Improved Sensitivity and Analysis Time for Semivolatile Organic Compounds Using GC-TOFMS : Can This Analysis Really be Performed in Less Than 10-Minutes?

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Desires of GC Analysts

- **Higher Sample Throughput**
  - Lowers cost/sample
  - Increases sample capacity
  - Fewer instruments to accomplish same workload
- **Better Resolution**
  - Can allow for shorter run times
  - Improves quantitation
 - Can allow for analysis of very complex matrices

USEPA Method 8270

- **GC-MS, Full Scan**
  - 6 to 7 data points across peak is minimum recommendation
  - 20 to 25 minute analysis time is practical limitation if using "conventional" MSD's
  - 20 to 160 ng calibrations – will overload most columns suitable for the analysis
  - Extracts may have high concentration of co-extractable compounds
  - Instrumentally intensive – routine maintenance

How Many data points are enough to characterize a peak?

Sampling Frequency Limitations of Quads and Ion Traps Can Cause Peak Biasing
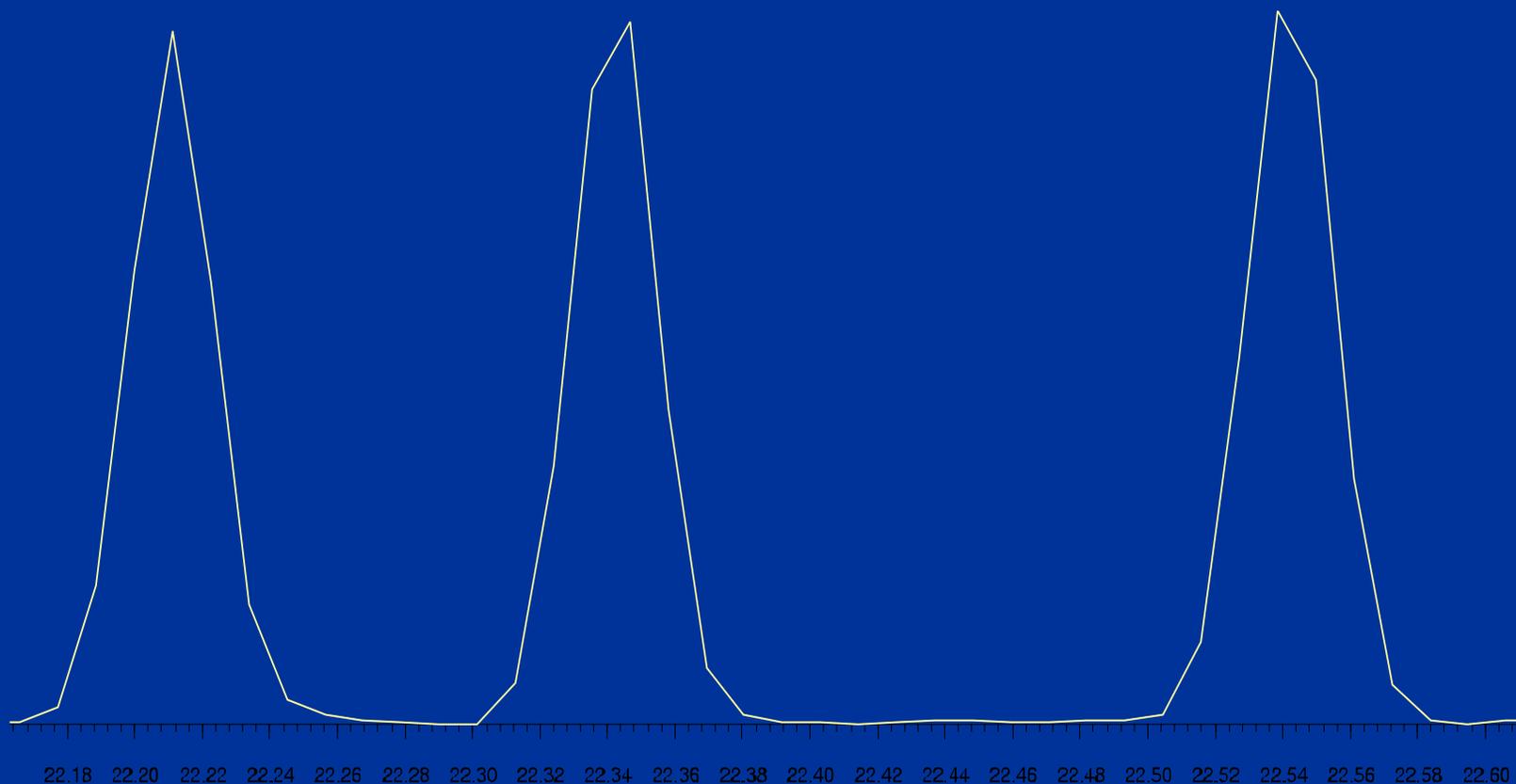
If we want to approach the 10-minute analysis time range, we will need to change something…

- Scan rate?
  - Most are running as fast as possible
- Scan Range
  - Not practical
- Time-of-Flight MS?
  - Can't sacrifice sensitivity, or calibration range
 - Can't add significant amount of maintenance
  - Feasible???

Major Benefits of TOFMS

- Full mass spectrum acquired
- 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
- Automated peak find
  - Find compounds buried beneath matrix
  - Locate non-target compounds
- Spectral deconvolution
  - Produce quality mass spectra from coeluting peaks
  - Library search deconvoluted spectra

LECO Pegasus III GC-TOFMS

- Make ions
- Pulse them down a flight tube
- Arrival at detector is by time-of-flight
  - Low mass = faster
 - High mass = slower
- Detect ions

Push Pulse Plate
Electron Focusing Optics
Electron Beam
Vial with Calibration Compound
Heated Transfer line
Sampling
Ion Source Chamber
Gas Chromatograph
Carrier Gas Flow
Turbomolecular Pump
Ion Focusing Optics
Capillary Column
He Gas (99.9995%) Tank
Z Steering and Deflection Plates
Signal Out
Rough Pump
Detector
Einzel Lens
Main Analysis Chamber
Y Steering Plates
Turbomolecular Pump
Reflectron
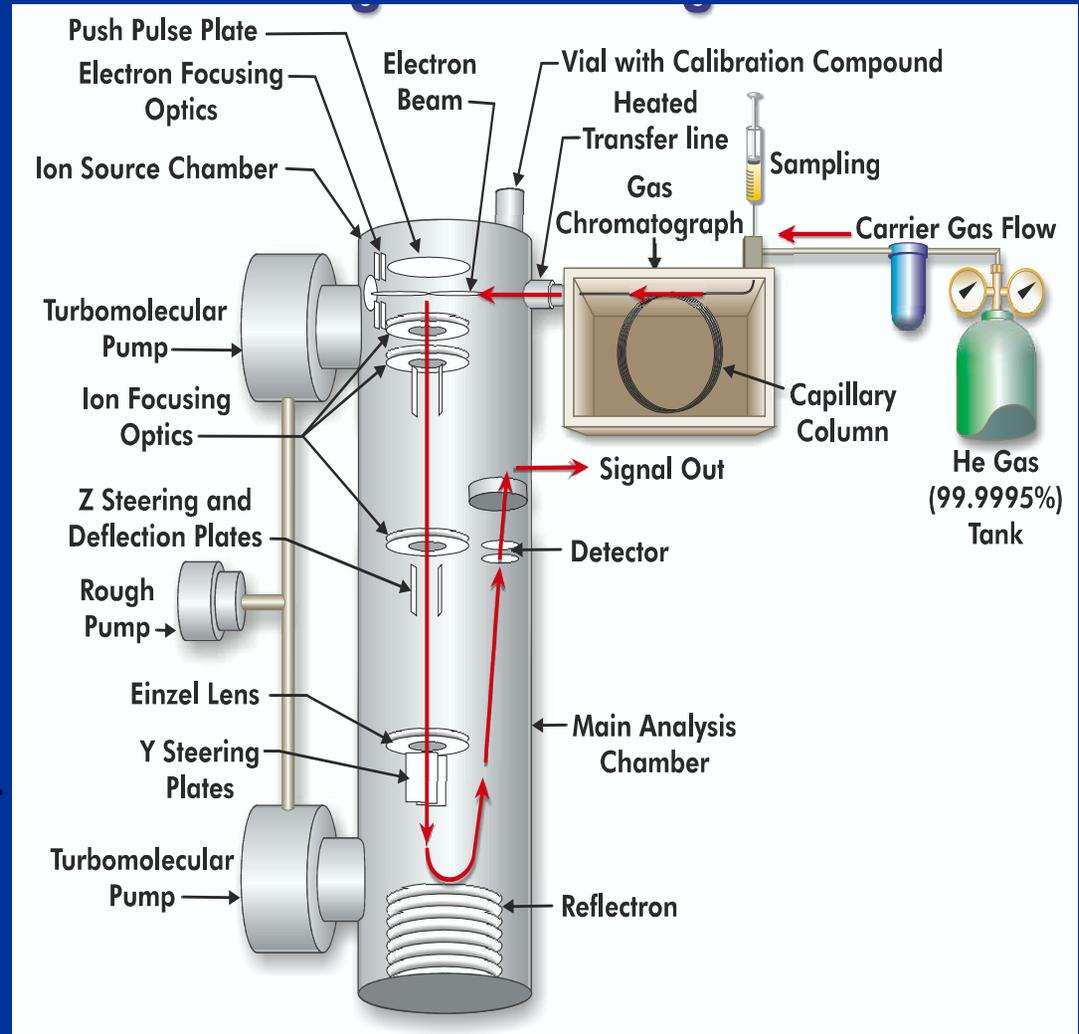
Sampling Frequency Limitations of Quads and Ion Traps Can Cause Peak Biasing
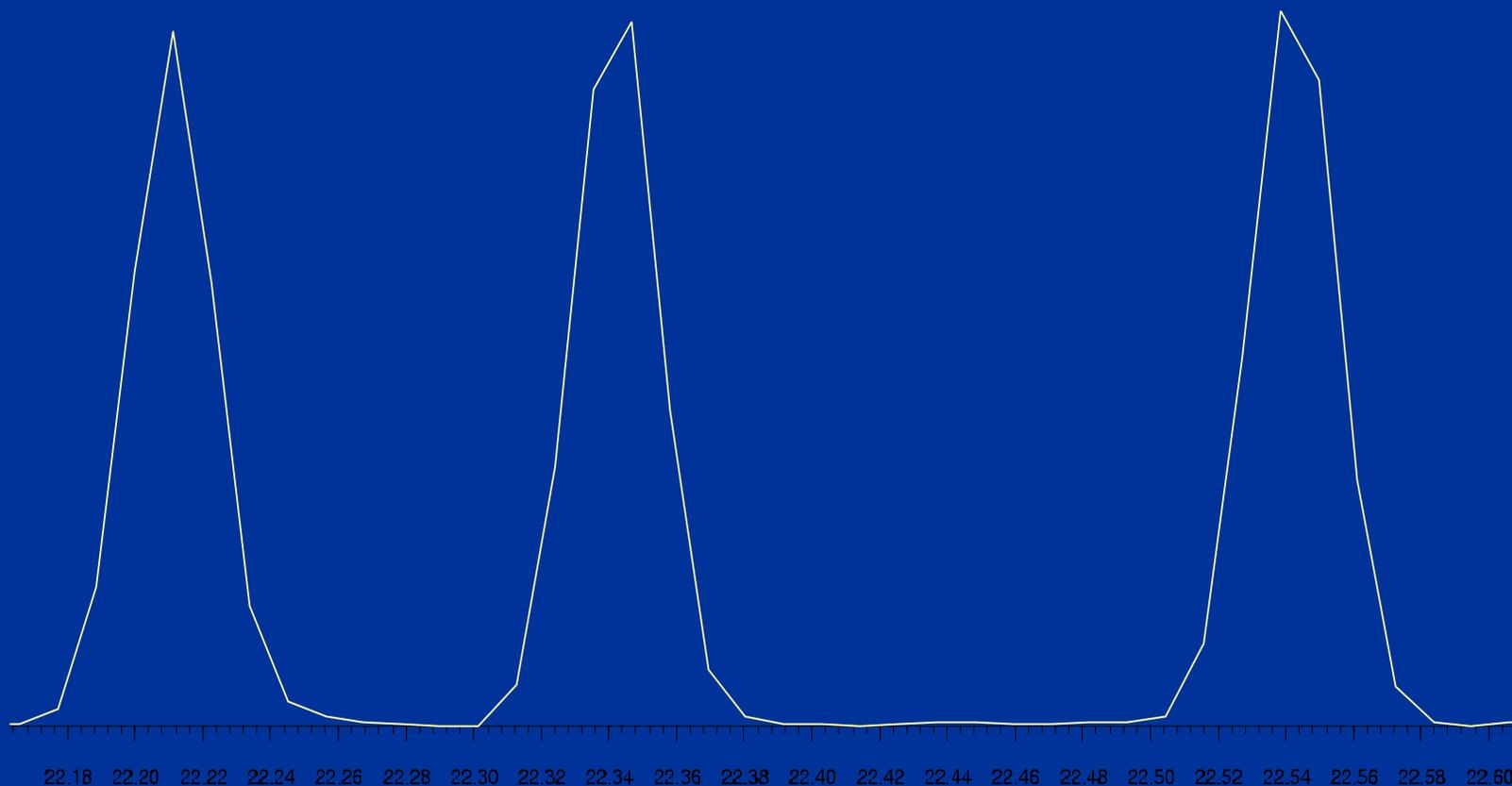
PAH Standard – TIC
# Phenanthrene-D10, Phenanthrene, Anthracene
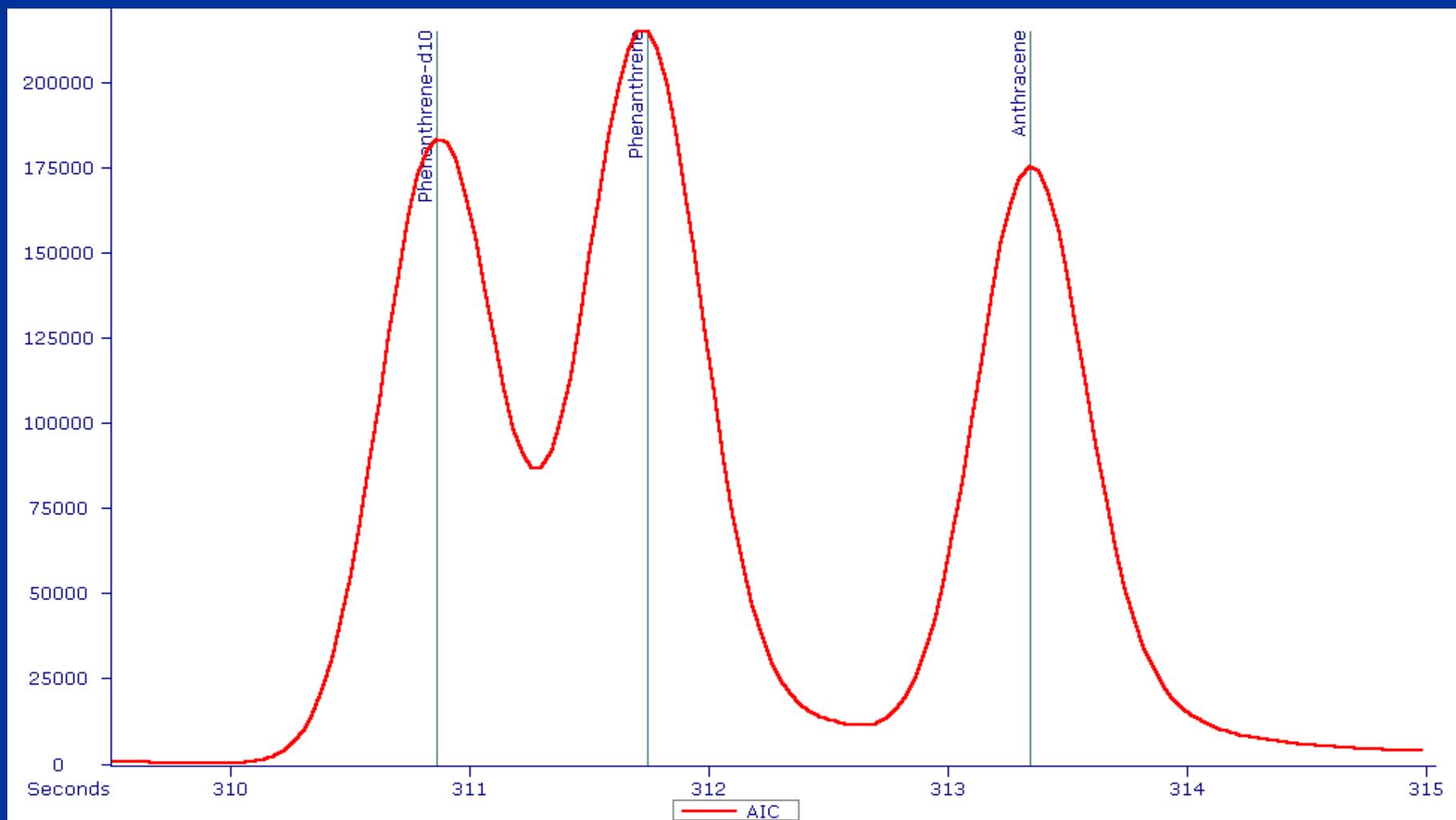
Spectral Reproducibility
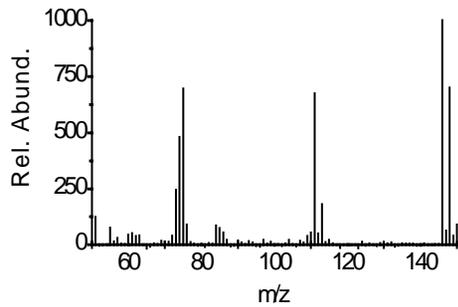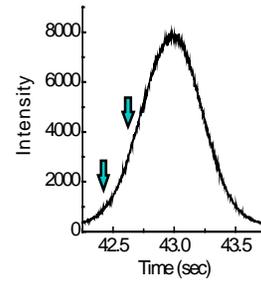
TOFMS
GC Peak
Scanning MS
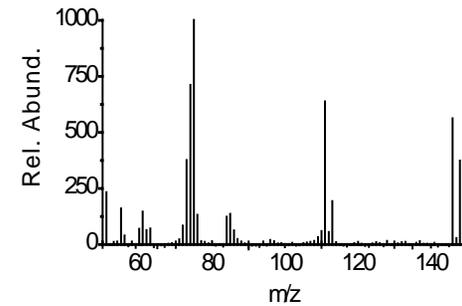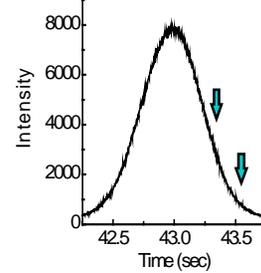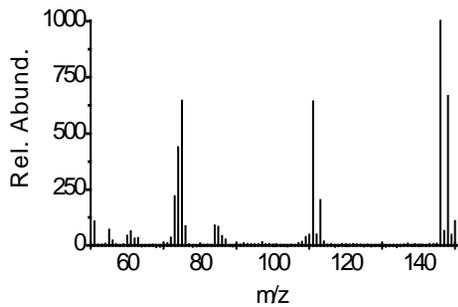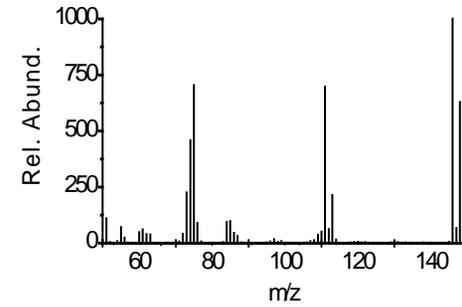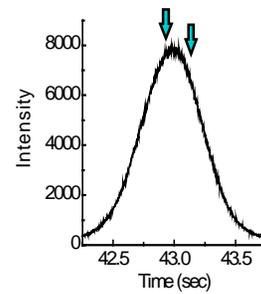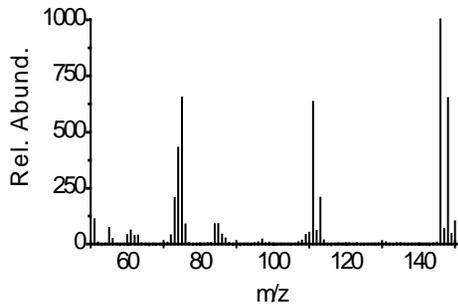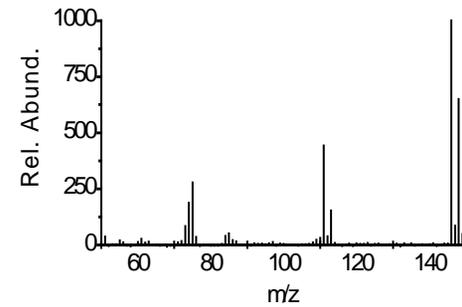
# Peak Find at 40 Spectra/sec

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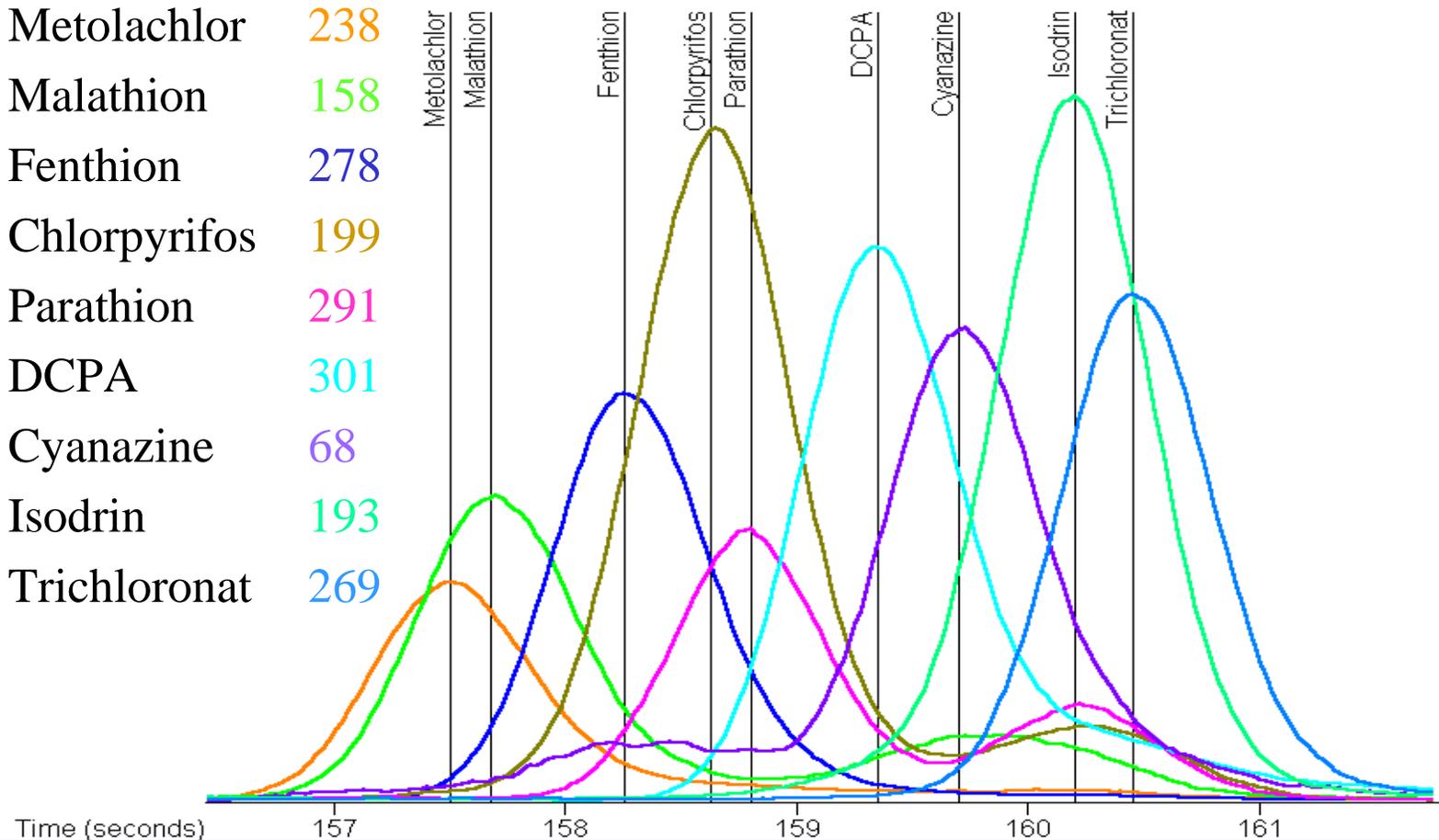
9 peaks located.

2 Spectra/sec

Typical scanning instrument rate

Automated peak find is not possible.

Time (seconds)   157   158   159   160   161
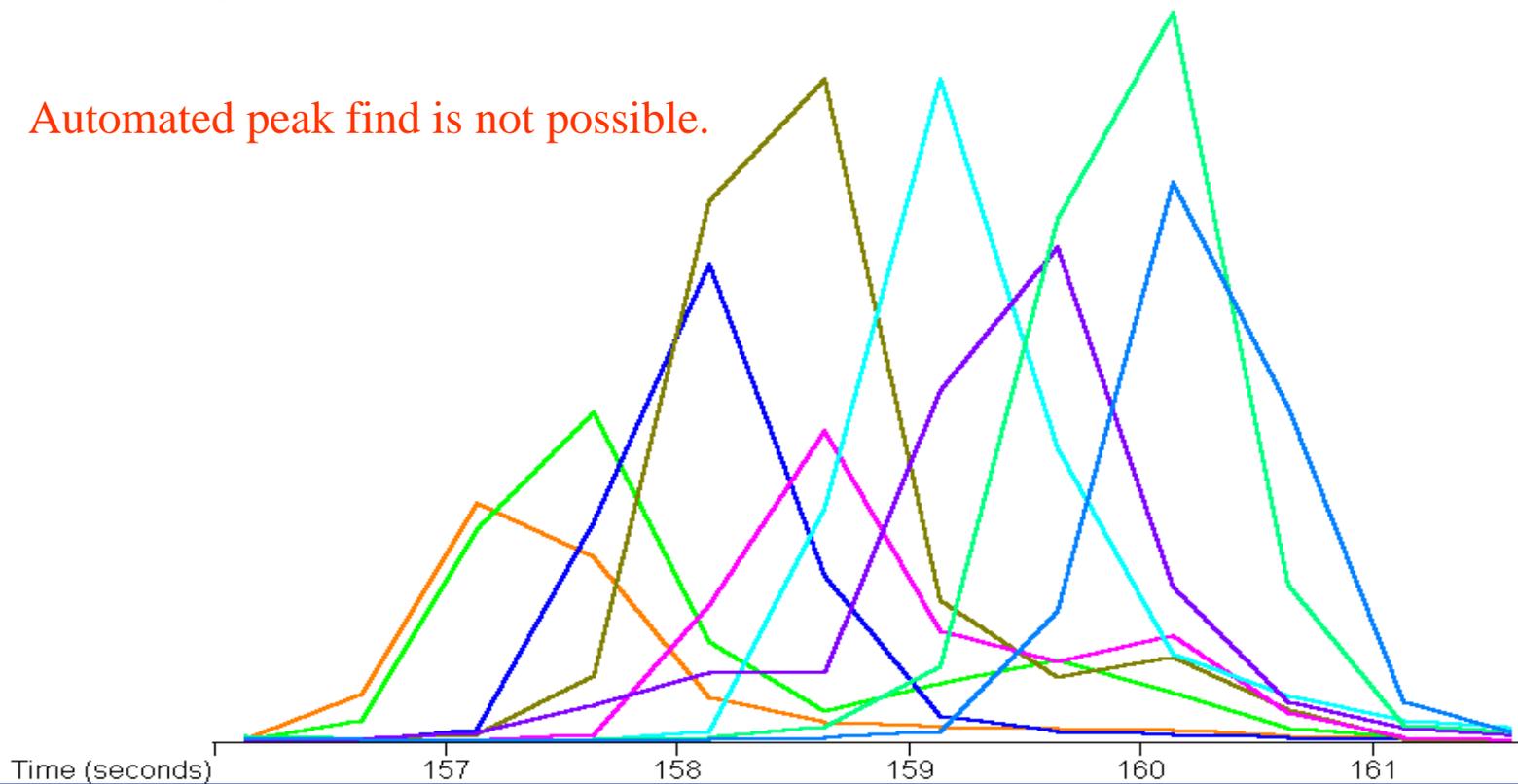
8270 Experiment

- Silarylene-based, Rtx-5Sil MS GC column
  - Low bleed, high Tmax
- Split Injection
  - Sharper Peaks, narrower peak width
  - Better sample handling for contaminated samples
- TOFMS
  - Record full scan data at necessary rate
- Analyze "real" samples and compare to "accepted values"
  - Technique needs to be equivalent, at a minimum for acceptance by environmental community

GC Conditions

- Split injection
  - 4mm Restek Siltek liner with Siltek wool
  - One microliter at 250°C
  - Split ratio 50:1
  - 10m x 0.18mm x 0.18μm Restek Rtx-5SilMS column
  - Constant flow helium, 2 mL/minute

- GC oven program
  - 40°C (0.1 min), 30°/min to 340°(0 min)
  - 25 sec solvent delay
  - Total run time: 10 min

GC Column Selection

- Short and narrow bore for rapid analysis
  - 10m x 0.18mm x 0.18µm Rtx-5SilMS
  - 2 mL/min He = ~130 cm/sec linear velocity
- Maximum operating temperature of 340°C
  - Necessary when fast oven programming is used so all compounds elute on ramp
  - Low bleed means low background to MS
- High degree of inertness
  - Analyzing many active compounds, including acids and bases

TOFMS Conditions
LECO Pegasus III

- Source temperature: 250°C
- Electron ionization: 70 eV
- Stored mass range: 35 to 500 u

- Acquisition rate: 20 spectra/sec

Calibration

- **20 to 160 ng/uL**
  - At 50:1 split ratio

- **Can we go even lower?**
  - Go as far as reasonably possible until we have linearity or sensitivity issues…
  - 8270, and 525 in 1 run?

160 ng/uL 8270 Calibration Standard - tic
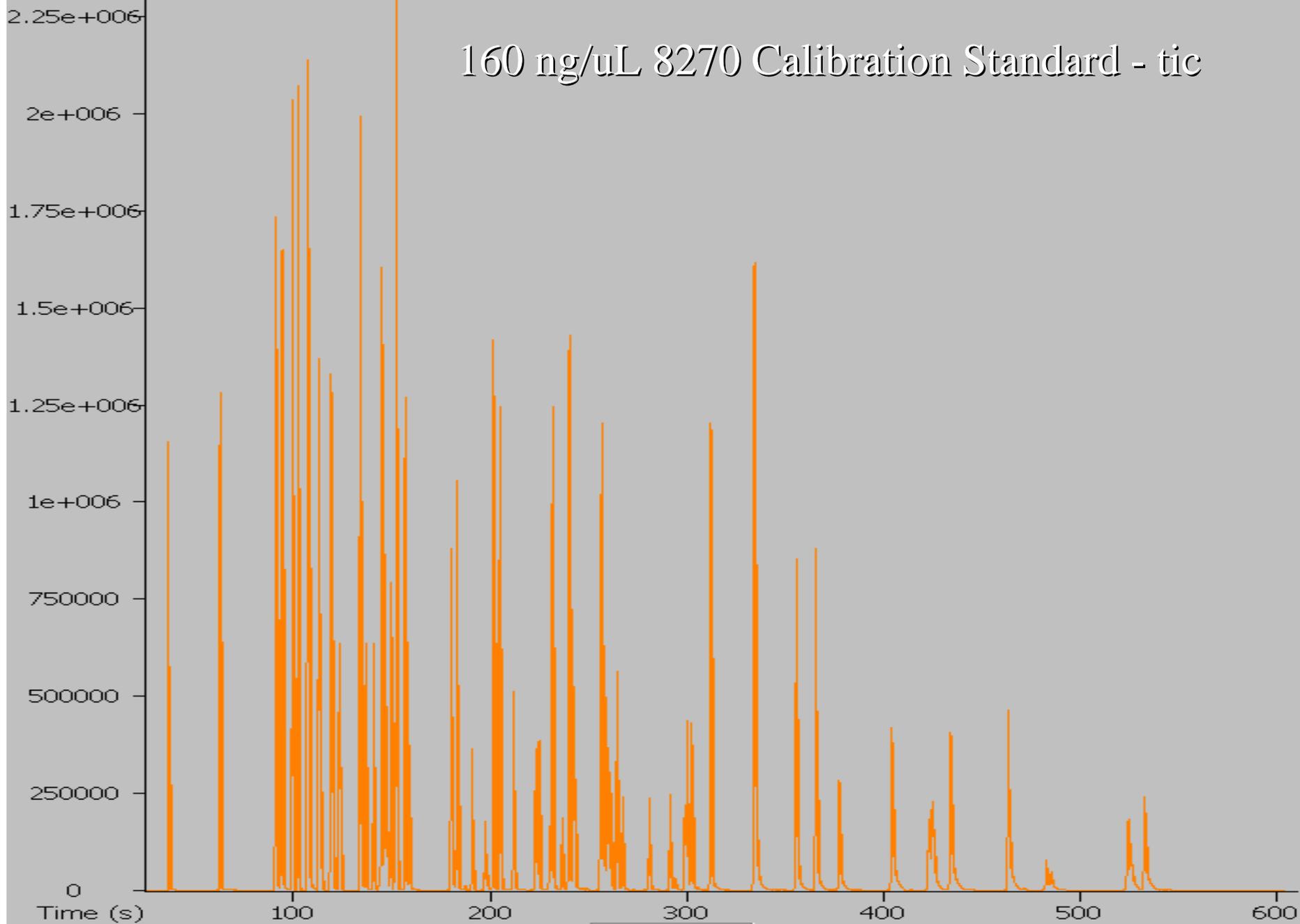
20ng/uL 8270 Calibration Standard - tic
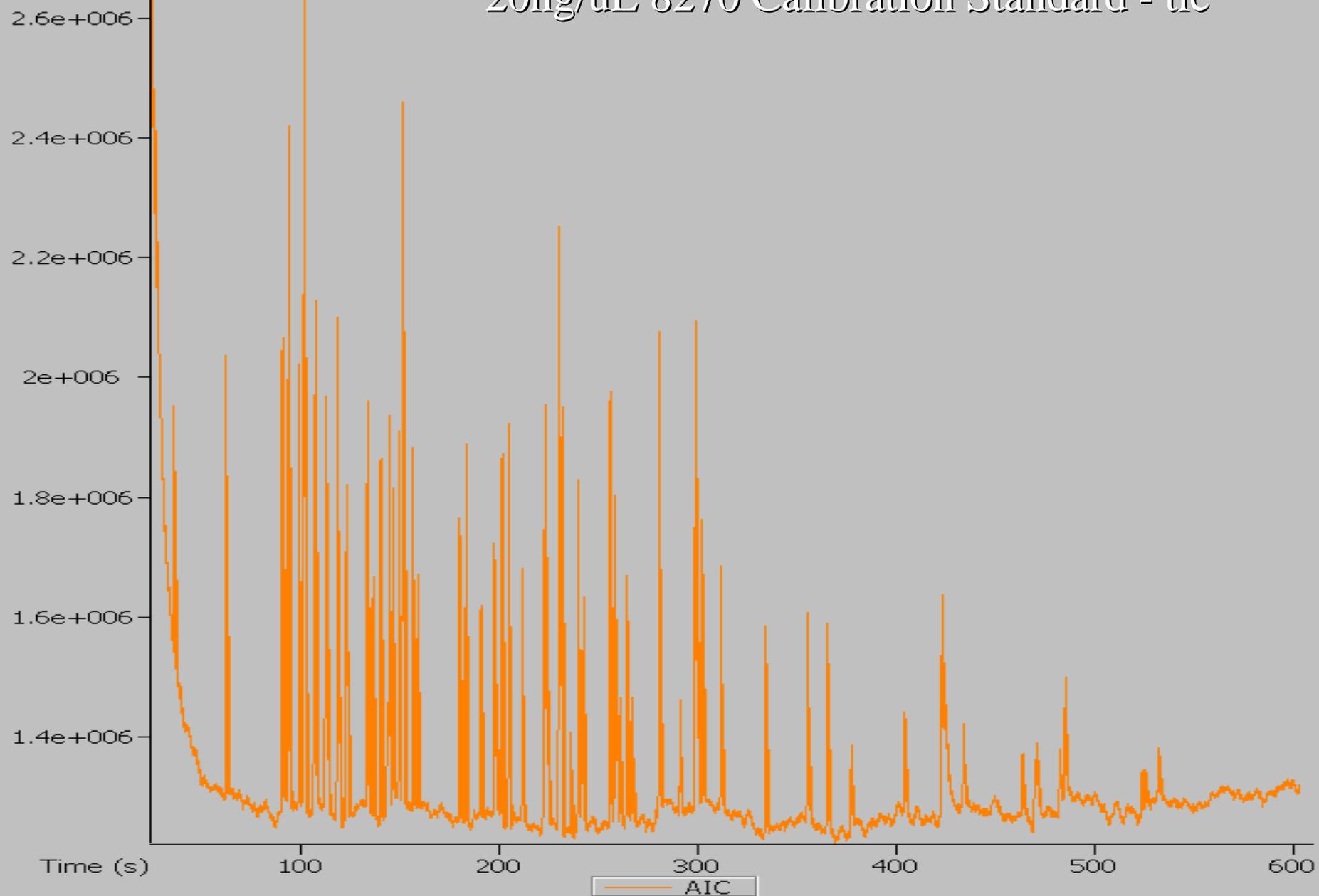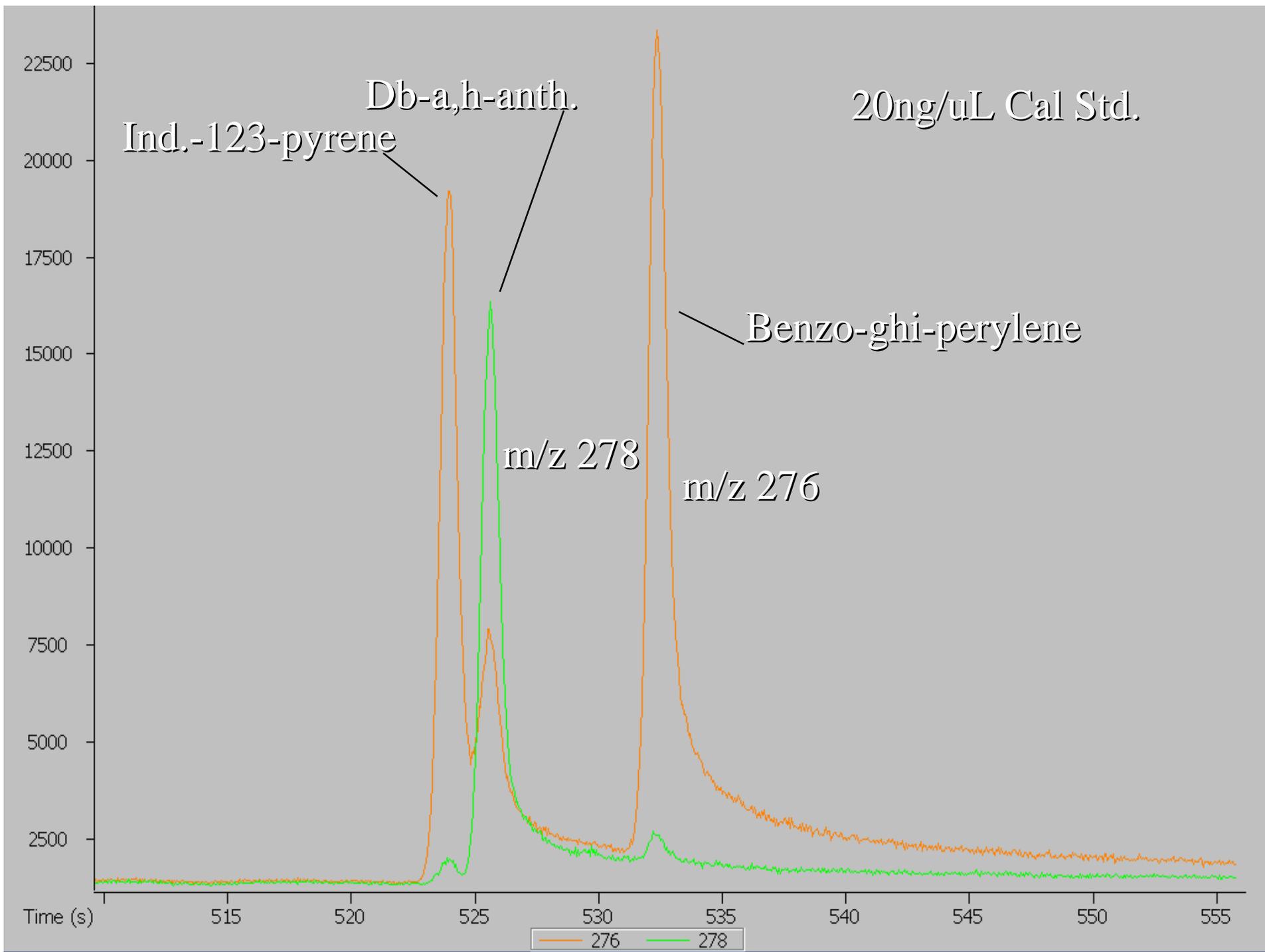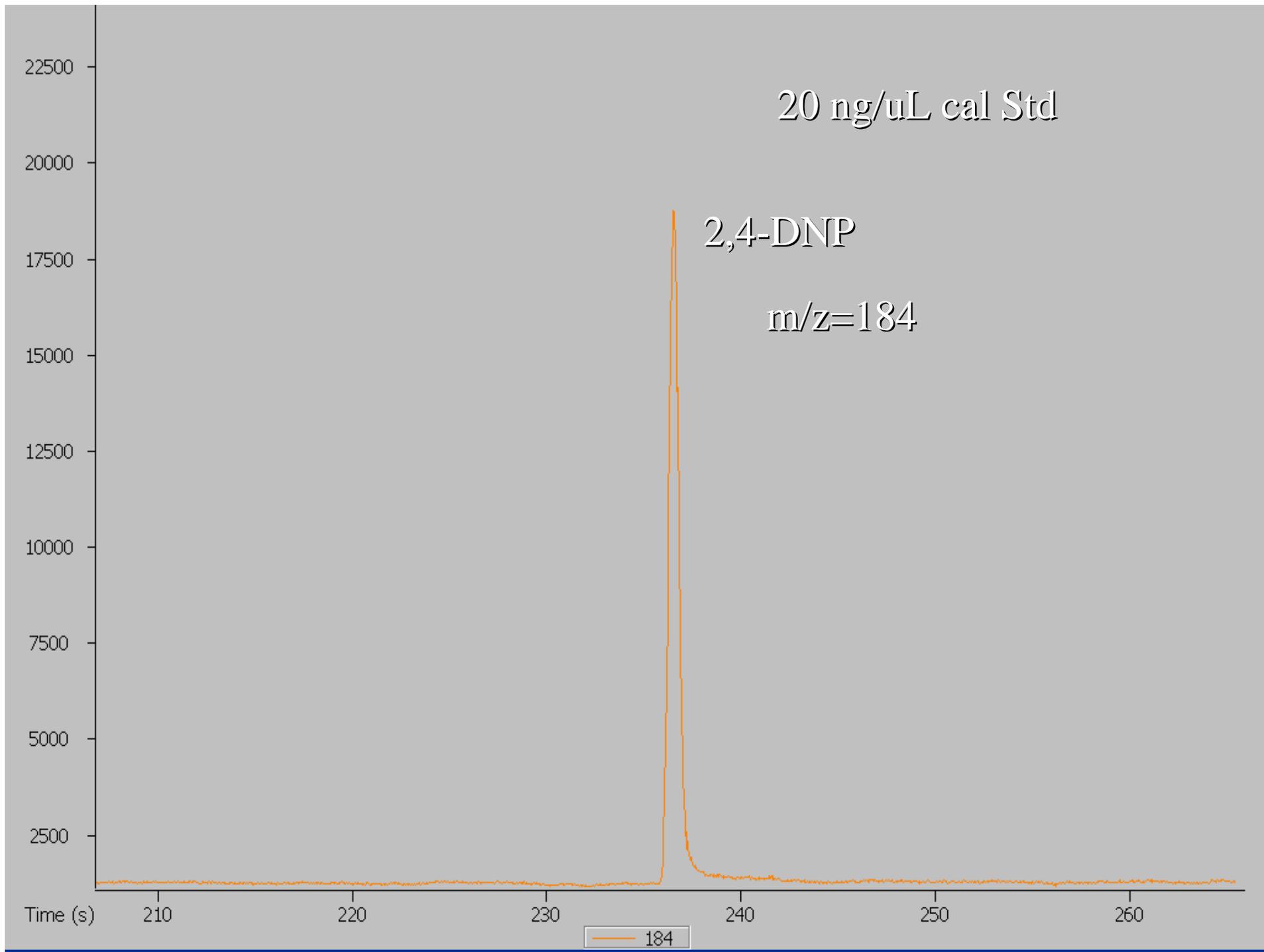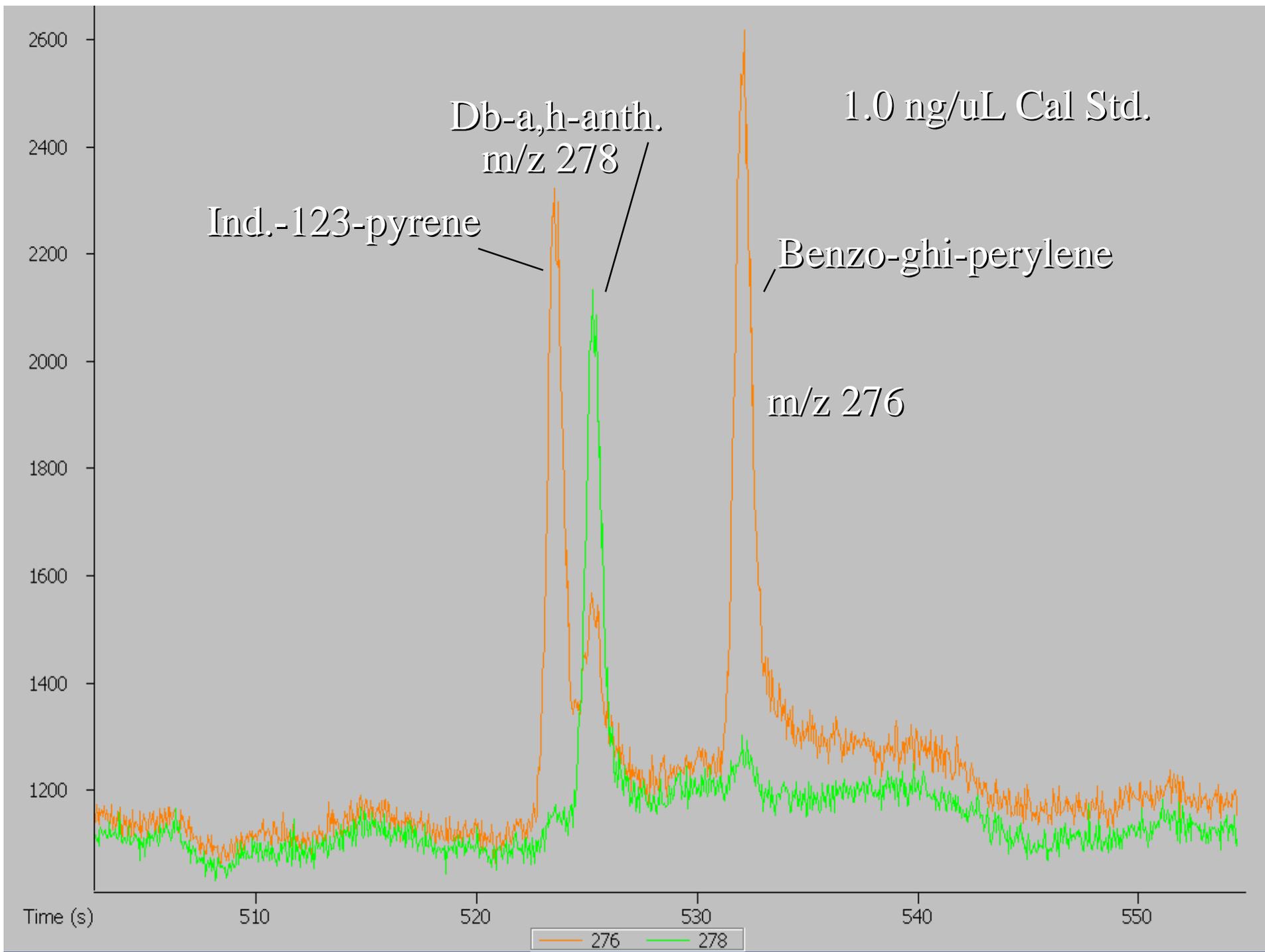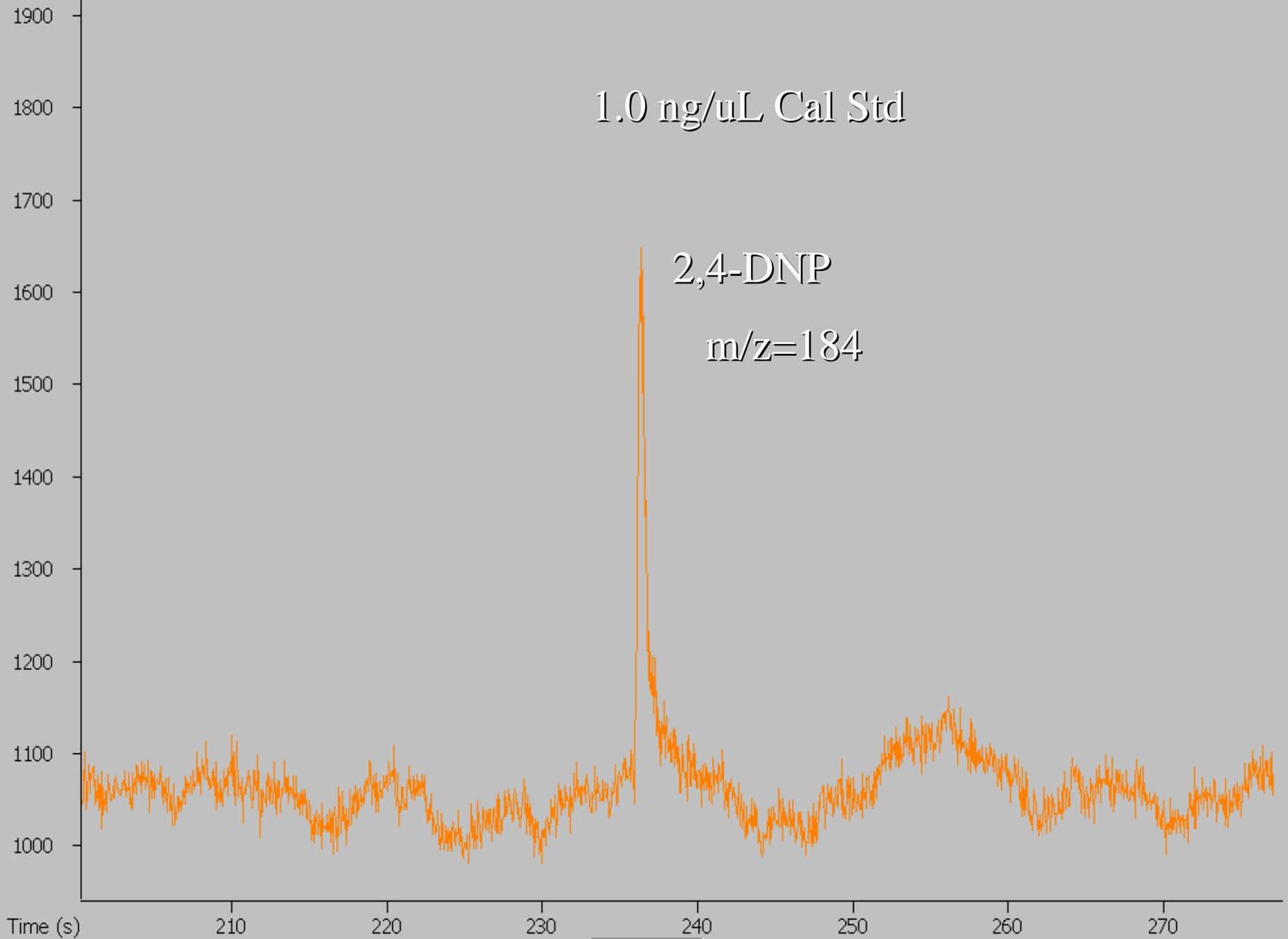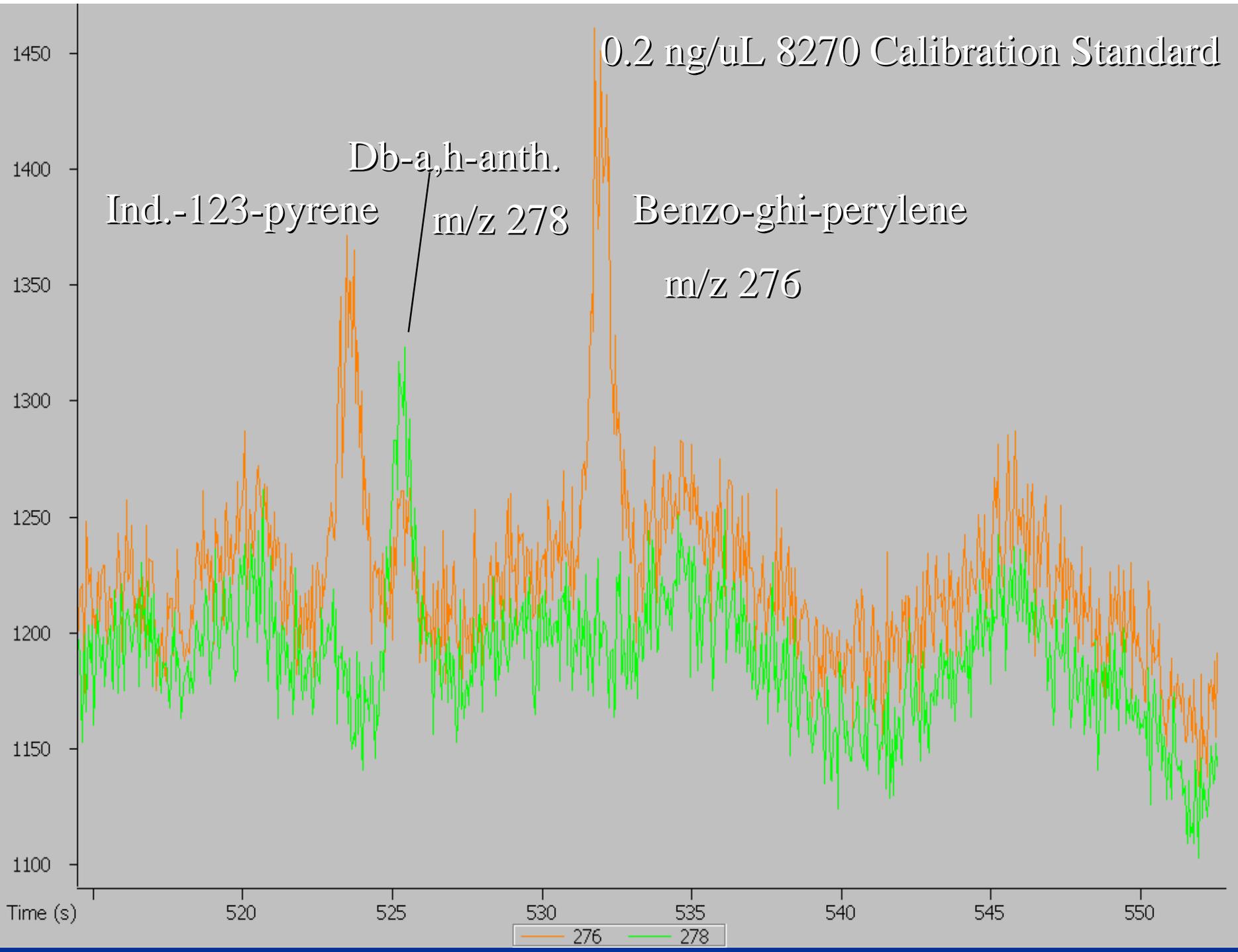
N-nitrosodipropylamine Calibration Curve 0.2 to 160 ppm
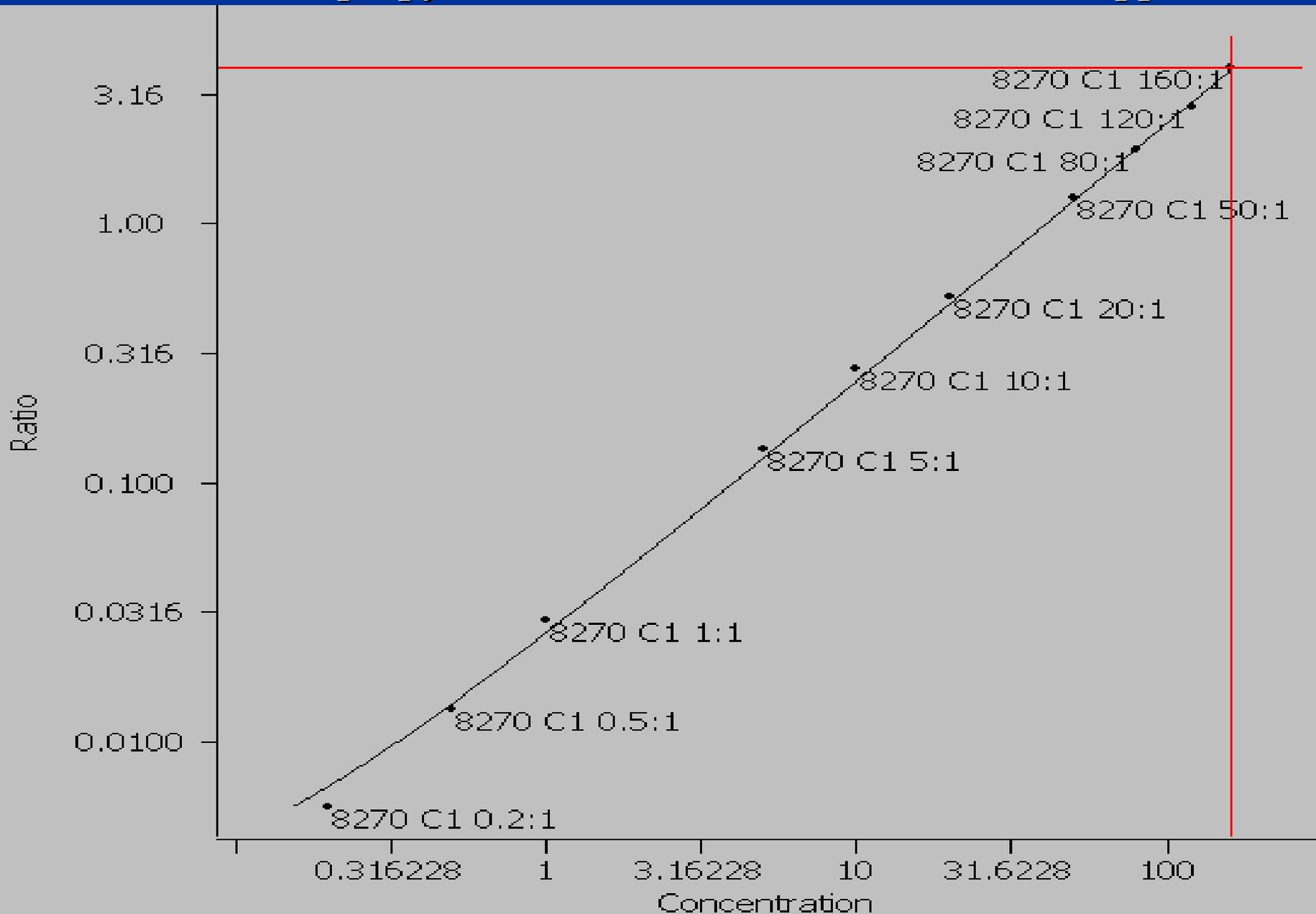
Hexachlorobutadiene Calibration Curve 0.2 to 160 ng/uL

Ratio

8270 C1 160:1
8270 C1 120:1
8270 C1 80:1
8270 C1 50:1
8270 C1 20:1
8270 C1 10:1
8270 C1 5:1
8270 C1 1:1
8270 C1 0.5:1
8270 C1 0.2:1

0.316
0.100
0.0316
0.0100
0.00316

0.316228   1   3.16228   10   31.6228   100

Concentration

$y = +0.00495725x + 0.000296213$
$r = 0.99784$
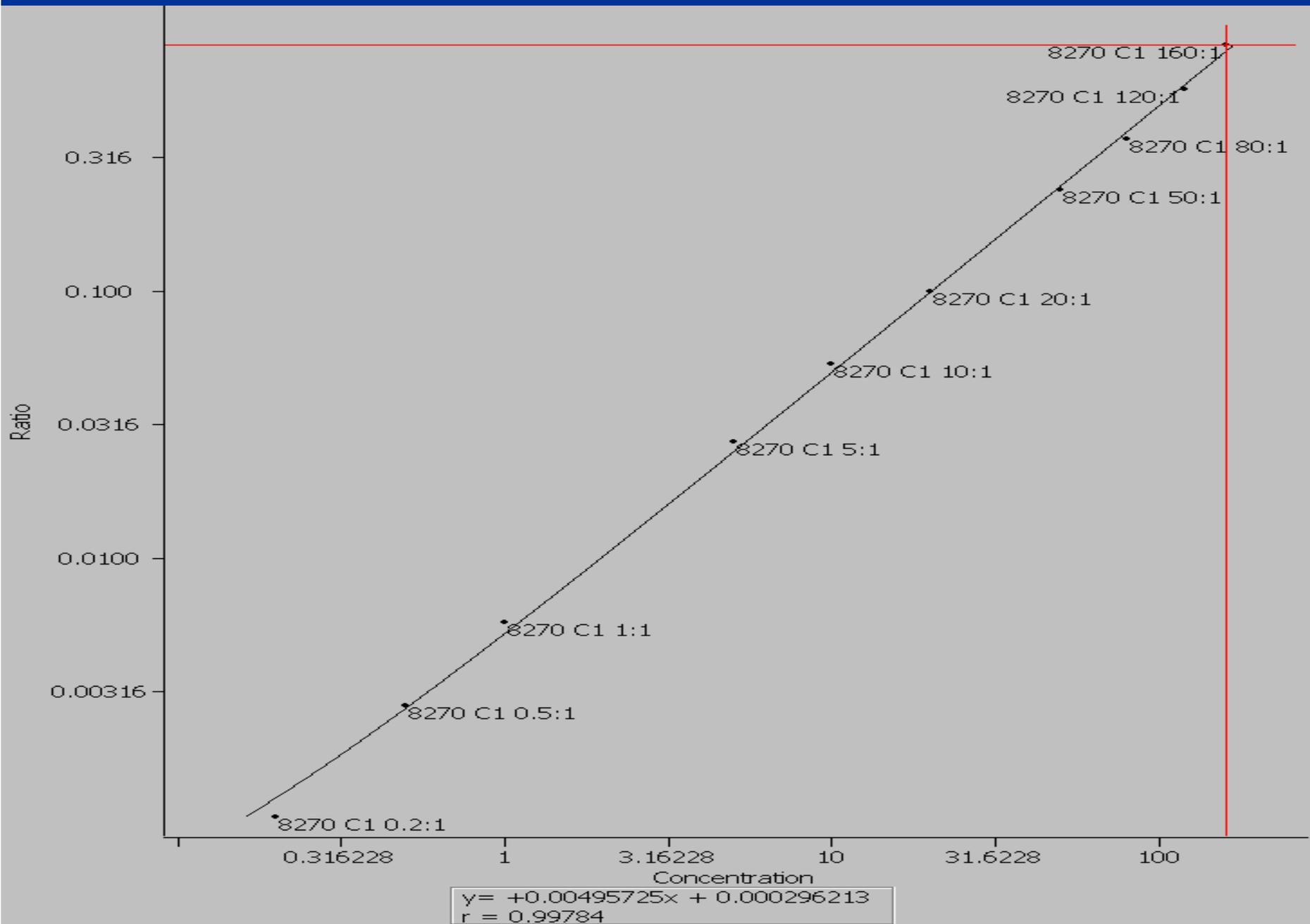
Indeno-1,2,3-cd pyrene Calibration Curve 0.2 – 160 ng.uL
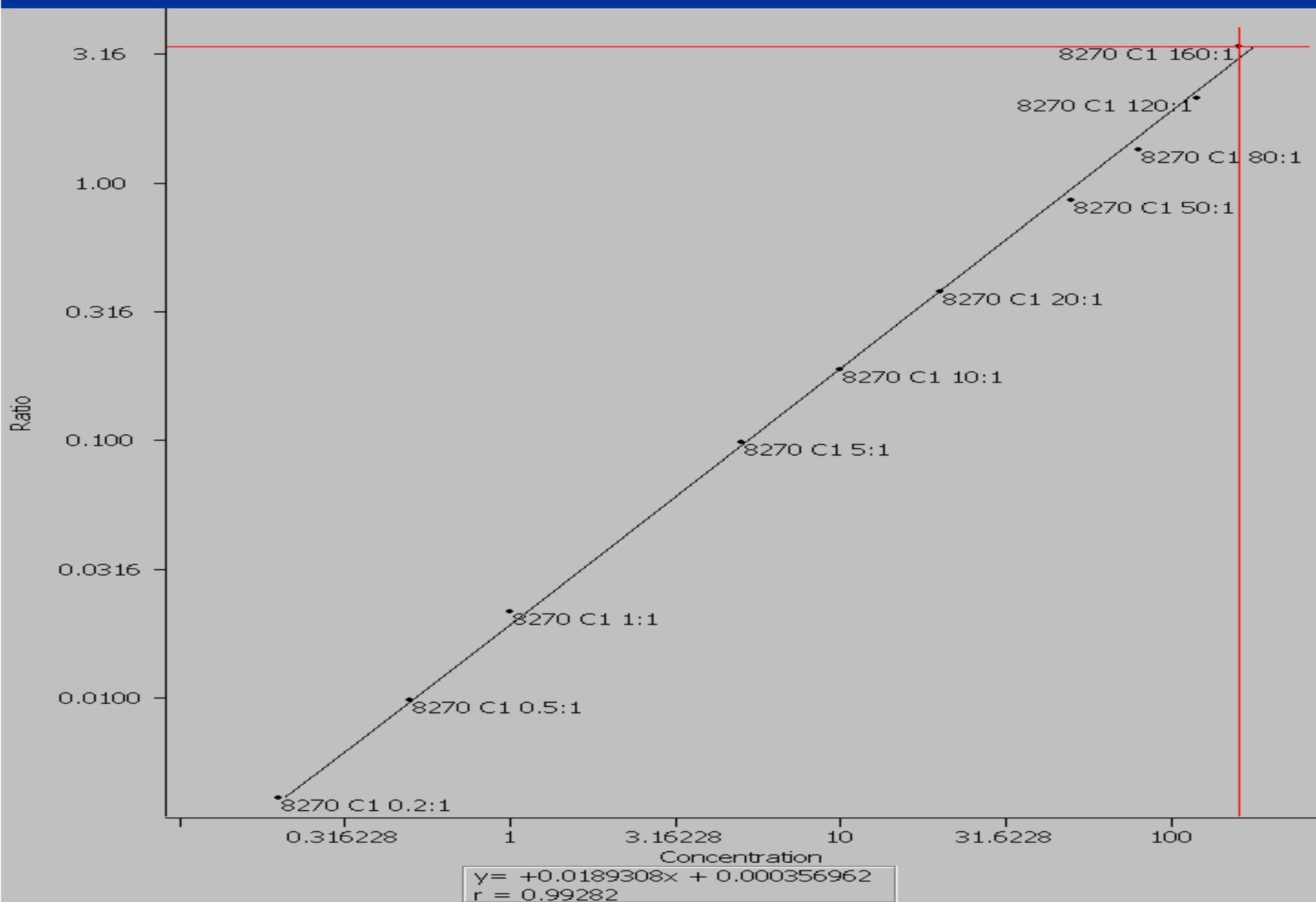
Calibration: 0.2 – 160 ng/uL

Analyte	Name	RF	% RSD RF
1	N-nitrosodimethylamine	1.0355	8.2945
2	2-Fluorophenol	1.2680	7.6450
3	Phenol-d6	.3376	6.7295
4	Phenol	1.7126	8.1128
5	2-Chlorophenol-d4	1.2784	8.7205
6	Bis(2-chloroethyl) ether	1.7656	10.312
7	2-Chlorophenol	1.3272	8.3891
8	1,3-Dichlorobenzene	1.4816	8.8188
10	1,4-Dichlorobenzene	1.5300	9.3936
12	1,2-Dichlorobenzene	1.4162	9.8743
13	Benzyl alcohol	0.62129	5.4928
14	2-Methylphenol	1.0014	7.5679
15	Bis(2-Chloroisopropyl) ether	4.0564	10.865
16	N-nitrosodipropylamine	1.0531	6.8509
17	4-Methylphenol	1.3962	7.6146
18	Hexachloroethane	0.63759	6.3153
20	Nitrobenzene	0.79893	5.7447

Calibration: 0.2 – 160 ng/uL

Analyte	Name	RF	% RSD RF
25	2,4-Dichlorophenol	0.45040	5.4932
26	Benzoic acid	0.28141	6.0157
27	1,2,4-Trichlorobenzene	0.50528	6.2814
30	4-Chloroaniline	0.76842	5.8820
31	Hexachlorobutadiene	0.20824	7.2981
32	4-Chloro-3-methyl phenol	0.52651	4.2807
33	2-Methylnaphthalene	0.77941	7.0069
34	Hexachlorocyclopentadiene	0.58097	4.9004
35	2,4,6-Trichlorophenol	0.65494	6.3512
36	2,4,5-Trichlorophenol	0.75073	4.2657
37	2-Fluorobiphenyl	2.0950	8.7763
38	2-Chloronaphthalene	2.3569	7.4887
39	2-Nitroaniline	1.2166	3.4748
40	Dimethyl phthalate	2.4481	5.8420
41	Acenaphthylene	3.3182	8.2350
42	2,6-Dinitrotoluene	0.54913	5.3293
44	3-Nitroaniline	0.68362	11.639
45	Acenaphthene	1.7045	8.1745
46	2,4-Dinitrophenol	0.25791	8.7682

Calibration: 0.2 – 160 ng/uL

Analyte	Name	RF	% RSD RF
47	Dibenzofuran	2.7990	8.3769
48	4-Nitrophenol	0.56334	7.9127
49	2,4-Dinitrotoluene	0.75561	7.4913
50	Fluorene	1.9027	6.7142
51	Diethyl phthalate	2.7242	5.1845
52	4-Chlorophenyl phenyl ether	0.96773	6.5160
53	4-Nitroaniline	0.68371	11.678
54	4,6-Dinitro-2-methylphenol	0.17243	12.039
55	N-Nitrosodiphenylamine	0.74167	5.7546
56	2,4,6-Tribromophenol	0.16120	6.6840
59	Pentachlorophenol	0.17331	7.8475
61	Phenanthrene	1.5889	9.3179
62	Anthracene	1.6295	5.2792
63	Carbazole	1.4902	4.5625
64	Dibutyl phthalate	2.3977	4.8314
65	Fluoranthene	1.3318	4.1521
66	Pyrene	2.8087	14.550
68	Butyl benzyl phthalate	1.3279	9.5554

Data Comparison

15 samples analyzed, ranging from extraction blanks and LCS's to highly contaminated soils

K5LCS

Target Compound	TOF Concentration	STL Value	% Difference TOF -vs- STL
N-nitrosodimethylamine	35.15	28	-25.5
2-Fluorophenol	78.94	77	-2.5
Phenol-d6	76.99	78	1.3
Phenol	43.18	34	-27.0
2-Chlorophenol-d4	81.98	78	-5.1
Bis(2-chloroethyl) ether	38.91	34	-14.4
2-Chlorophenol	37.81	33	-14.6
1,3-Dichlorobenzene	35.01	31	-12.9
1,4-Dichlorobenzene	35.42	30	-18.1
1,2-Dichlorobenzene-d4	55.47	56	0.9
1,2-Dichlorobenzene	34.99	30	-16.6
Benzyl alcohol	35.91	35	-2.6
2-Methylphenol	34.18	35	2.3
Bis(2-Chloroisopropyl) ether	37.34	34	-9.8
N-nitrosodipropylamine	28.72	33	13.0

575095

Target Compound	TOF Concentration	STL Value	% Difference TOF -vs- STL
2-Fluorophenol	65.61	67.95	3.4
Phenol-d6	62.26	70.2	11.3
2-Chlorophenol-d4	66.53	67.46	1.4
1,2-Dichlorobenzene-d4	45.11	46.97	4.0
2-Methylphenol	1.33	1.4	5.0
4-Methylphenol	1.19	1.3	8.5
Nitrobenzene-d5	43.77	46.94	6.8
2-Fluorobiphenyl	40.11	37.16	-7.9
2,4,6-Tribromophenol	48.67	47.38	-2.7
p-Terphenyl-d14	0.42	0.38	-10.5
Bis(2-ethylhexyl) phthalate	1.67	4.8	65.2
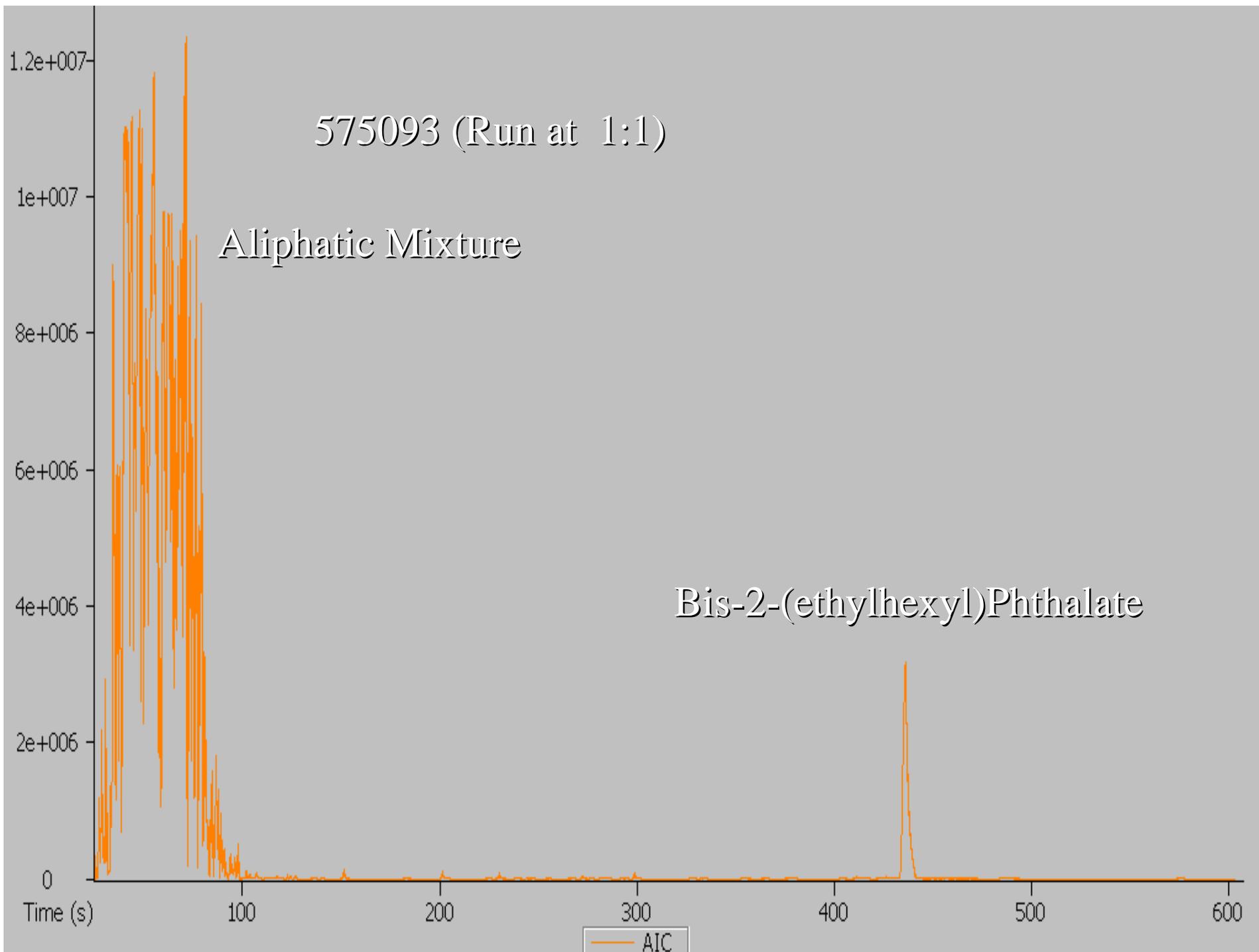
575093 D1

Target Compound	TOF Concentration	STL Value	% Difference TOF -vs- STL
2-Fluorophenol	0	32	100.0
Phenol-d6	64.83	34	-90.7
2-Chlorophenol-d4	68.25	35	-95.0
1,2-Dichlorobenzene-d4	36.39	27	-34.8
Nitrobenzene-d5	32.14	20	-60.7
2-Fluorobiphenyl	34.81	24	-45.0
Bis(2-ethylhexyl) phthalate	6500	4025	-61.5

575093MS

Target Compound	TOF Concentration	STL Value	% Difference TOF -vs- STL
N-nitrosodimethylamine	93.81	40.1	-133.9
2-Fluorophenol	ND	ND	
Phenol-d6	96.83	62.1	-55.9
Phenol	52.97	16.03	-230.4
2-Chlorophenol-d4	60.64	64.98	6.7
Bis(2-chloroethyl) ether	29.48	28.47	-3.5
2-Chlorophenol	30.12	30.47	1.1
1,3-Dichlorobenzene	28.48	25.53	-11.6
1,4-Dichlorobenzene	29.19	26.04	-12.1
1,2-Dichlorobenzene-d4	42.89	45.5	5.7
1,2-Dichlorobenzene	29.5	25.54	-15.5
Benzyl alcohol	26.46	29.91	11.5
2-Methylphenol	29.24	29.58	1.1
Bis(2-Chloroisopropyl) ether	30.1	26.73	-12.6
N-nitrosodipropylamine	19.92	28.06	29.0

574951 7:1000 Dilution - tic

PAH Contamination Sample
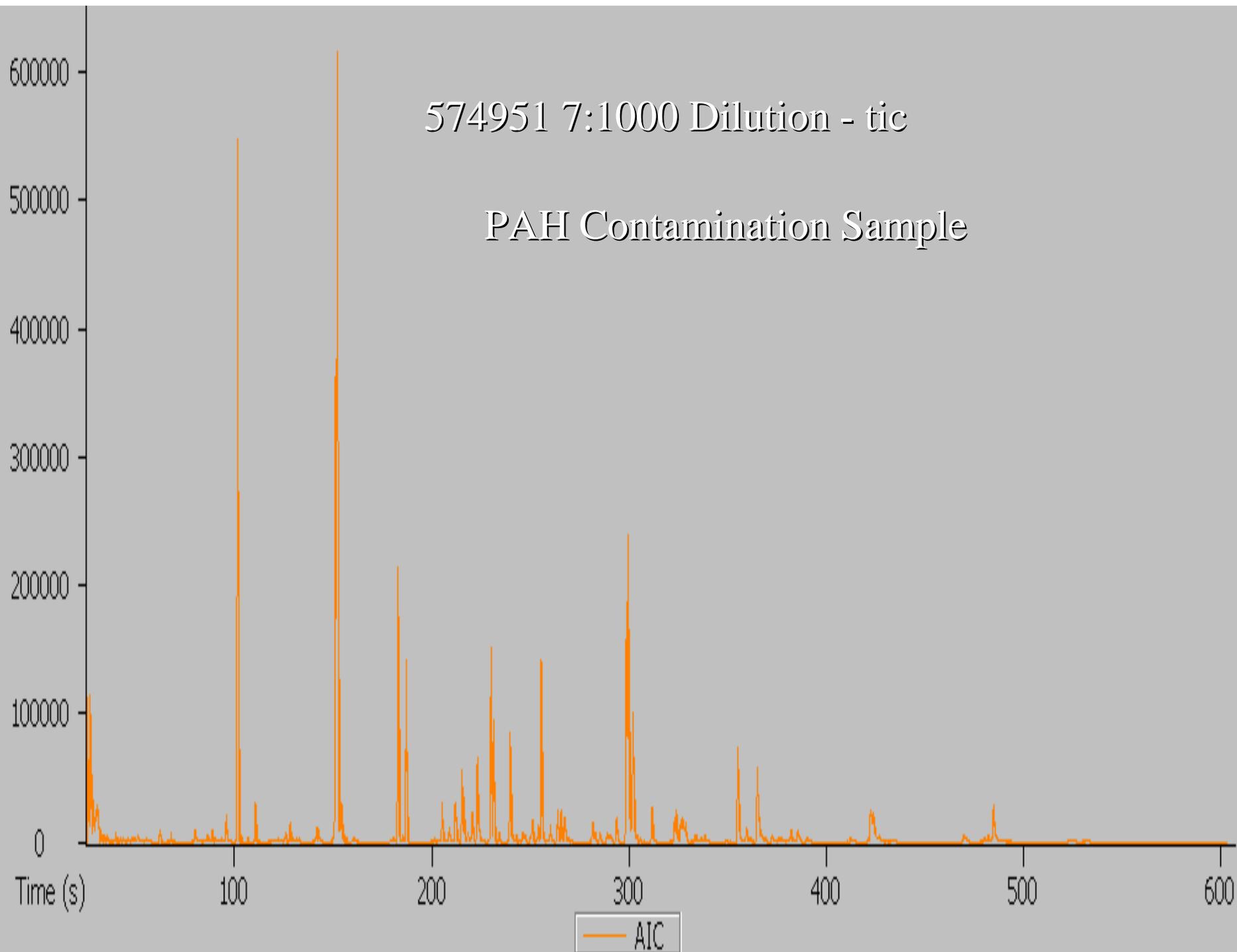
574951

Target Compound	TOF Concentration at DF=142.9	Corrected Concentration	STL Value	% Difference TOF -vs- STL
2-Fluorophenol	0.43	61.4	49.25	-24.8
Phenol-d6	0.46	65.7	ND	
2-Chlorophenol-d4	0.43	61.4	55.42	-10.9
1,2-Dichlorobenzene-d4	0.27	38.6	73.14	47.2
Nitrobenzene-d5	0.32	45.7	ND	
Naphthalene	53.61	7660.9	6560	-16.8
2-Methylnaphthalene	16.84	2406.4	2378	-1.2
2-Fluorobiphenyl	0.31	44.3	68.99	35.8
Acenaphthylene	7.45	1064.6	861	-23.6
Acenaphthene	8.75	1250.4	1148	-8.9
Dibenzofuran	10.7	1529.0	1312	-16.5
Fluorene	13.64	1949.2	1681	-16.0
2,4,6-Tribromophenol	0.61	87.2	42.82	-103.6
Phenanthrene	33.72	4818.6	4510	-6.8

574951 - continued

Target Compound	TOF Concentration at DF=142.9	Corrected Concentration	STL Value	% Difference TOF -vs- STL
Anthracene	15.12	2160.6	2132	-1.3
Carbazole	4.3	614.5	ND	
Fluoranthene	17.28	2469.3	2501	1.3
Pyrene	15.27	2182.1	1845	-18.3
p-Terphenyl-d14	0.27	38.6	76.88	49.8
Benzo[a]anthracene	8.29	1184.6	1066	-11.1
Chrysene	5.65	807.4	943	14.4
Bis(2-ethylhexyl) phthalate	0.34	48.6	ND	
Benzo[b]fluoranthene	6.17	881.7	533	-65.4
Benzo[k]fluoranthene	1.82	260.1	697	62.7
Benzo[a]pyrene	3.55	507.3	738	31.3
Indeno[123-cd]pyrene	2.4	343.0	254	-35.0
Dibenz[ah]anthracene	0.69	98.6	127	22.4
Benzo[ghi]perylene	1.42	202.9	221	8.2

Did we pass?

- **Data are comparable**
  - Very few values are outside the accepted error range
- **Data processing time is similar**
  - Spectral quality from TOFMS is generally more accurate, and automatic
- **Analysis time goals were met**
- **Calibration passes all USEPA method requirements (8270, OLM, 625, 525, etc…)**
- **Sensitivity improvement by 10 to 20 fold**
  - Even using split injection

Conclusions

- Fast GC-TOFMS
  - Quantification of actual samples similar to "accepted" technique
    » Analysis time improved versus conventional GC-MS
    » Sensitivity Improvement
  - Analysis times of less than 10 minutes are possible
  - Low pg sensitivity with full mass spectrum
  - Automated data handling
- Rtx-5Sil MS column performed very well
  - Inertness, even at low concentrations, was excellent
  - Met all separation needs
- Fast GC-TOFMS should have little downtime
  - Split injection
  - Inert, high temperature stable GC column
  - No mass spectrometer source cleaning
- Complete data comparison is available