

Fa. Leco [*Christian Zühlke*]

**„Vorzüge der GC-TOFMS und GCxGC-TOFMS
anhand von applikativen Beispielen
aus dem Bereich der Wasseranalytik“**

Langenauer Wasserforum

Langenau, 9. – 10. November 2009

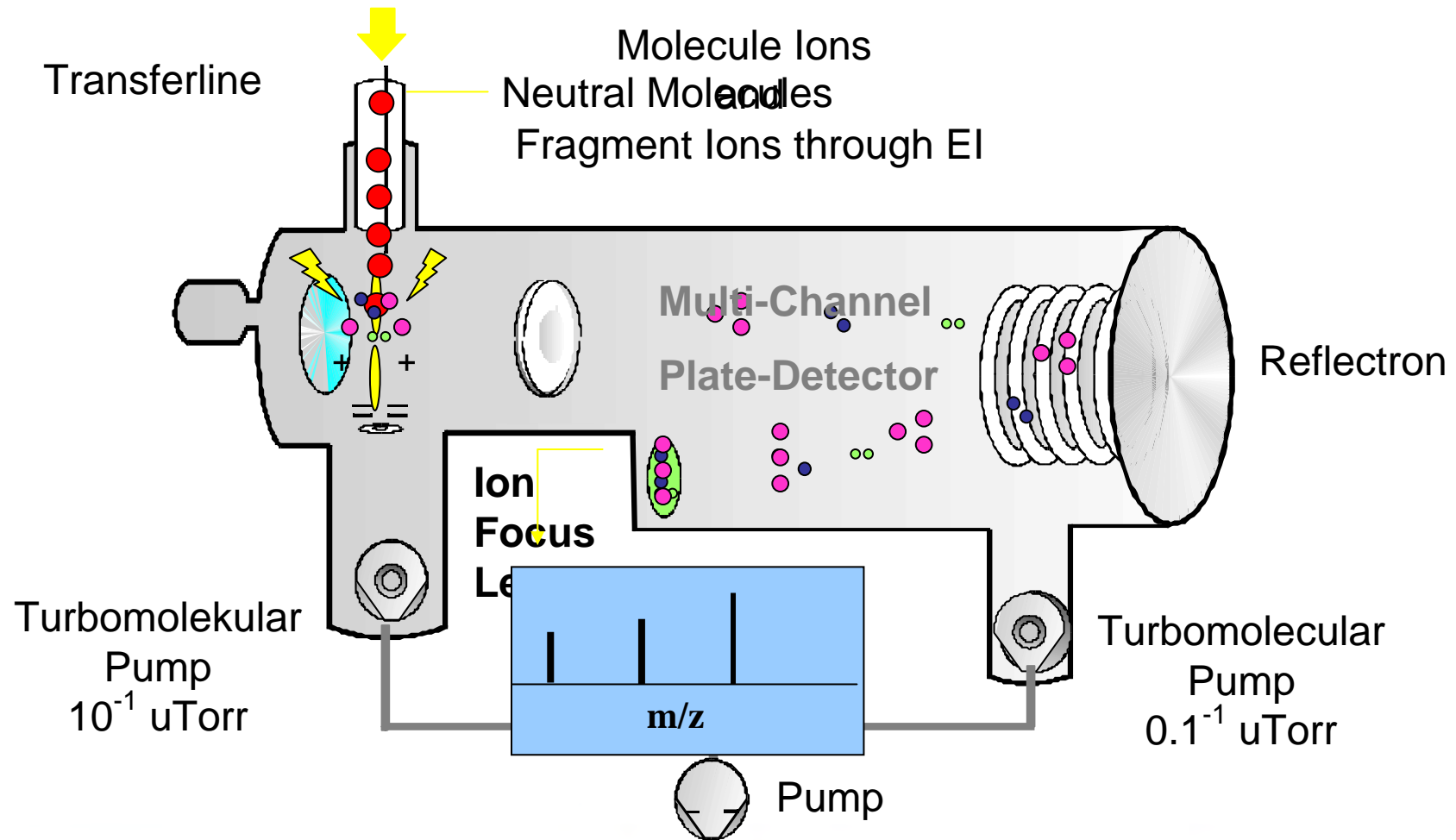
**“ Applikative Möglichkeiten mittels GC-TOFMS
und GCxGC TOFMS ”**

Outline

- **Introduction to GC TOFMS Technique**
 - *Description*
 - *Features and Benefits*
 - *One Dimensional Water Application Example*
- **Introduction to Comprehensive GCxGC TOFMS**
 - *Description and Overview*
 - *Water Application Example*
 - *Power of Classification Feature*
- **Conclusions**

Overview and Function of TOF

Injection of the Sample



GC TOFMS – Instrument Configuration



Pegasus[®] HT GC-TOFMS including Gerstel Autosampler and other Sample Prep Equipment



TruTOF HT GC-TOFMS

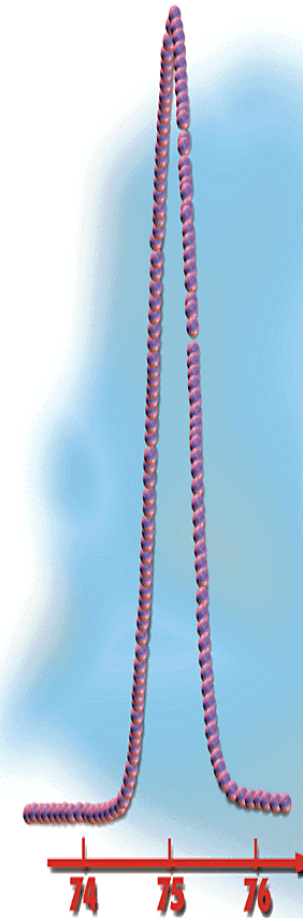
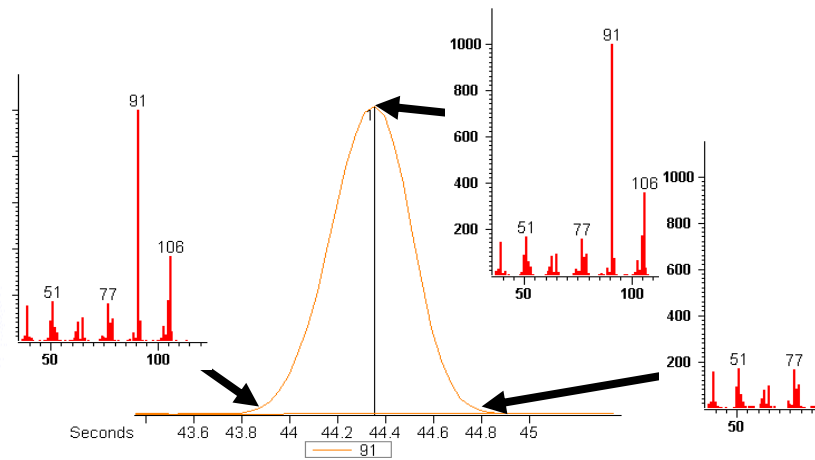
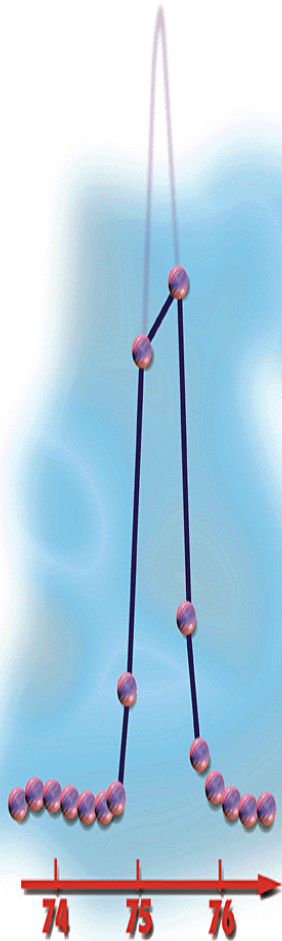


Major Benefits of TOFMS

- Full mass spectrum acquired
 - Powerful confirmation of compound in sample
- Full mass range sensitivity
 - Low pg range for most compounds
- Fast acquisition rates
 - Up to hundreds of spectra/sec
 - Defines narrow peaks from fast GC techniques

LECO Time-of-Flight Mass Spectrometer

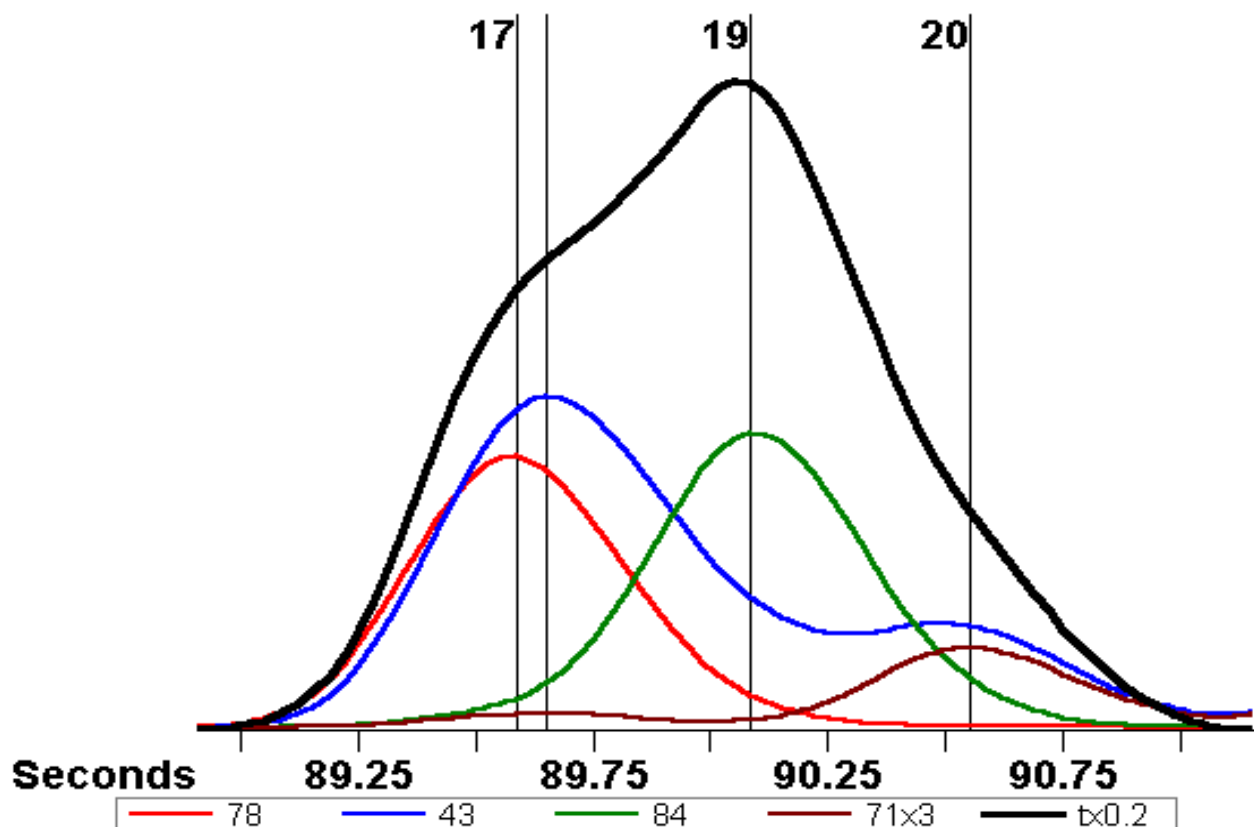
„Full Spectra“
Maximum 500 Spectren/sek



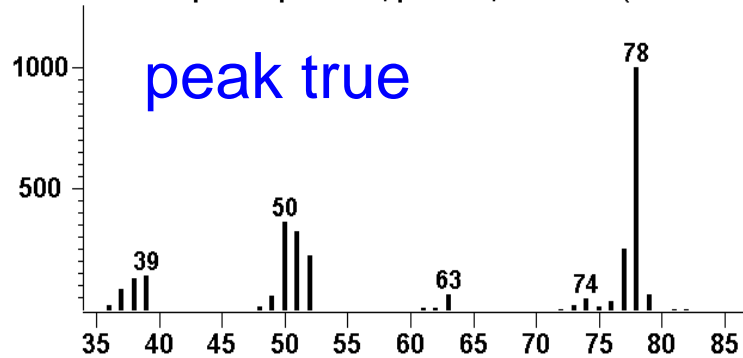
Major Benefits of TOFMS

- **Automated peak find**
 - Find compounds in normal or complex matrix
 - Locate non-target compounds
- **Spectral deconvolution**
 - Quality mass spectra from coeluting peaks
 - Easy Library search with deconvoluted spectra
 - Time-compressed chromatography

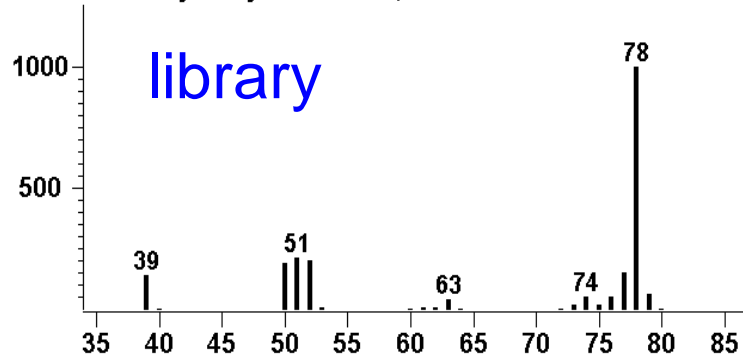
LECO ChromaTOF[®] - Software Deconvolution



Peak True - sample "Naphtha:5", peak 17, at 89.586 (scan 2685)

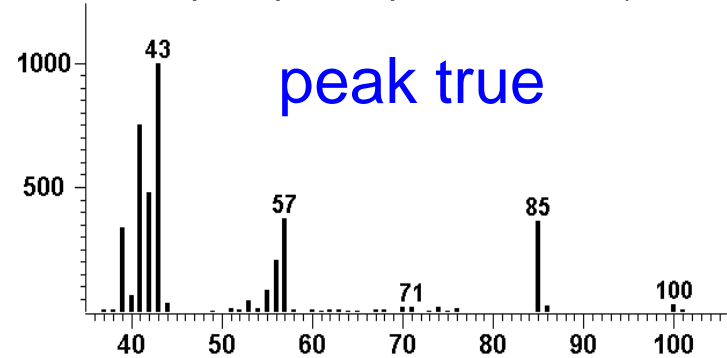


Peak Hit - library entry "Benzene", match 888

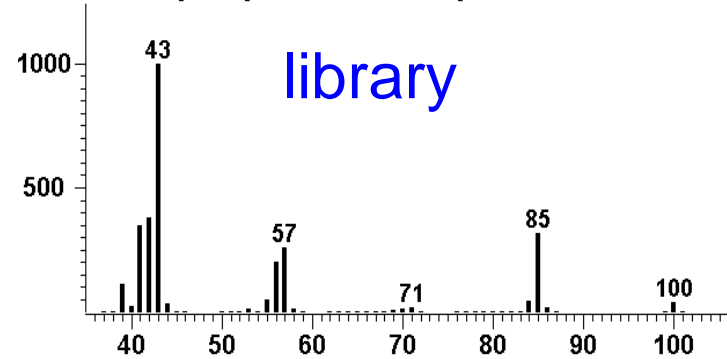


Benzene - 888

Peak True - sample "Naphtha:5", peak 18, at 89.6527 (scan 2687)



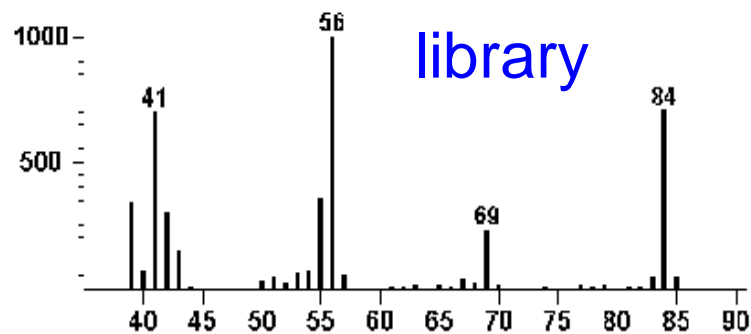
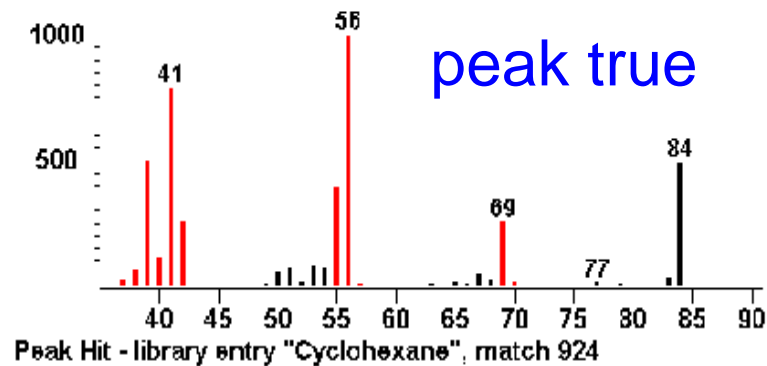
Peak Hit - library entry "Hexane, 2-methyl-", match 863



2-Methyl-hexane - 863

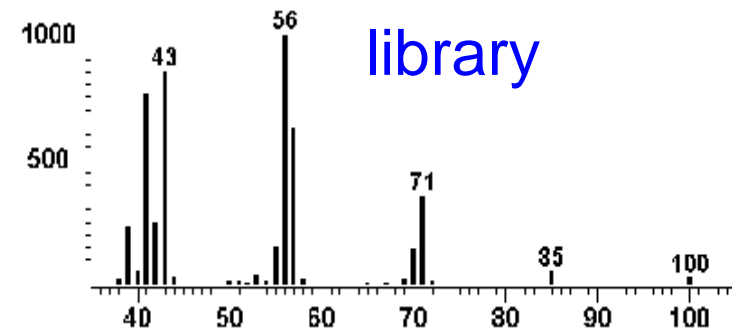
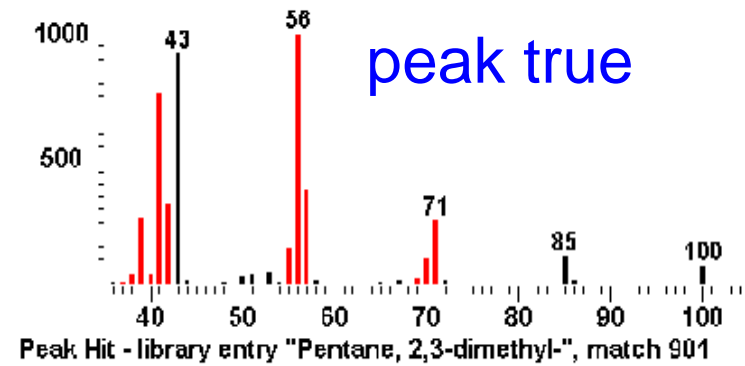
Coeluting Peaks will be right detected automatically !

Peak True - sample "Naphtha:5", peak 19, at 90.086 (scan 2700)



Cyclohexane - 924

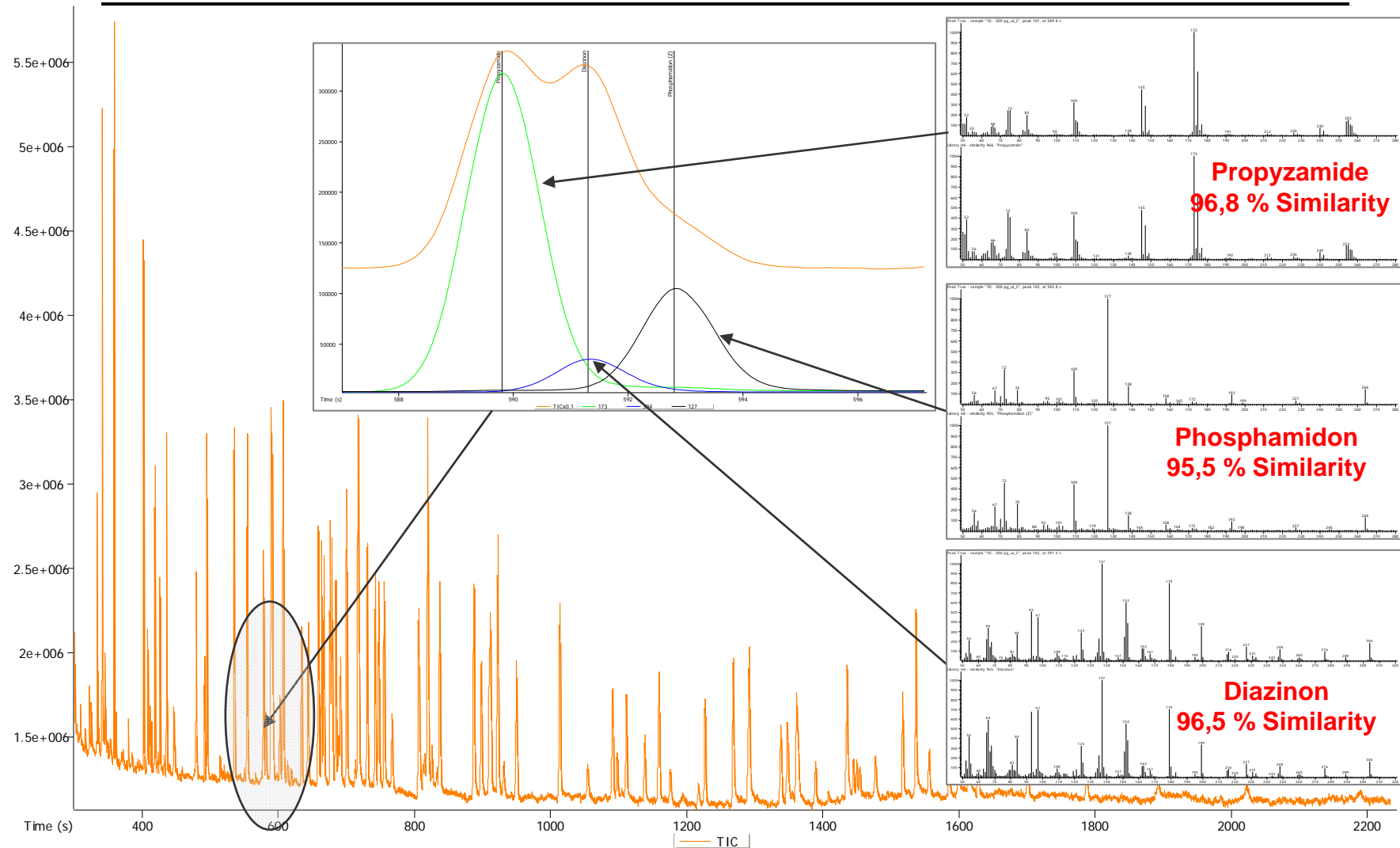
Peak True - sample "Naphtha:5", peak 20, at 90.5527 (scan 2714)



2,3-Dimethyl-pentane - 901

Also valuable for Compounds with same Masses !

LECO ChromaTOF[®]-Software Deconvolution

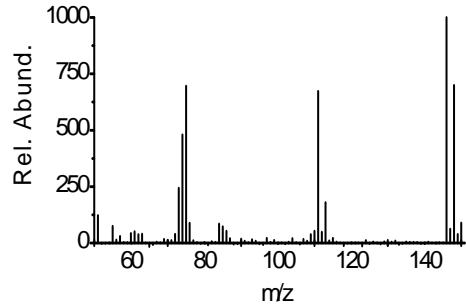


TOFMS Spectral Reproducibility

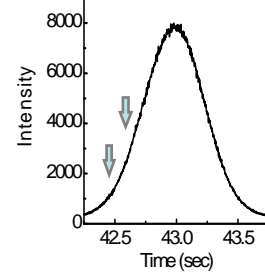
- **5000 pulsed transients (spectra) per second**
 - Ion packets are formed, extracted, and mass analyzed almost simultaneously
 - “Snapshot” technique
- **Concentration changes occurring in the source during GC peak elution don't affect spectral quality in TOFMS**
 - Non-skewed mass spectra
 - Makes deconvolution algorithms easier and reliable

Spectral Reproducibility

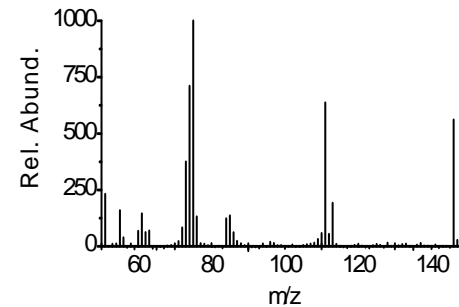
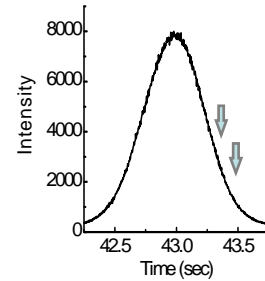
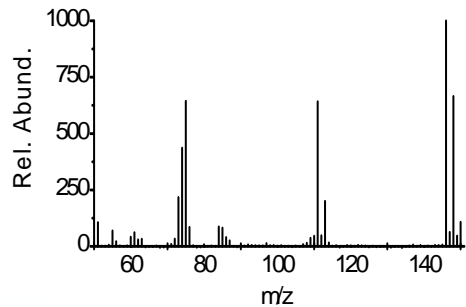
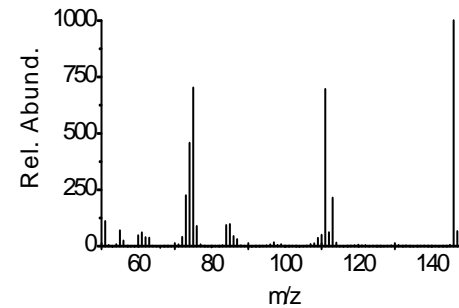
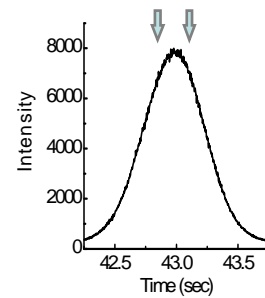
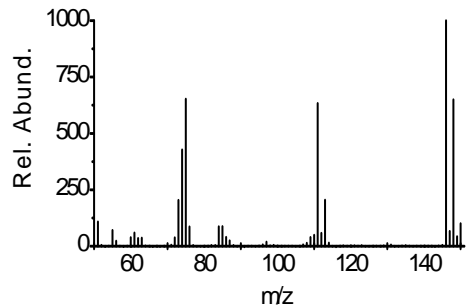
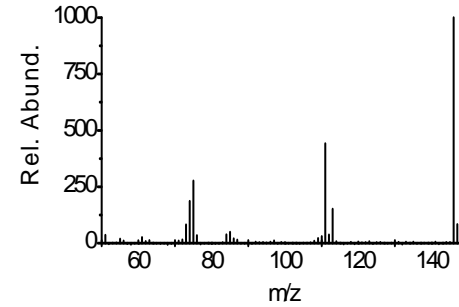
Simultaneous Sampling



GC Peak



Scannen



Automated Peak Find

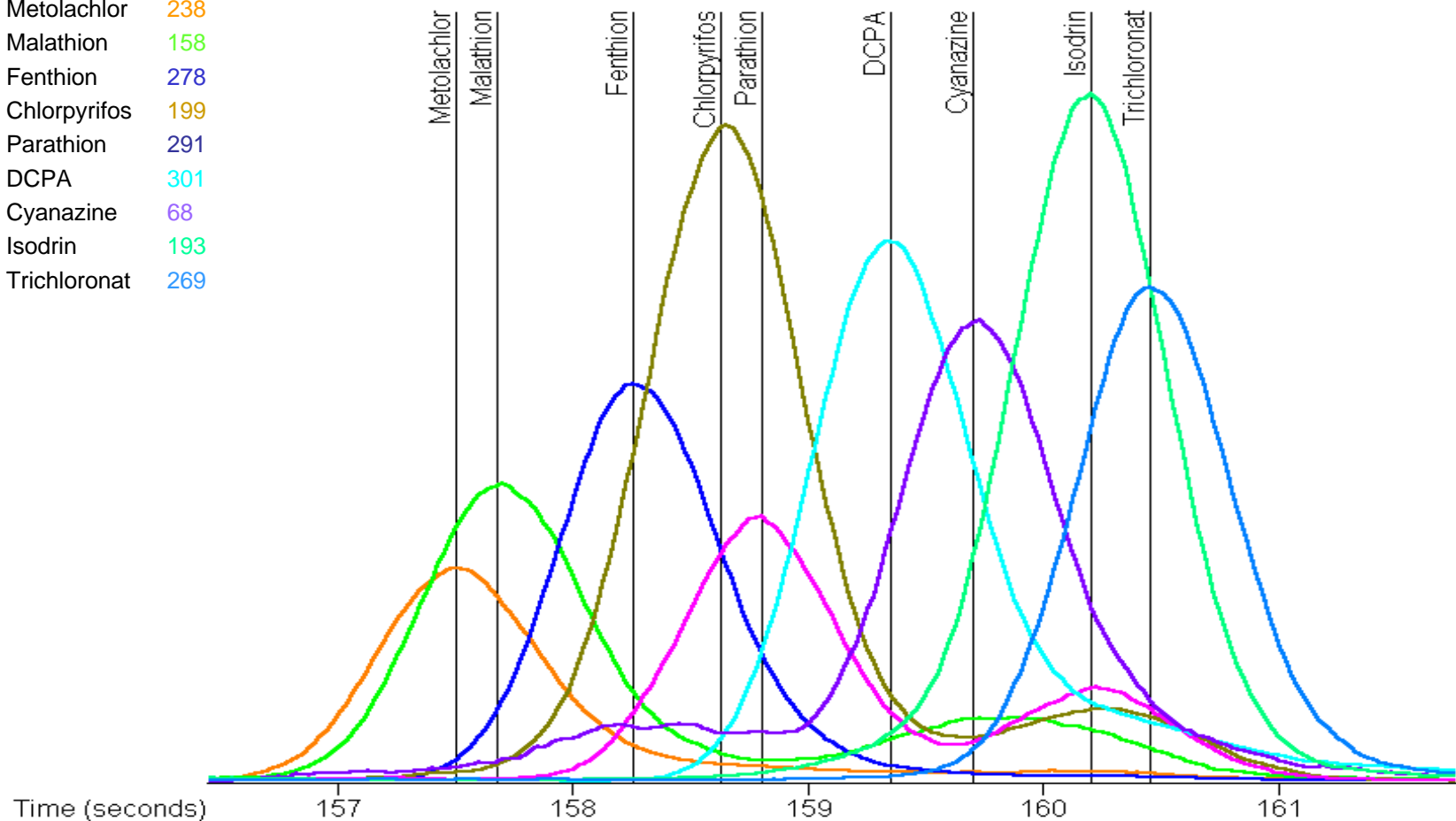
- **Mass spectrometer requirements**
 - Acquisition rate sufficient to define peaks
 - Reproducible mass spectra across peak
- **Software requires:**
 - Estimated peak width
 - Signal-to-noise desired
 - “How many peaks do I find?”

Acquisition Rate for Peak Find

- Important for closely eluting peaks
- Faster rate can improve peak find
- Spectral deconvolution may also improve
- Example: nine pesticides eluting in 4 sec
 - Peak widths = 1.5 to 2 sec

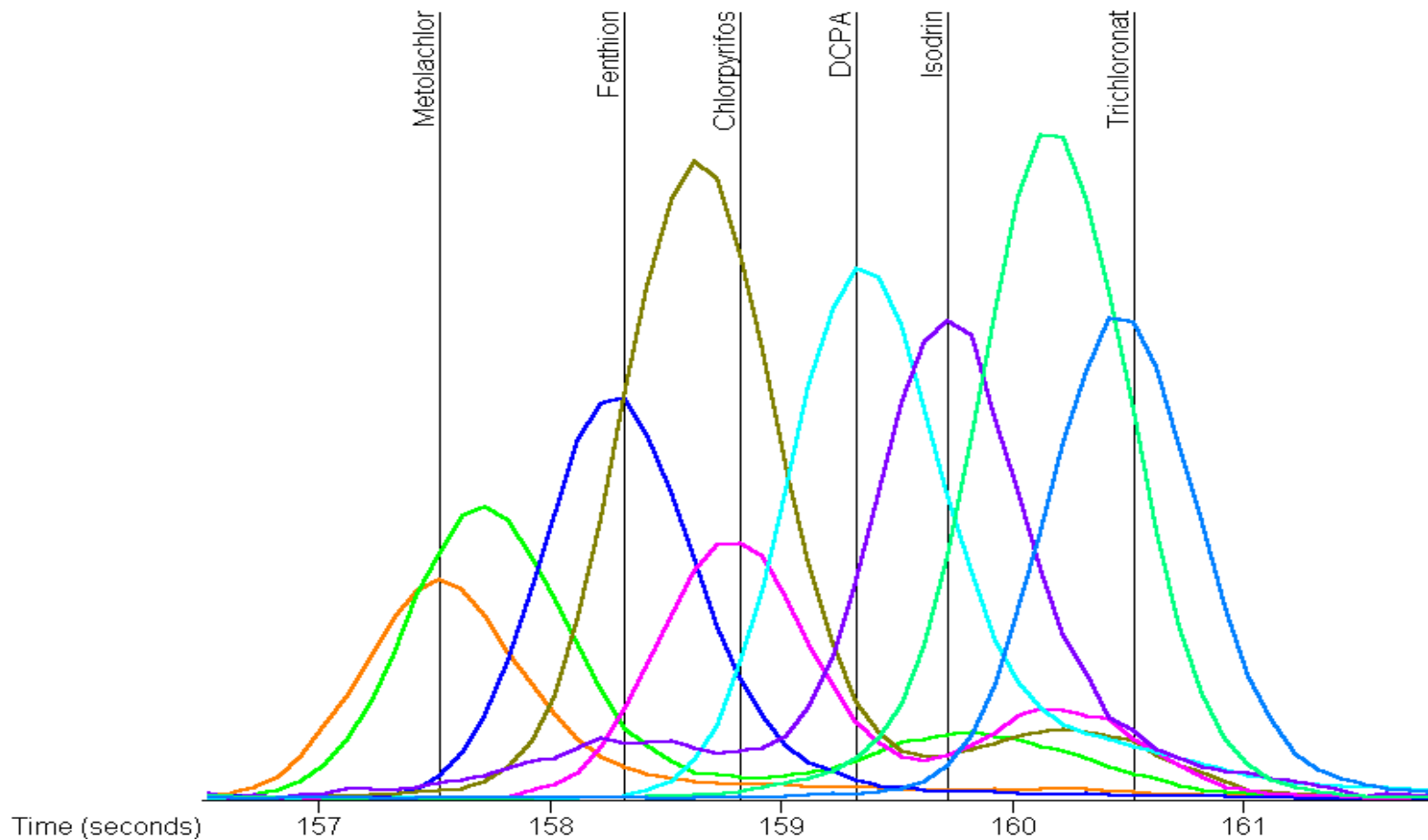
Peak Find at 40 Spectra/sec

Metolachlor	238
Malathion	158
Fenthion	278
Chlorpyrifos	199
Parathion	291
DCPA	301
Cyanazine	68
Isodrin	193
Trichloronat	269



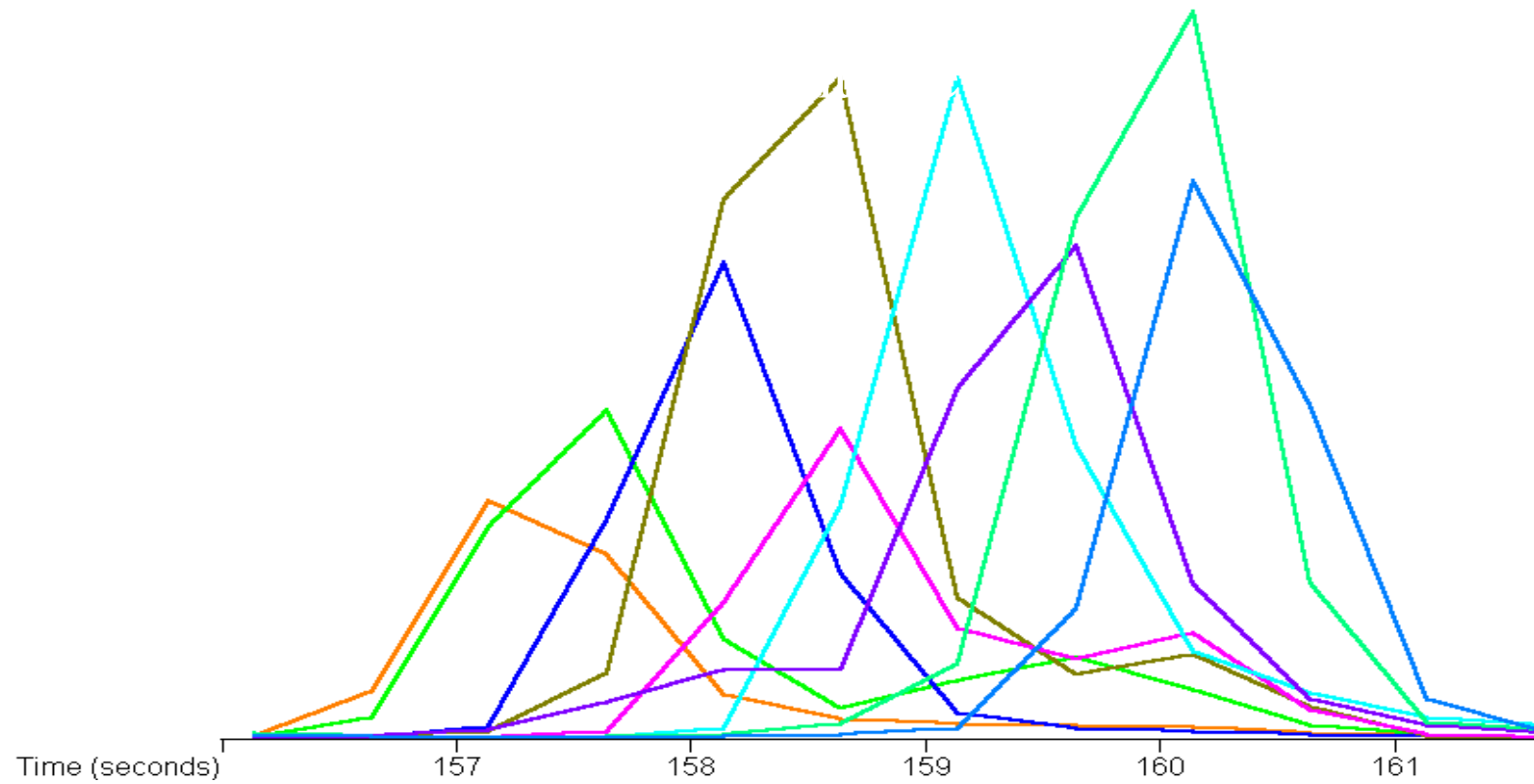
9 peaks located

Peak Find at 10 Spectra/sec



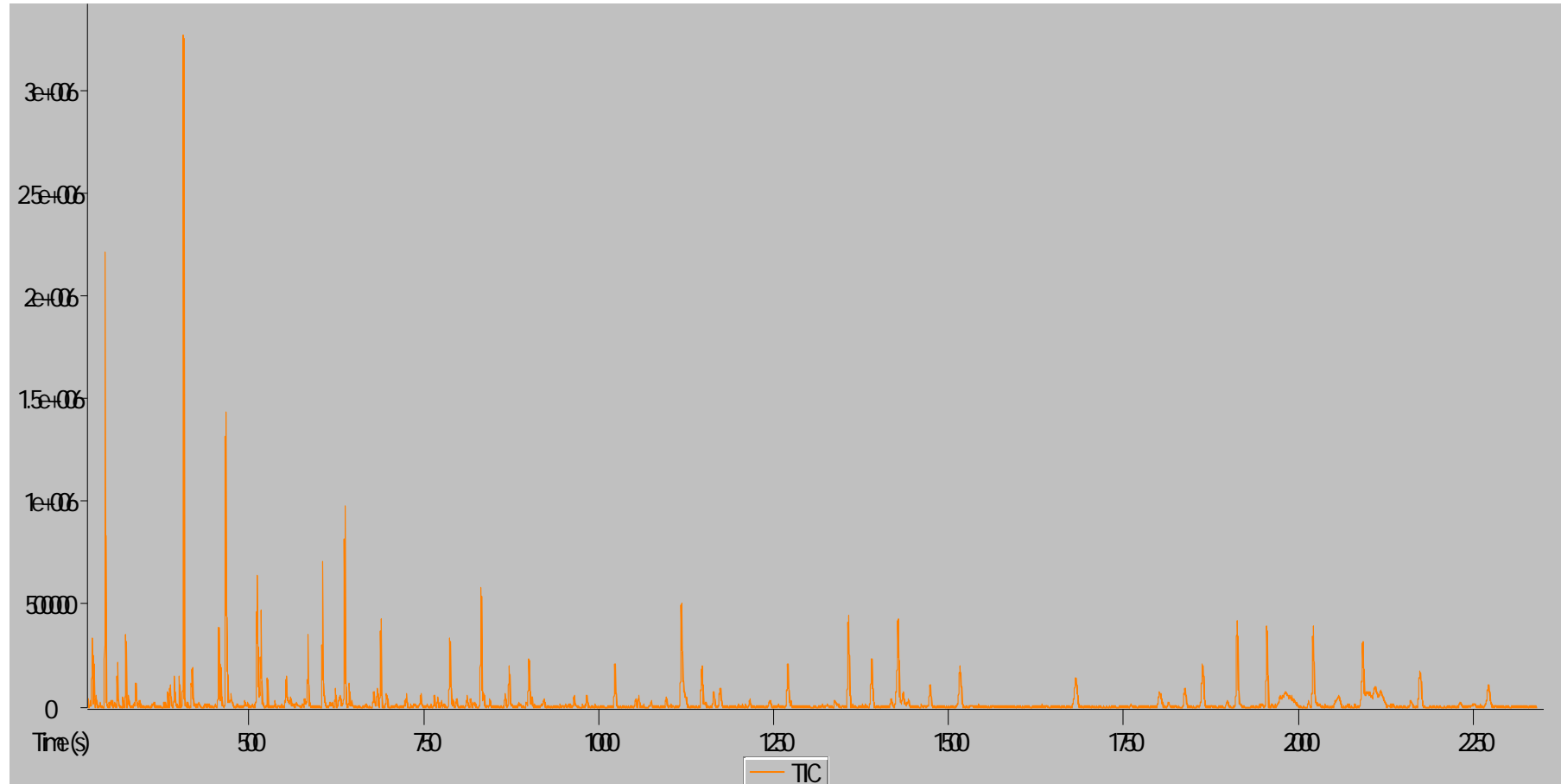
6 peaks located

2 Spectra/sec



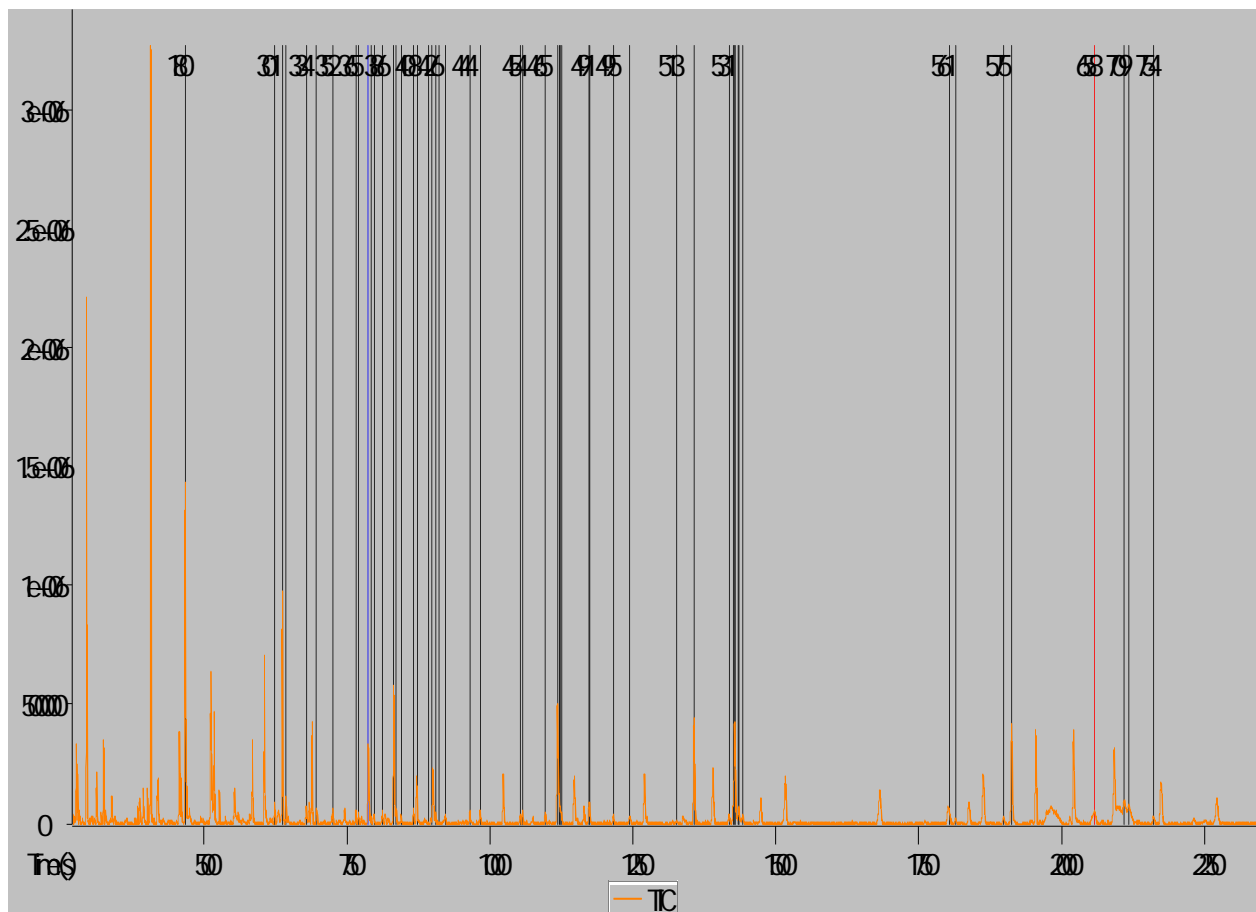
Automated peak find is not possible !

TIC of Drinking Water Sample



Showing the TIC Chromatogramm !

TIC of Drinking Water Sample

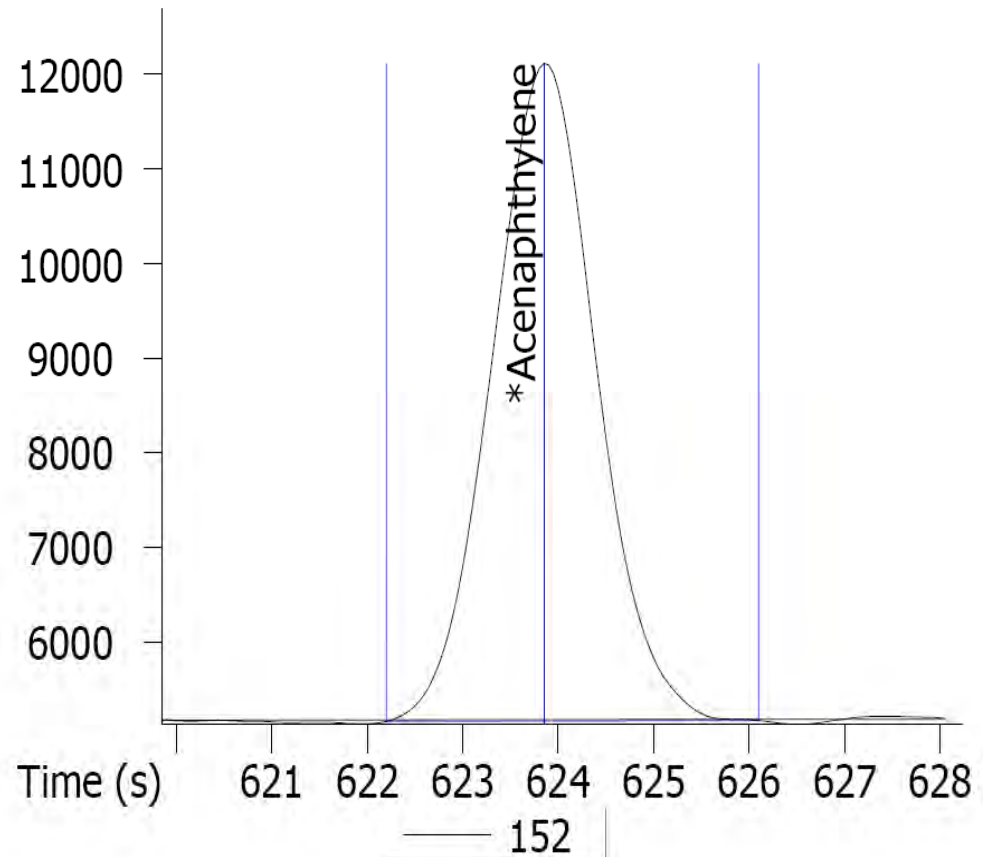
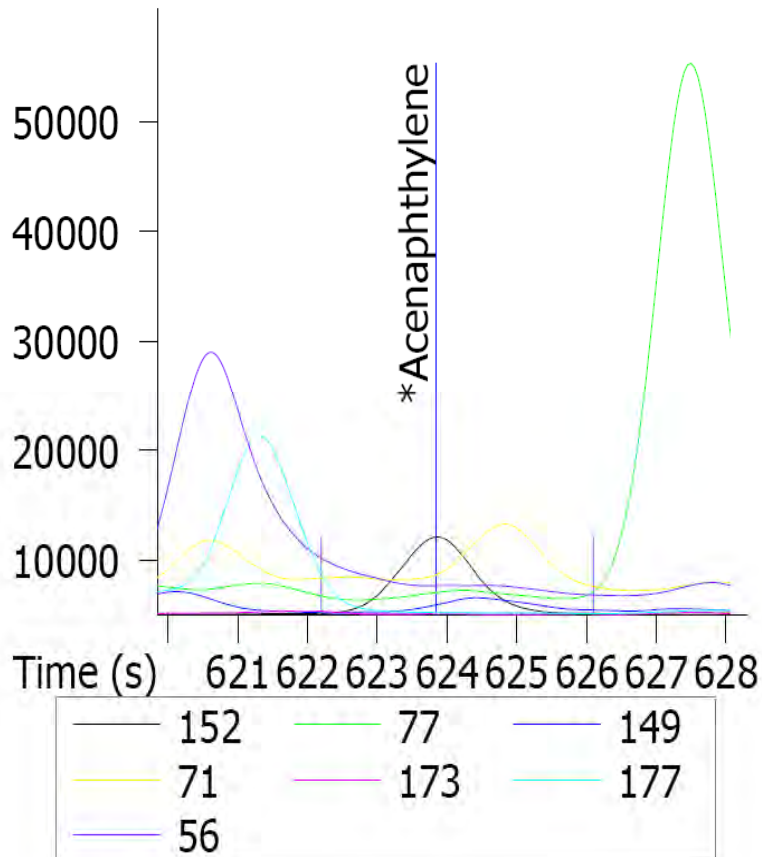


R.T. (s)	Name	Quant Masses	Quant S/N	Concentration	Match
623.7	*Acenaphthylene	152	1615	53	978
643.5	*2-Chlorobiphenyl	188	1360	50	977
678.9	*Diethyltoluamide	119	540	46	970
696.4	*Fluorene	165	646	50	982
725.4	*Triallyl isocyanurate	249	191	51	975
765.7	*2,3-Dichlorobiphenyl	222	497	57	940
769.9	*Benzene, hexachloro-	284	161	40	901
787.1	*Simazine	201	121	NA	682
792.0	*Atrazine	200	281	61	897
797.4	*Tri(2-chloroethyl) phosphate	249	81	45	954
811.9	*α-Lindane	181	195	59	935
836.1	*Phenanthrene	170	932	52	966
841.8	*Anthracene	178	787	55	970
866.8	*Galaxolide 1	243	519	56	998
872.8	*Caffeine	194	197	51	924
872.8	*1,1'-Biphenyl, 2,3,6-trichloro-	258	473	58	965
893.0	*Galaxolide 2a	243	15	39	941
897.6	*Galaxolide 2:2	243	15	43	932
905.1	*Alachlor	188	205	67	831
910.8	*Galaxolide 2	243	31	58	959
922.0	*Heptachlor	272	83	43	944
965.4	*1,1'-Biphenyl, 2,2',4,4'-tetrachloro-	292	382	53	968
963.3	*Alolin	65	129	62	948
1053.1	*Heptachlor epoxide	353	82	45	764
1057.4	*1,1'-Biphenyl, 2,2',3',4',6-Pentachloro-	326	229	53	930
1096.8	*trans-Chlordane	373	128	43	834
1121.0	*cis-Chlordane	373	118	46	769
1122.9	*Pyrene	202	982	50	969
1125.4	*cis-Nonachlor	409	106	40	922
1173.4	*1,1'-Biphenyl, 2,2',3,4,5,5'-hexachloro-	360	239	54	921
1174.7	*Dieldrin	79	93	69	873
1216.2	*Erdrin	281	16	40	877
1244.9	*trans-Nonachlor	409	91	43	820
1326.5	*Carbamazepine	193	87	55	688
1418.5	*1,1'-Biphenyl, 2,2',3,3',4,4',6'-heptachloro-	394	134	50	903
1426.8	*Benz[a]anthracene	228	863	51	970
1428.8	*1,1'-Biphenyl, 2,2',3,3',4,5',6,6'-octachloro-	428	143	42	628
1434.9	*Chrysene	228	829	53	978
1435.7	*p,p'-Methoxychlor	227	644	51	970
1443.0	*Diazepam	256	166	56	862
1803.8	*Benzofluoranthene	252	494	61	952
1814.5	*Benz[k]fluoranthene	252	462	62	912
1898.5	*Benz[a]pyrene	252	567	58	943
2055.4	*Cholesterol	301	157	NA	370
2109.7	*Indeno[1,2,3-cd]pyrene	276	563	54	966
2118.4	*Dibenz[a,h]anthracene	278	541	54	964
2161.2	*Benz[ghi]perylene	276	664	55	972

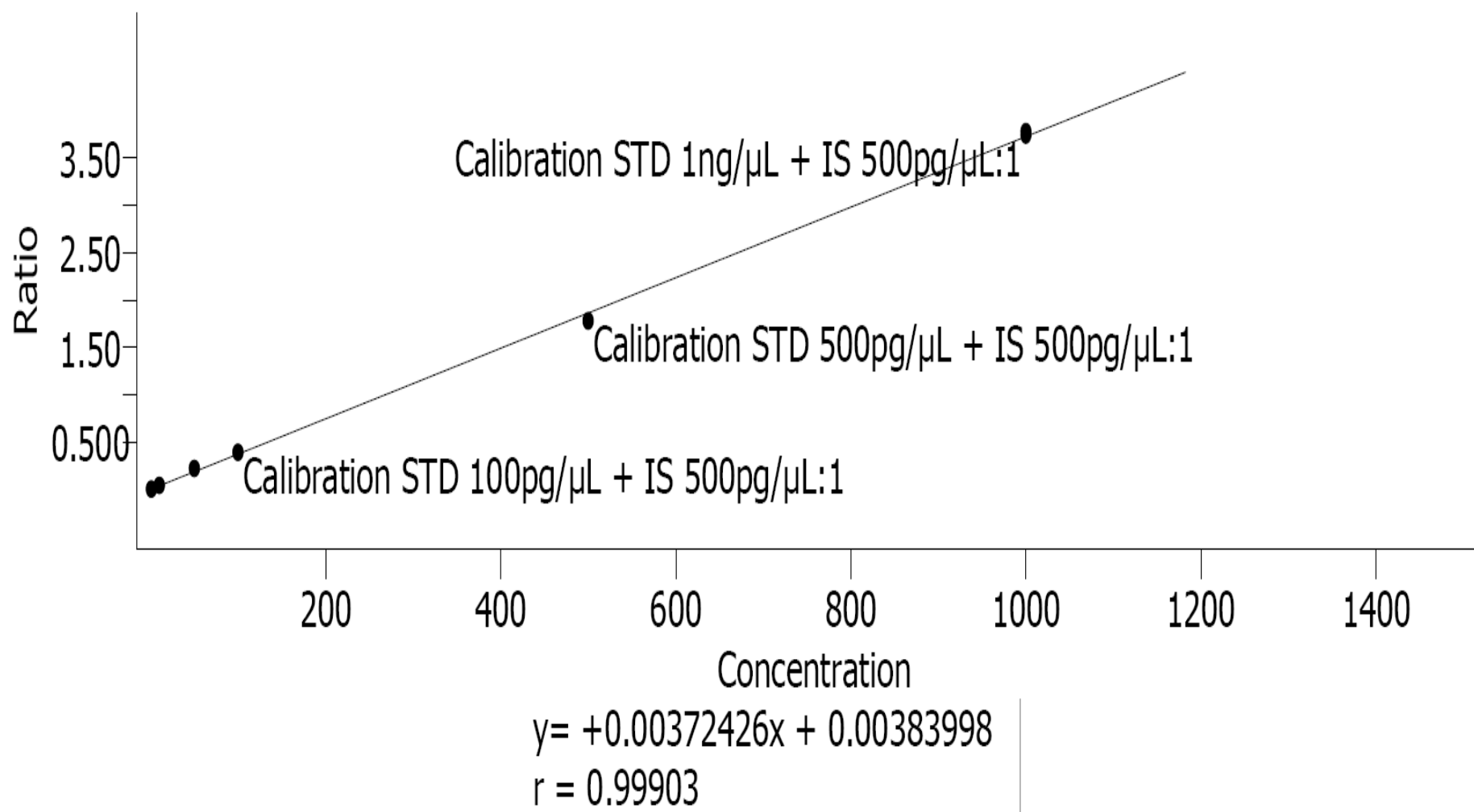
Showing only specified Target Compound Peaks !

Target Analysis – “Acenaphthylene”(10ppb)

EIC - Chromatogramm Co-eluierender Peaks & EIC - Chromatogramm der Quantifizierungsmassen

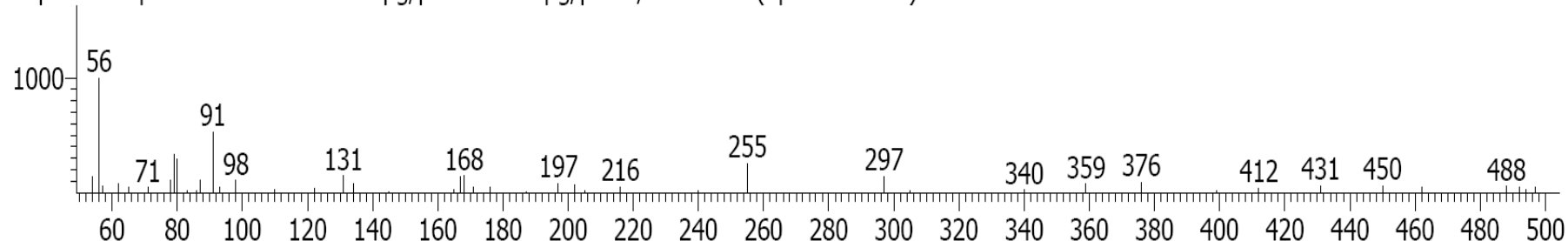


Calibration Curve Acenaphthylene (1-1000pg/μl)

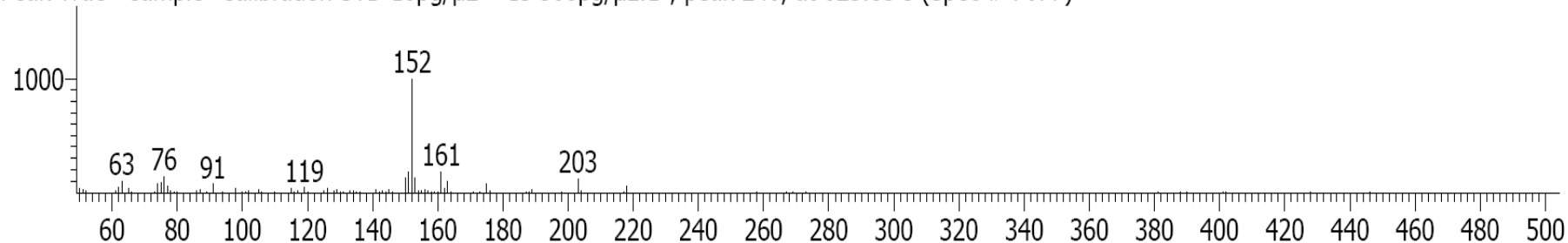


Mass Spectral Comparison of Acenaphthylene

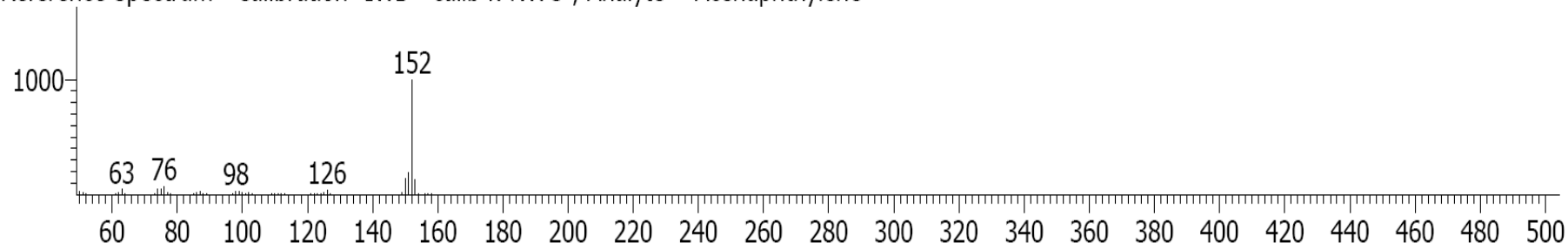
Caliper - sample "Calibration STD 10pg/ μ L + IS 500pg/ μ L:1", 0 s to 0 s (Spec # 0 to 0)



Peak True - sample "Calibration STD 10pg/ μ L + IS 500pg/ μ L:1", peak 240, at 623.85 s (Spec # 7077)

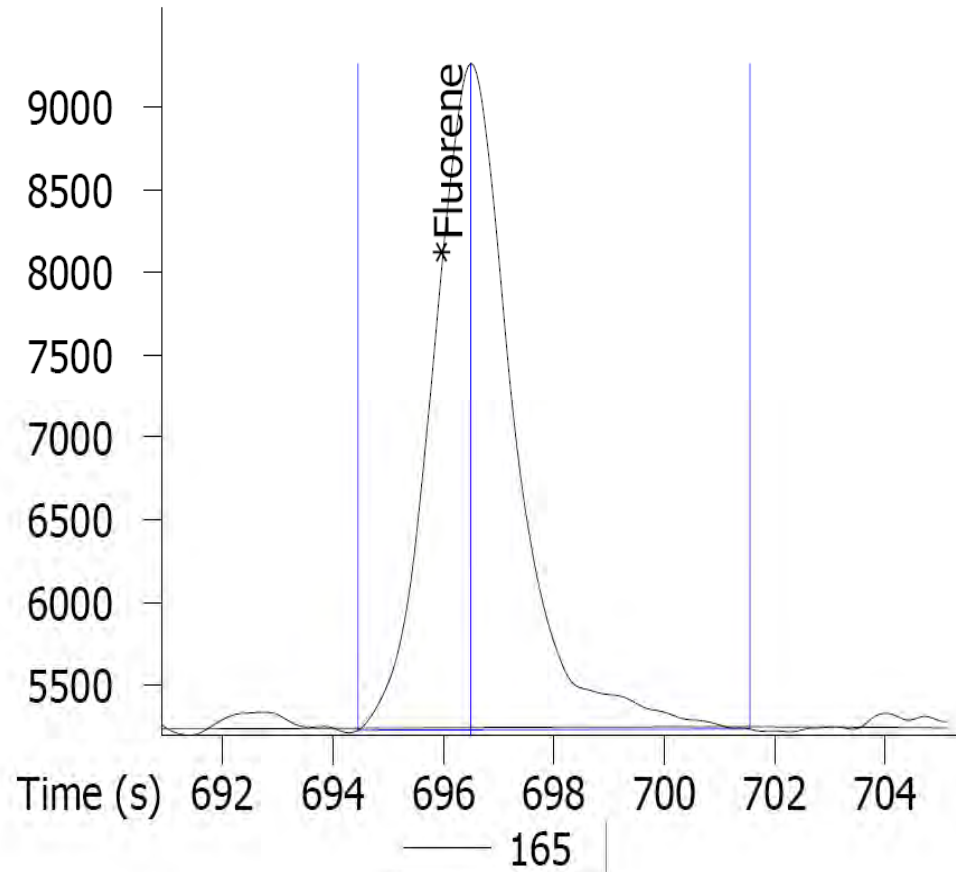
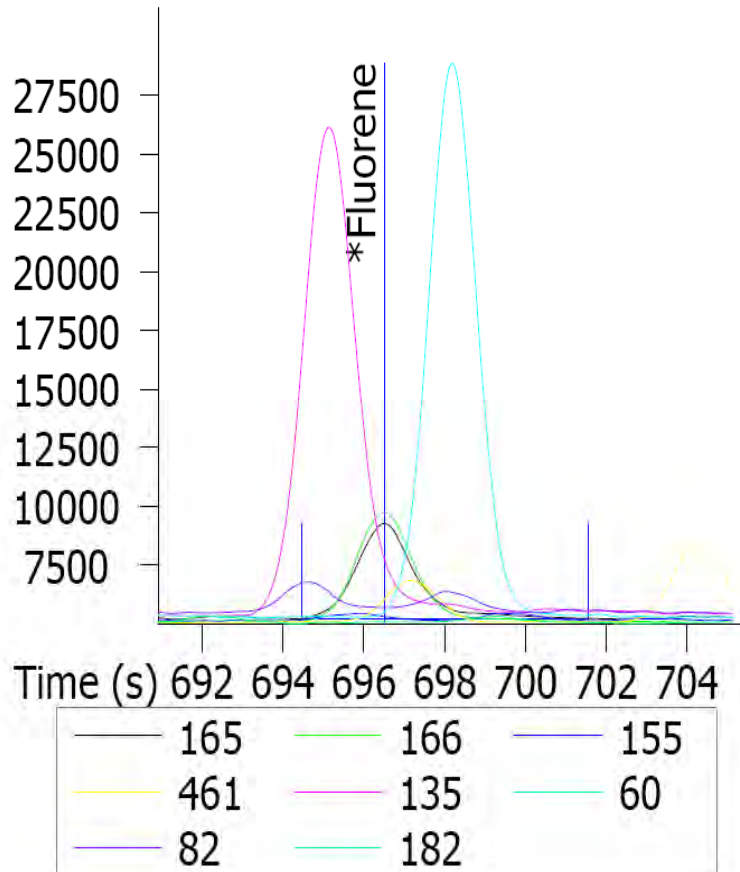


Reference Spectrum - Calibration "IWB - calib f. NWG", Analyte "*Acenaphthylene"

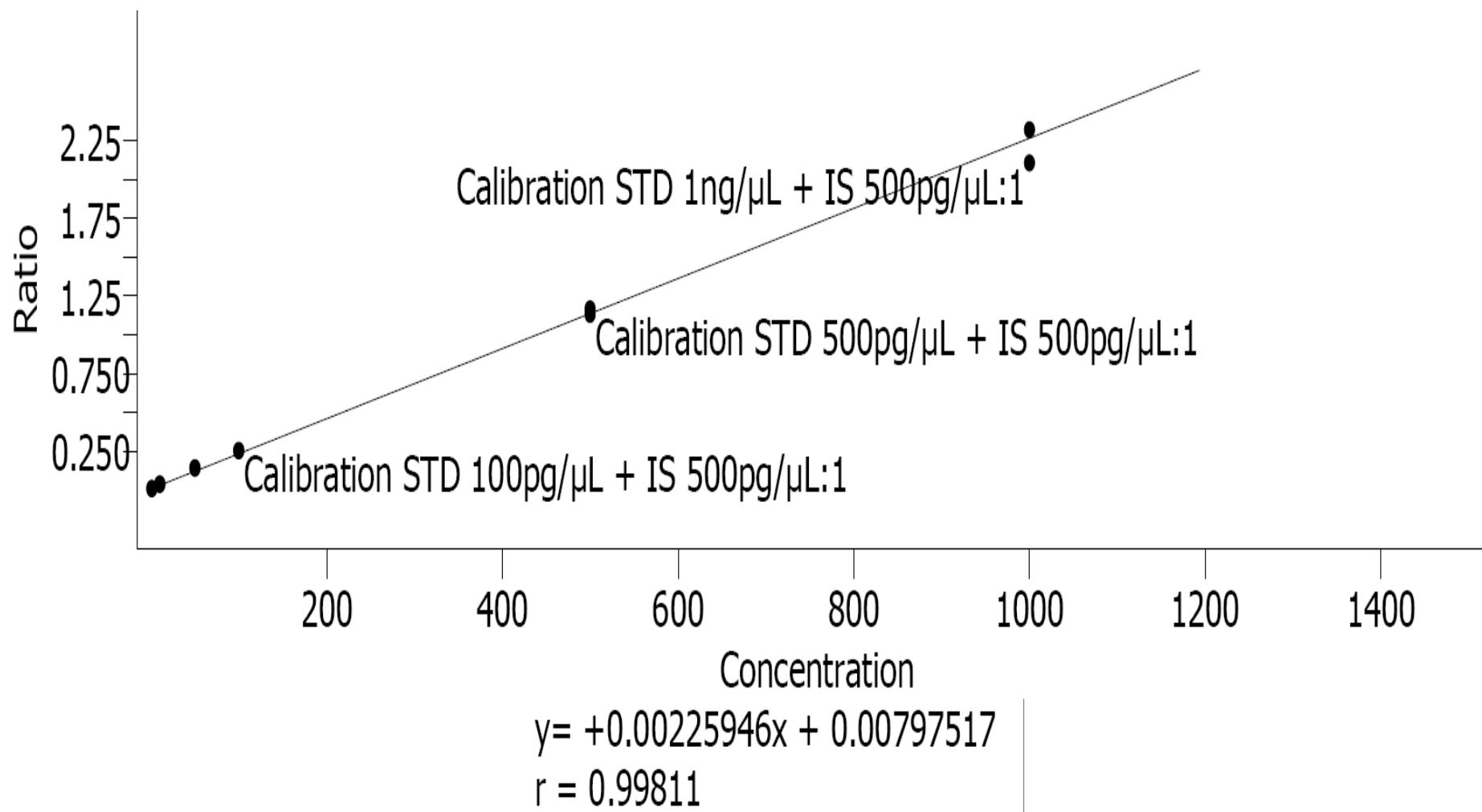


Target Analysis – “Flourene”(10ppb)

EIC - Chromatogramm Co-eluierender Peaks & EIC - Chromatogramm der Quantifizierungsmassen

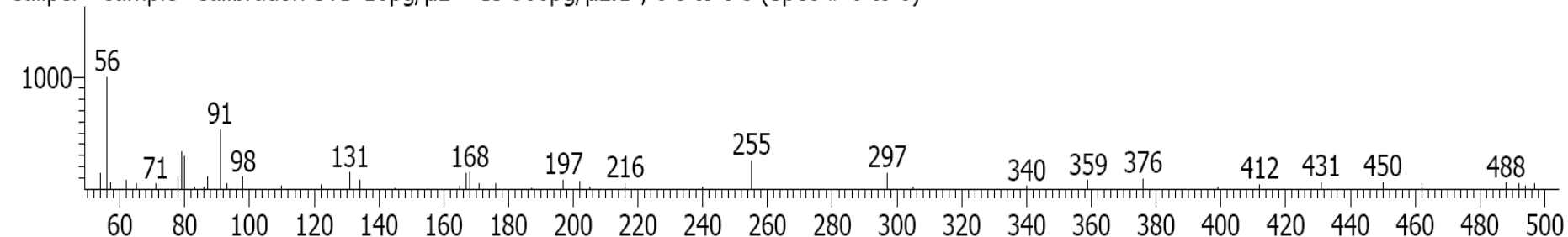


Calibration Curve Flourene (1-1000pg/μl)

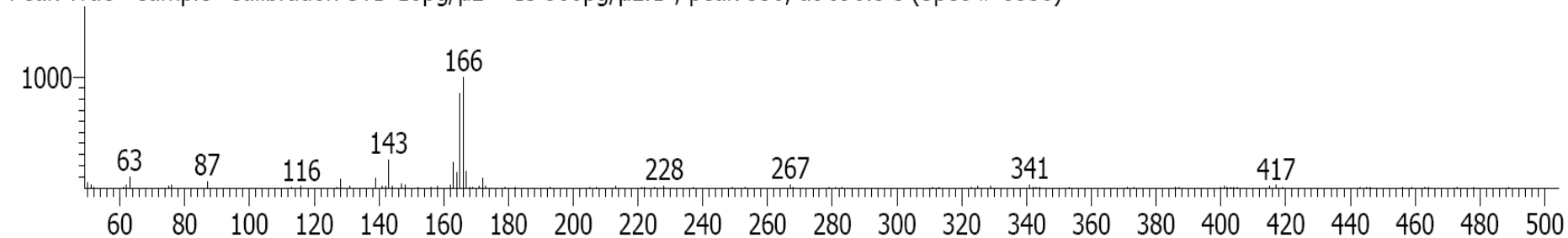


Mass Spectral Comparison of Fluorene

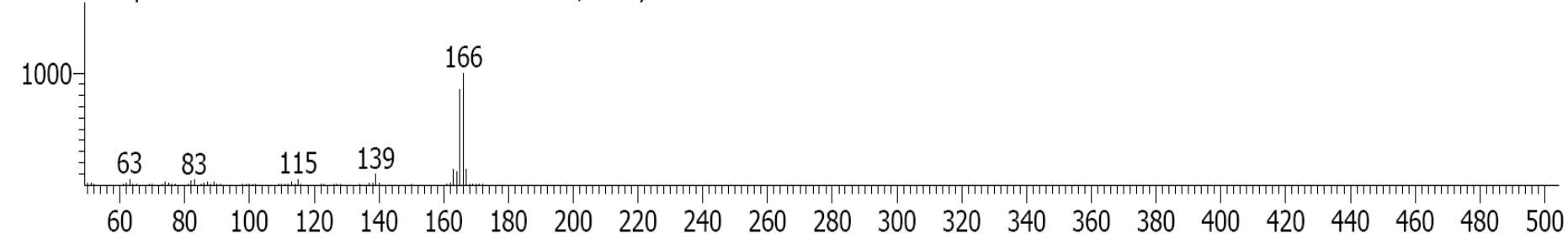
Caliper - sample "Calibration STD 10pg/ μ L + IS 500pg/ μ L:1", 0 s to 0 s (Spec # 0 to 0)



Peak True - sample "Calibration STD 10pg/ μ L + IS 500pg/ μ L:1", peak 336, at 696.5 s (Spec # 8530)

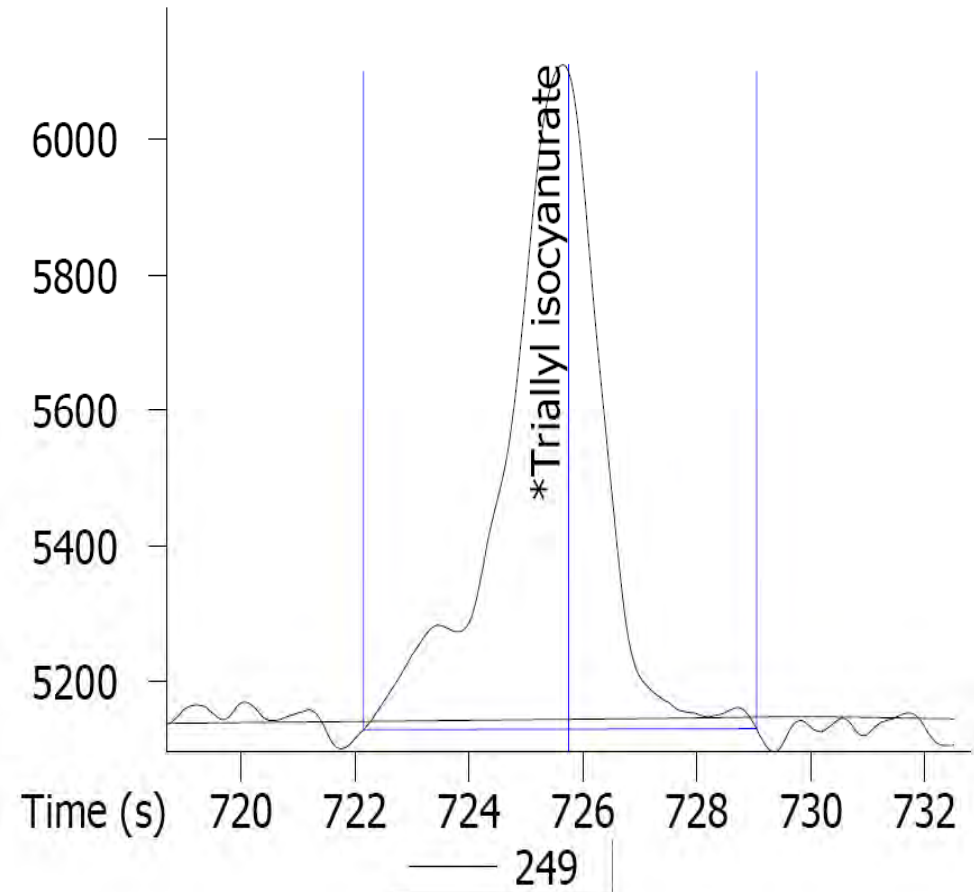
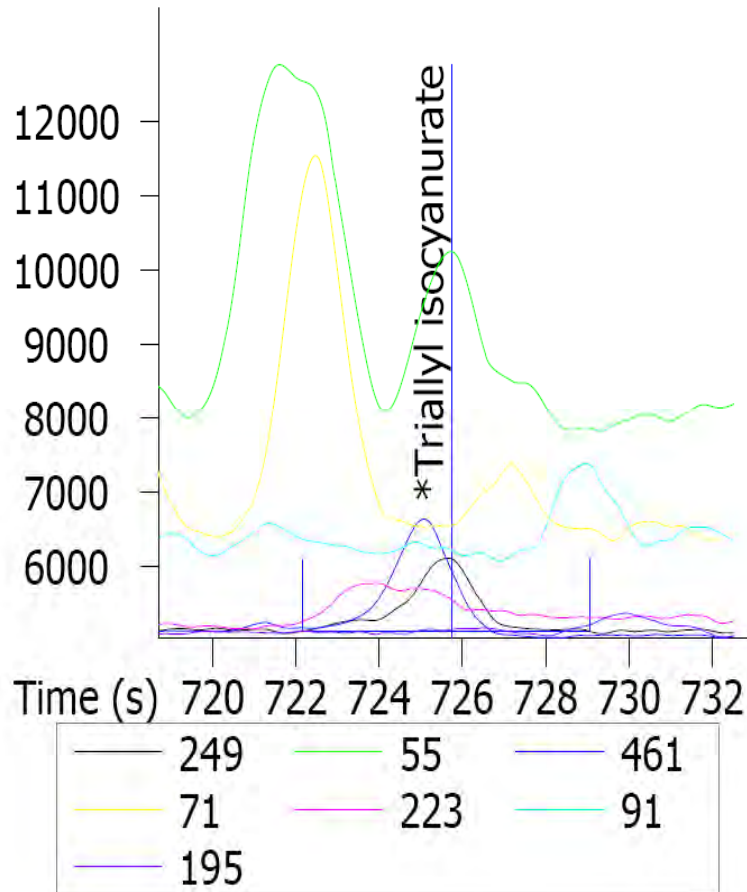


Reference Spectrum - Calibration "IWB - calib f. NWG", Analyte "*Fluorene"

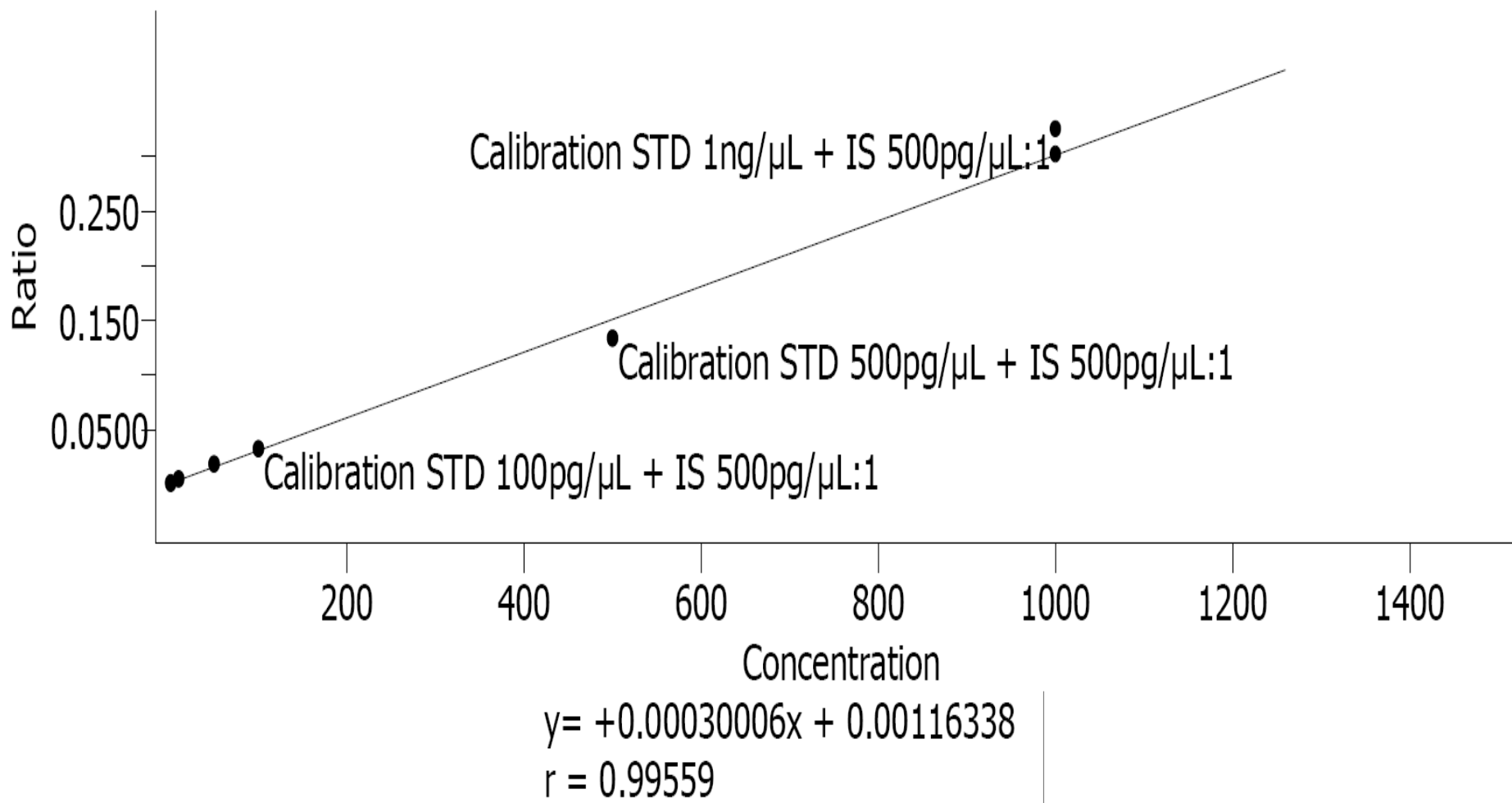


Target Analysis – “Triallyl isocyanurate” (10ppb)

EIC - Chromatogramm Co-eluierender Peaks & EIC - Chromatogramm der Quantifizierungsmassen

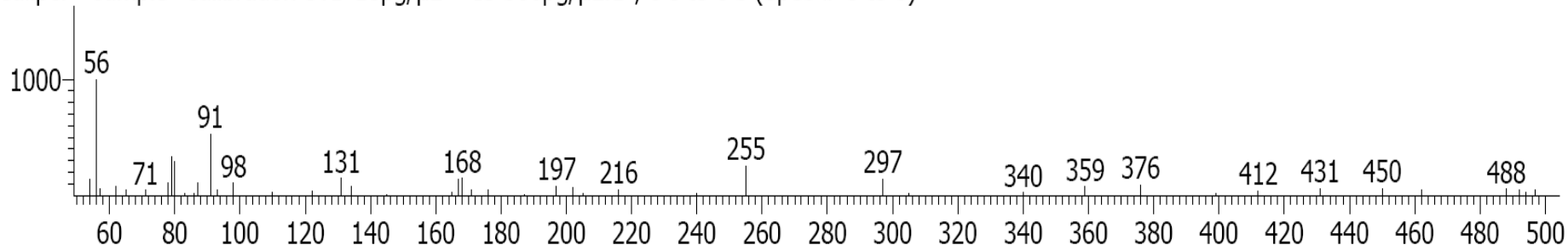


Calibration Curve Triallyl isocyanurate (1-1000pg/μl)

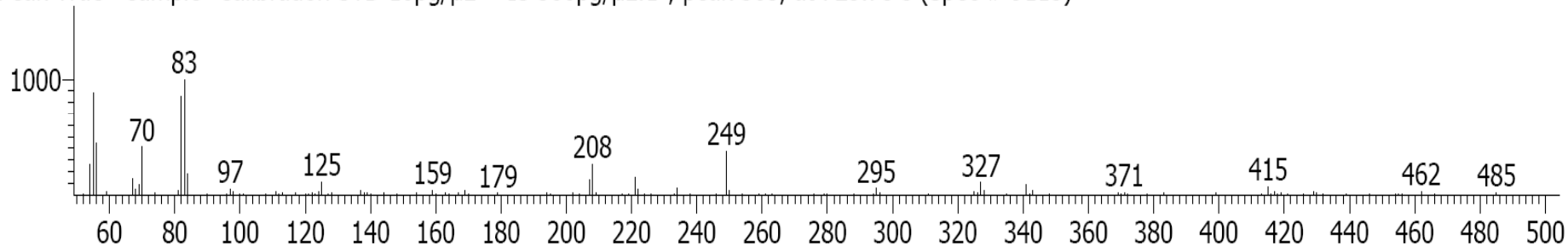


Mass Spectral Comparison of Triallyl isocyanate

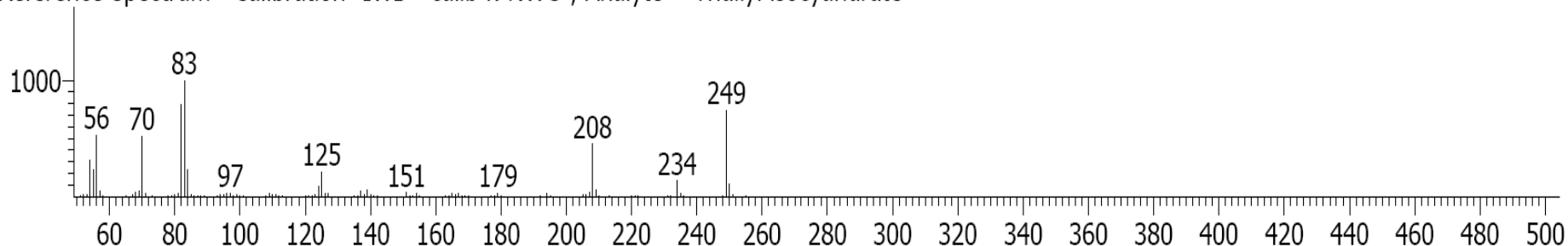
Caliper - sample "Calibration STD 10pg/ μ L + IS 500pg/ μ L:1", 0 s to 0 s (Spec # 0 to 0)



Peak True - sample "Calibration STD 10pg/ μ L + IS 500pg/ μ L:1", peak 365, at 725.75 s (Spec # 9115)



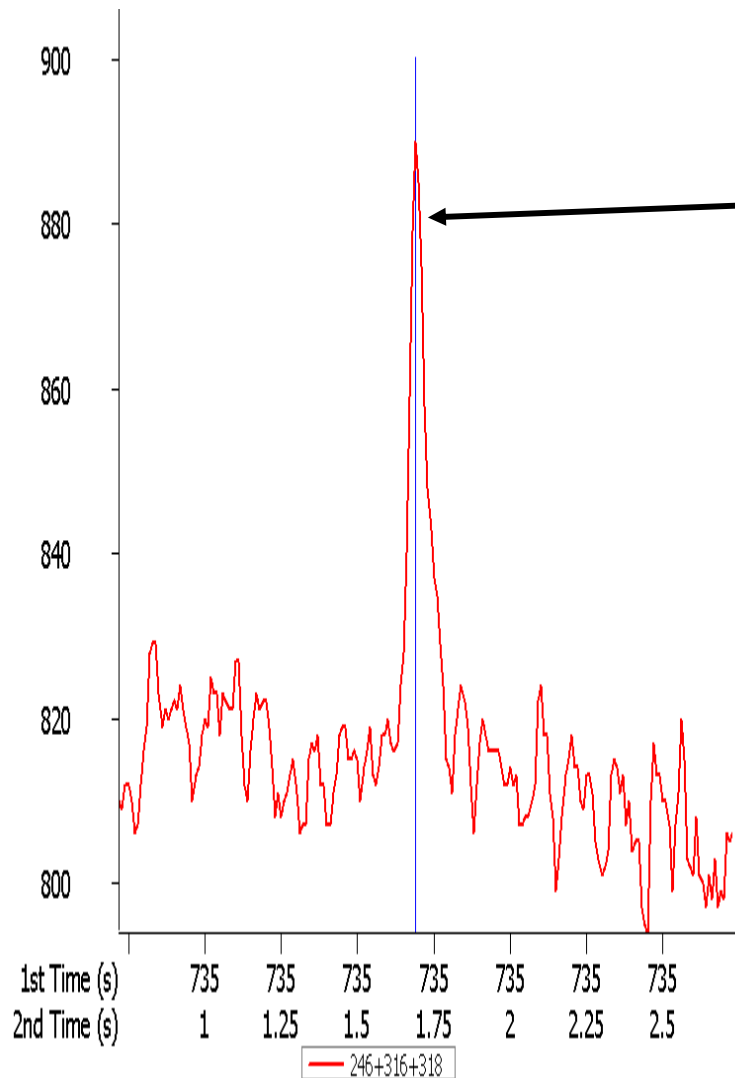
Reference Spectrum - Calibration "IWB - calib f. NWG", Analyte "*Triallyl isocyanurate"



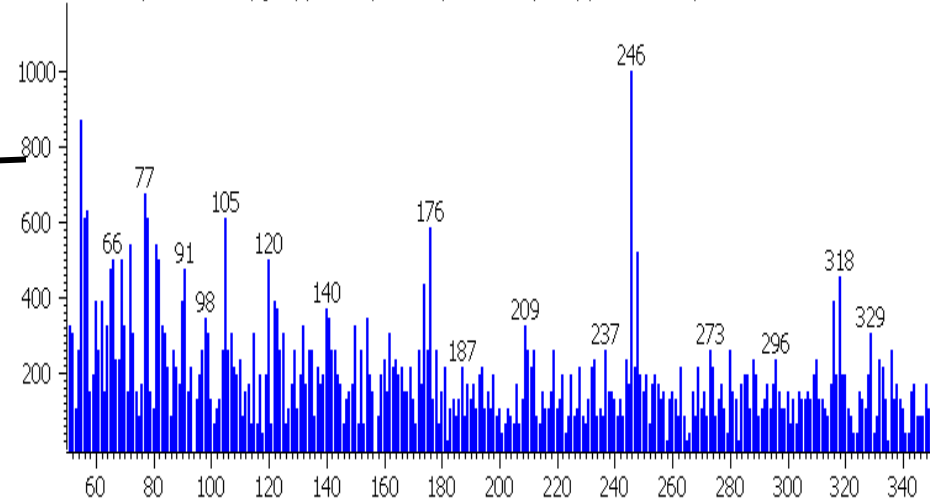
Detection Limits of Target Components (calculated on 10 ppb Standard)

R.T. (s)	Name	Similarity	Quant Masses	LOD S/N 3	LOQ S/N 10
623.85	*Acenaphthylene	928	152	0.1	0.2
643.6	*2-Chlorobiphenyl	945	188	0.1	0.3
679.1	*Diethyltoluamide	905	119	0.2	0.7
696.6	*Fluorene	906	165	0.1	0.6
725.76	*Triallyl isocyanurate	897	249	0.6	1.8
765.76	*2,3-Dichlorobiphenyl	944	222	0.2	0.8
770.06	*Benzene, hexachloro-	937	284	0.5	1.8
788.2	*Simazine	644	201	0.1	0.2
792.2	*Atrazine	957	200	0.4	1.3
797.15	*Tri(2-chloroethyl) phosphate	942	249	1.3	4.5
812.15	*à-Lindane	947	181	0.6	2.0
836.06	*Phenanthrene	951	178	0.1	0.3
844.96	*Anthracene	948	178	0.1	0.4
866.9	*Galaxolide 1	825	243	0.2	0.6
872.85	*Caffeine	765	194	0.5	1.6
872.85	*1,1'-Biphenyl, 2,3,6-trichloro-	765	258	0.2	0.8
	*Galaxolide 2a	645	243	NA	NA
	*Galaxolide 2:2	810	243	NA	NA
905.35	*Alachlor	922	188	0.6	1.9
910.8	*Galaxolide 2	711	243	2.2	7.5
922.06	*Heptachlor	933	272	1.0	3.4
965.4	*1,1'-Biphenyl, 2,2',4,4'-tetrachloro-	943	292	0.3	0.9
983.45	*Aldrin	932	66	0.7	2.4
1053.5	*Heptachlor epoxide	913	353	1.2	4.1
1057.65	*1,1'-Biphenyl, 2,2',3',4,6-Pentachloro-	901	326	0.5	1.5
1096.65	*trans-Chlordane	948	373	0.8	2.6
1121.1	*cis-Chlordane	903	373	0.8	2.8
1122.95	*Pyrene	940	202	0.1	0.4
1125.55	*cis-Nonachlor	838	409	0.9	2.9
1173.4	*1,1'-Biphenyl, 2,2',3,4,5,5'-hexachloro-	922	360	0.4	1.5
1174.9	*Dieldrin	955	79	1.0	3.2
1215.6	*Endrin	920	281	2.3	7.5
1244.8	*trans-Nonachlor	927	409	1.1	3.7
1327.06	*Carbamazepine	930	193	1.7	5.7
1418.6	*1,1'-Biphenyl, 2,2',3,3',4,4',6-heptachloro-	835	394	0.7	2.4
1425.8	*Benz[a]anthracene	902	228	0.1	0.6
1429.3	*1,1'-Biphenyl, 2,2',3,3',4,5',6,6'-octachloro-	857	428	0.7	2.4
1434.75	*Chrysene	906	228	0.2	0.6
1435.6	*p,p'-Methoxychlor	834	227	0.2	0.7
1443.15	*Diazepam	935	256	0.8	2.6
1804.2	*Benzo[b]fluoranthene	900	252	0.3	0.9
1814.9	*Benzo[k]fluoranthene	919	252	0.3	1.0
1898.6	*Benzo[a]pyrene	932	252	0.2	0.8
2055.3	*Cholesterol	578	301	NA	NA
2110.2	*Indeno[1,2,3-cd]pyrene	918	276	0.2	0.7
2118.35	*Dibenz[a,h]anthracene	956	278	0.2	0.8
2161.3	*Benzo[ghi]perylene	915	276	0.2	0.6

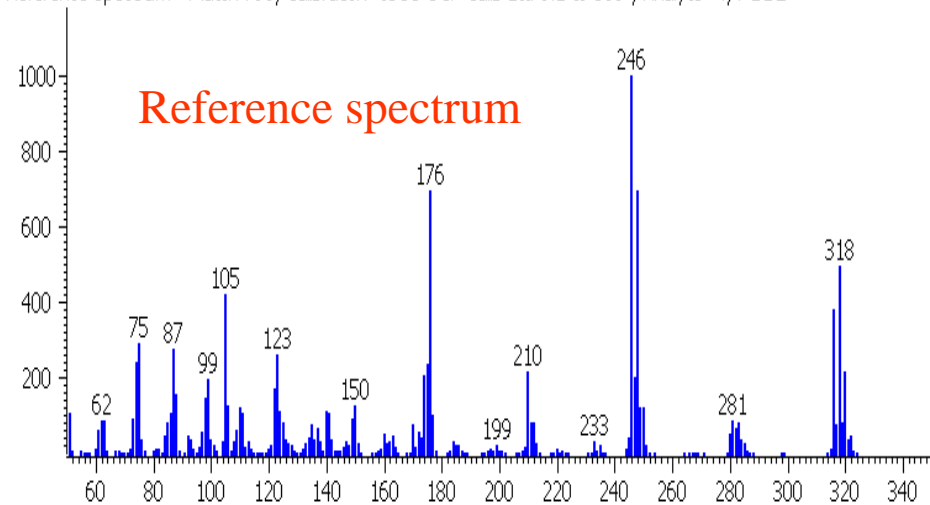
200 fg DDE in Drinking Water



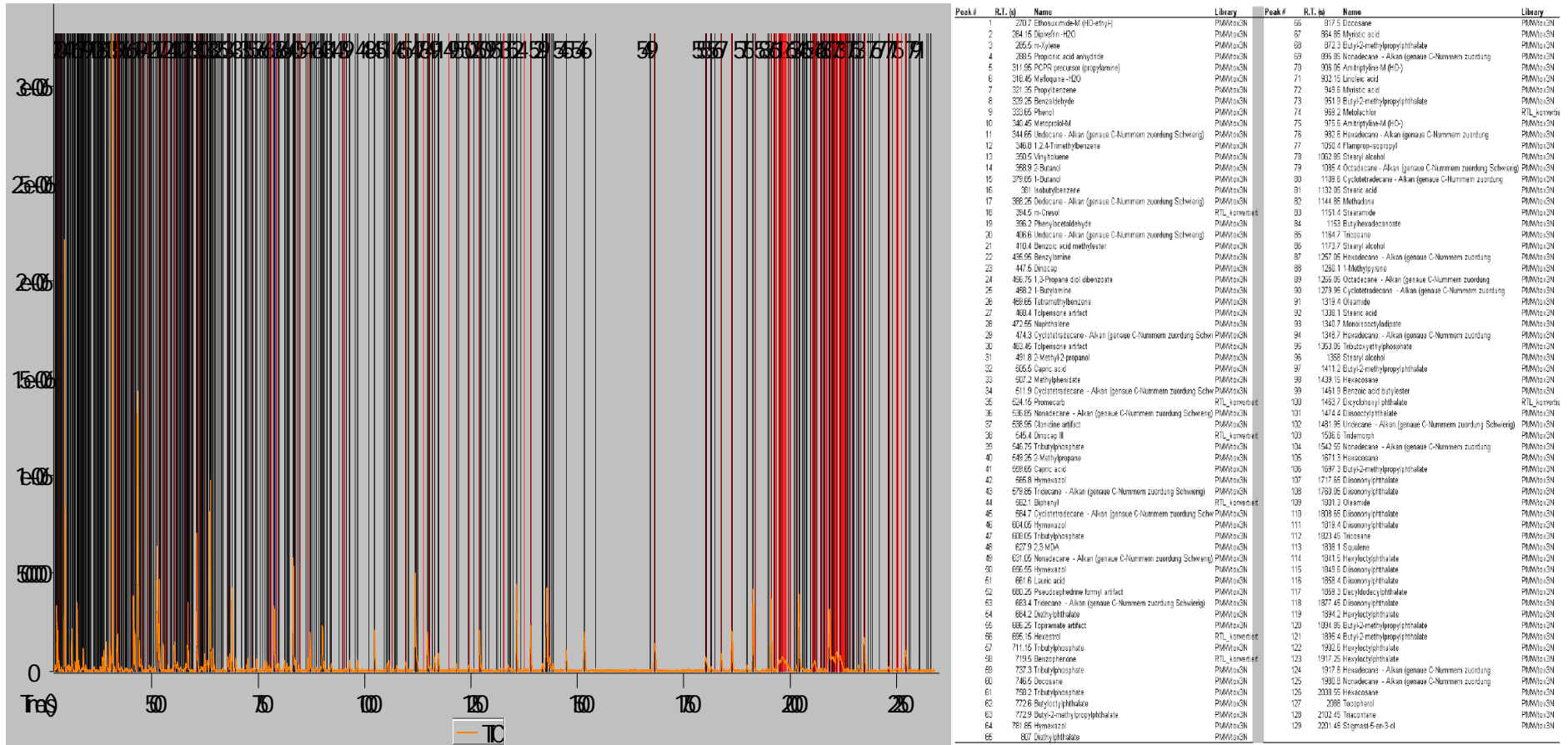
Peak True - sample "OCP 0.2 pg:1", peak 38, at 735 , 1.690 sec,sec (Spec # 43669)



Reference Spectrum - Match 790, Calibration "ISCC OCP Calb Ltd 0.2 to 500", Analyte "4,4'-DDE"



Non Target Screening of Drinking Water Sample



Showing all Peak Markers = additionally 700 Peaks identified
(288 with similarity > 70 %)

LECO Pegasus[®] 4D

- Agilent 7890 GC
- Agilent or Gerstel Autosampler
- LECO quad-jet, dual-stage modulator
 - Modulates C₄ to C₄₀
- LECO consumable free modulator
 - Modulates C₈ to C₄₀
- LECO secondary column oven
- LECO Pegasus[®] 4D TOFMS
 - Acquisition rates up to 500 spectra/s
 - Mass range from 5 to 1000 u
- LECO ChromaTOF[®] software
 - GC x GC control and data processing
 - Automated peak find
 - Spectral Deconvolution
 - Classification, Scripting and Compare

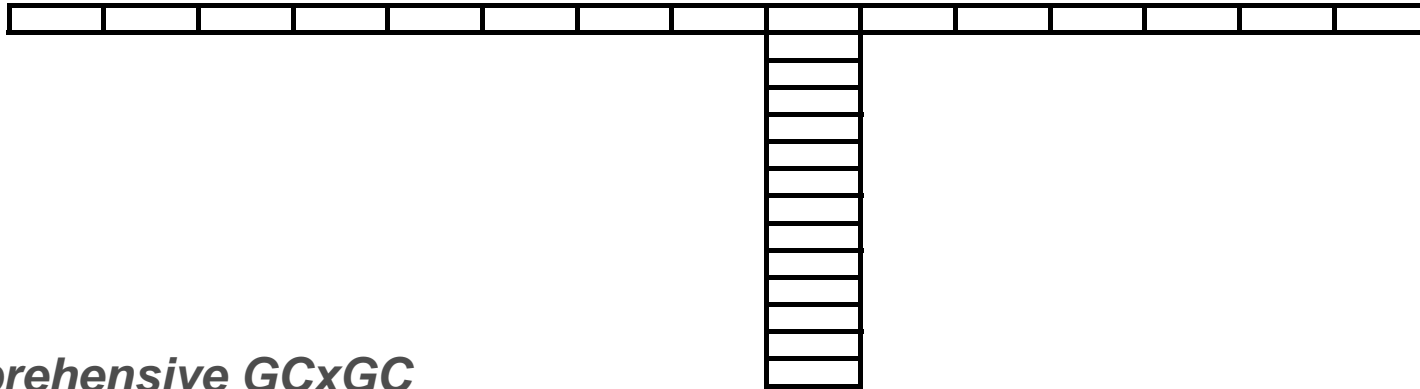


Principle of Comprehensive GC

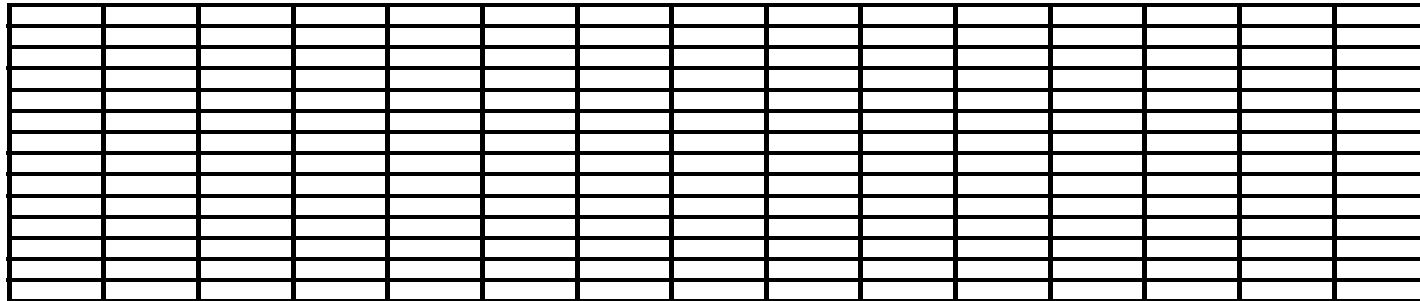
Normal Chromatography



Heart-cut 2D Chromatography (Multi-Dimensional GC (2DGC))

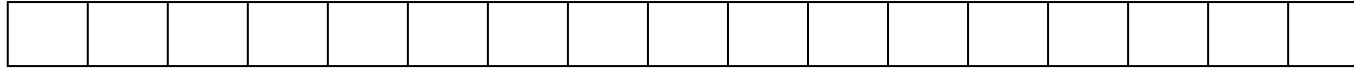


Comprehensive GCxGC



Principle of Comprehensive GC

Peak Capacity Normal GC

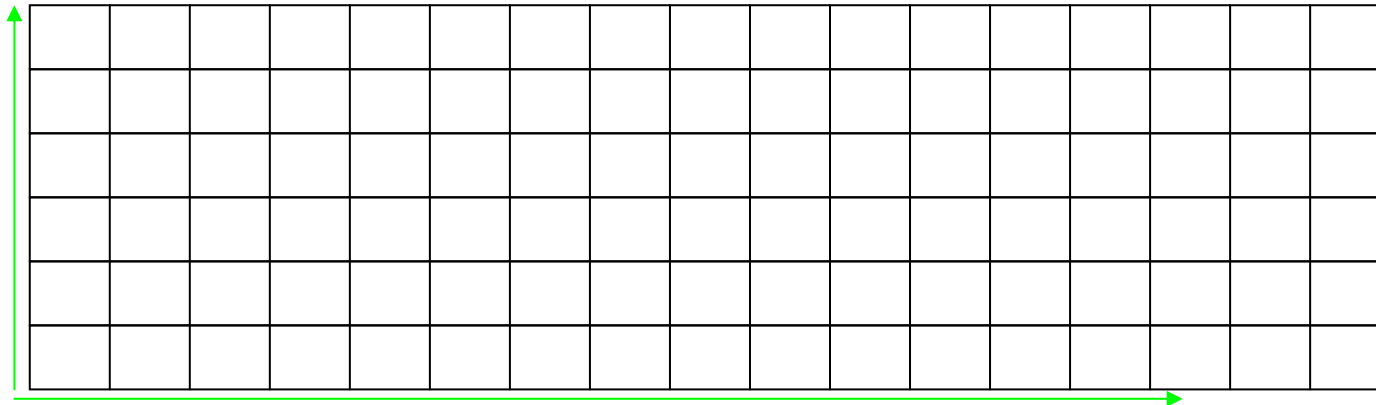


$$SN = \left(\frac{\Delta t_r}{(W_{1/2})_1 + (W_{1/2})_2} \right) - 1$$

$$SN_t = \sum_i^j (SN + 1)$$

= 85 peaks

Peak Capacity Comprehensive GC



$$SN = \left(\frac{\Delta t_r}{(W_{1/2})_1 + (W_{1/2})_2} \right) - 1$$

X

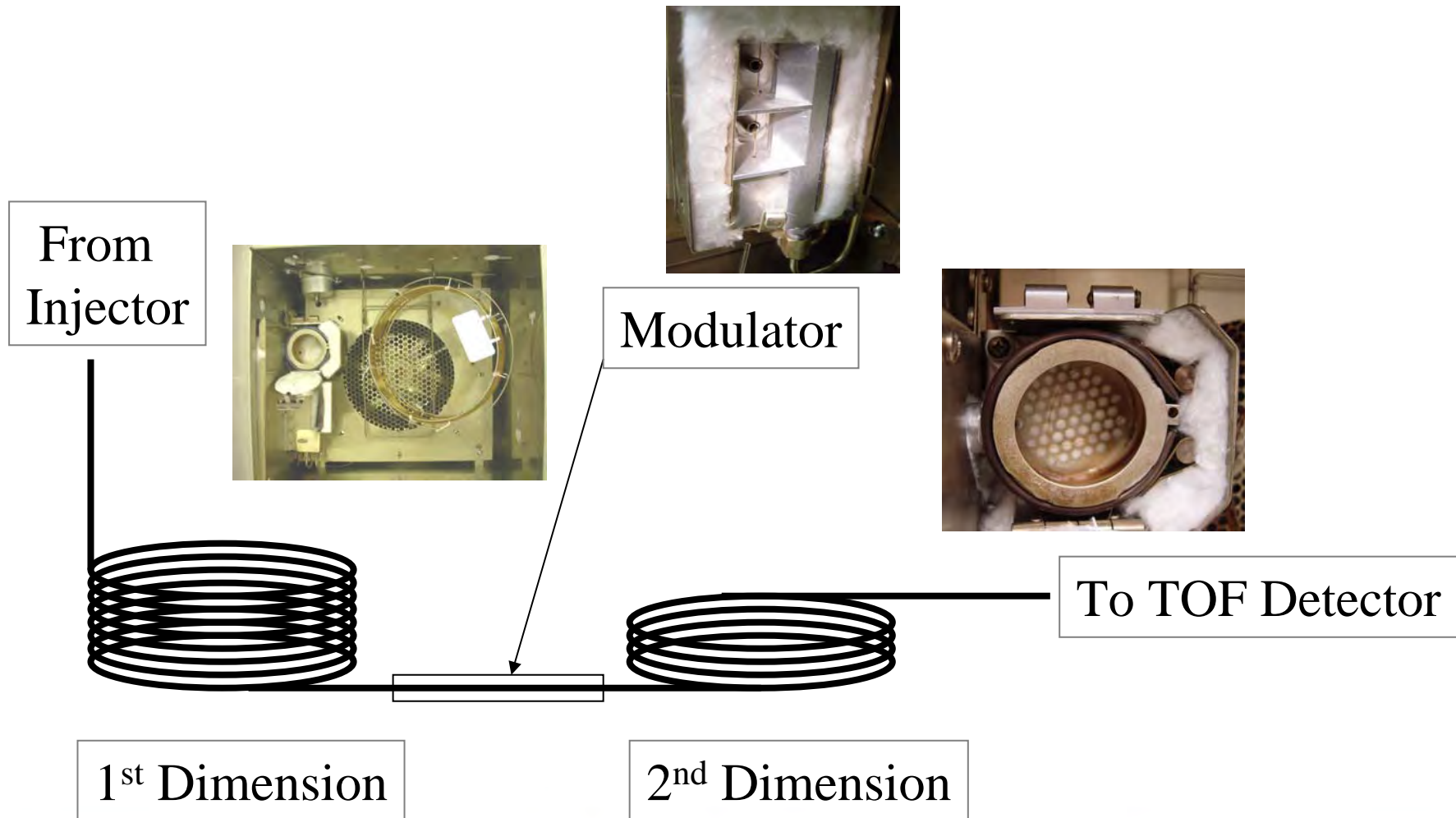
$$Cp = 1 + \frac{\sqrt{N}}{4R_s} \ln \left[\frac{t_{r(last)}}{t_m} \right]$$

= 2550 peaks

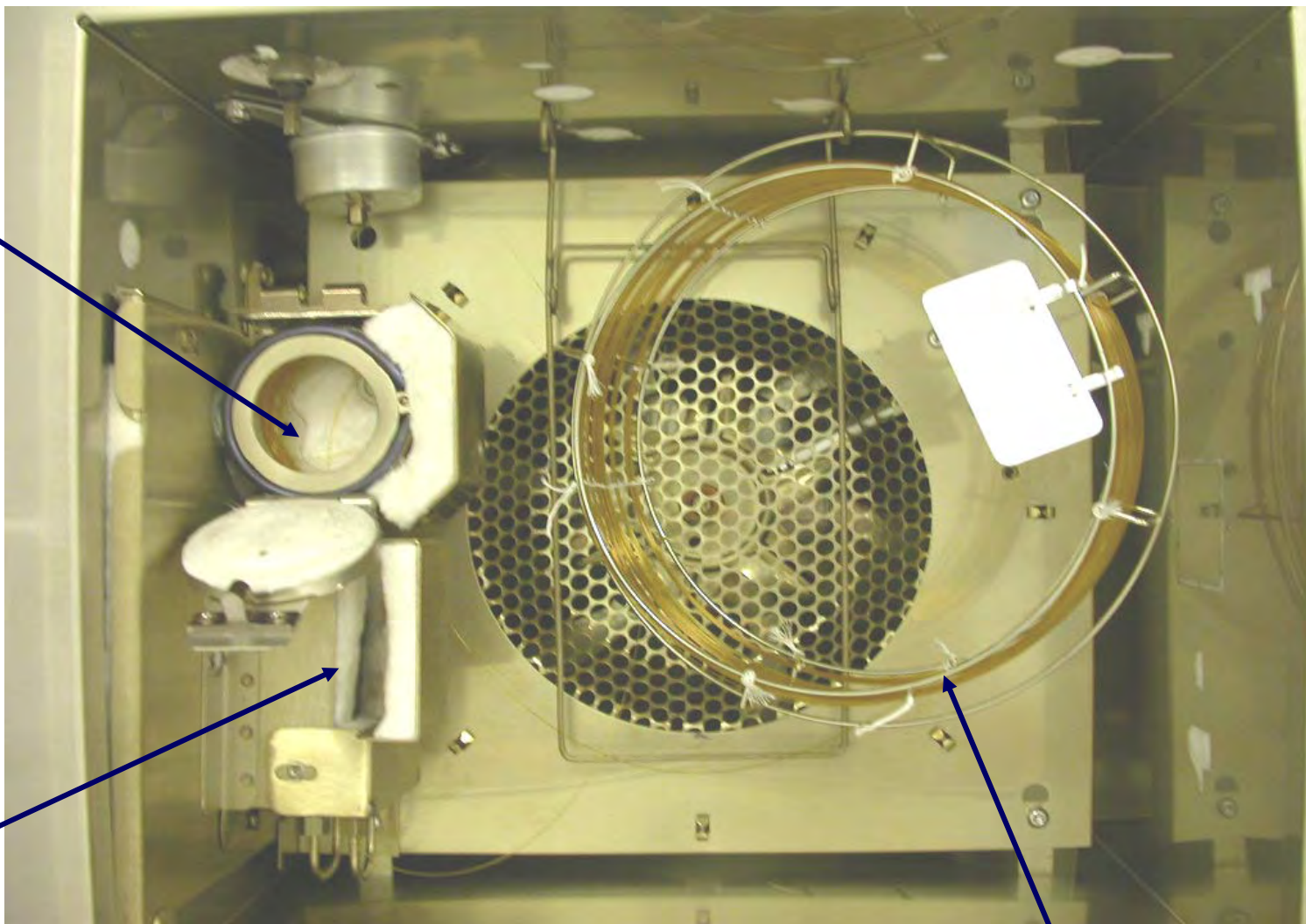
Typical GCxGC Setup

- **Primary column (1st dimension)**
 - Longer, wider bore, thicker film
 - Mostly 30 m and Non-polar
- **Modulator**
 - Thermal in nature (LN2 Cooling) or Consumable Free Modulator (Air Cooling)
 - Focuses effluent from primary column
 - “Injects” this effluent onto secondary column
- **Secondary column (2nd dimension)**
 - Very short, narrow bore, thinner film
 - Mostly 1-3 m and Polar or Selective

GCxGC Schematic Overview



**Secondary
Oven**
including
2nd Dimension
Column



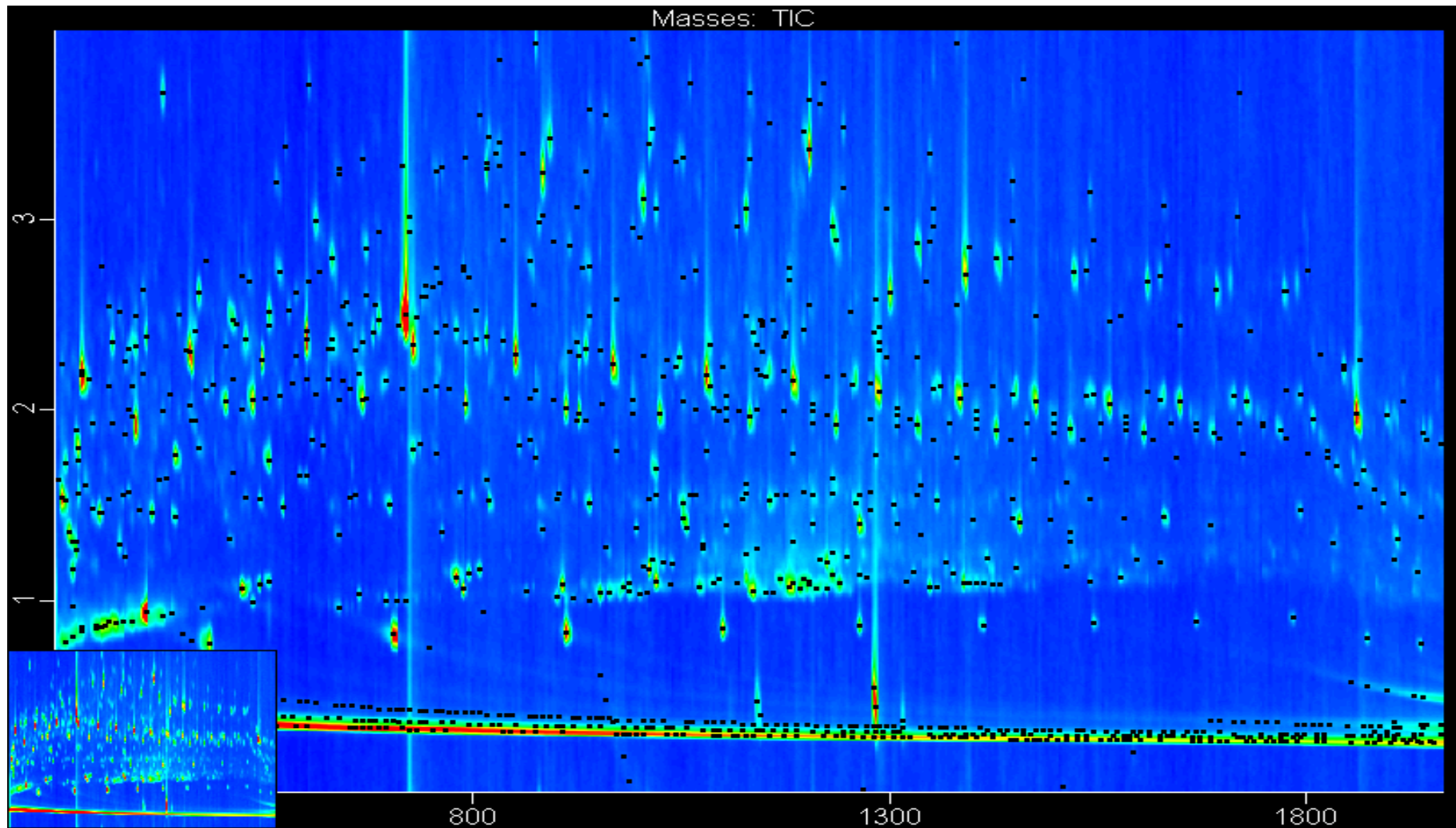
Modulator

1st Dimension Column

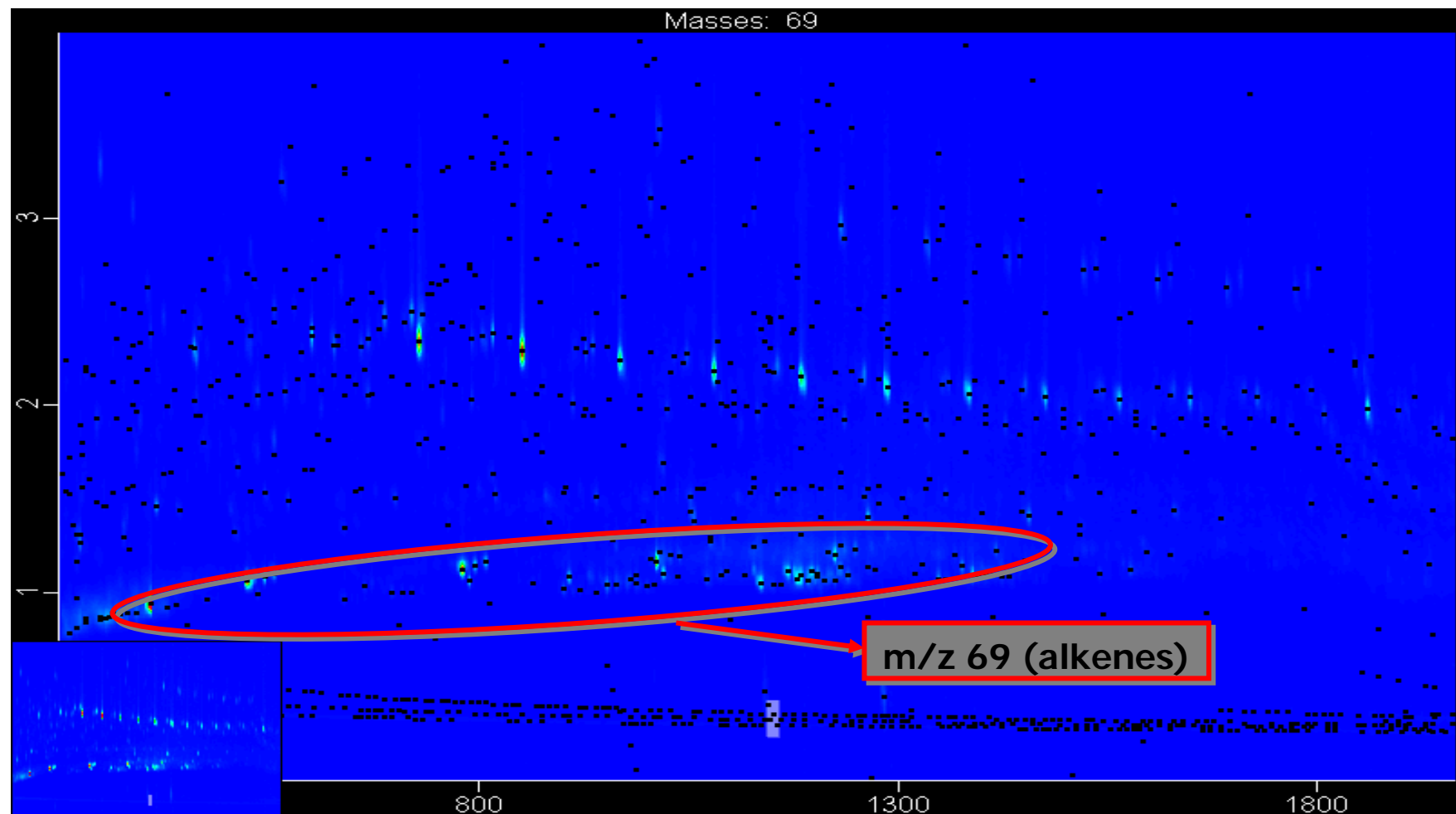


Delivering the Right Results

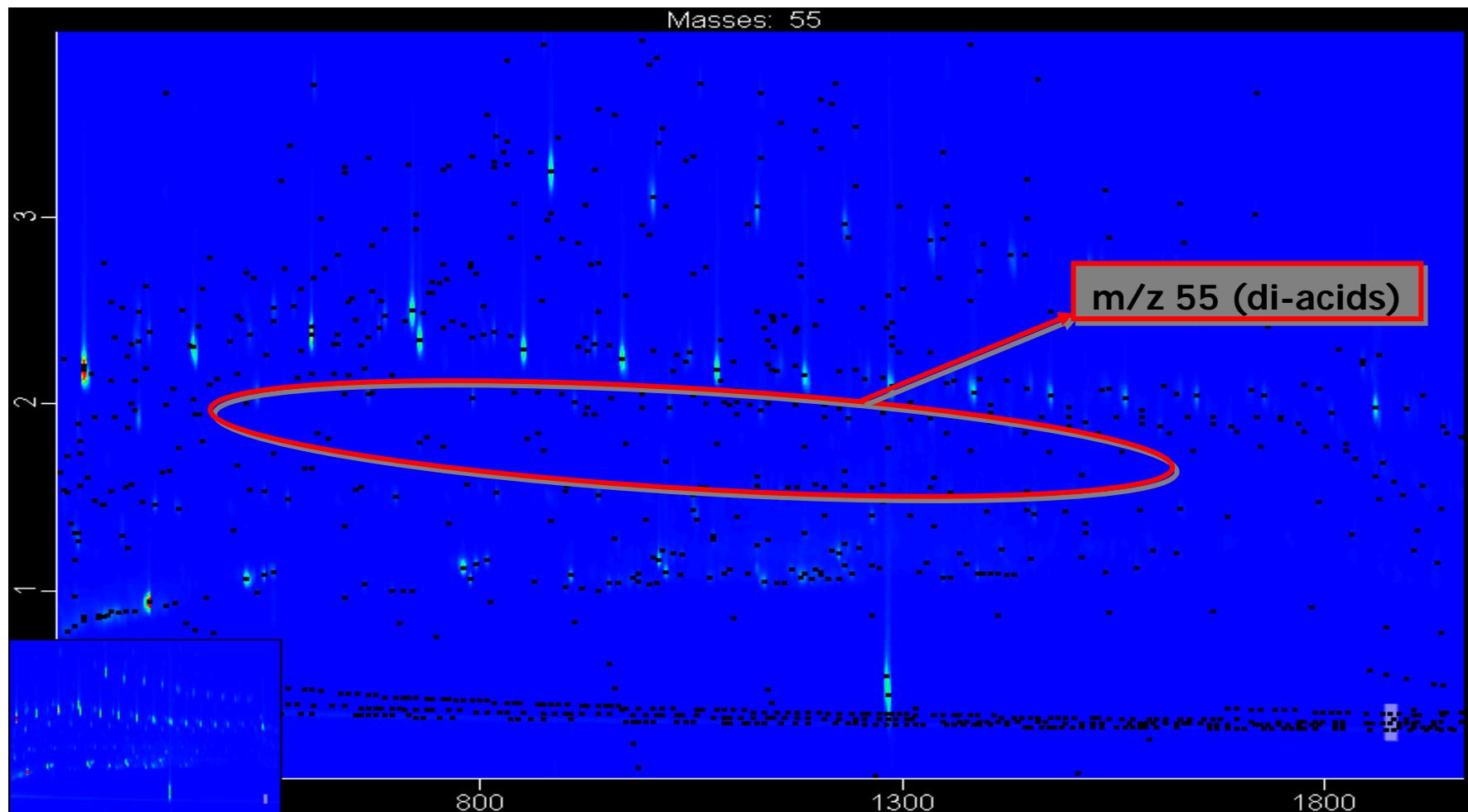
2D-plot of extract of River water



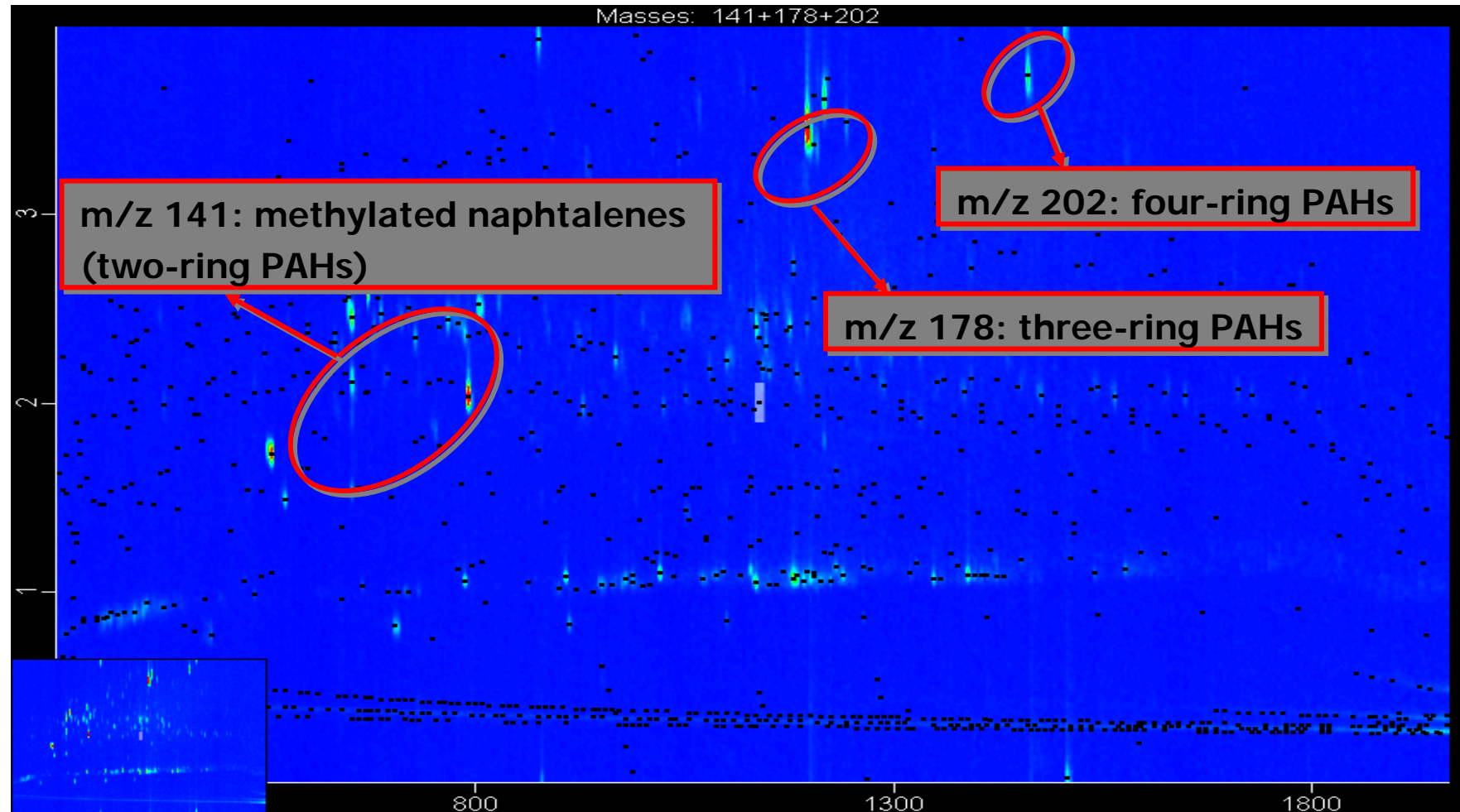
Non-target analysis example: River Water



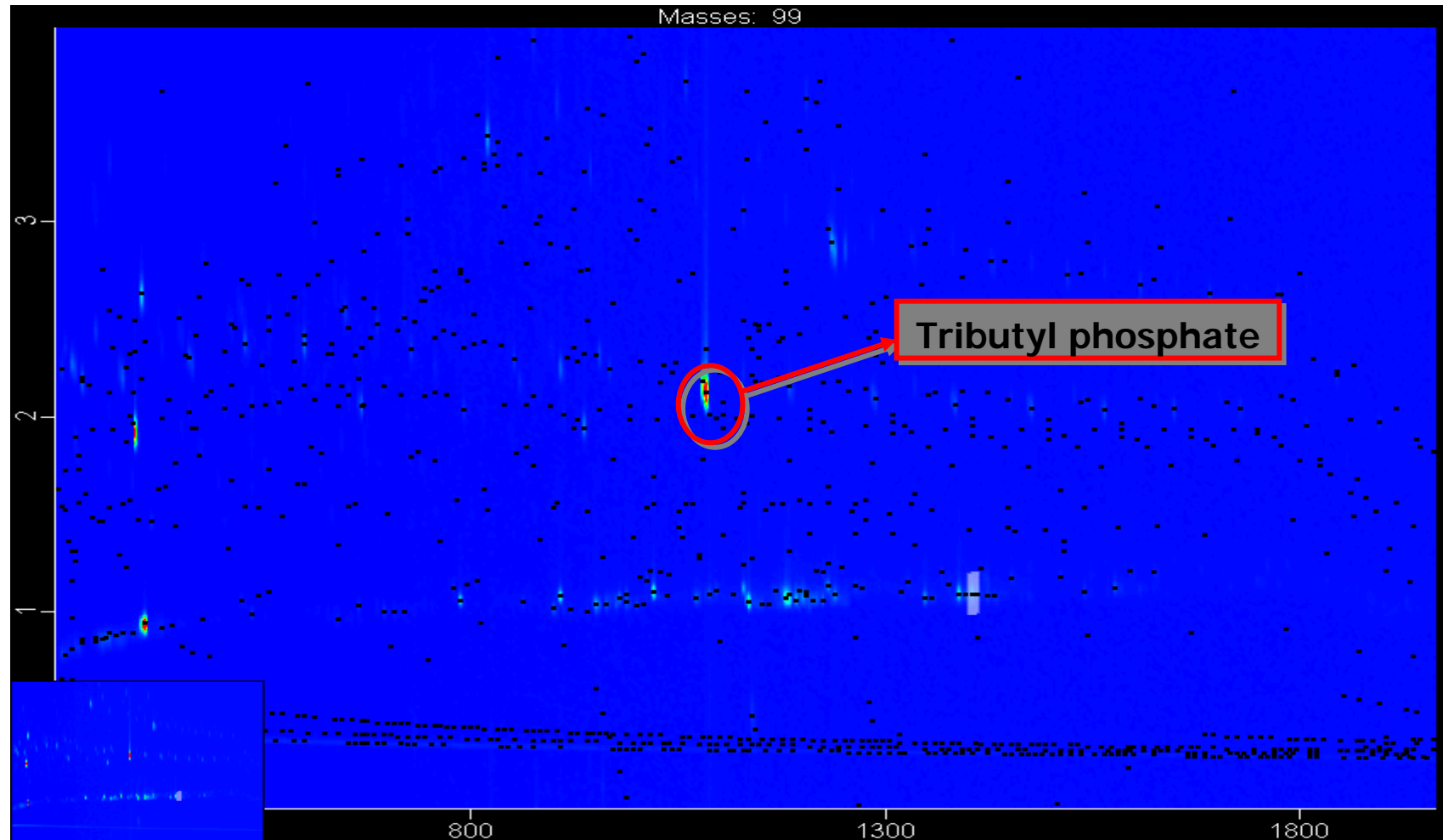
Non-target analysis example: River Water



Non-target analysis example: River Water



Non-target analysis example: River Water



Conclusions

- **TOFMS is not a new technique**
- **But many innovations have occurred for chromatographic uses of TOFMS**
 - **Fast acquisition is possible because of improvements in electronics**
- **Automated data processing routines**
 - **Peak find**
 - **Intergrated Spectral deconvolution**
 - **Library Search**
 - **Qualification and Quantification**
 - **Classification and Statistic Compare**

Conclusions

- **TOFMS is an excellent MS choice for fast GC techniques that produce narrow peaks**
 - **Smaller bore capillary columns (0.10 or 0.18mm)**
 - **GCxGC**
- **TOFMS instrumentation is robust**
 - **Simple, no complicated magnetic or electric fields**
 - **No mass spectrometer source cleaning !**

Conclusions

- **TOFMS has full mass range, pg level sensitivity for trace level work**
 - **Environmental applications**
 - **Pesticides in food and water**
 - **Allergens or other compounds in fragrances**
 - **Important, but low level compounds in flavors**
- **TOFMS has a wide dynamic range**
 - **Flavors and fragrances**
 - **Metabolomics**

Many Thank's for your Attention !!!

Any Questions ???

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Zweckverband
Landeswasserversorgung 

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Delivering the Right Results