ROYAL SOCIETY OF CHEMISTRY
Approved training

AnthiasConsulting Ltd
Bridging the Gap

Adding more Power to your GC-MS Analysis through Deconvolution

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Director & Senior Consultant

Anthias Consulting Ltd

- Analytical training & consultancy services focusing on specialist subject fields of gas chromatography, mass spectrometry & periphery techniques
  - Scheduled and bespoke training from many industries & all levels of experience in techniques, hardware & software
  - Applications support to help choose the best techniques
  - Our consulting & instrument business areas to advise & support from assistance with method development to application support & technical authoring.
  - Teaching theory, hardware, software, method development, troubleshooting and maintenance and impart our knowledge and many years of experience in these subject areas
  - Customers from UK, to Middle East including PetroChemical companies like Saudi Aramco

Course Accreditation

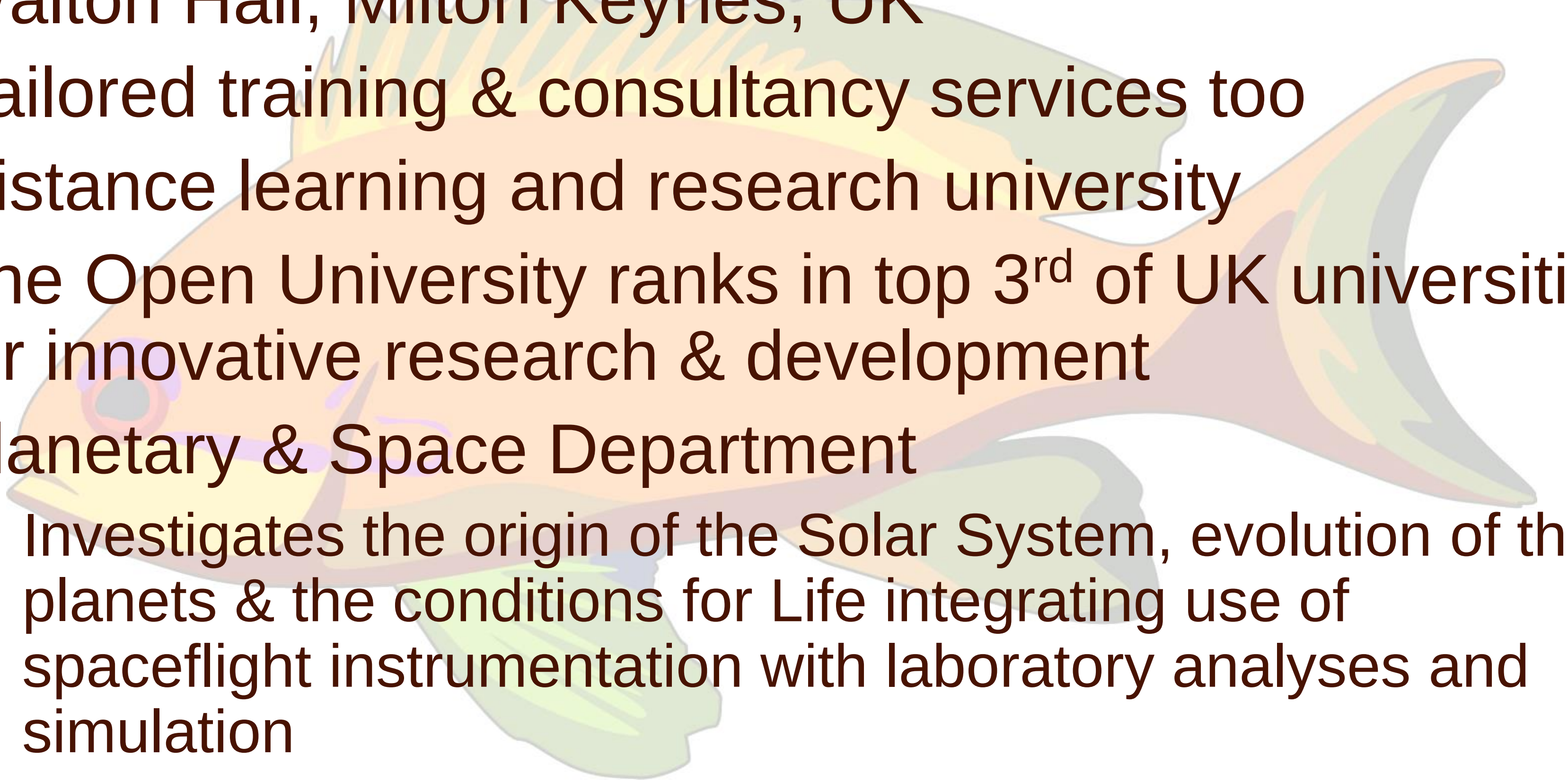
20+ training courses formally approved by Royal Society of Chemistry

> *"The objectives of course approval are to highlight good quality training available to the community & encourage members' continuing professional development (CPD)…The approval process is one of peer review, involving assessment against set criteria by members that are experts in their field"*

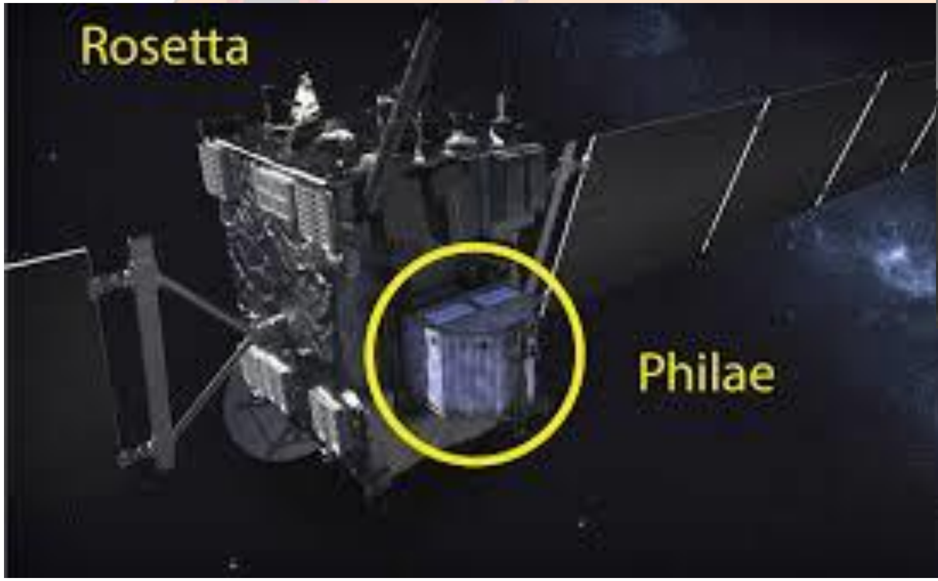
Dr Andrea McGhee, RSC Accreditation Development Specialist

The Open University

AnthiasConsulting Ltd
Bridging the Gap



- All practical scheduled courses take place here at Walton Hall, Milton Keynes, UK
- Tailored training & consultancy services too
- Distance learning and research university
- The Open University ranks in top 3rd of UK universities for innovative research & development
- Planetary & Space Department
  - Investigates the origin of the Solar System, evolution of the planets & the conditions for Life integrating use of spaceflight instrumentation with laboratory analyses and simulation
  - Instruments developed have been utilised for applications in health care, such as TB & cancer detection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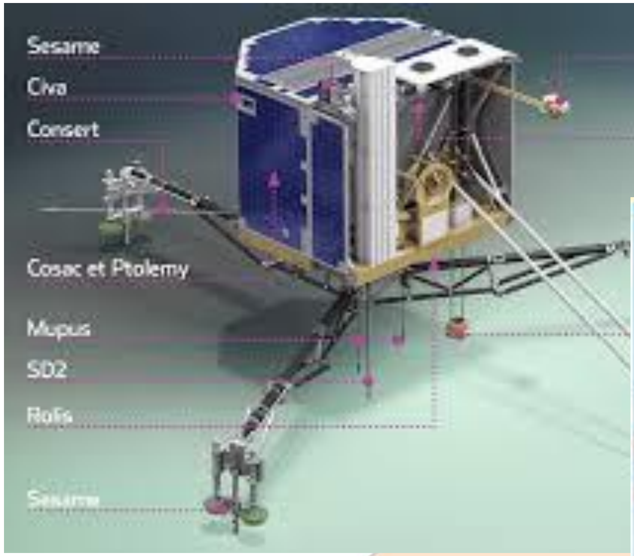
Sesame
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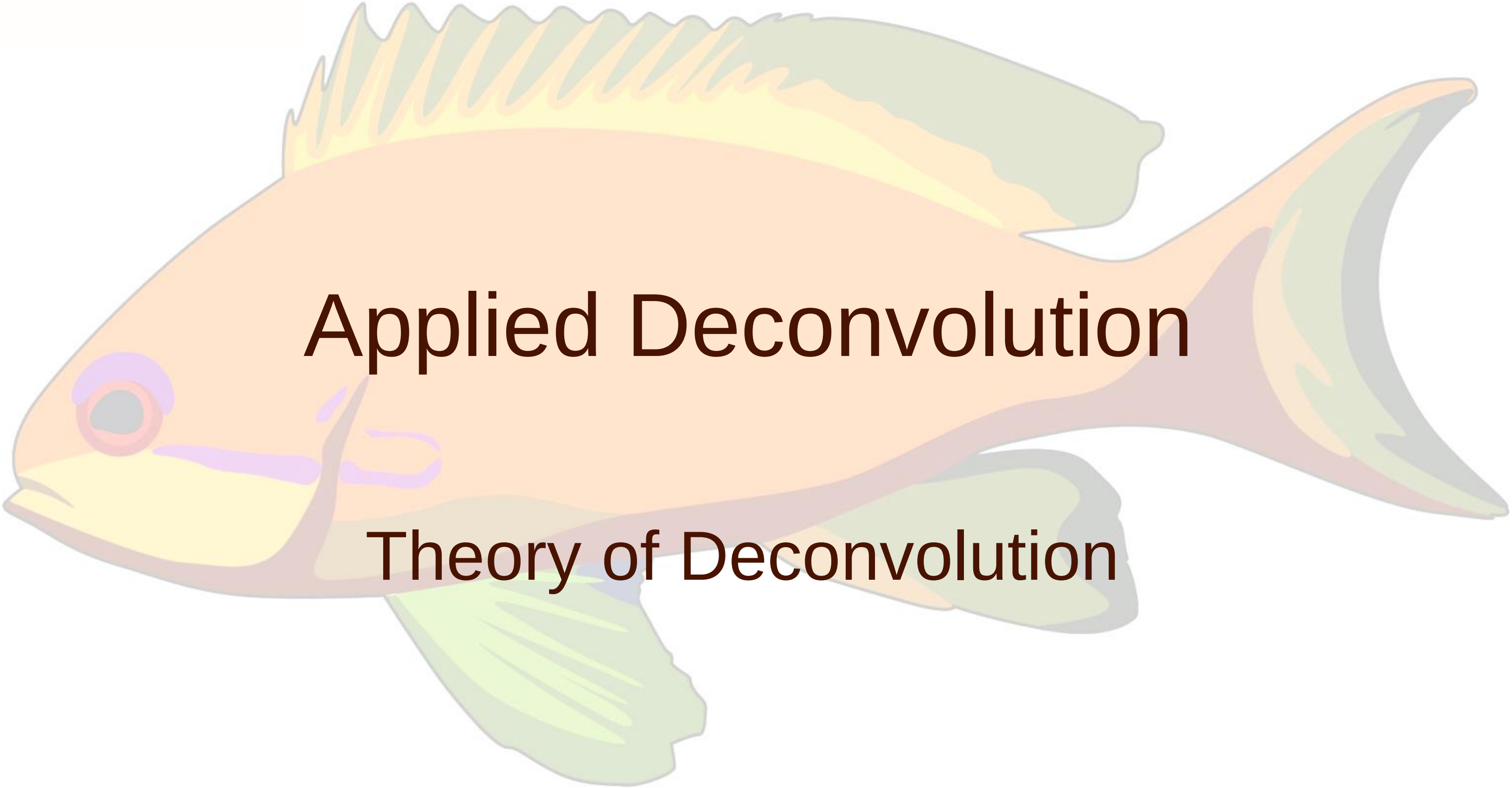
QM Post Vibration Test : E-Box Panels Removed to Reveal PCBs 2002/ 1/ 3



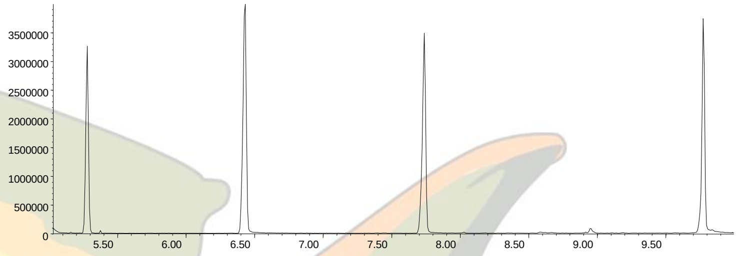
Applied Deconvolution

Theory of Deconvolution

GC-MS separation methods

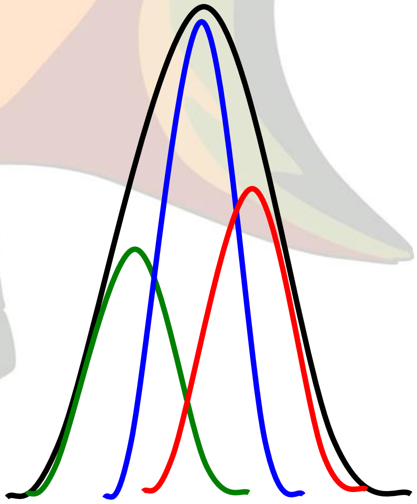
- Chromatographic resolution

  Analytes are physically separated by their selective interaction with stationary phase of analytical column & elute at different retention times



- Analytical resolution

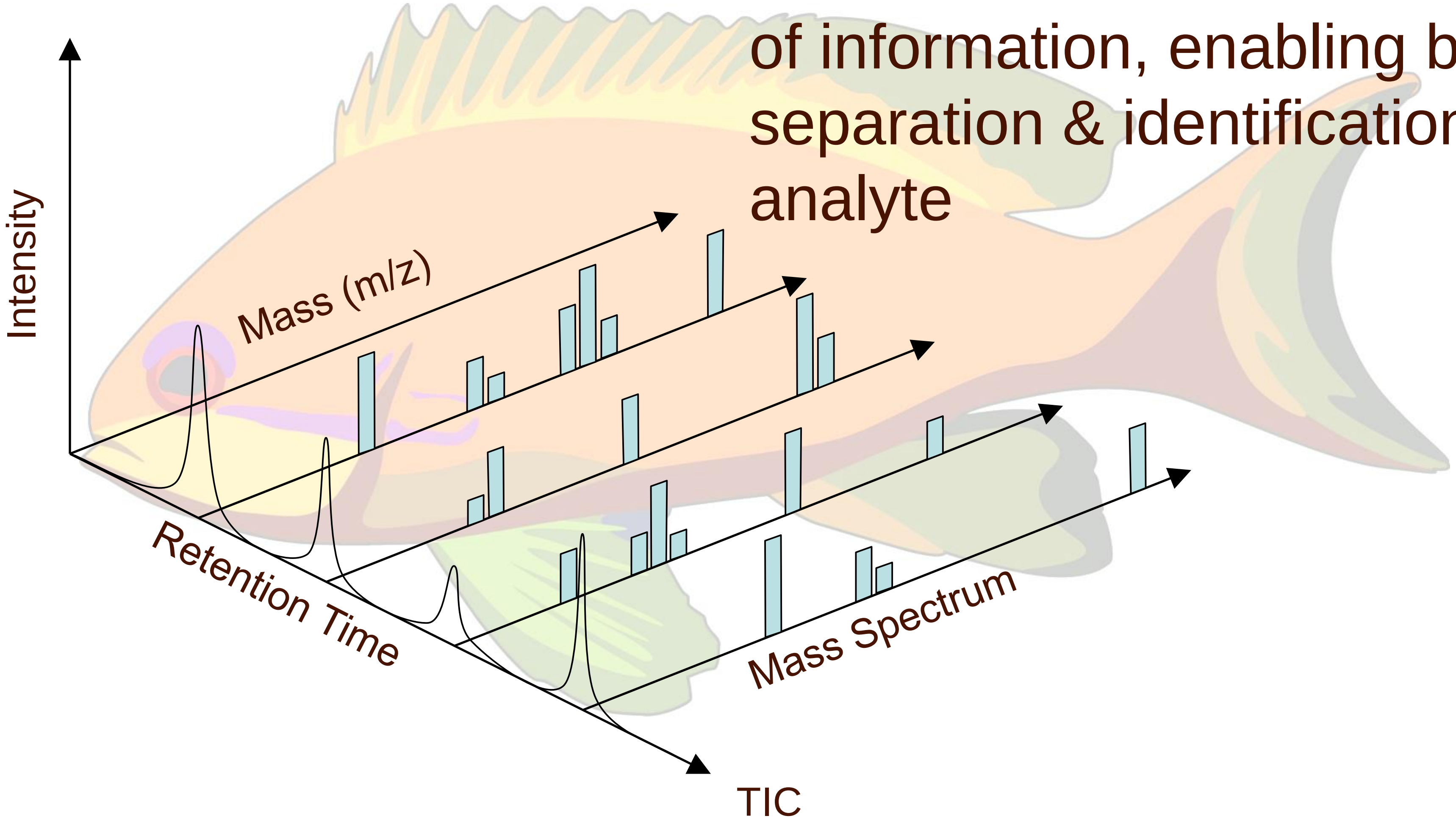
  Analytes eluting at similar retention times are separated by their different (unique) masses



Those analytes with same retention time AND all same masses cannot be separated

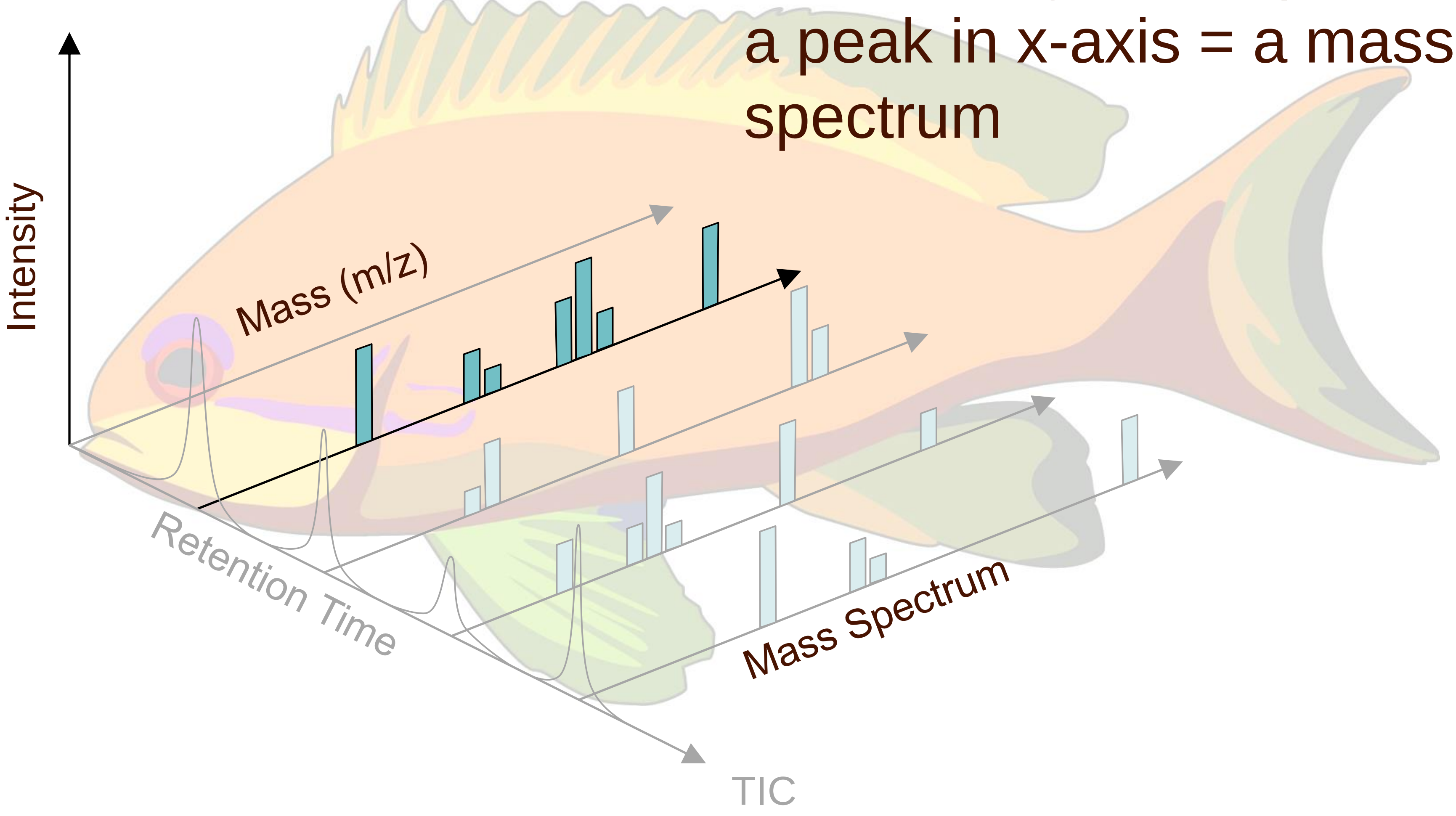
GC-MS = 3D data

MS adds another dimension of information, enabling both separation & identification of analyte



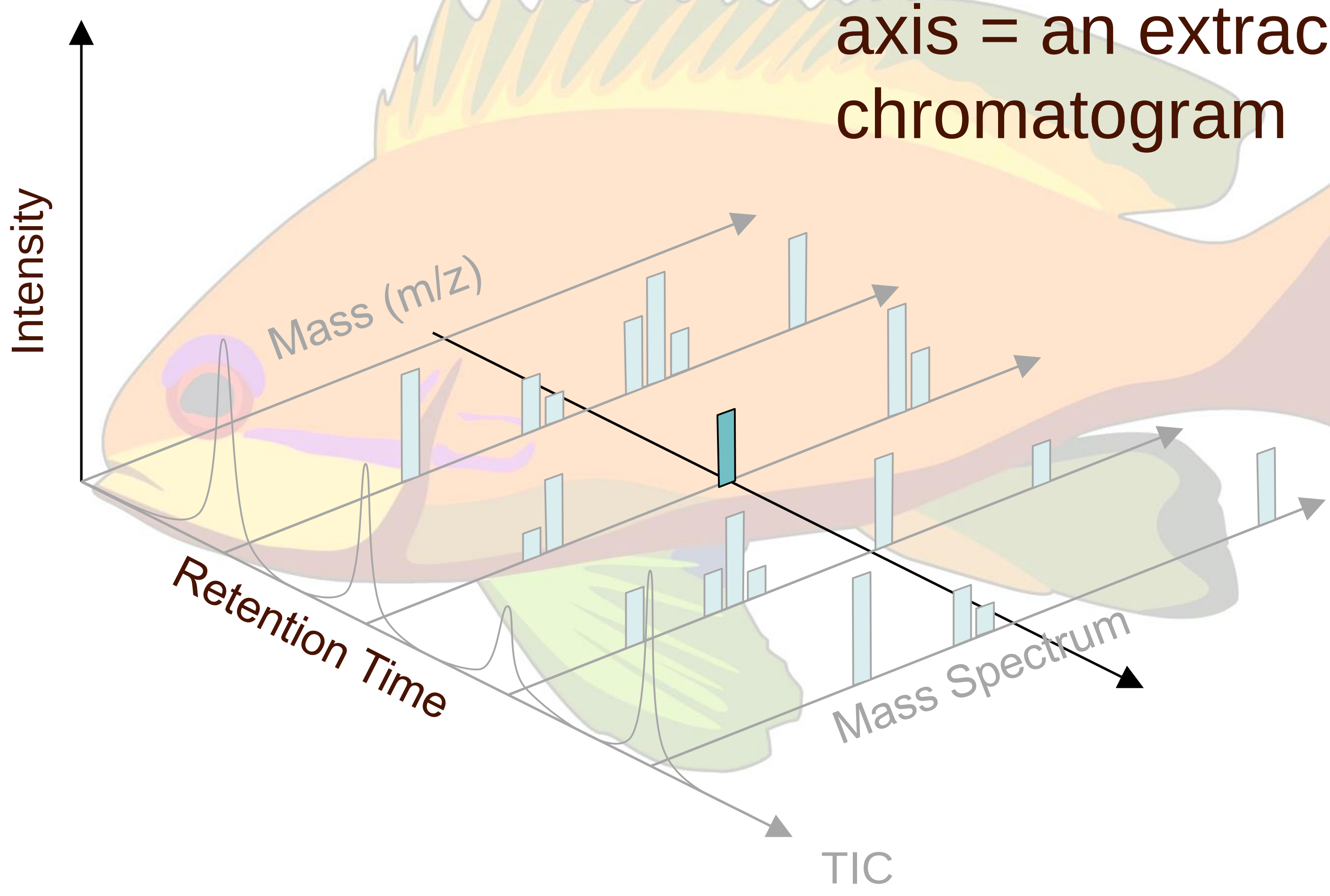
GC-MS = 3D data

Take a single data point on a peak in x-axis = a mass spectrum



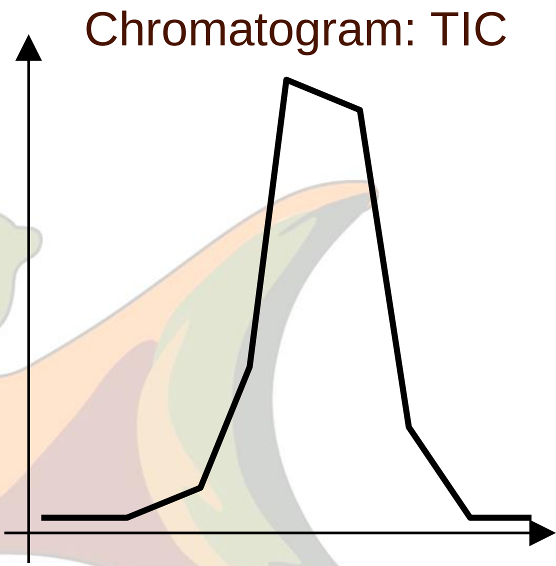
GC-MS = 3D data

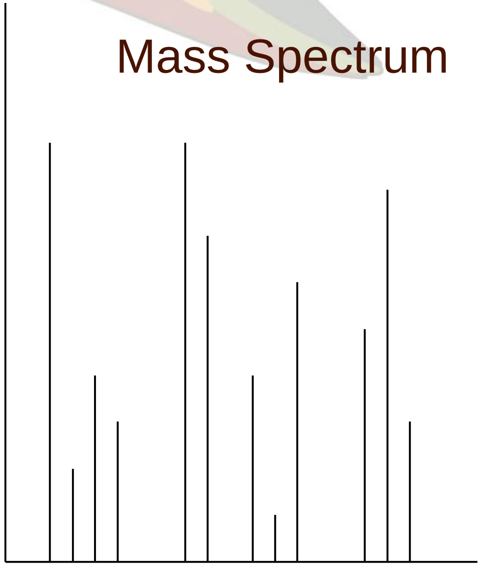
Extract a single ion from z-axis = an extracted ion chromatogram



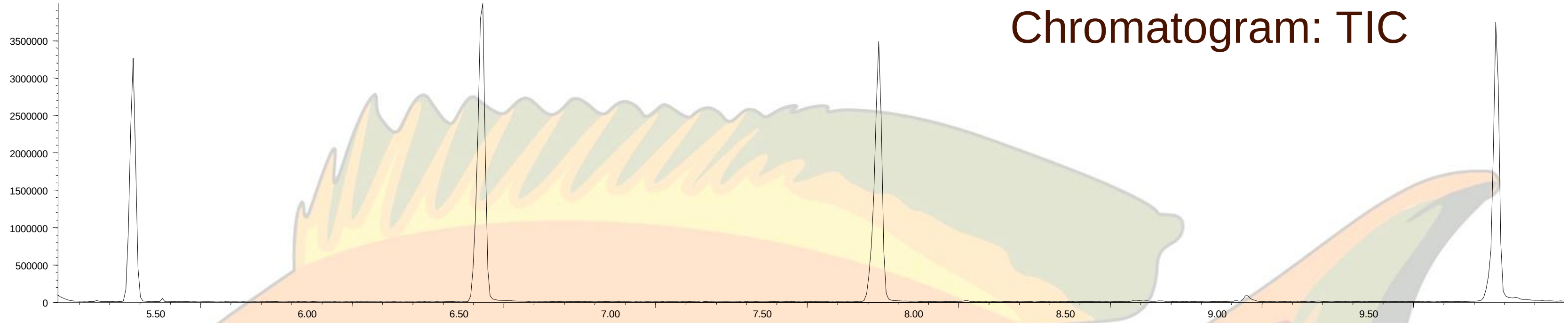
TIC

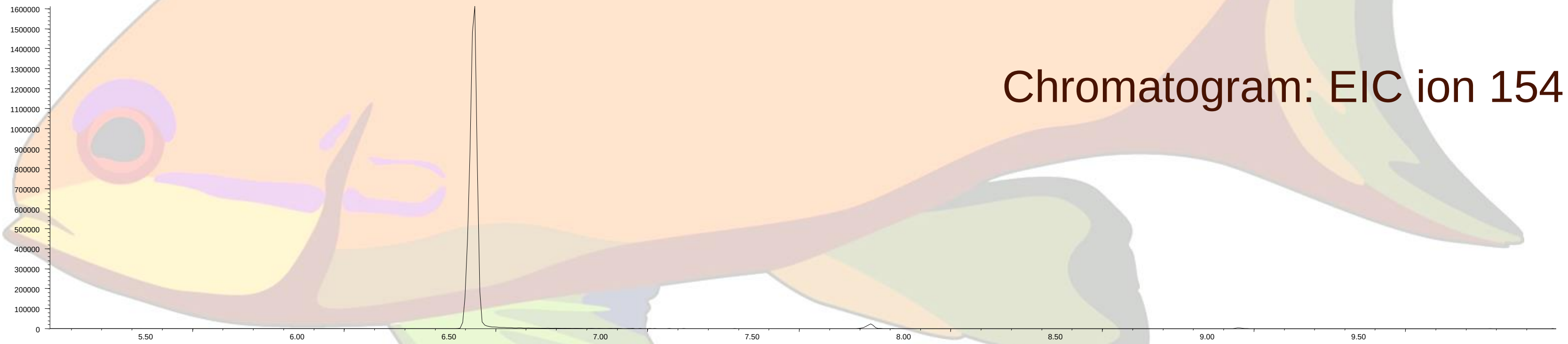
- Abundance of each mass at a particular data point is summed to produce a total ion current
- This is plotted for each data point (or scan)
- A 2D total ion chromatogram (TIC) is produced of retention time versus total ion current
- Selecting a single data point will then give a mass spectrum at that point in time
- If two peaks are co-eluting it will give a mixed mass spectrum of both peaks plus any background like column bleed





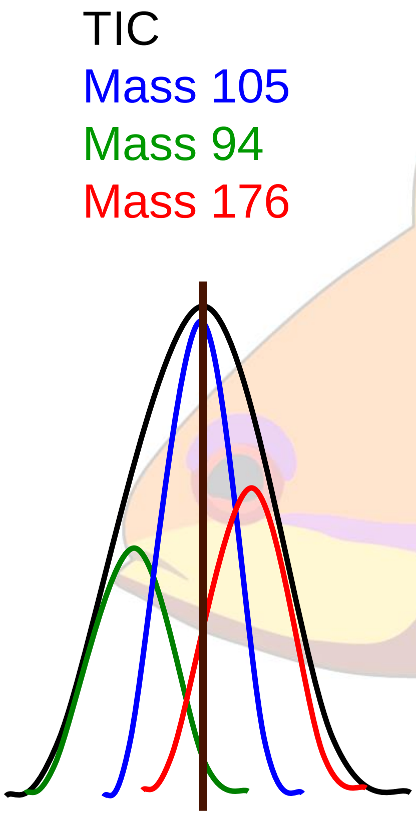
EIC





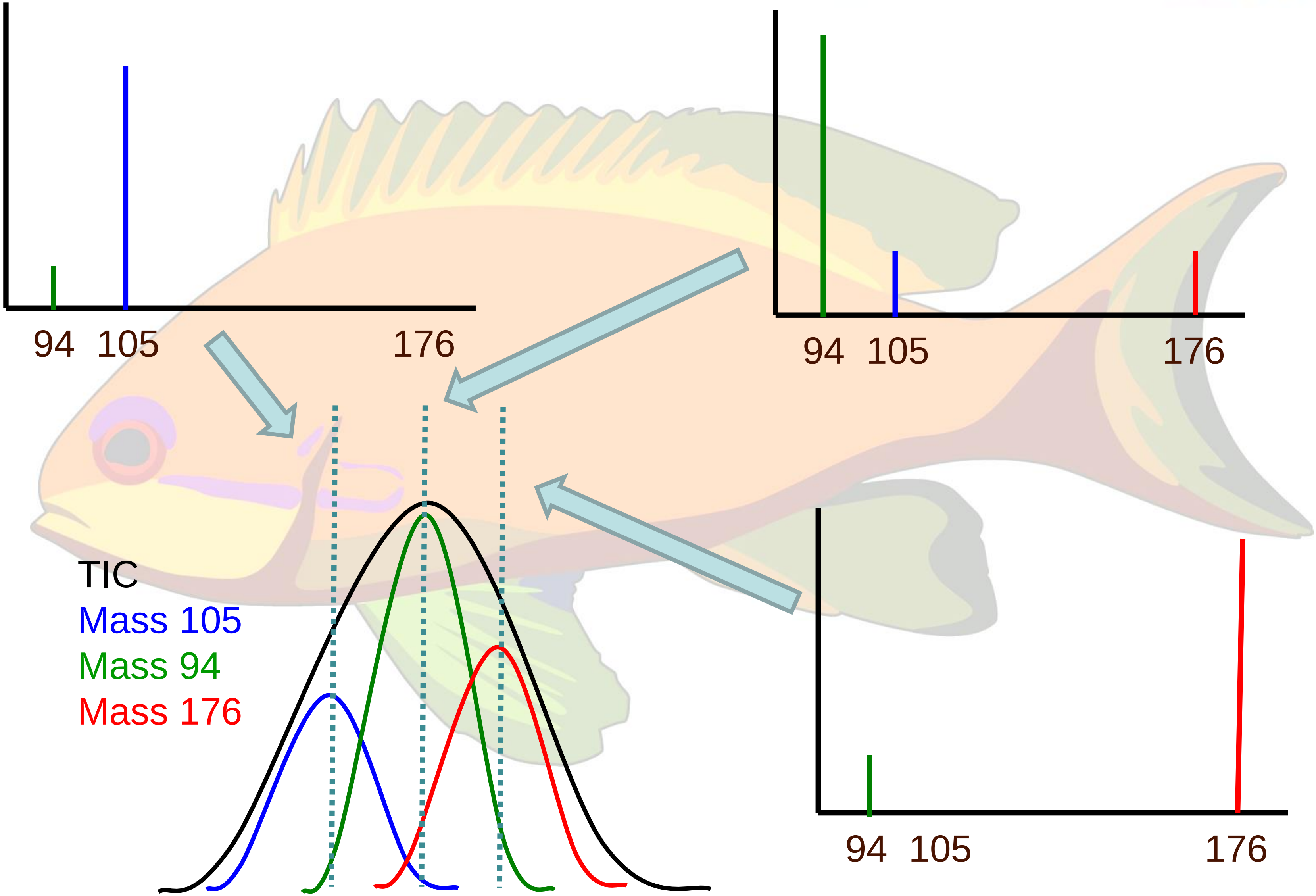
- Extracted ion chromatogram of 154 ion
  - Only peaks containing 154 ion can be seen
- Useful for looking for a particular known analyte
- Multiple ions can be extracted and summed if required

Why use deconvolution?



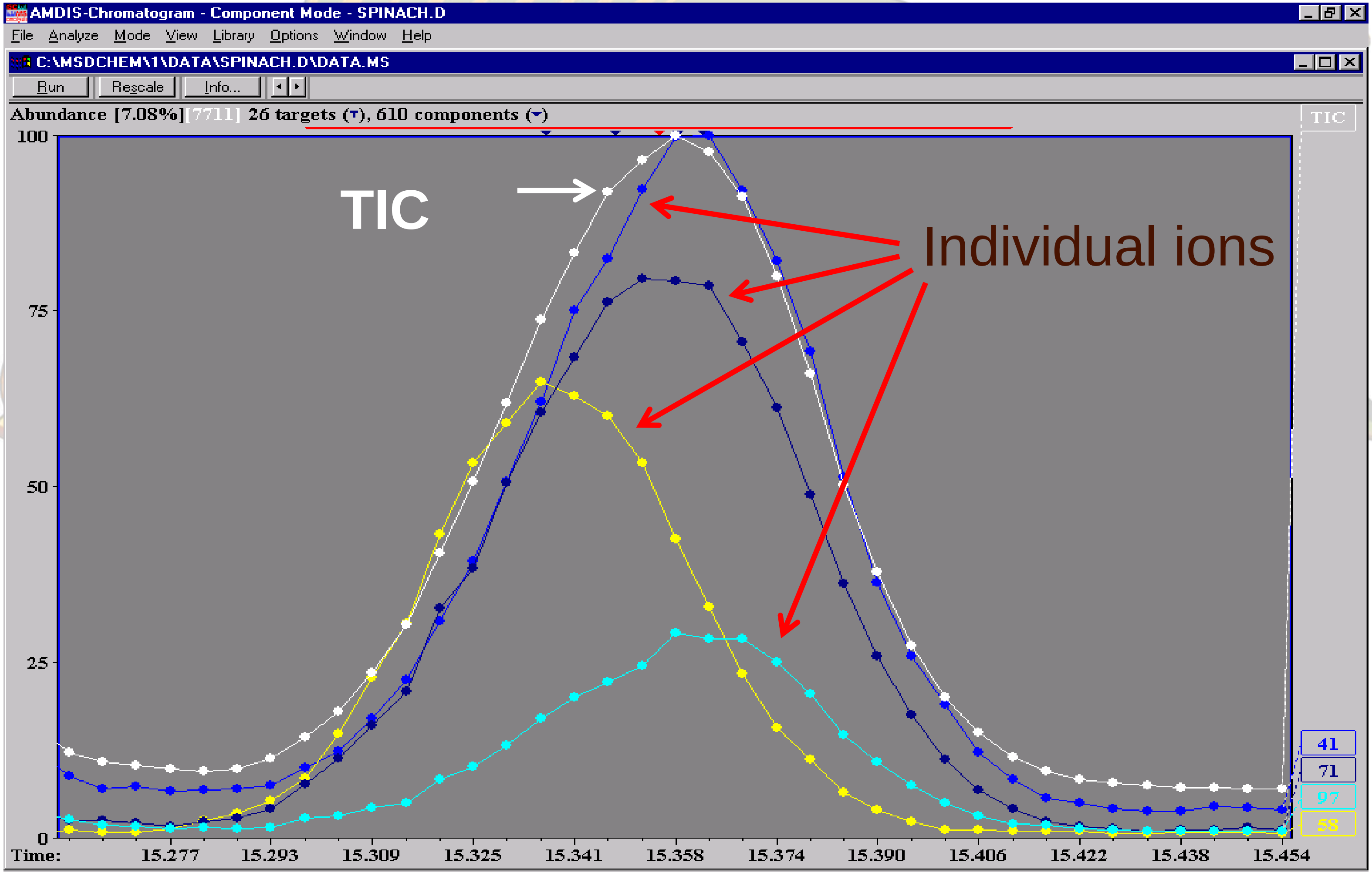
- If individual standards analysed – could get retention time & mass spectrum for each peak
- For target analysis where retention times & ions are known can identify & quantify analytes on unique masses
- For unknown samples:
  - Can you see if there are coelutions?
  - Can you get a high quality mass spectrum for library searching & identification?
- For target analytes, scan & SIM:
  - Coeluting peaks
  - Matrix interferences

Analytical resolution

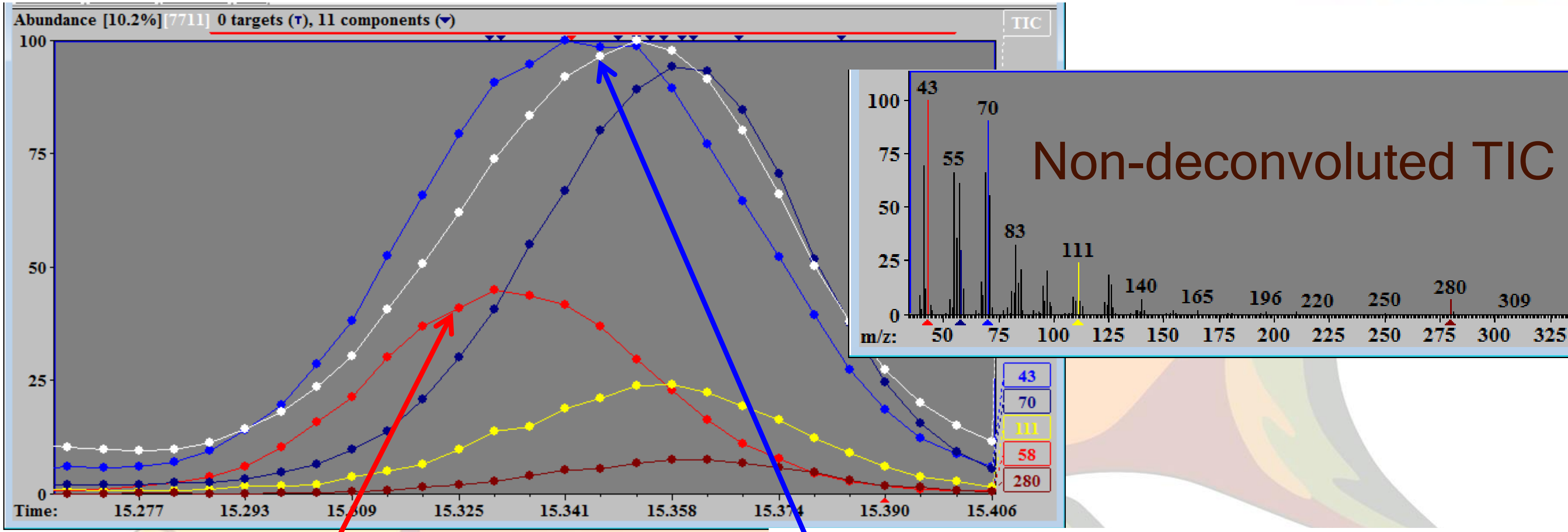


Deconvolution definition

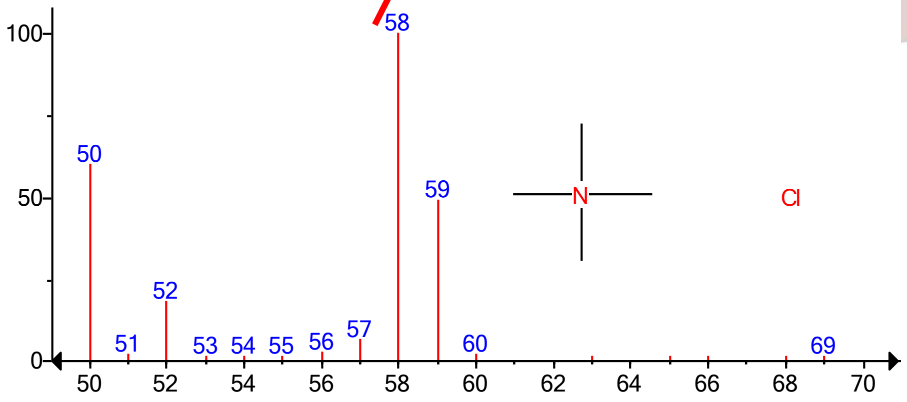
"…in the broad sense of extracting one signal from a complex mixture..." (From AMDIS)



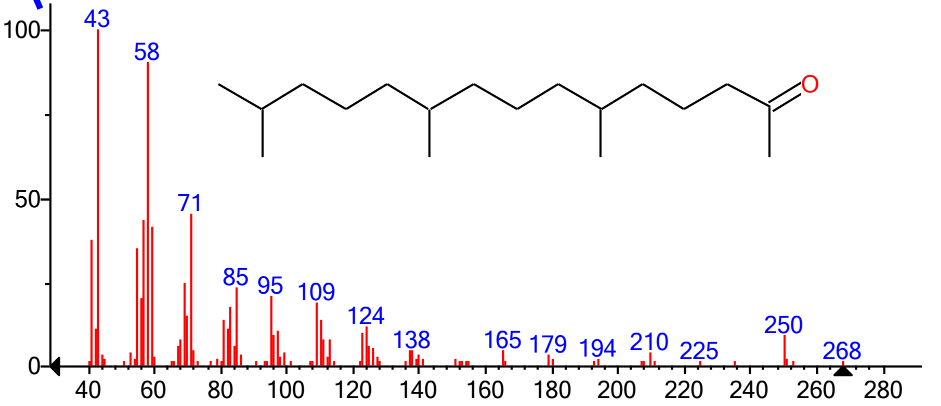
Deconvolution example



Non-deconvoluted TIC

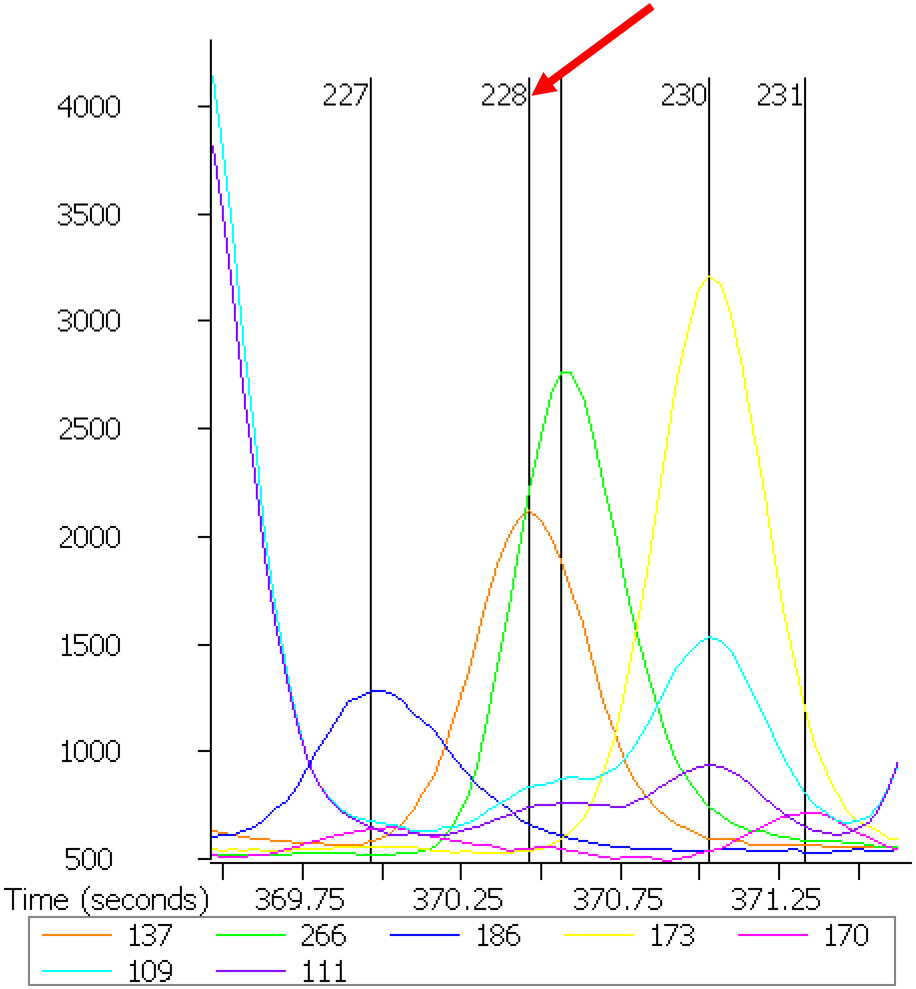


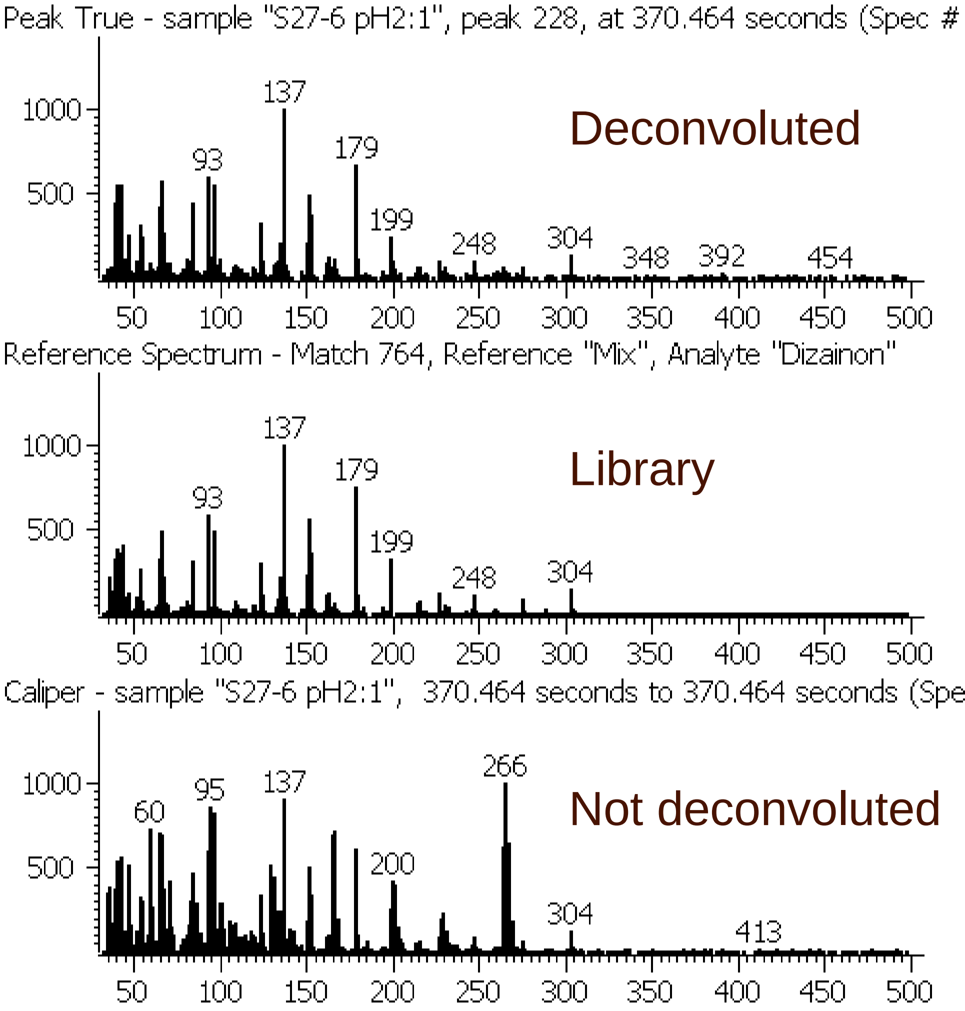
Tetramethylammonium chloride



Perhydrofarnesyl acetone

Deconvolution




Peak True - sample "S27-6 pH2:1", peak 228, at 370.464 seconds (Spec #

Deconvoluted

Reference Spectrum - Match 764, Reference "Mix", Analyte "Dizainon"

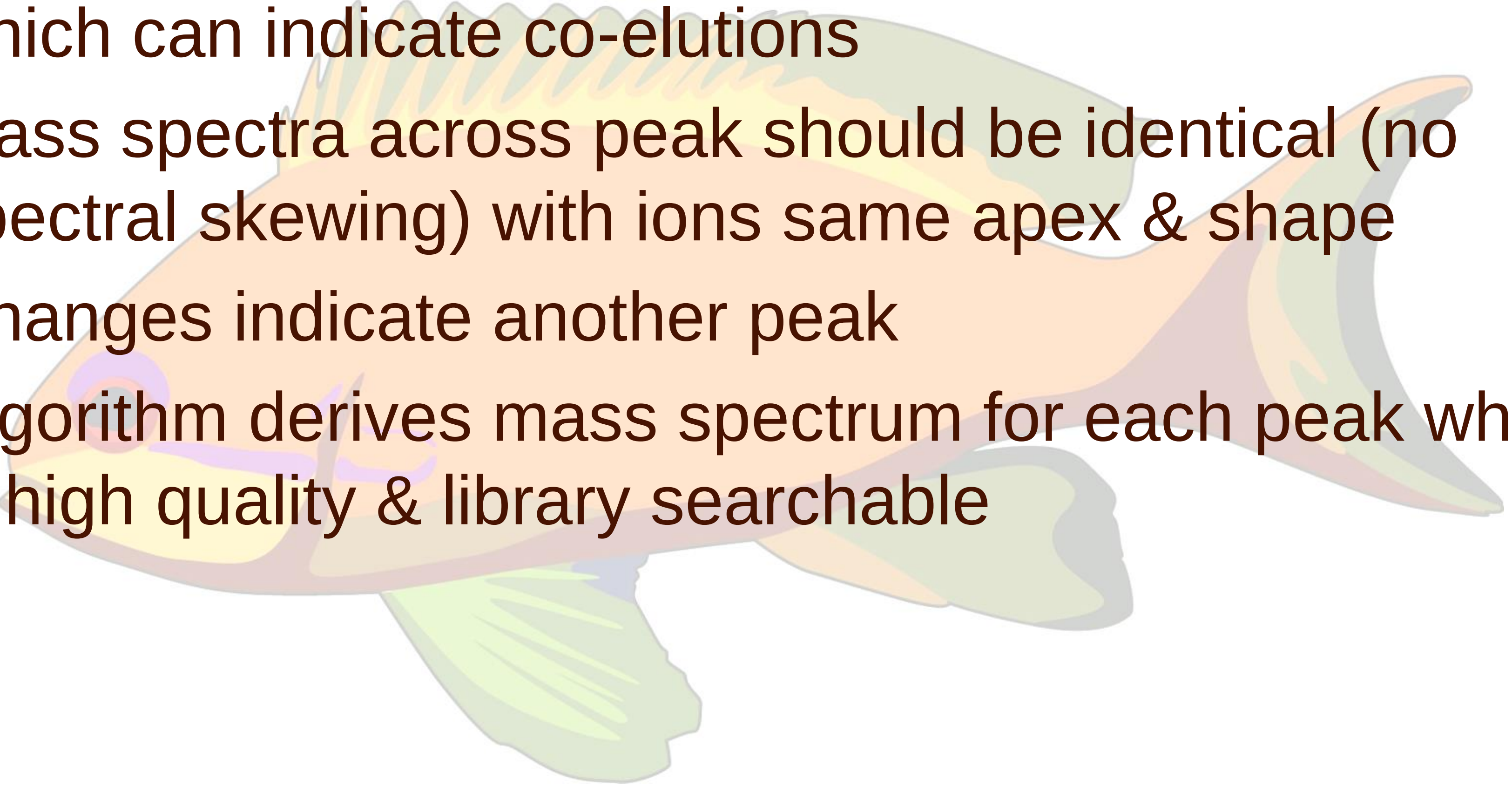
Library

Caliper - sample "S27-6 pH2:1", 370.464 seconds to 370.464 seconds (Spe

Not deconvoluted

Courtesy of Leco Instruments

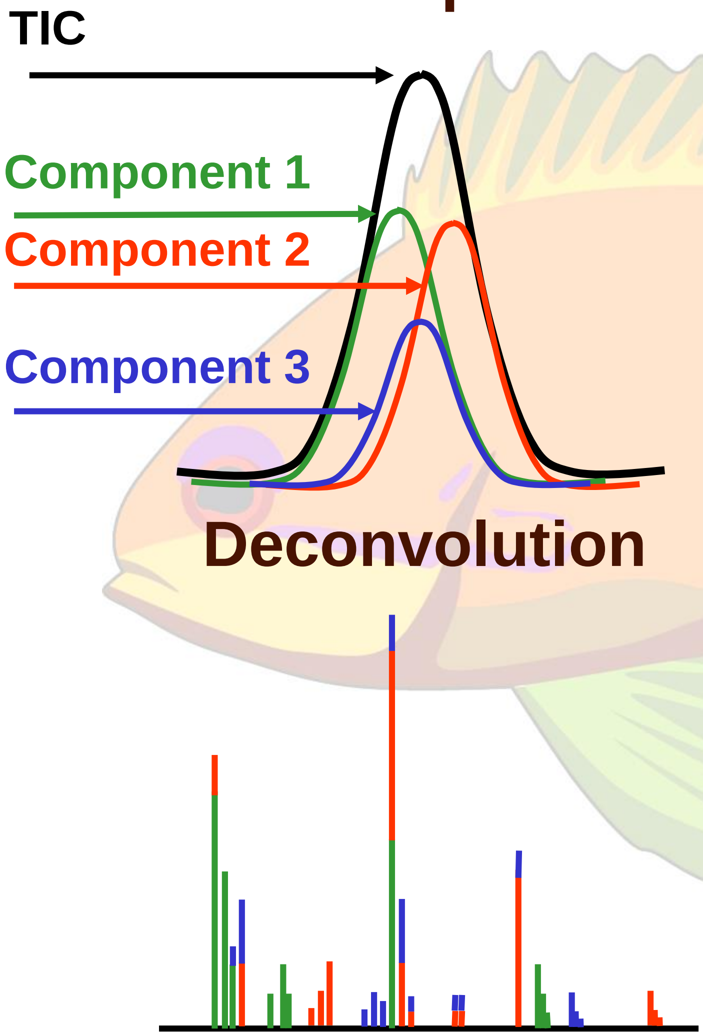
Deconvolution summary



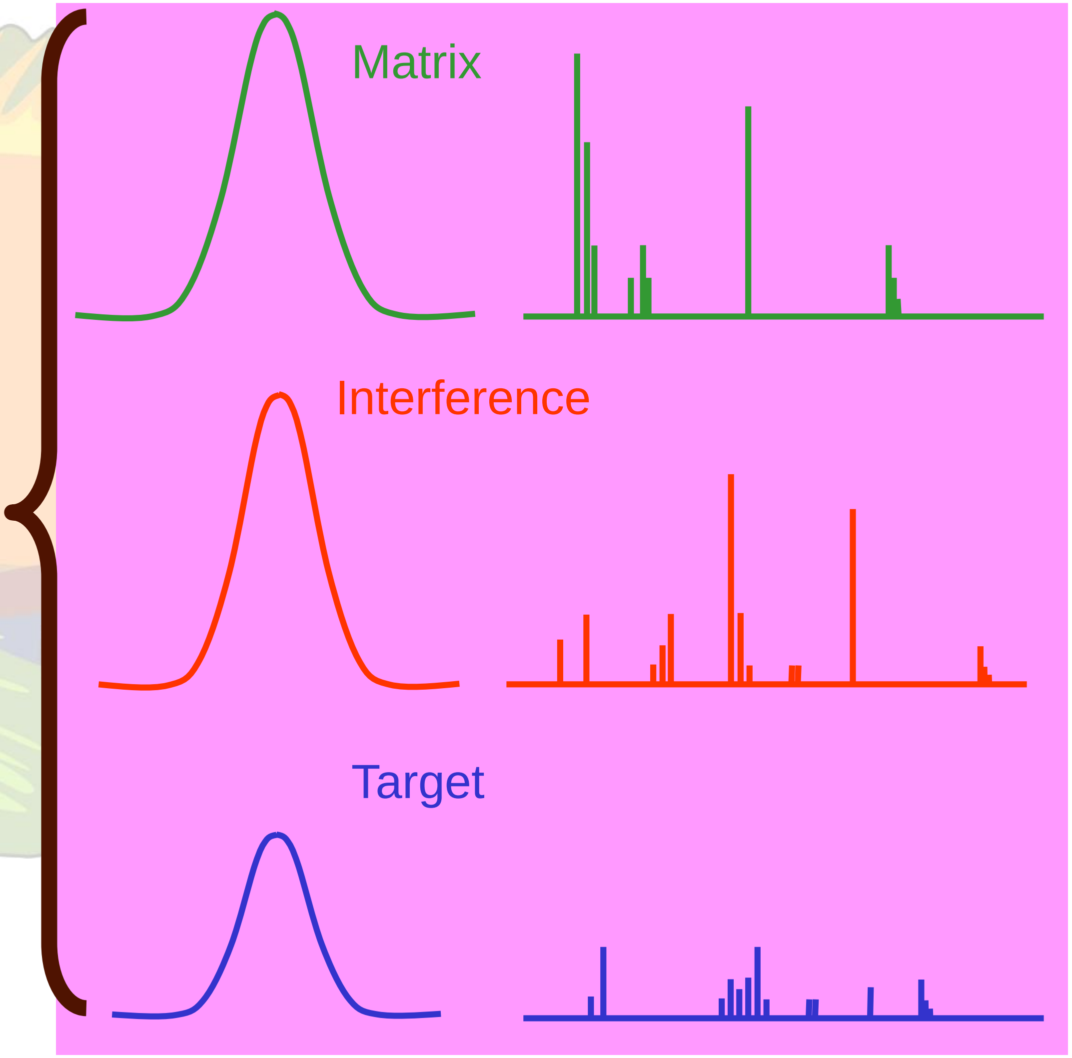
- Detects differences in mass spectra across a peak which can indicate co-elutions
- Mass spectra across peak should be identical (no spectral skewing) with ions same apex & shape
- Changes indicate another peak
- Algorithm derives mass spectrum for each peak which is high quality & library searchable

Deconvolution example

TIC & Spectrum



Deconvoluted Peaks and Spectra

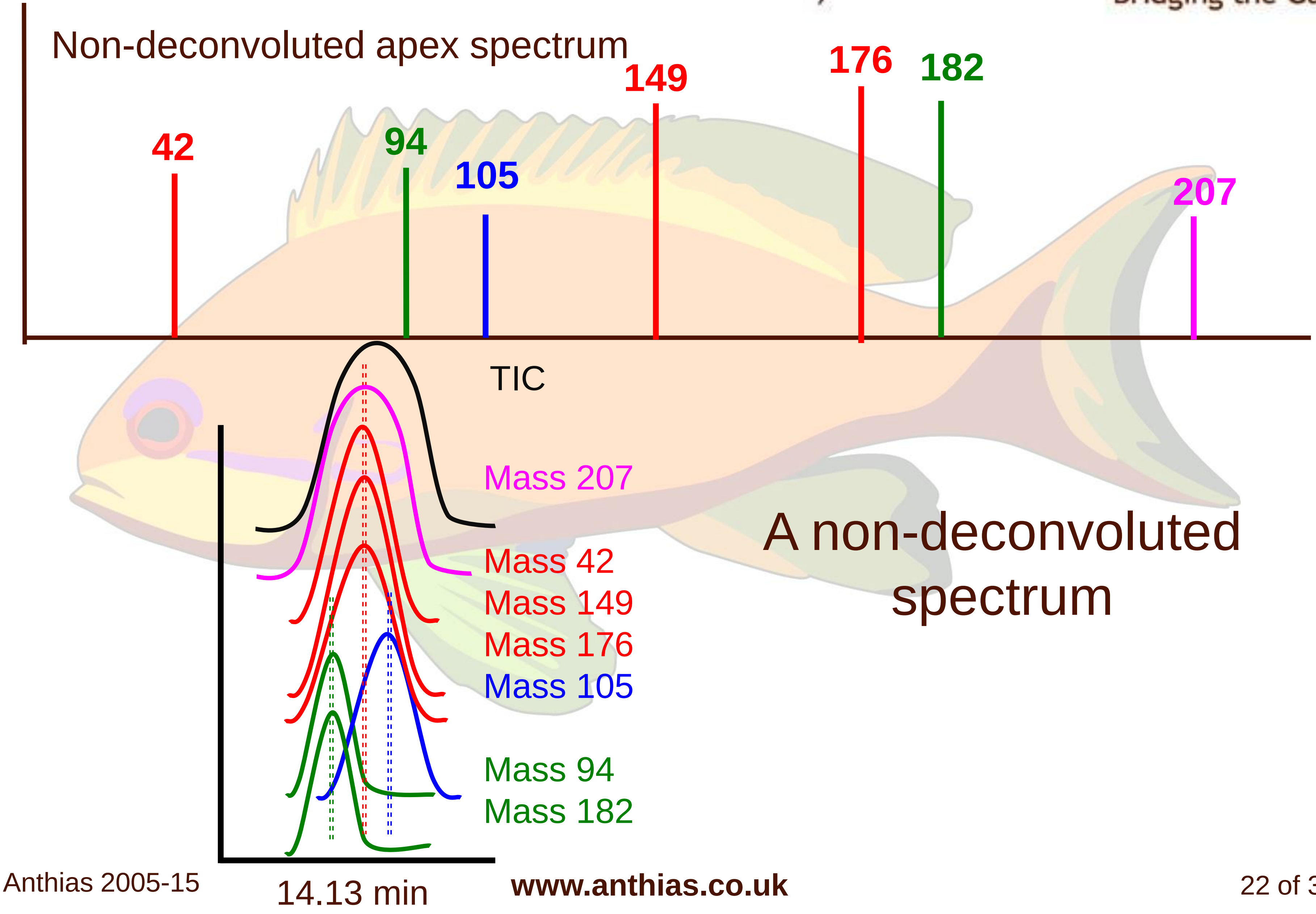


Deconvolution: Basic Steps

Exact steps dependent on deconvolution software:

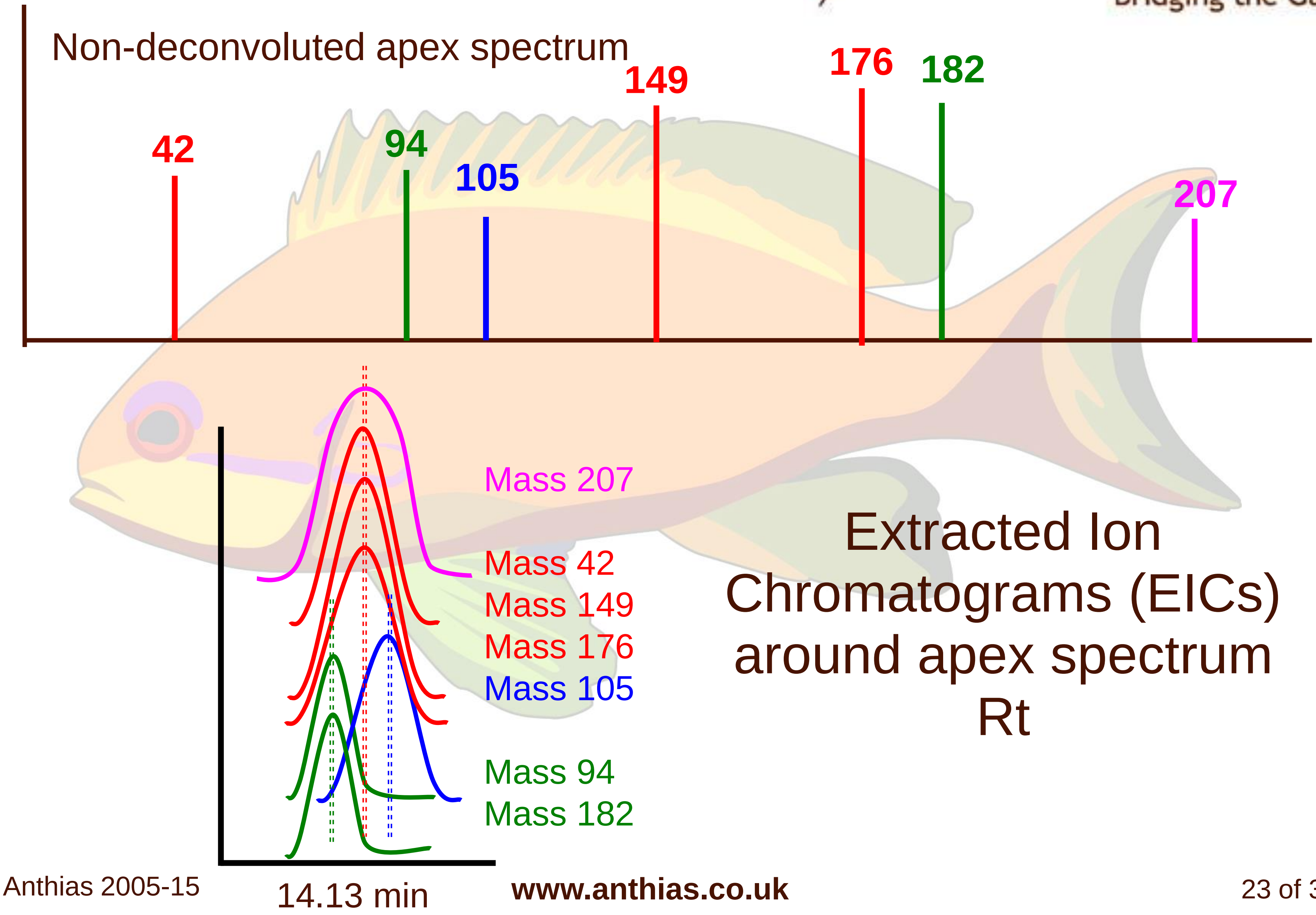
- Noise is defined & compensated for
- Scan skew is corrected
- True peak maximum found for each ion
- Ion profiles are tracked, rate of rise/fall
- Ions present in mass spectrum of that peak should have
  - Same apex
  - Rise up & fall together (have same shape)
- Deconvoluted mass spectrum produced for each peak found according to settings/integration parameters
- Deconvoluted mass spectra can be library searched
- Retention index can be used as a qualifier to check correct isomer identified

Deconvolution process



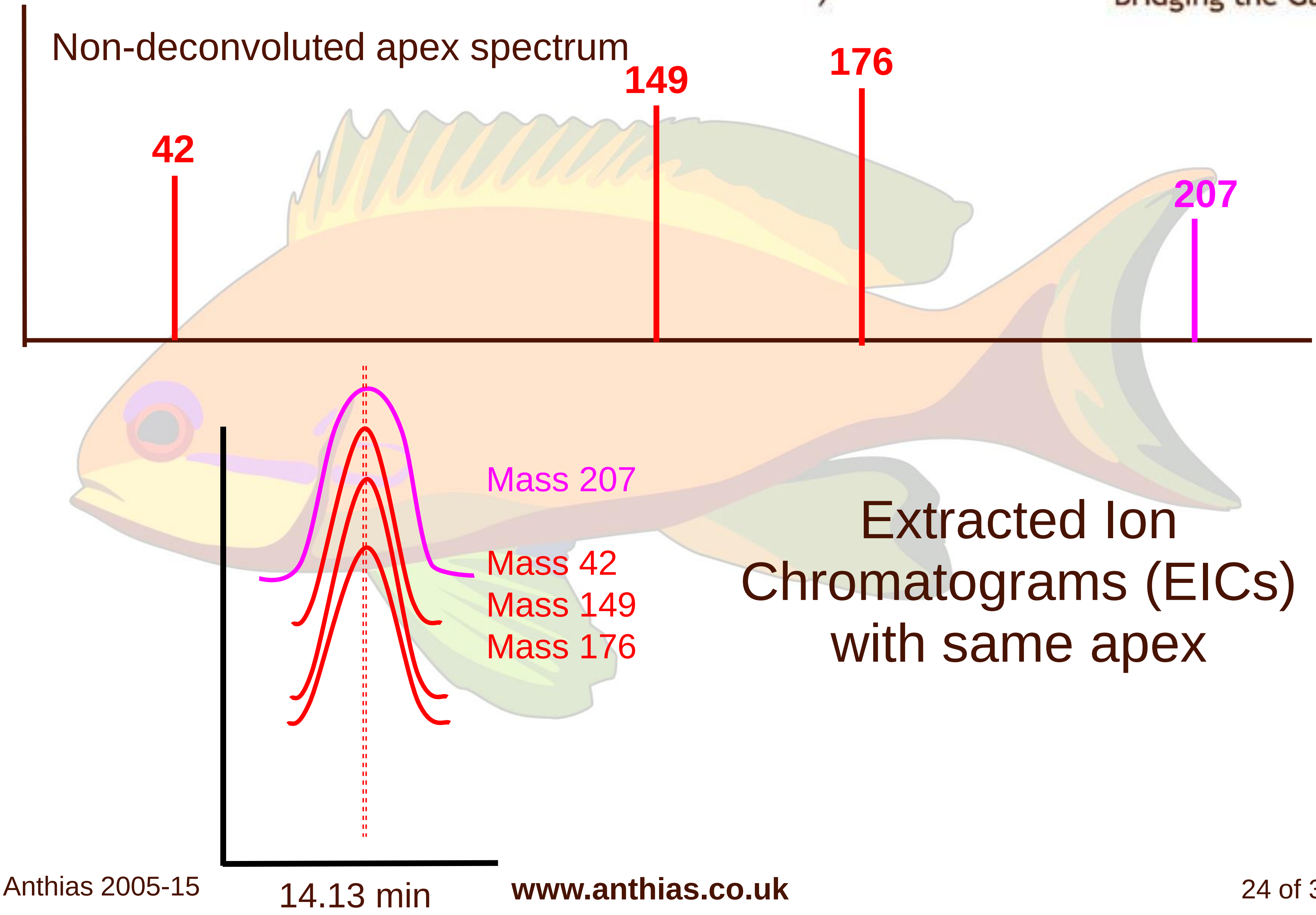
A non-deconvoluted spectrum

Deconvolution process



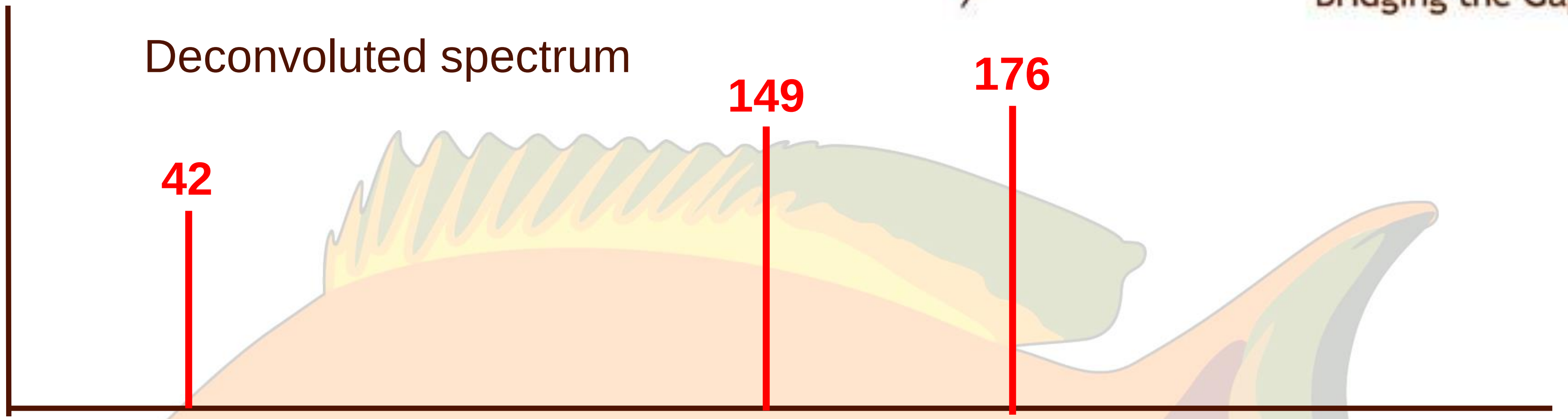
Extracted Ion Chromatograms (EICs) around apex spectrum Rt

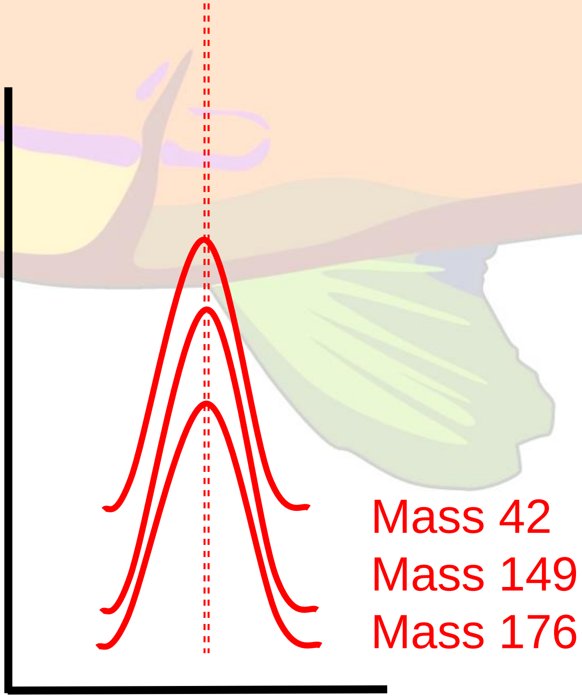
Eliminate ions: different apex



Extracted Ion Chromatograms (EICs) with same apex

Eliminate ions: different shape



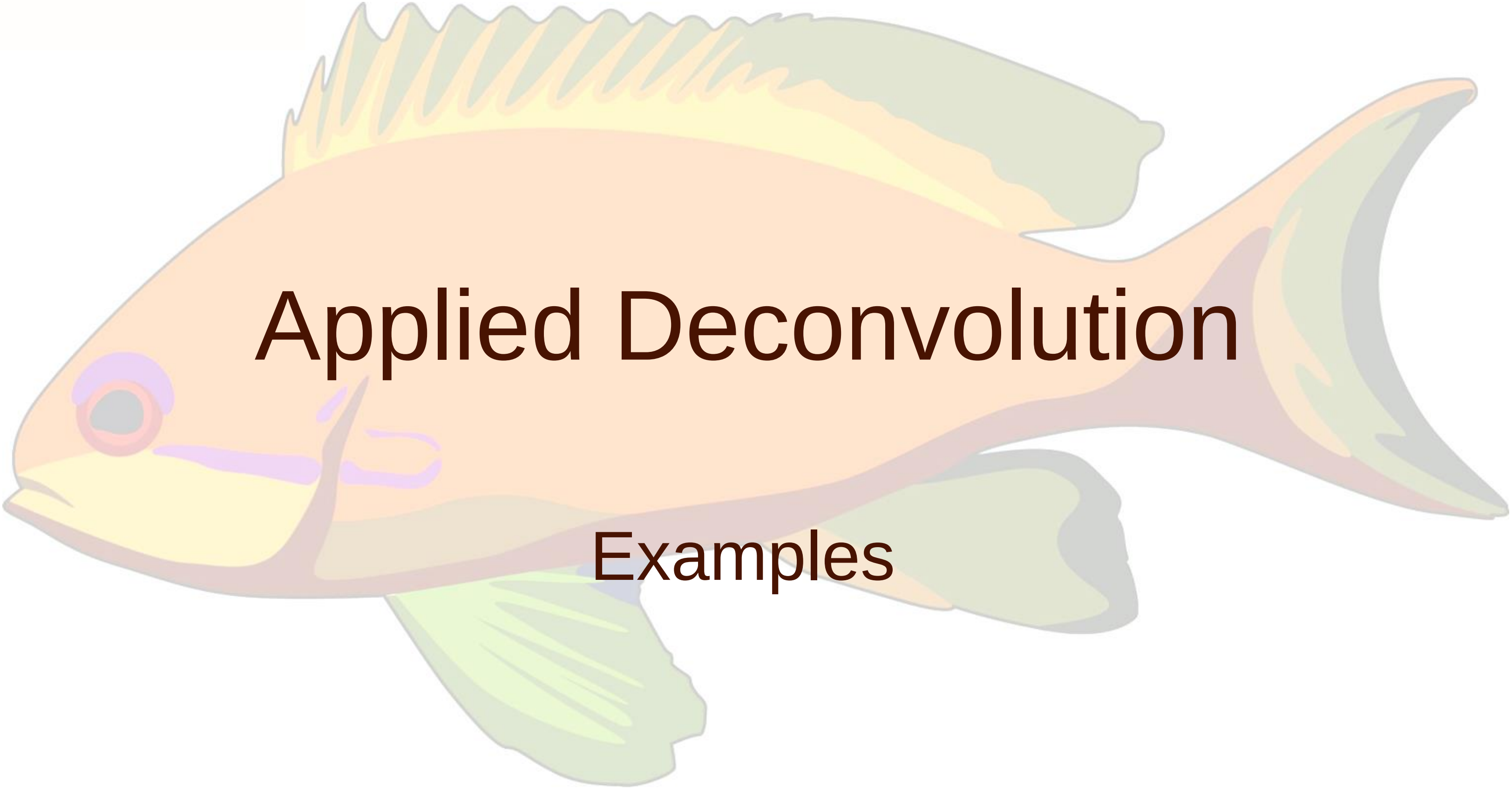


Extracted Ion Chromatograms (EICs) that have same shape & apex

'Clean-up' or 'deconvoluted' mass spectrum

High quality GC-MS data

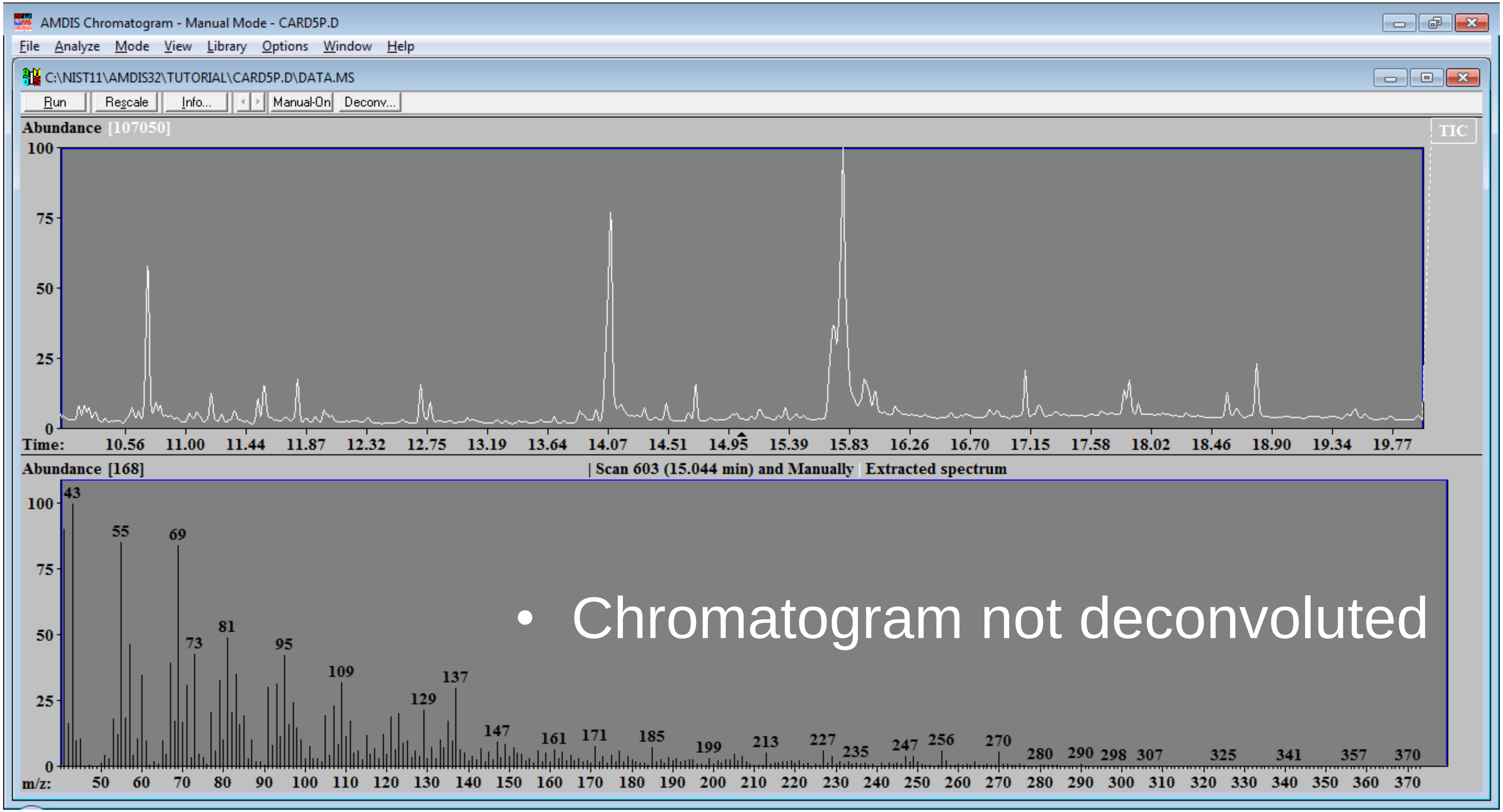
- Always some chromatographic resolution
  - Total co-elution (apex & same shape) can not be deconvoluted
- Always obtain good peak shapes
  - Sharp, Gaussian peaks are easier to deconvolute
- Ensure correct mass range is obtained for deconvolution
- Ensure there are enough data points across peak
  - Improves peak shape, enables accurate identification of apex, enables deconvolution of closely co-eluting peaks
- Get good signal to noise
  - Any data system will handle large, sharp peaks better than working in noise region
  - Reducing noise & improving signal can be applied throughout GC-MS system from carrier gas to MS detector & sample prep



Applied Deconvolution

Examples

AMDIS Deconvolution

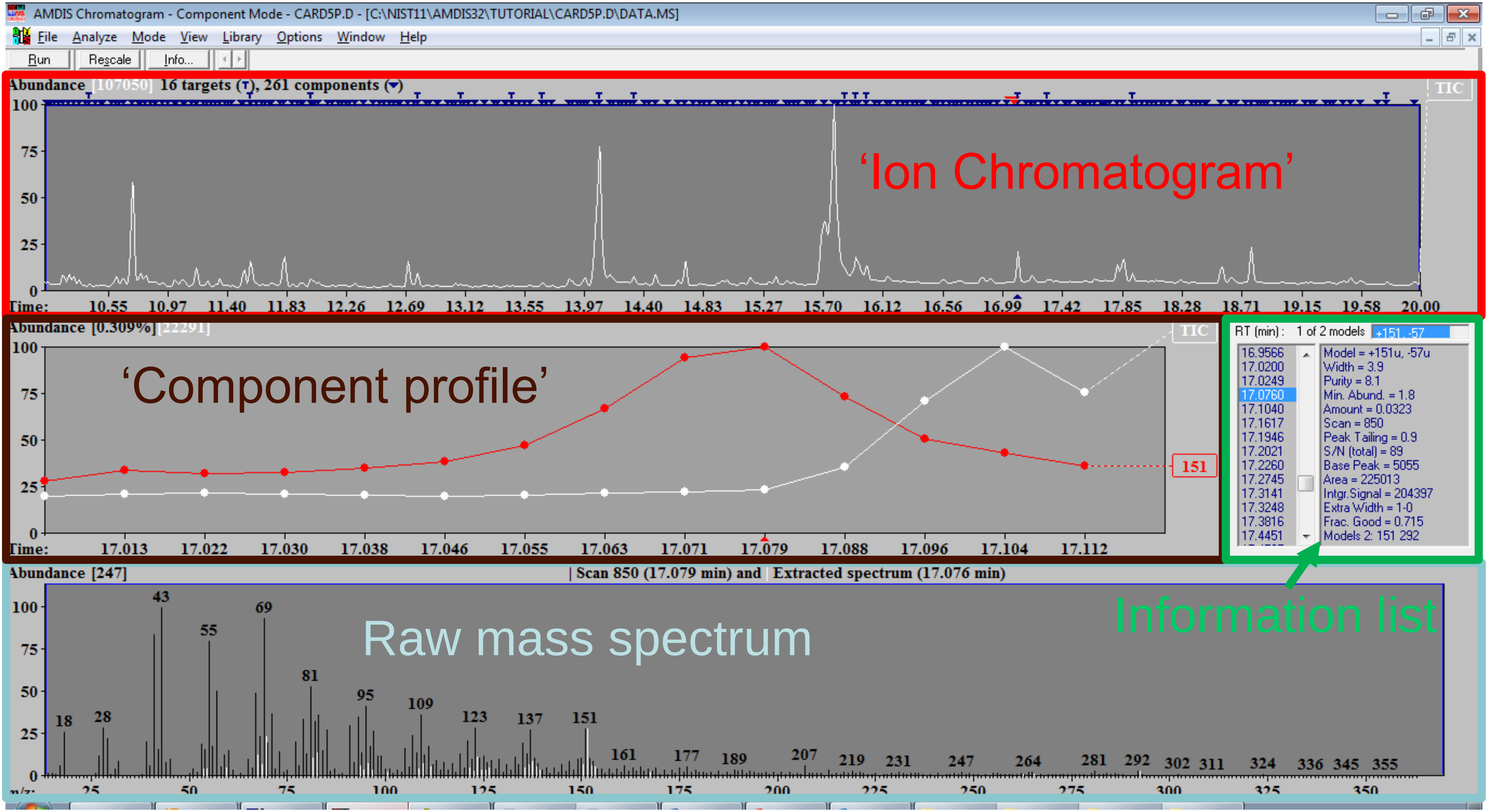


- Chromatogram not deconvoluted

Pesticides in cardamon oil

AMDIS Deconvolution

Individual components (peaks): selected component in red



AMDIS Chromatogram - Component Mode - CARD5P.D - [C:\NIST11\AMDIS32\TUTORIAL\CARD5P.D\DATA.MS]

RT (min): 1 of 2 models +151, -57

16.9566
17.0200
17.0249
17.0760
17.1040
17.1617
17.1946
17.2021
17.2260
17.2745
17.3141
17.3248
17.3816
17.4451

Model = +151u, -57u
Width = 3.9
Purity = 8.1
Min. Abund. = 1.8
Amount = 0.0323
Scan = 850
Peak Tailing = 0.9
S/N (total) = 89
Base Peak = 5055
Area = 225013
Intgr.Signal = 204397
Extra Width = 1-0
Frac. Good = 0.715
Models 2: 151 292

'Ion Chromatogram'

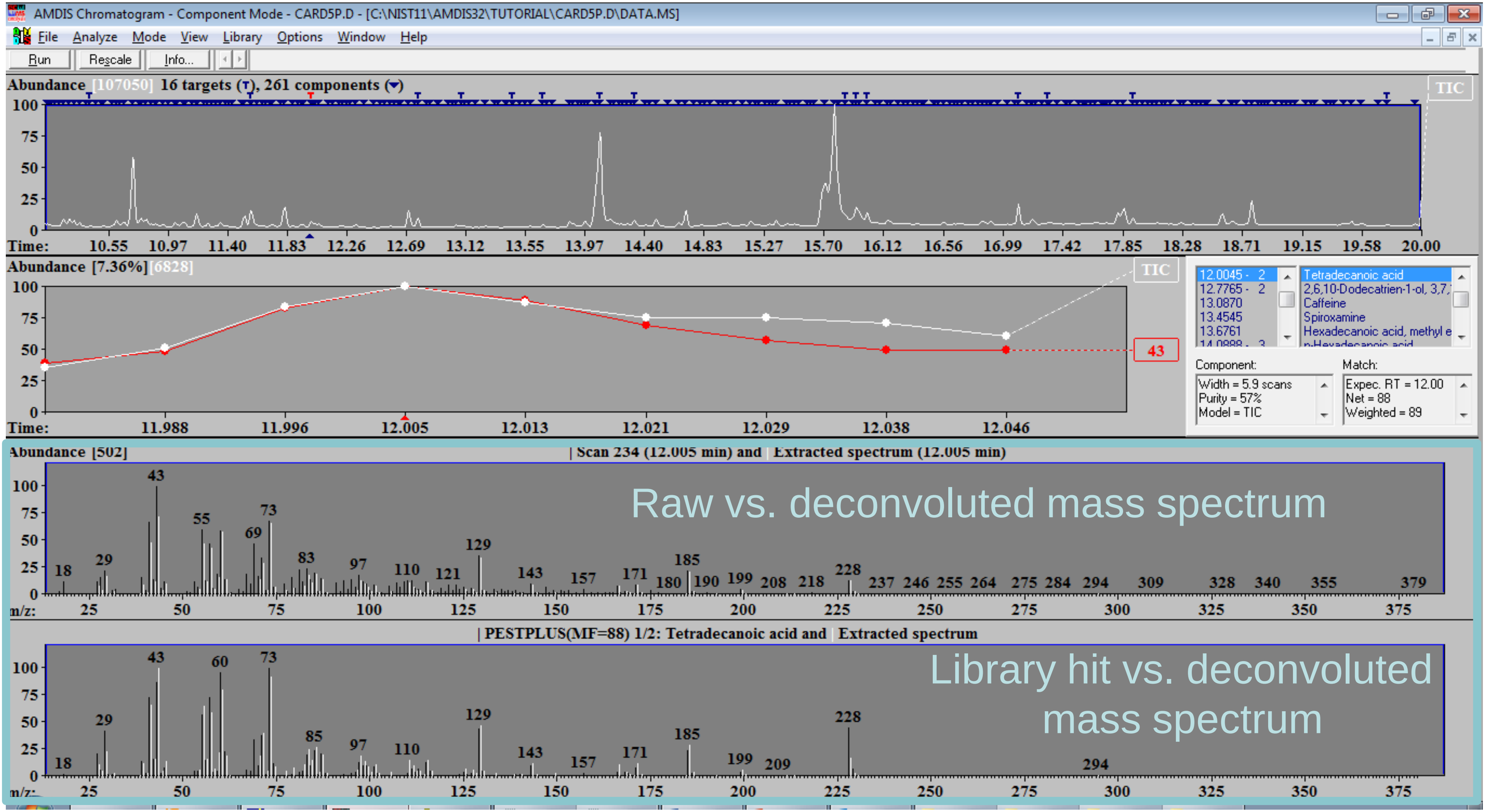
'Component profile'

Raw mass spectrum

Information list

AMDIS Deconvolution

Target components (T) found: match against the target library



12.0045 - 2 | Tetradecanoic acid
12.7765 - 2 | 2,6,10-Dodecatrien-1-ol, 3,7,
13.0870 | Caffeine
13.4545 | Spiroxamine
13.6761 | Hexadecanoic acid, methyl e
14.0888 - 3 | n-Hexadecanoic acid

Component:
Width = 5.9 scans
Purity = 57%
Model = TIC

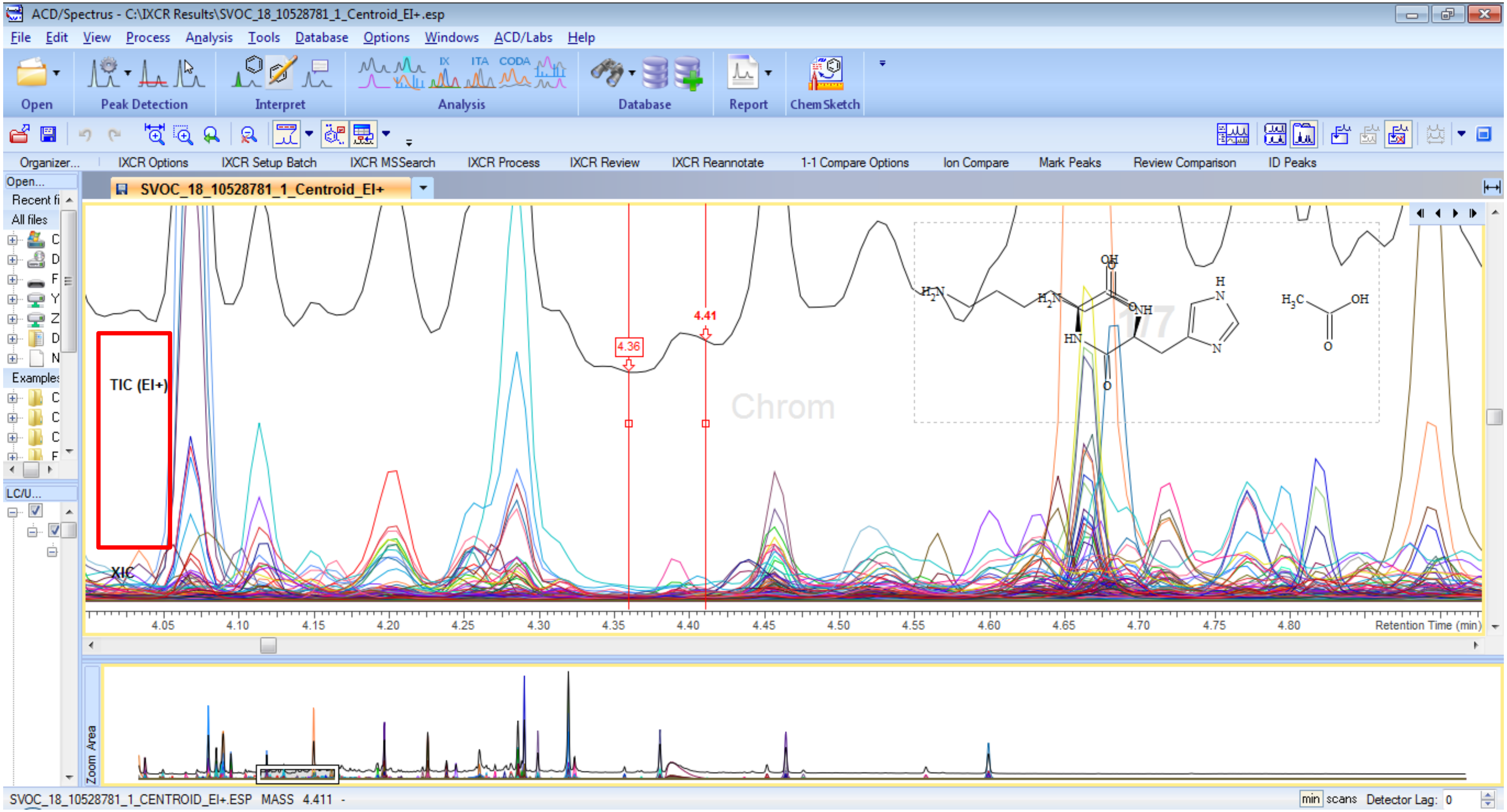
Match:
Expec. RT = 12.00
Net = 88
Weighted = 89

Raw vs. deconvoluted mass spectrum

Library hit vs. deconvoluted mass spectrum

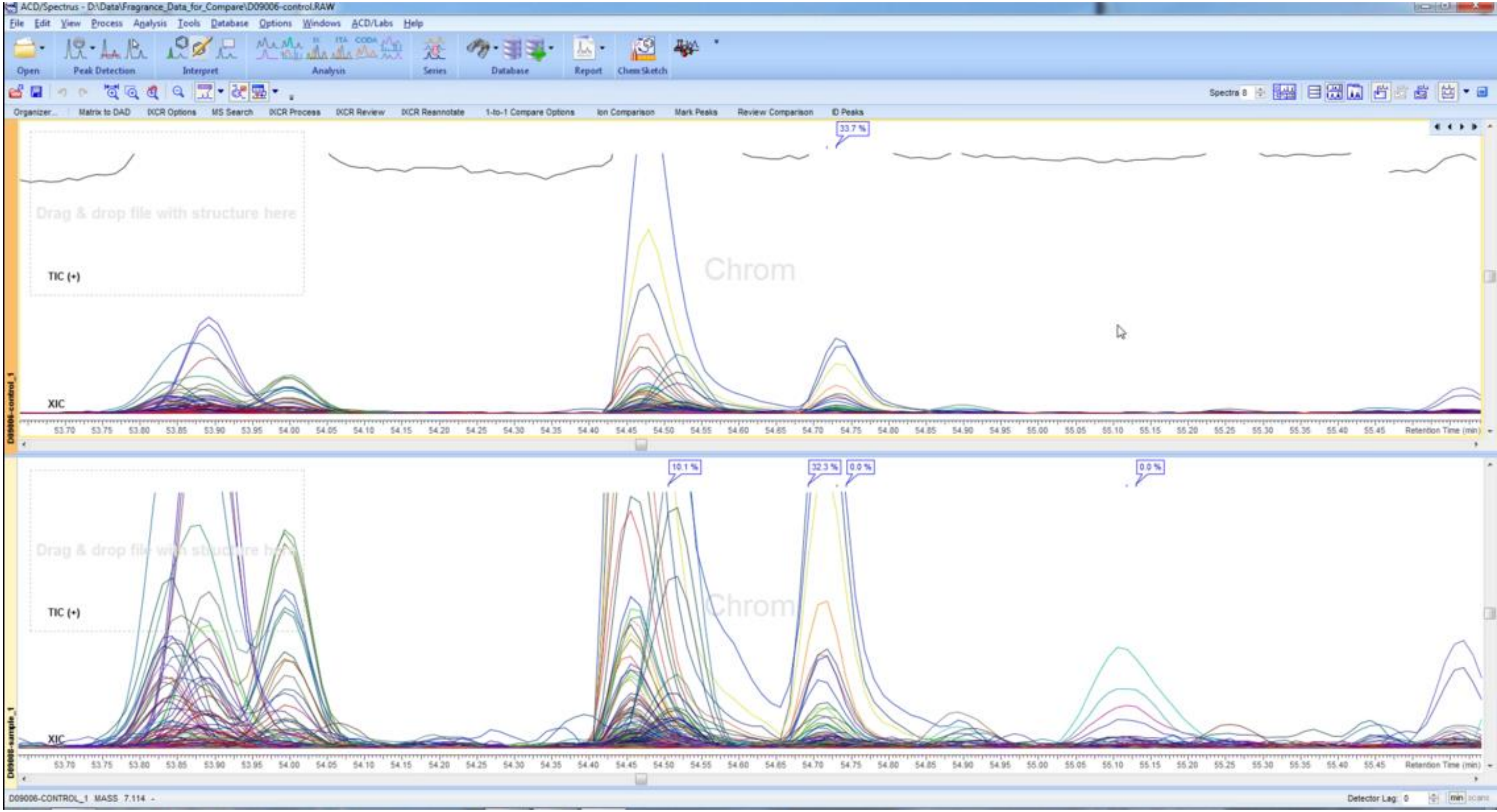
ACD/Spectrus Deconvolution

SVOCs in an Environmental sample



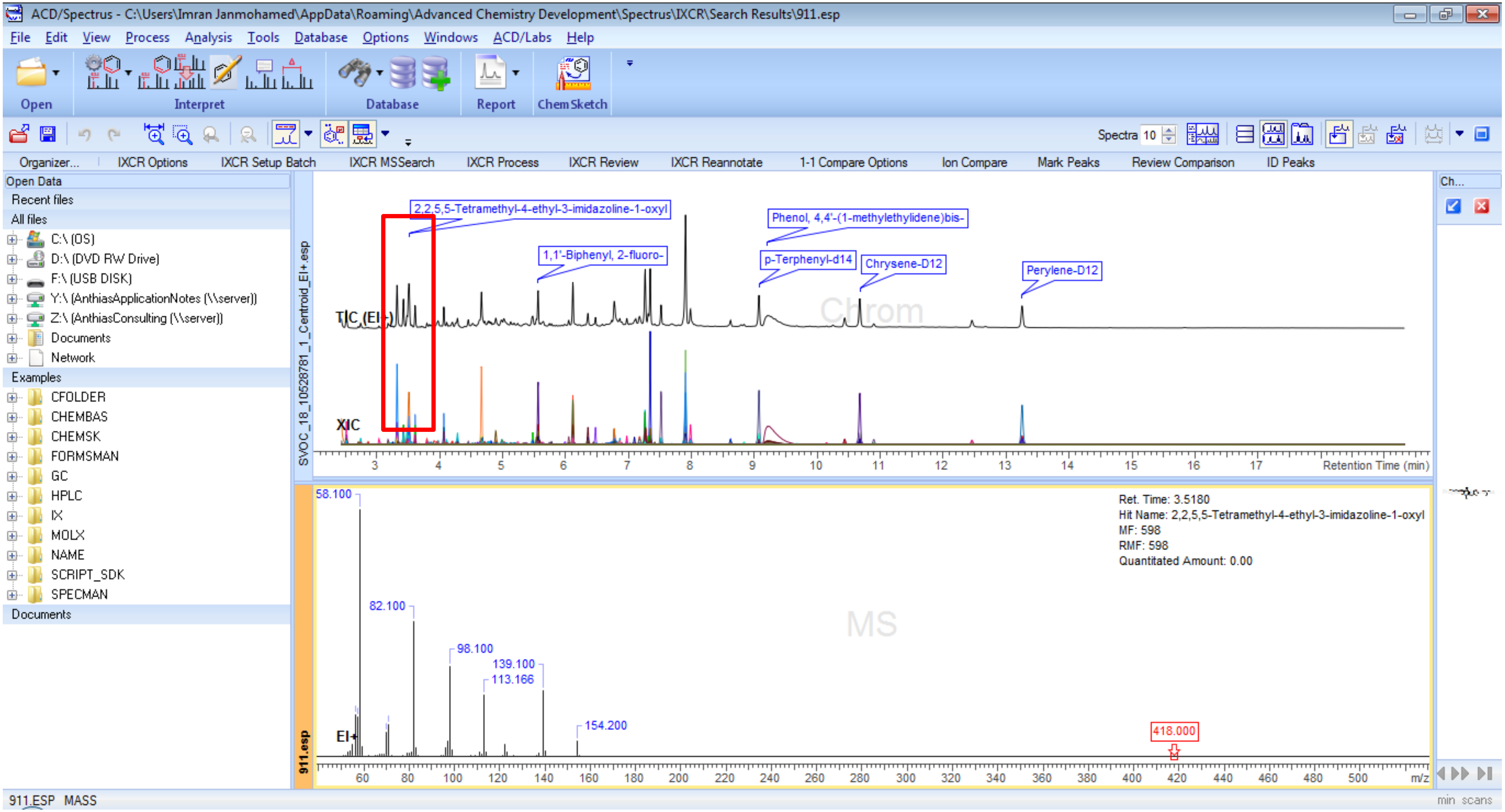
Courtesy of ACD/Labs

ACD/Spectrus Deconvolution



Courtesy of ACD/Labs

ACD/Spectrus Deconvolution


ACD/Spectrus - C:\Users\Imran Janmohamed\AppData\Roaming\Advanced Chemistry Development\Spectrus\IXCR\Search Results\911.esp

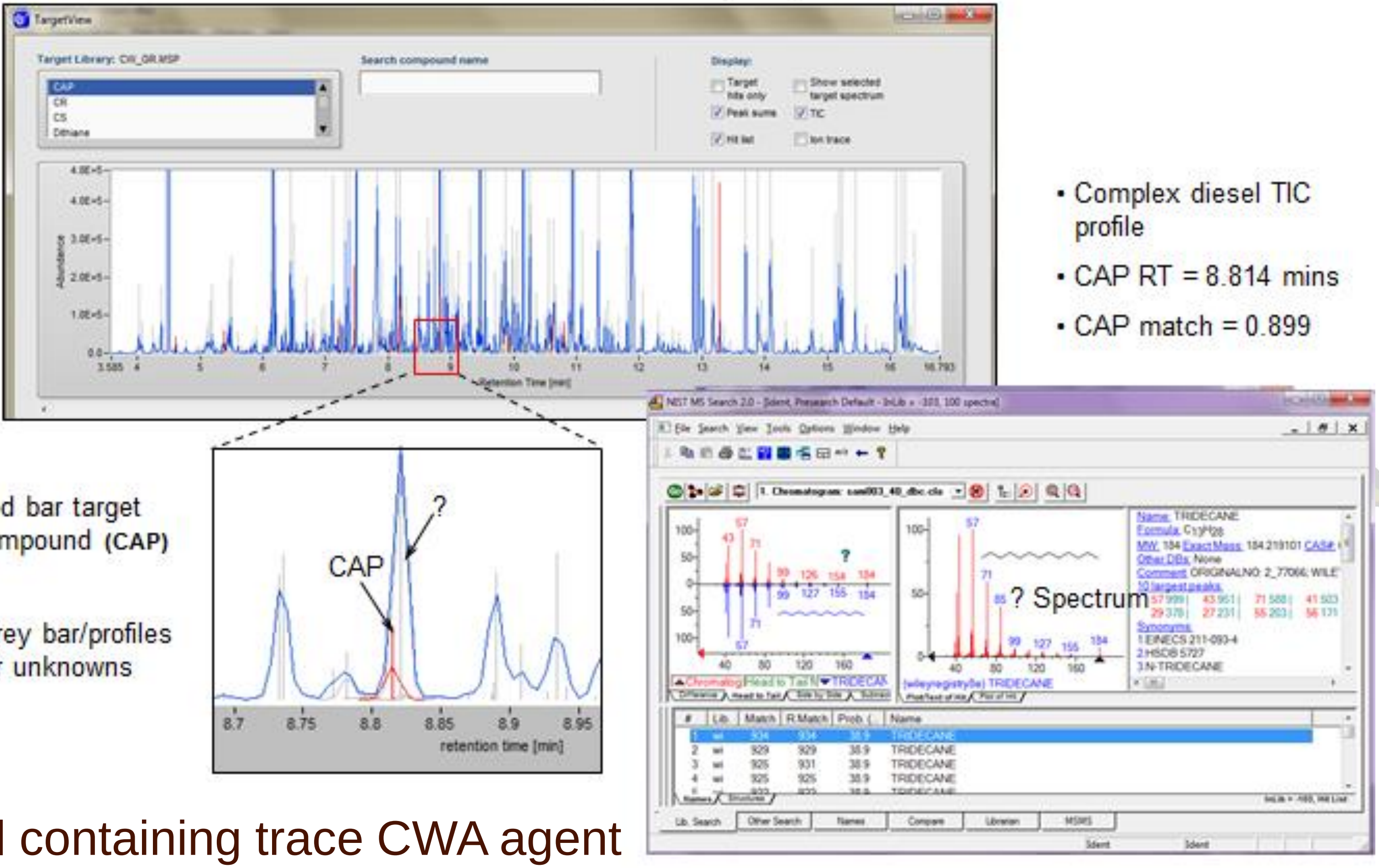
Ret. Time: 3.5180
Hit Name: 2,2,5,5-Tetramethyl-4-ethyl-3-imidazoline-1-oxyl
MF: 598
RMF: 598
Quantitated Amount: 0.00

Courtesy of ACD/Labs

TargetView deconvolution

Deconvolution of co-eluting compounds

- Identification of 2-Chloroacetophenone (CAP)



#	Lib.	Match	R.Match	Prob.	Name
1	wi	934	934	38.9	TRIDECANE
2	wi	929	929	38.9	TRIDECANE
3	wi	925	931	38.9	TRIDECANE
4	wi	925	925	38.9	TRIDECANE

- Complex diesel TIC profile
- CAP RT = 8.814 mins
- CAP match = 0.899

Red bar target compound **(CAP)**

Grey bar/profiles for unknowns

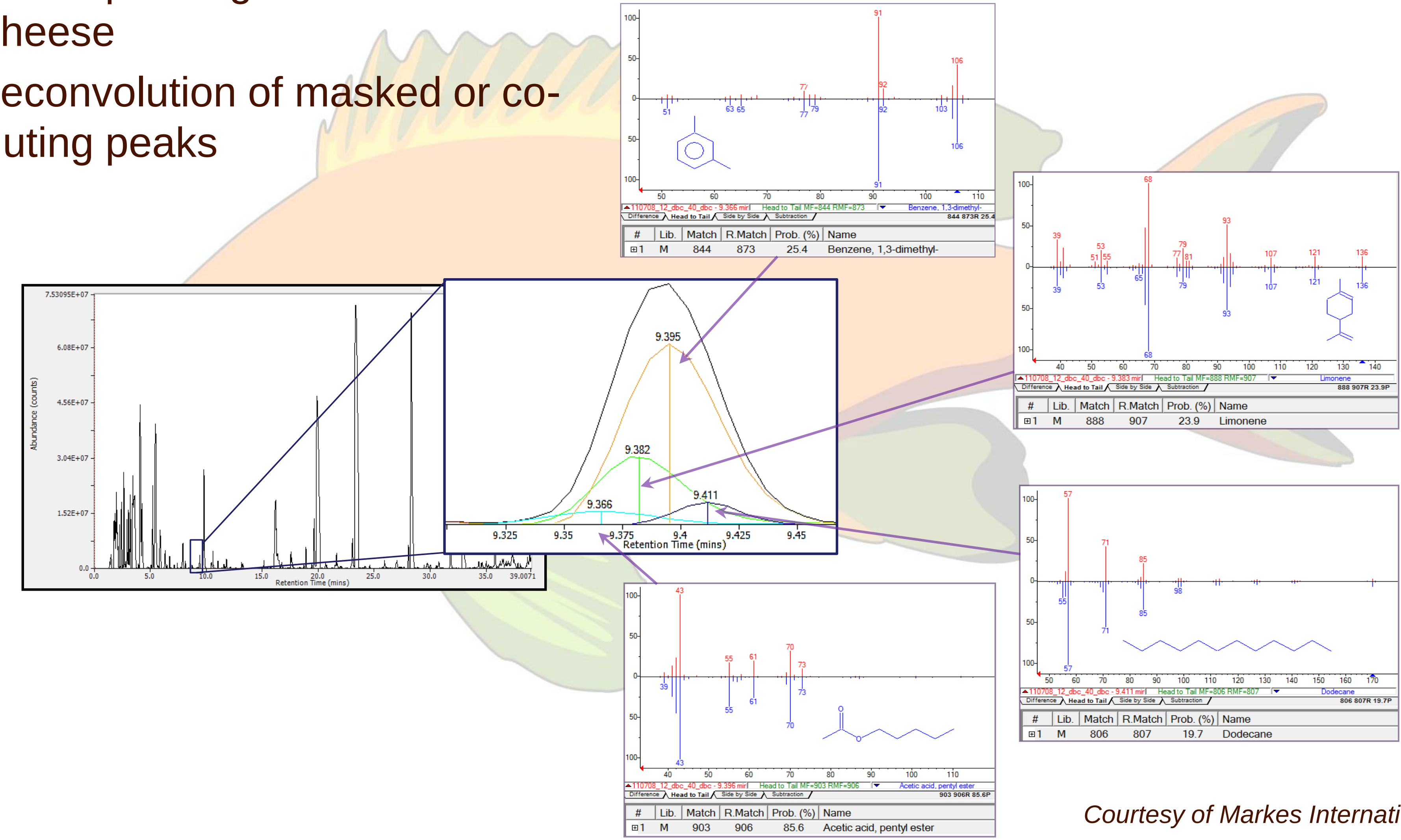
Diesel Oil containing trace CWA agent compounds

Courtesy of Markes International

TargetView deconvolution

Aroma profiling of Cheddar Cheese

Deconvolution of masked or co-eluting peaks



#	Lib.	Match	R.Match	Prob. (%)	Name
⊞1	M	844	873	25.4	Benzene, 1,3-dimethyl-

#	Lib.	Match	R.Match	Prob. (%)	Name
⊞1	M	888	907	23.9	Limonene

#	Lib.	Match	R.Match	Prob. (%)	Name
⊞1	M	806	807	19.7	Dodecane

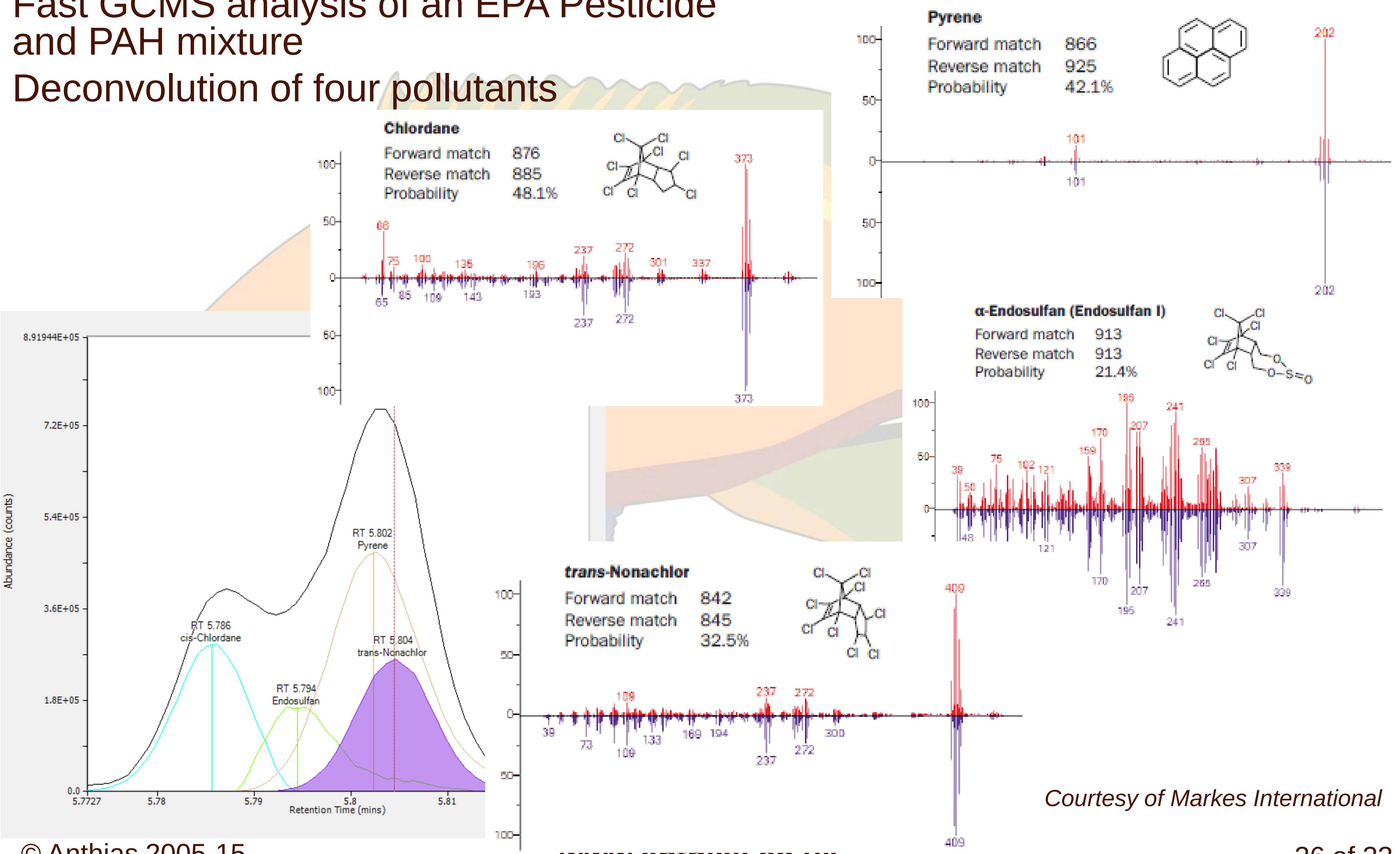
#	Lib.	Match	R.Match	Prob. (%)	Name
⊞1	M	903	906	85.6	Acetic acid, pentyl ester

Courtesy of Markes International

TargetView deconvolution

Fast GCMS analysis of an EPA Pesticide and PAH mixture

Deconvolution of four pollutants



Pyrene

Forward match	866
Reverse match	925
Probability	42.1%

Chlordane

Forward match	876
Reverse match	885
Probability	48.1%

α-Endosulfan (Endosulfan I)

Forward match	913
Reverse match	913
Probability	21.4%

trans-Nonachlor

Forward match	842
Reverse match	845
Probability	32.5%

Courtesy of Markes International

Pros & cons deconvolution

- Help to identify peaks you don’t know are there!
- Can provide cleaned-up mass spectra that is difficult to get manually
- Can be used on full scan + SIM/MRM data
- After peak finding & deconvolution, can search libraries automatically & use retention time/index as qualifier
- Software dependent, need to optimise settings to pull out all useful peaks
  - Too many ‘noise’ peaks vs. missing peaks of interest
- Cannot be used identify isomers
  - Can use retention indices automatically
- Cannot deconvolute peaks of identical retention time & shape

Questions?

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Thank you