Improved Separation and Quantification of Dioxin and Furan Congeners Using an Application-Specific Capillary Gas Chromatographic Column and GC-HRMS

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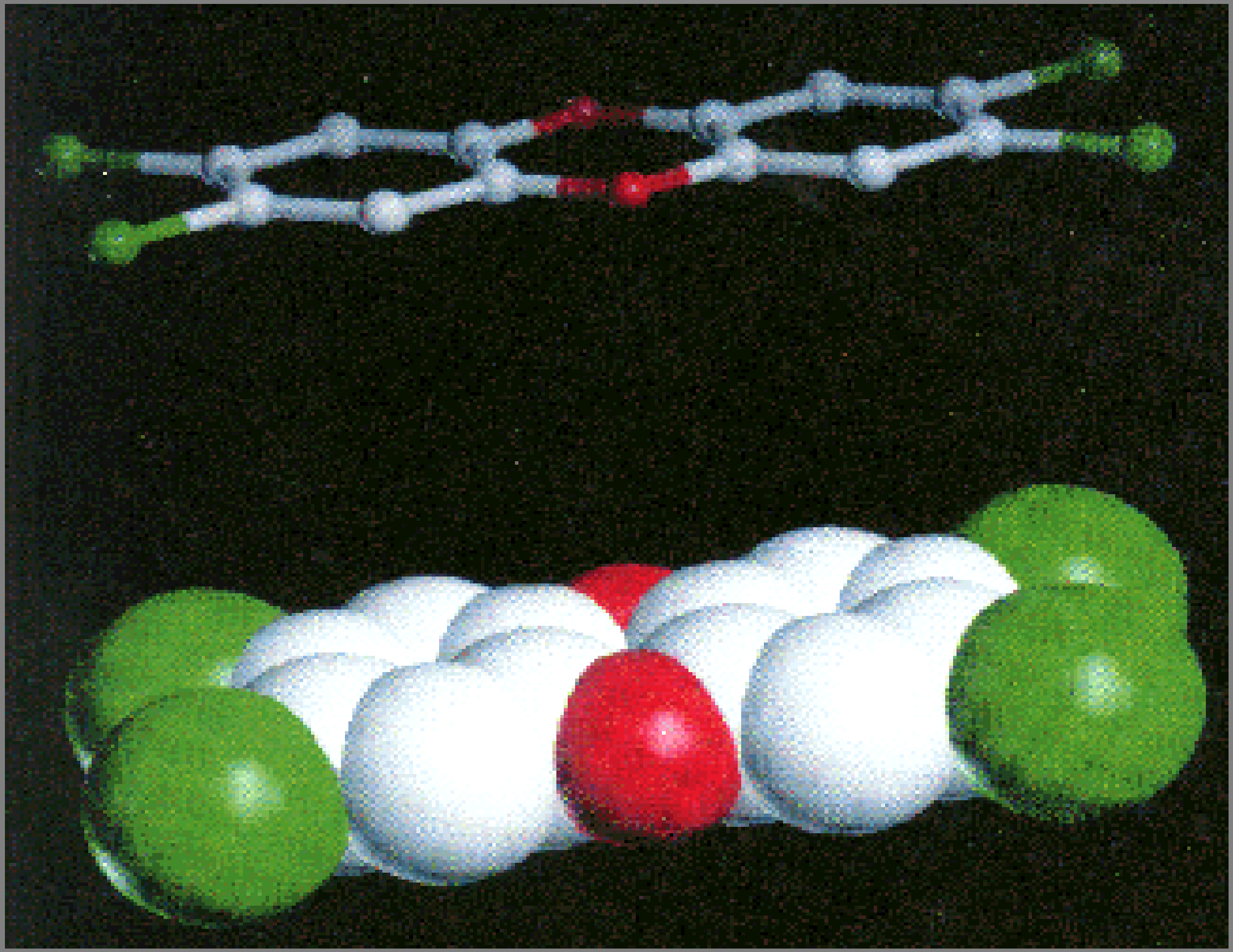
Analysis of Dioxins and Furans



http://dioxins-r-us.ucdavis.edu/TCDD

History
GC Analytical Methods

- All isomers/congeners can be separated from each other with a minimum of two columns (Ryan, J., 1991) and GC HRMS

- **Typically used:** 60-M GC column, 5% phenyl liquid phase, separates many congeners, but not with complete resolution

HOWEVER..

- Confirmation still required, generally with “high-cyano” liquid phases

    ex. for 2,3,7,8-TCDF Method 1613 suggests a 225-phase

Dioxin and Furan Analysis

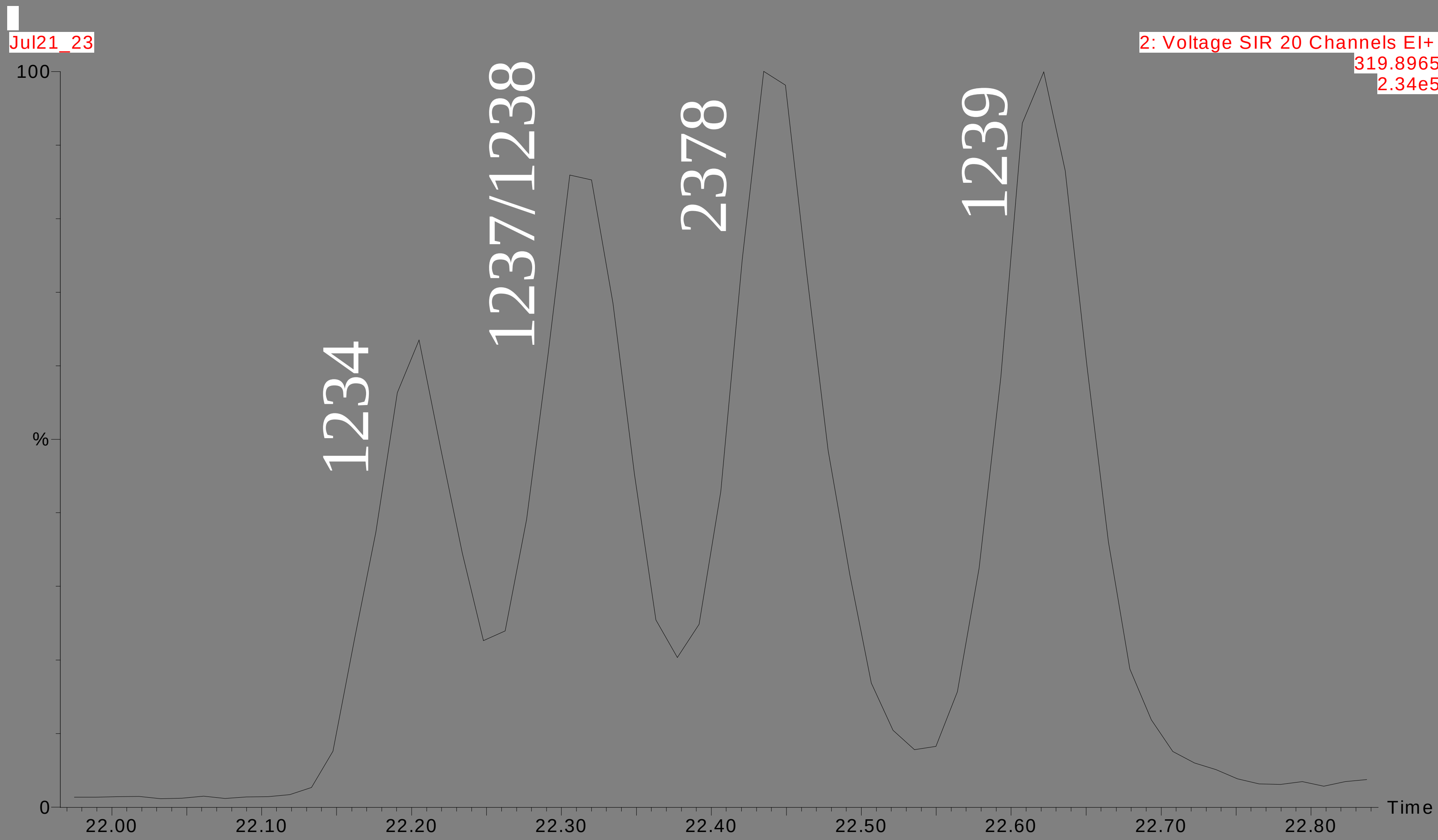
- Dual column method
  - Usually 5% diphenyl column and a high-cyano column (eg Rtx-225)
  - Cyano columns have poorer lifetimes and lower maximum operating temperatures
  - 5% diphenyl phases do not have the selectivity to accurately quantitate most samples
    - USEPA requires 2,3,7,8-tcdf to be confirmed on a X-225
- Desirable to have both columns in the same oven, and to improve the separation of the “5”, or employ a single column which achieves the necessary separation

PCDD and PCDF Target List

# of Chlorine	#Dioxins	#Furans
tetra	22(1)	38(1)
penta	14(1)	28(2)
hexa	10(3)	16(4)
hepta	2(1)	4(2)
octa	1(1)	1(1)

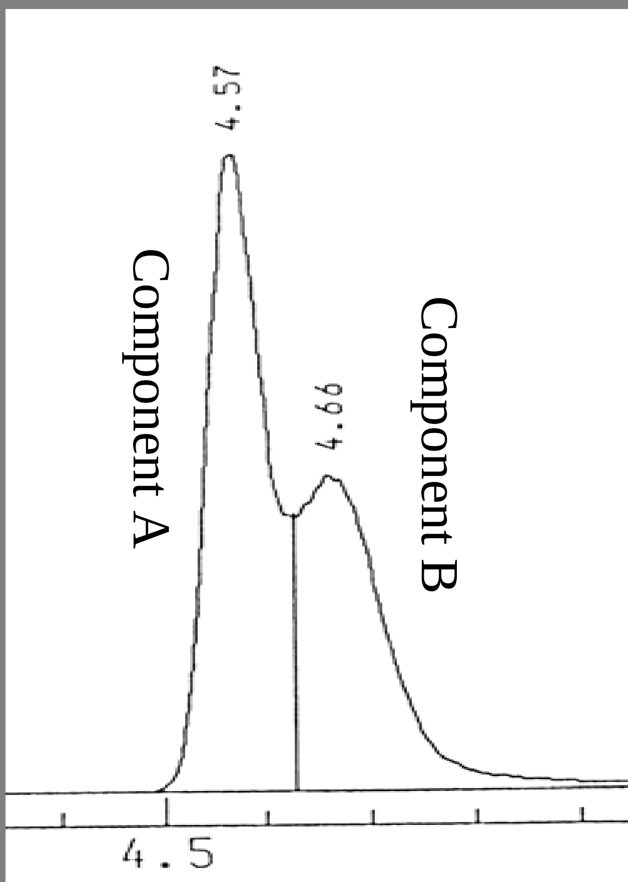
( ) numbers are 2,3,7,8-substituted congeners

Tetra-dioxin resolution check standard on 5% diphenyl / 95% dimethyl stationary phase



60-M X 0.25 mm i.d. X 0.25 um d.f.

How Resolution Affects Quantitation



Quantification of 20 ng/uL Reference Standard (Results Based on Multi-level/Multi-component Calibration):

Component A & B	***Rep 1***	***19.85***	***18.48***
	Rep 2	***19.29***	***18.48***
	Rep 3	***19.36***	***18.52***
Component A	***Rep 1***	***21.48***	
	Rep 2	***20.79***	
	Rep 3	***20.95***	
Component B	***Rep 1***		***16.3***
	Rep 2		***16.46***
	Rep 3		***16.25***

Achieving Analyte Separation

Resolution

$$R = 1/4 \sqrt{L / h} \times (k / k+1) \times (\alpha-1 / \alpha)$$

Capacity Factor

$$k = t_R - t_0 / t_0$$

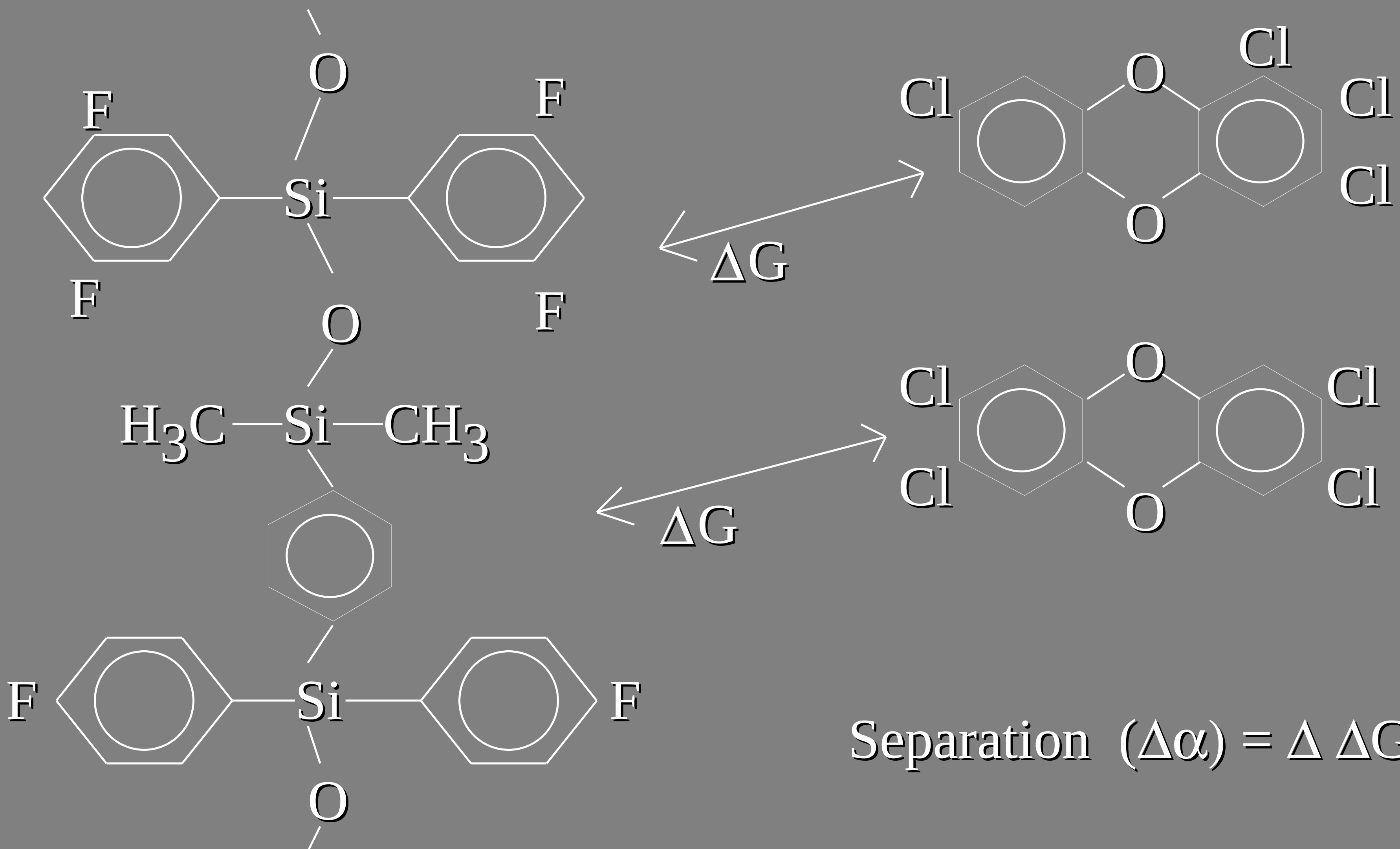
Selectivity

$$\alpha = k_2 / k_1$$

Thermodynamics:

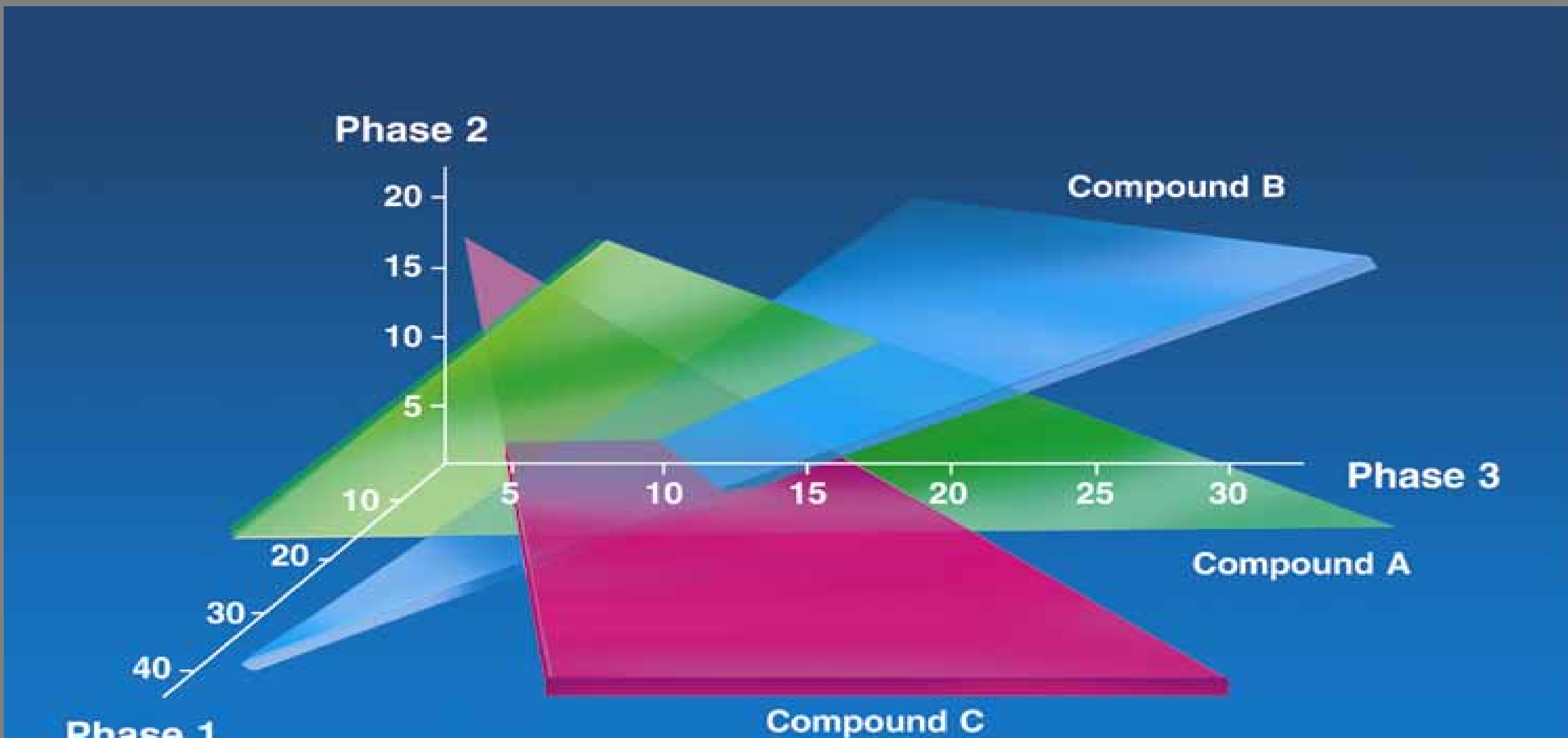
$$\Delta G = \Delta H - T\Delta S \qquad \Delta G = - RT \ln K_D$$

Modeling - Energies of Interaction

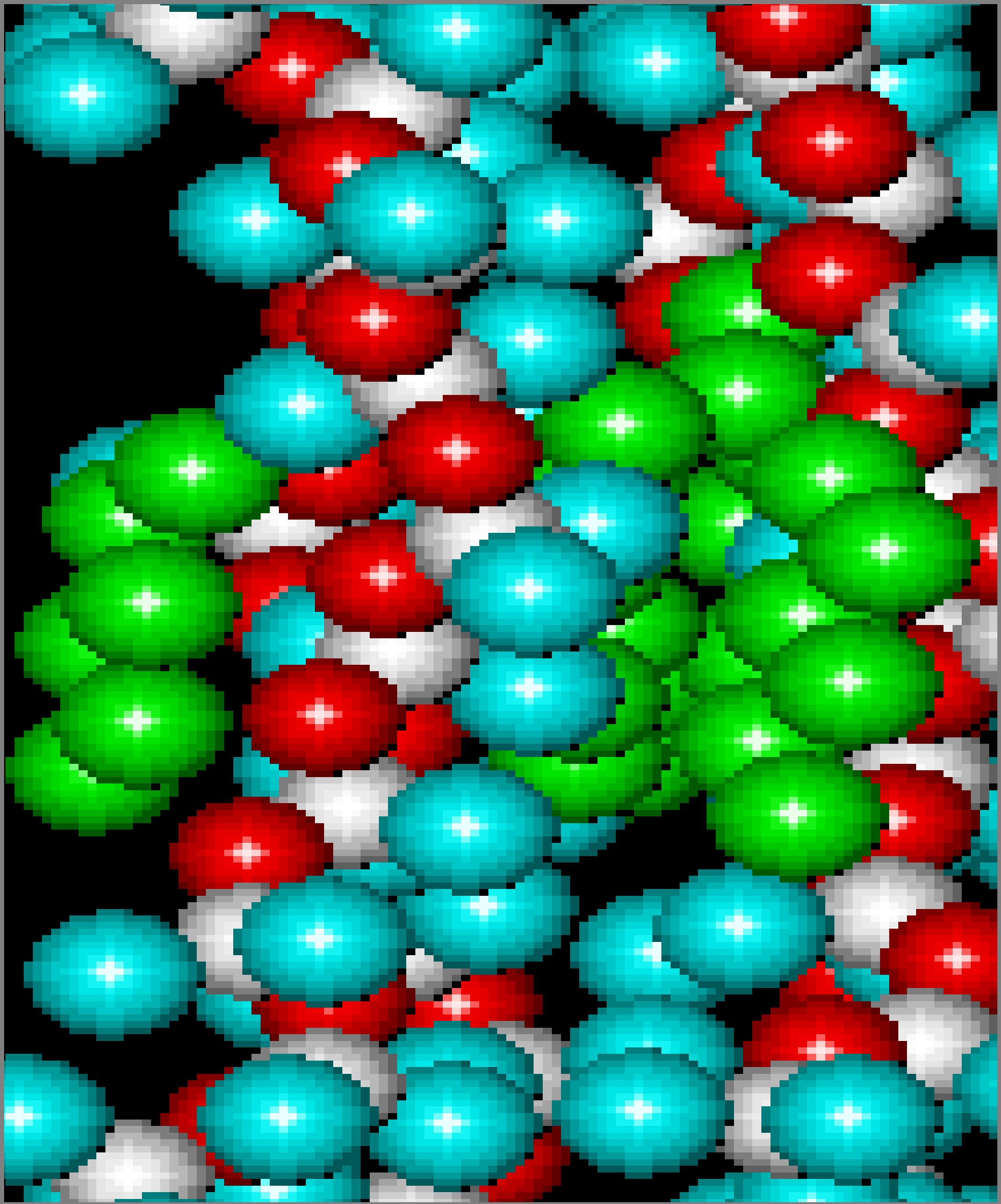


Separation $(\Delta\alpha) = \Delta\,\Delta G$

3-Space Selectivity Model for 3 Compounds



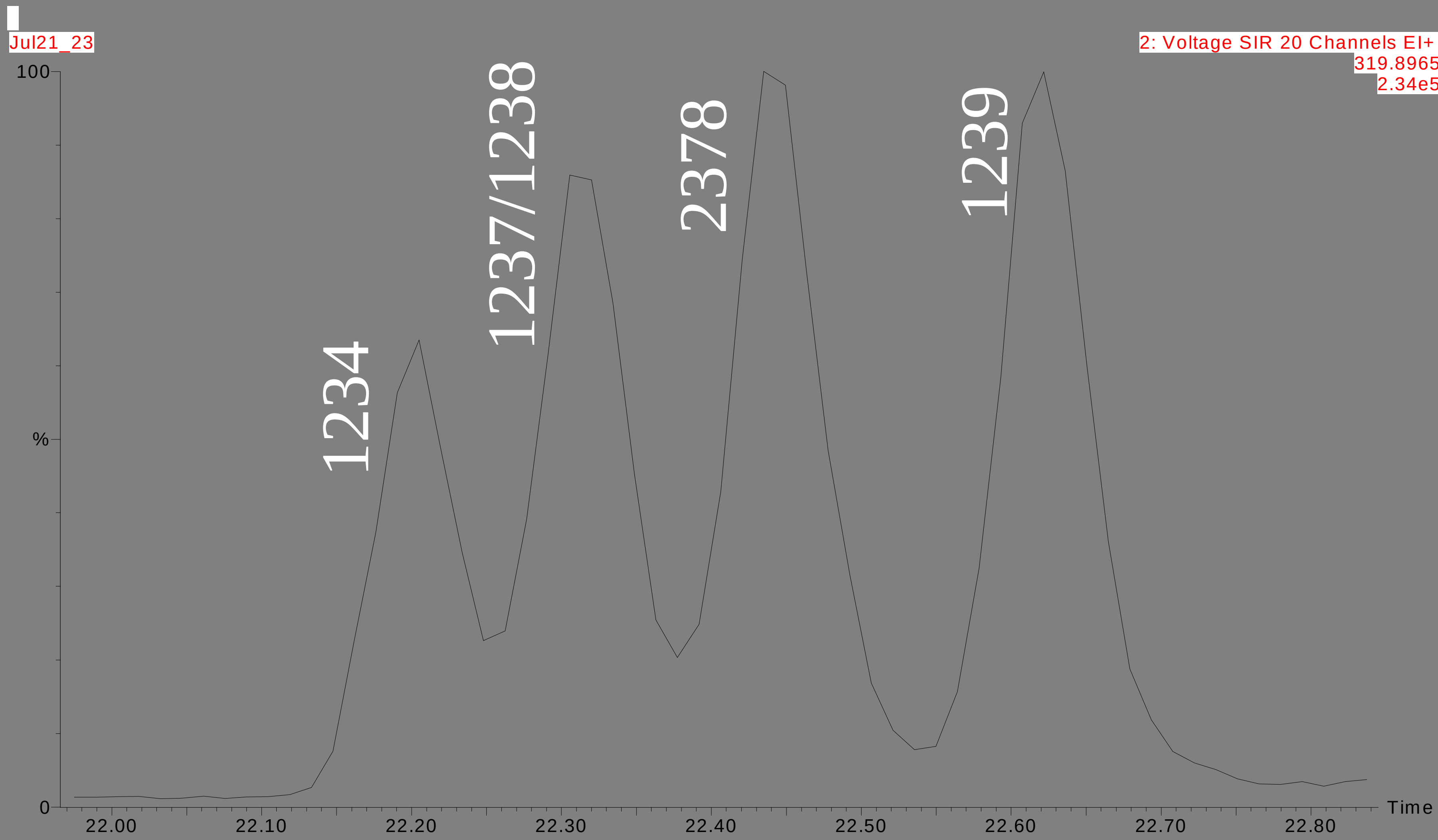
Surface=FΔHΔS



Example Result: Demeton-O on PDMS:

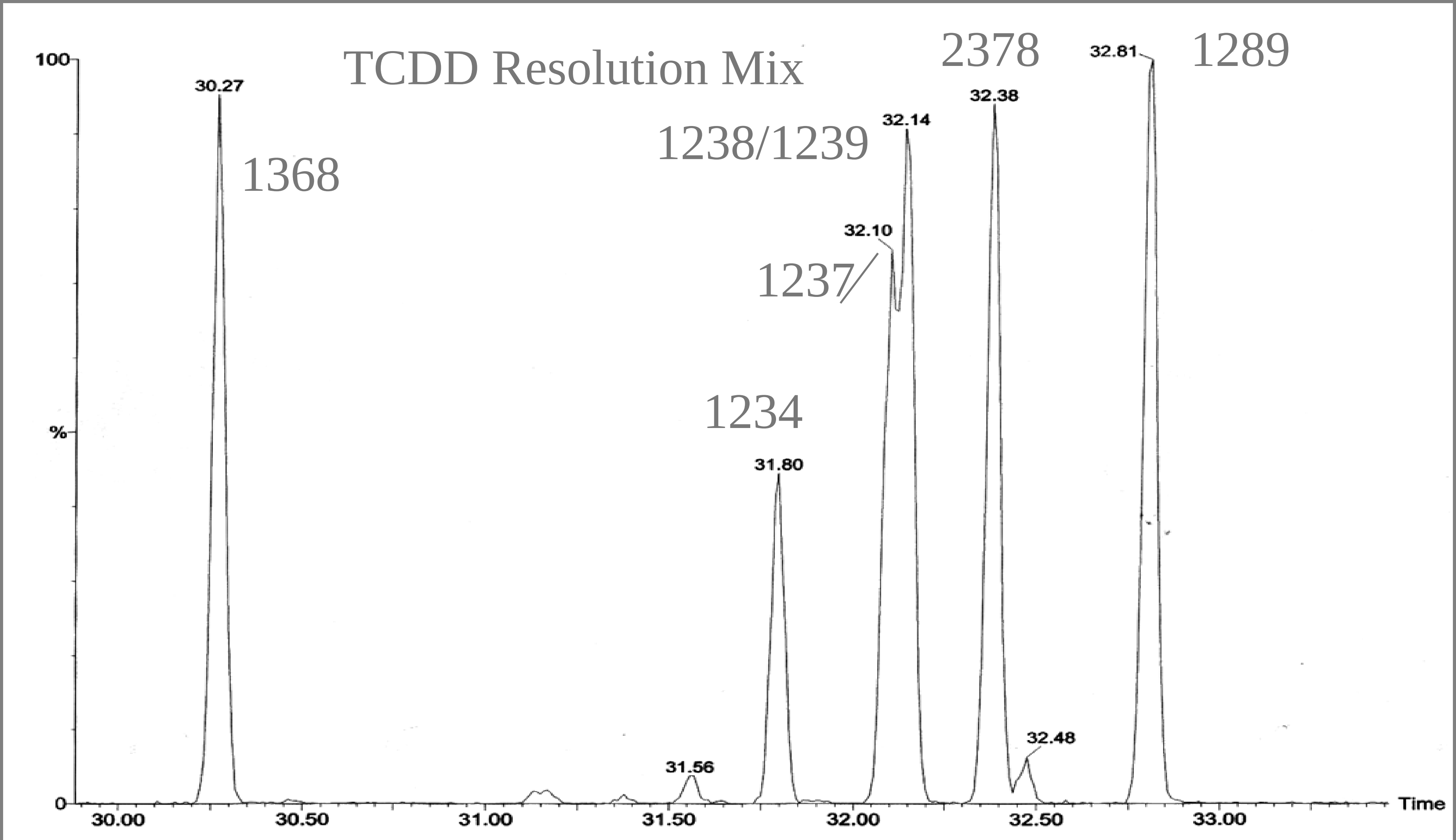
- Observed ΔG = -1.14E4 J/mol
- Calculated ΔG = -1.13E4 J/mol

Tetra-dioxin resolution check standard on 5% diphenyl / 95% dimethyl stationary phase

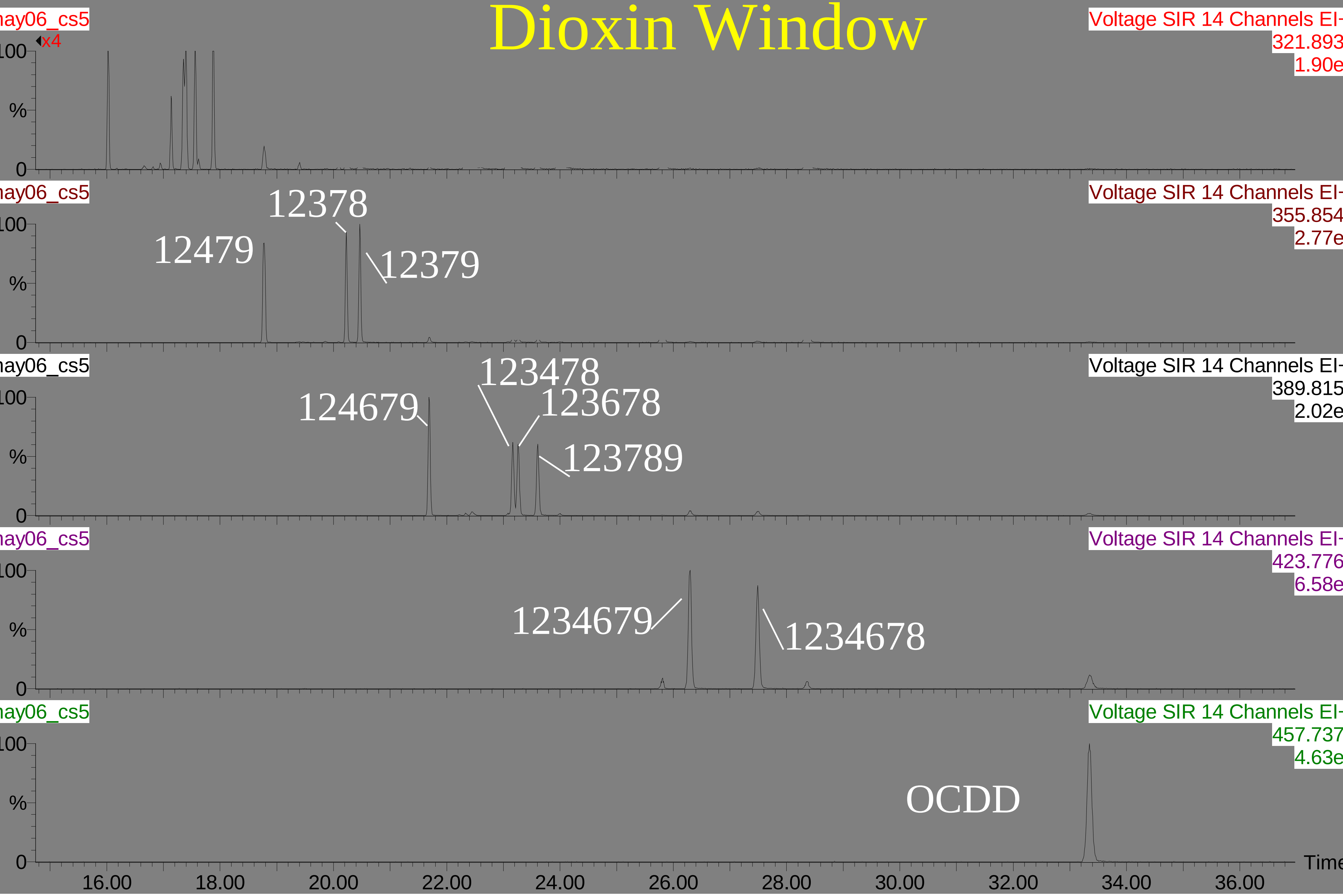


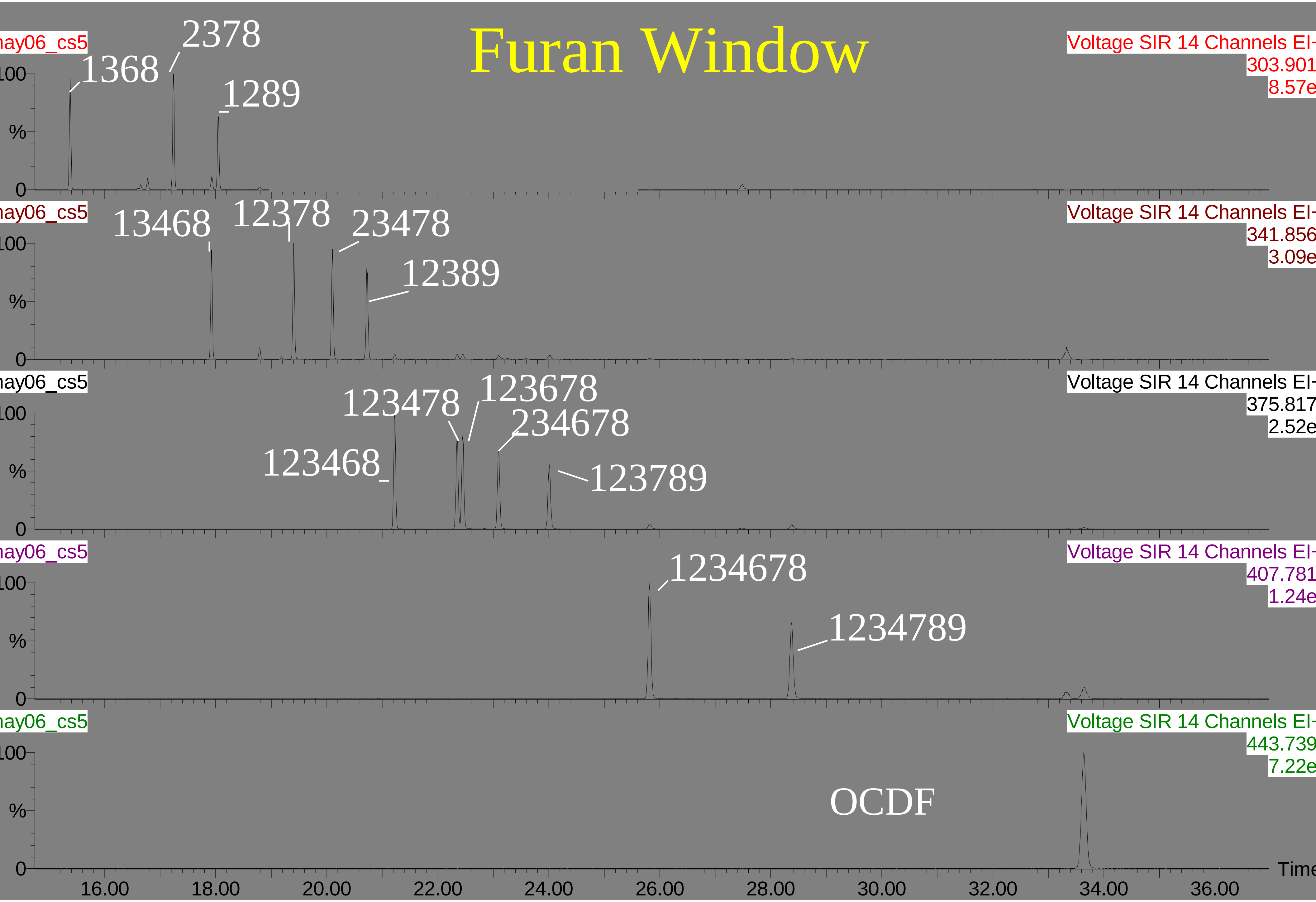
60-M X 0.25 mm i.d. X 0.25 um d.f.

Rtx-Dioxin2 Capillary GC Column



Dioxin Window



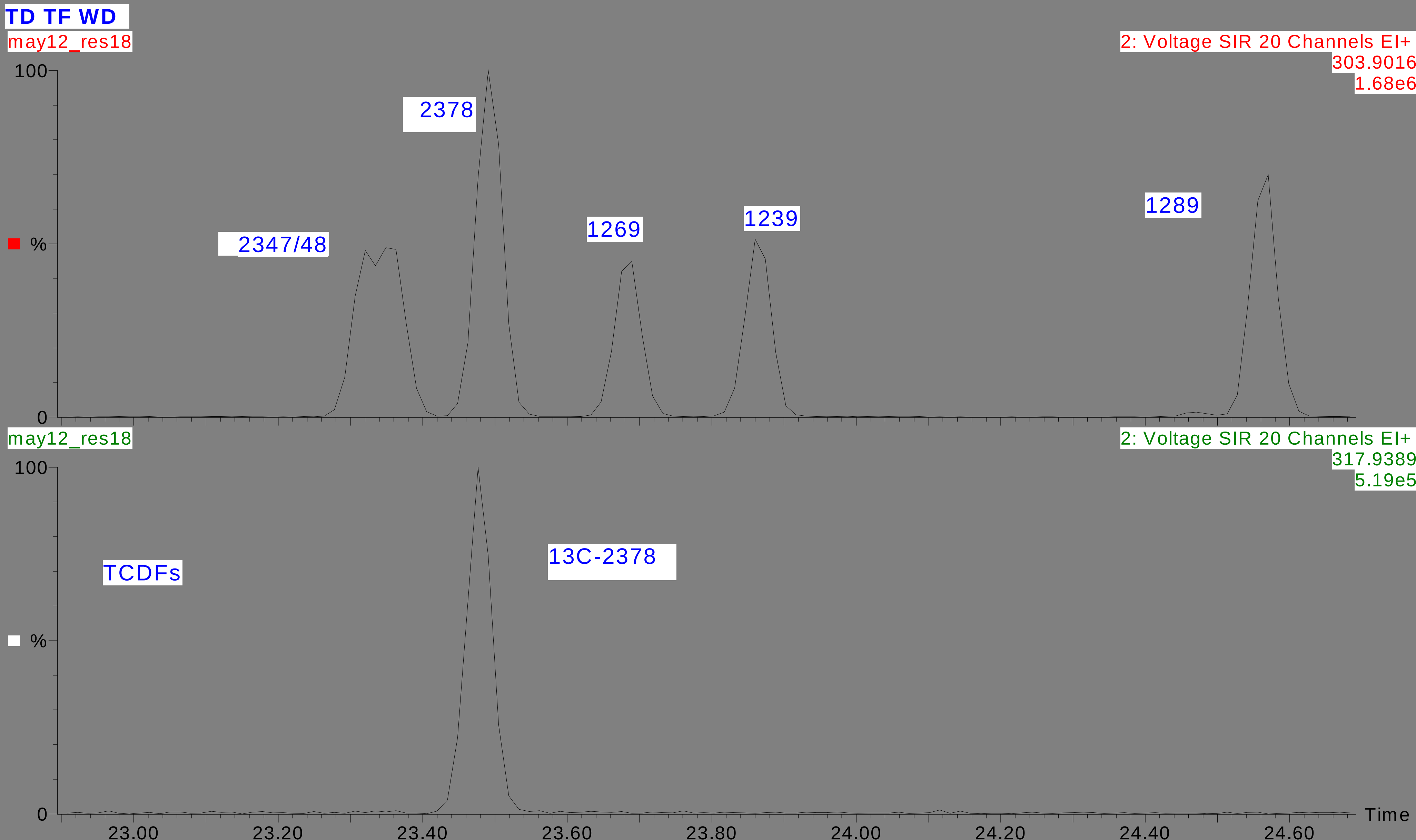


Furan Window
may06_cs5
Voltage SIR 14 Channels EI-
303.901
8.57e
1368
2378
1289
341.856
3.09e
13468
12378
23478
12389
375.817
2.52e
123478
123678
234678
123468
123789
407.781
1.24e
1234678
1234789
443.739
7.22e
OCDF
100
%
0
16.00
18.00
20.00
22.00
24.00
26.00
28.00
30.00
32.00
34.00
36.00
Time

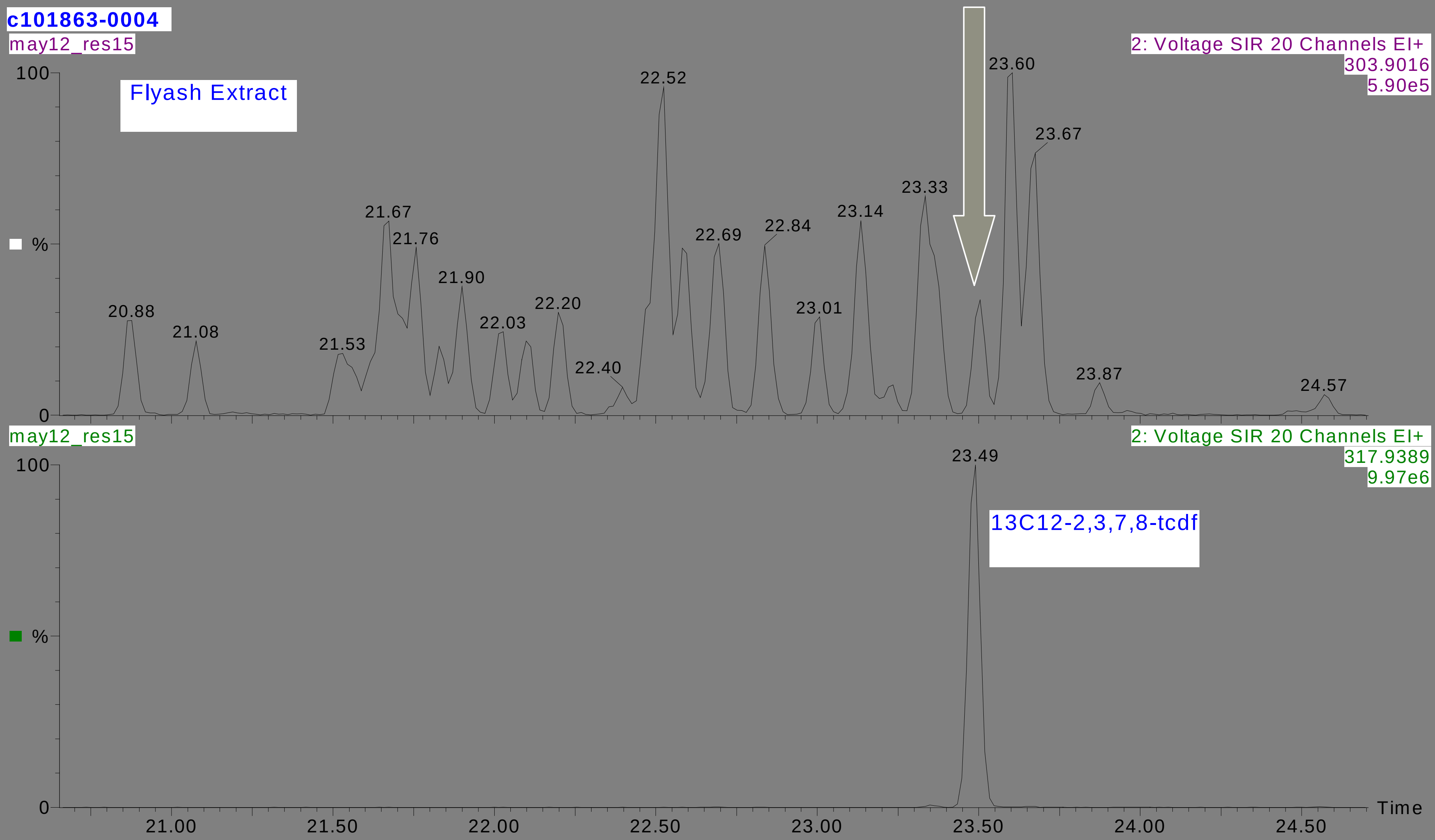
GC program for RTX-Dioxin2®

	60m x 0.25mm x 0.25µm
Gas Flow - constant	1.5mL/min
Initial Temp.	130 °C - hold 1min
1st Temp. Ramp	40 °C/min to 200 °C, 0 hold
2nd Temp. Ramp	3.0 °C/min to 235 °C, 0 hold
3rd Temp. Ramp	5 °C /min to 300 °C, hold ~5-10min.
Total Run Time	~43 min

TCDF Resolution on RTX-Dioxin2®



TCDF ion channel for flyash extract



TCDF ion channel for sewage sludge

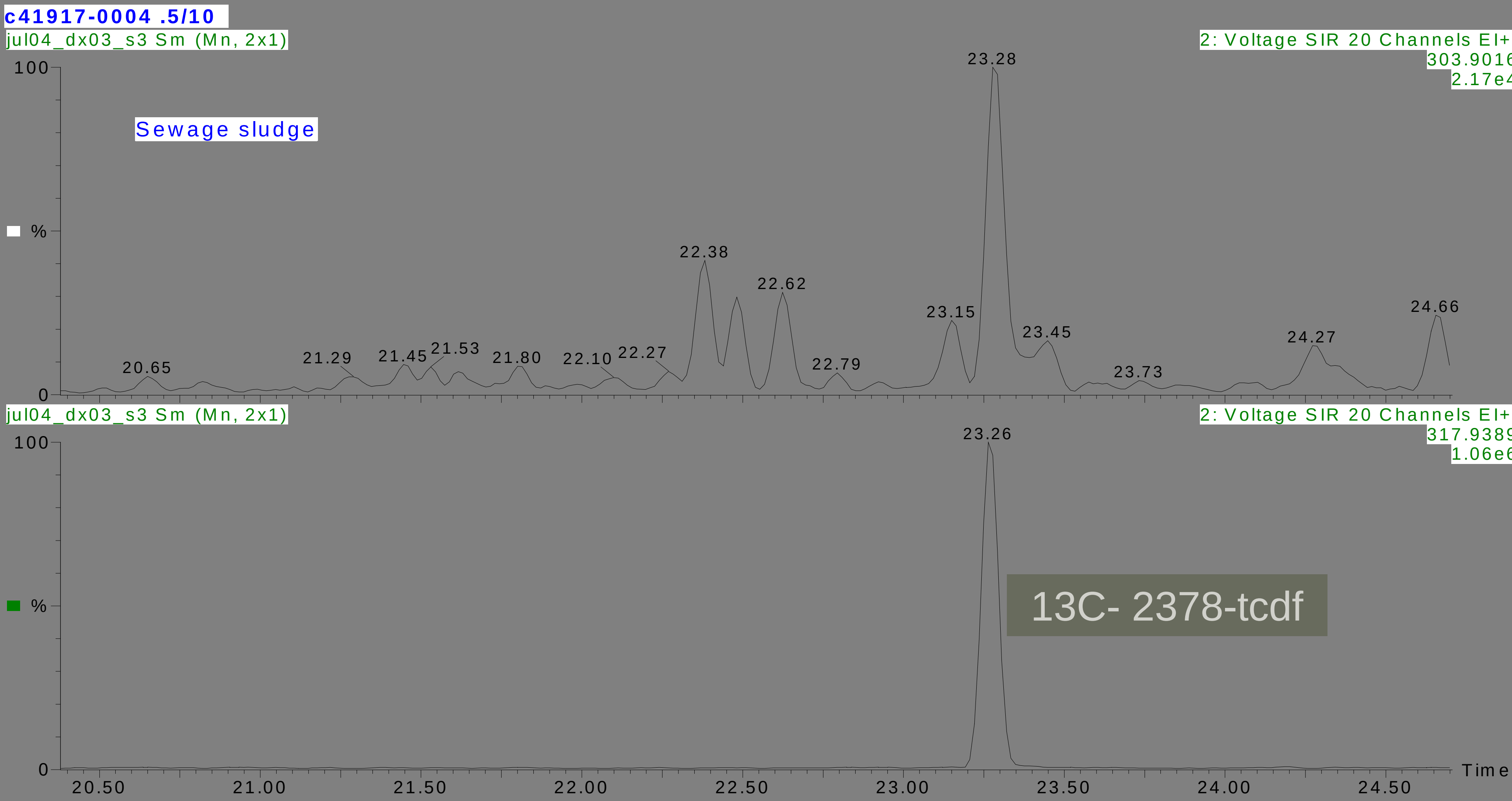
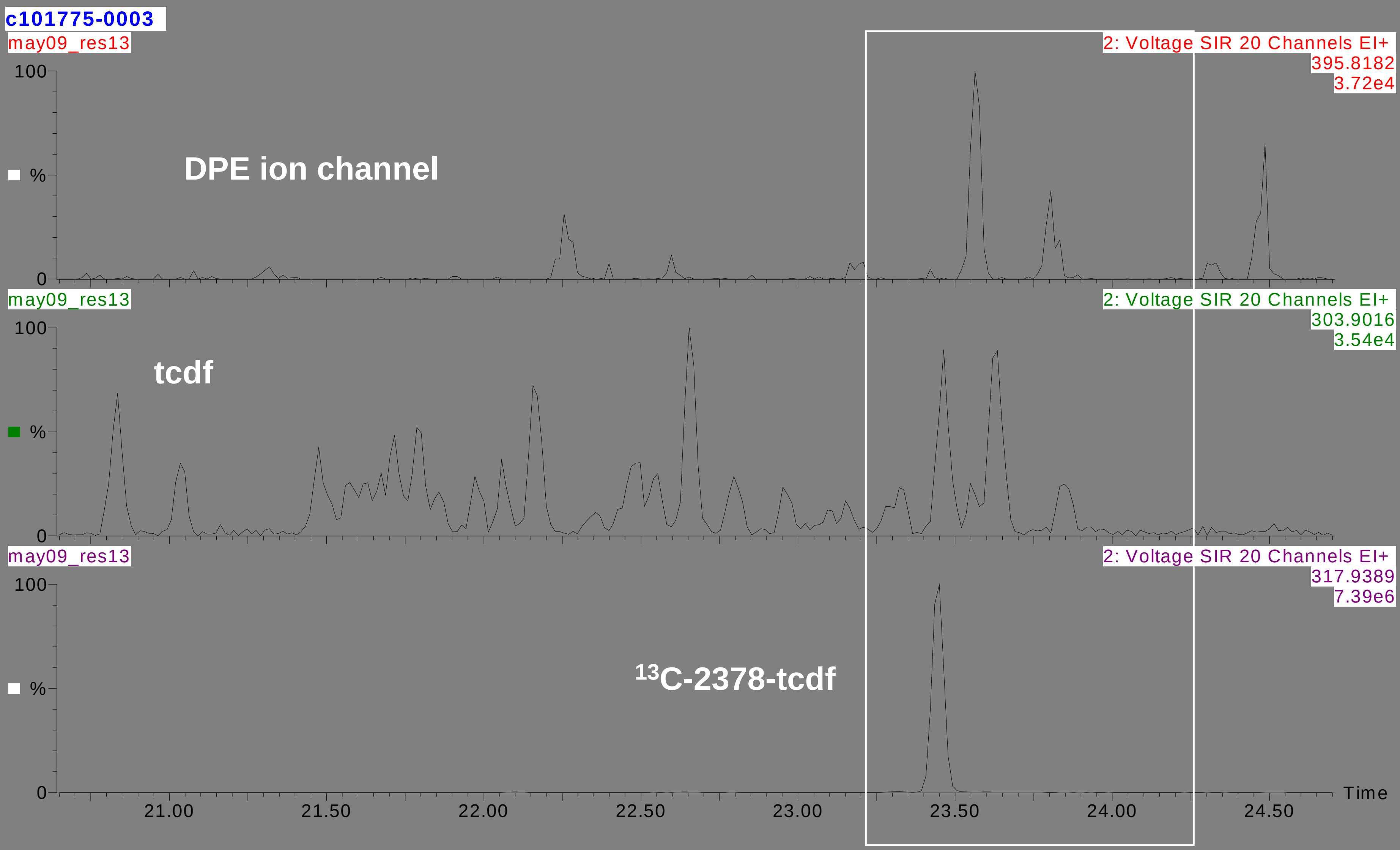


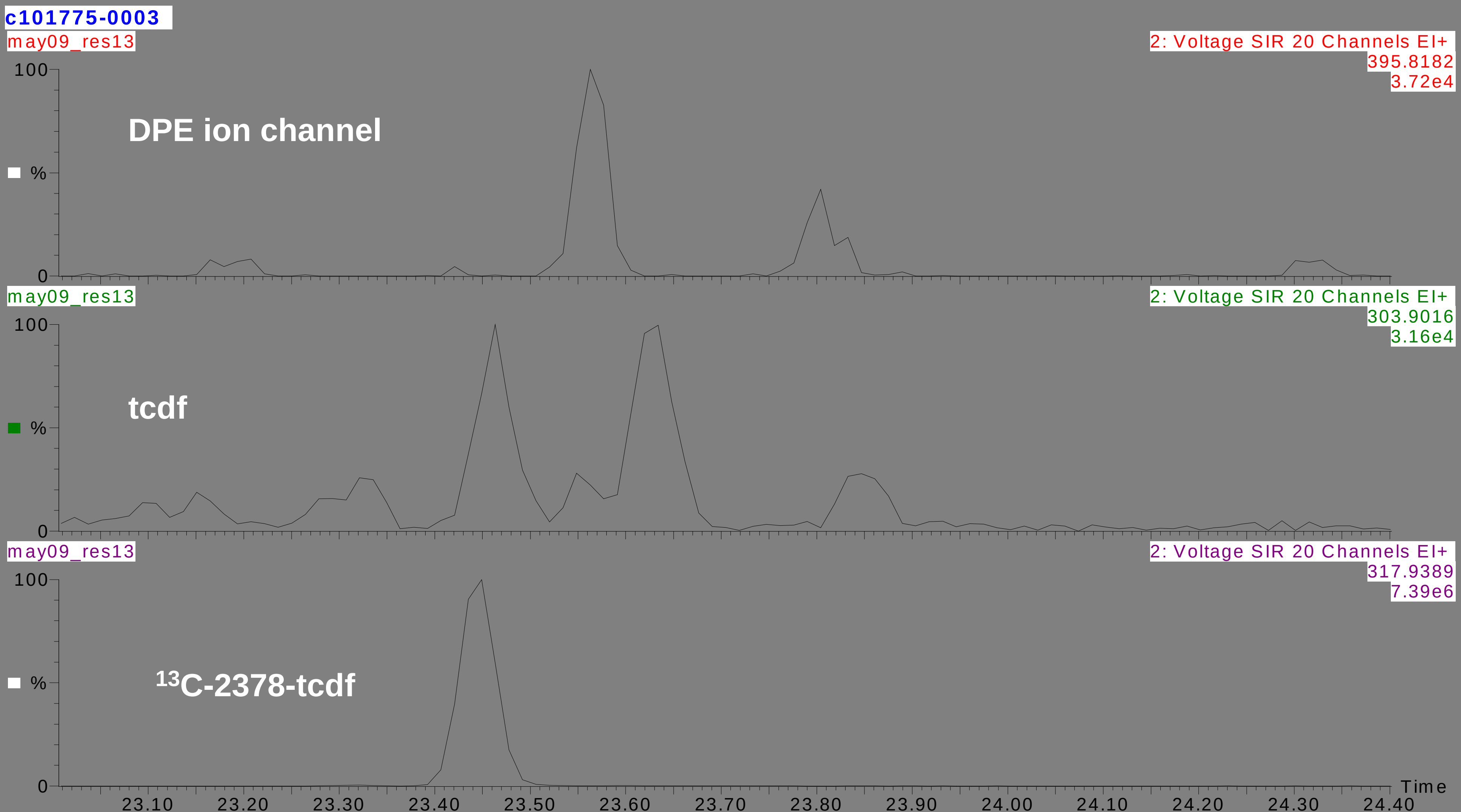
Table I - 2,3,7,8-TCDF (pg/g)

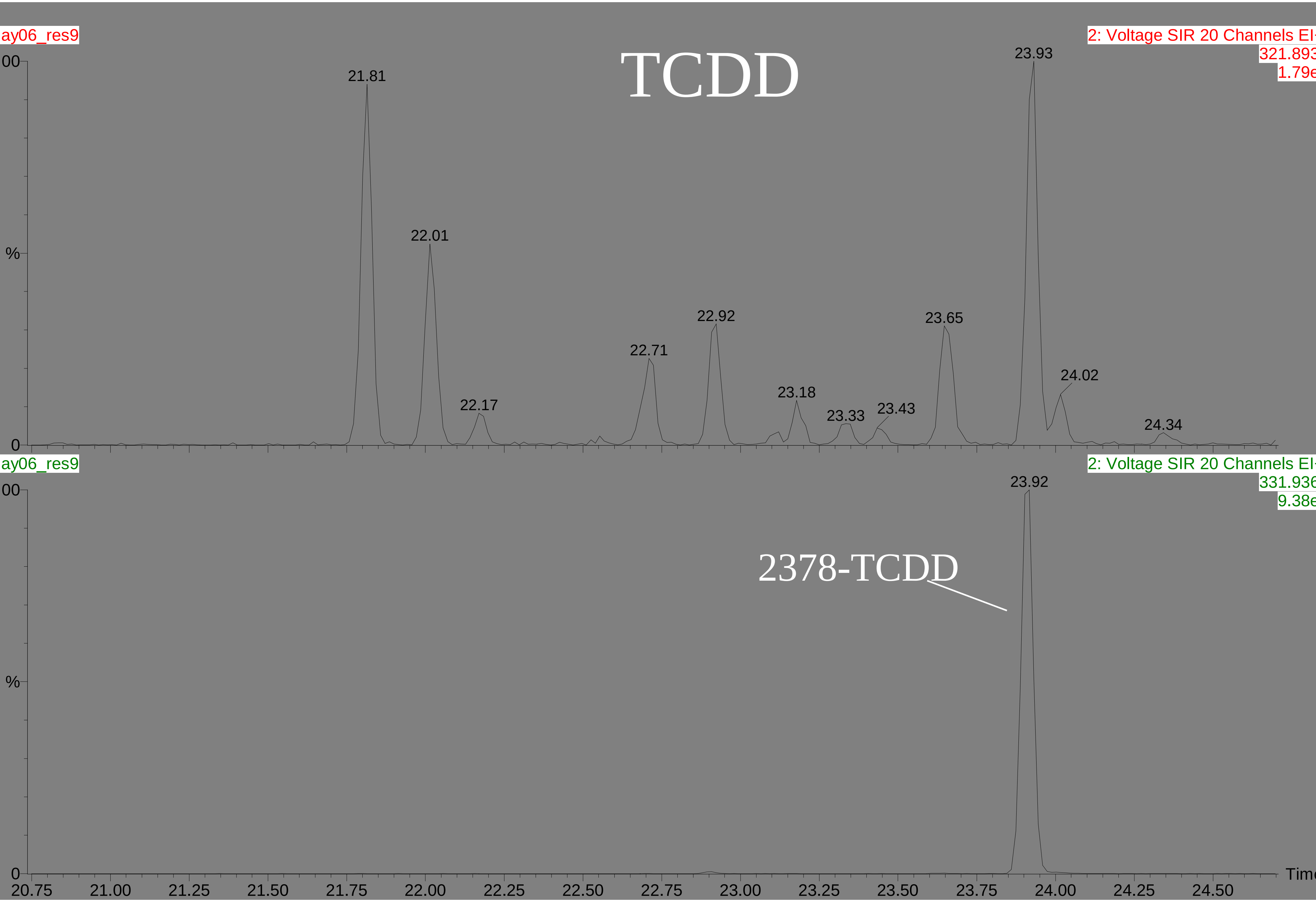
	5% phenyl	X-225	Rtx-DIOXIN2®	Certified Value
WMS-01	78	46	47	52.5 ± 16
EC-2(DX-1)	88	n/a	37	89 (±44)
Sediment	37	19	19	23
NIST 1974	4.7	n/a	3.3	-
Flyash	240	38	32	31
Flyash-2	250	40	32	28
Biota-1	1	1.3	0.8	1.25
Biota-2	4.3	4.3	2.2	1.45

TCDF ion channel for Biota sample



Potential resolution between DPEs and Furans





TCDD
ay06_res9
2: Voltage SIR 20 Channels EI
321.893
1.79e
21.81
22.01
22.17
22.71
22.92
23.18
23.33
23.43
23.65
23.93
24.02
24.34
ay06_res9
2: Voltage SIR 20 Channels EI
331.936
9.38e
23.92
2378-TCDD
00
%
0
Time
20.75
21.00
21.25
21.50
21.75
22.00
22.25
22.50
22.75
23.00
23.25
23.50
23.75
24.00
24.25
24.50

5% Phenyl Column Resolution Mix
Rtx-DIOXIN2 ®

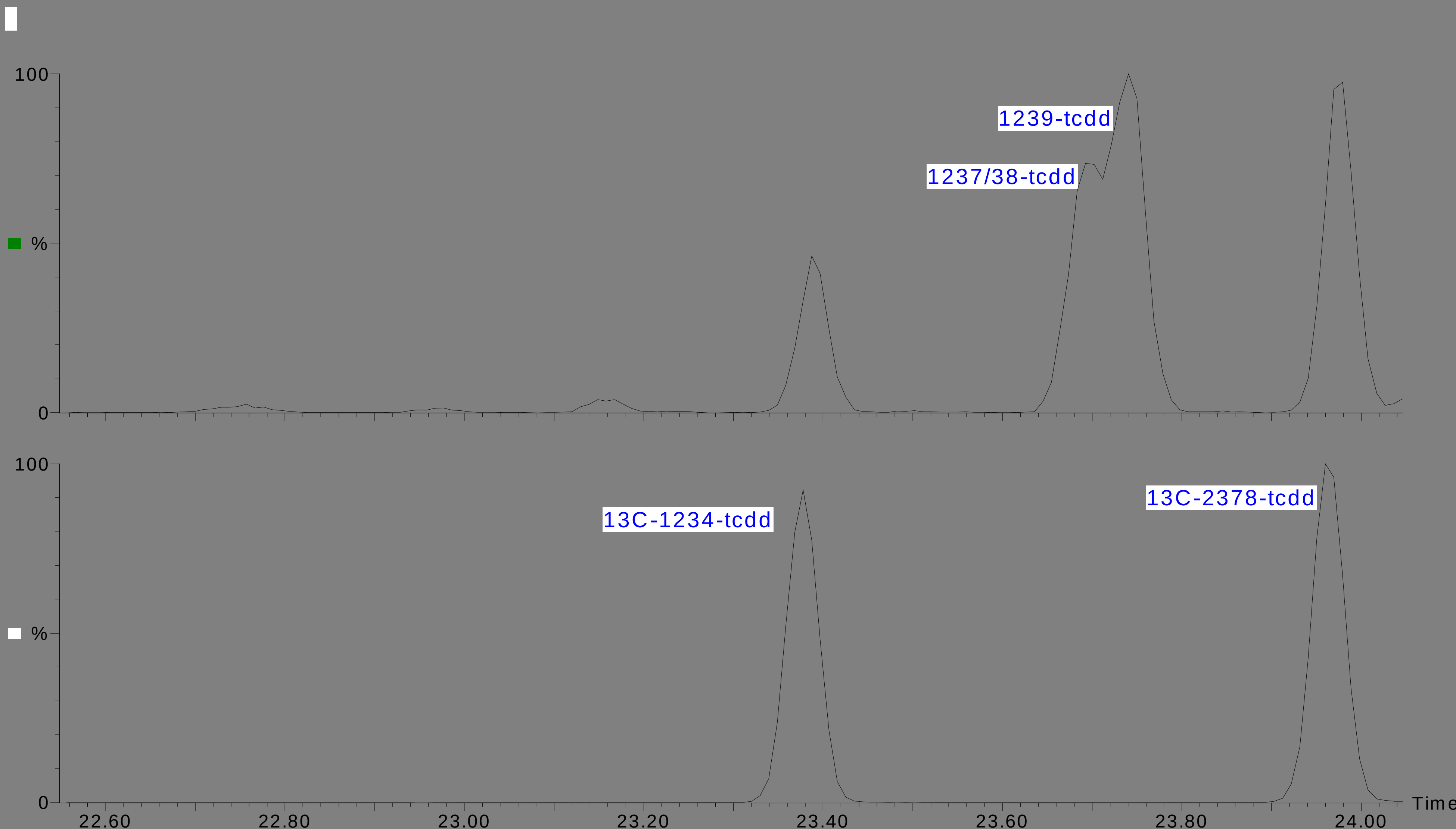
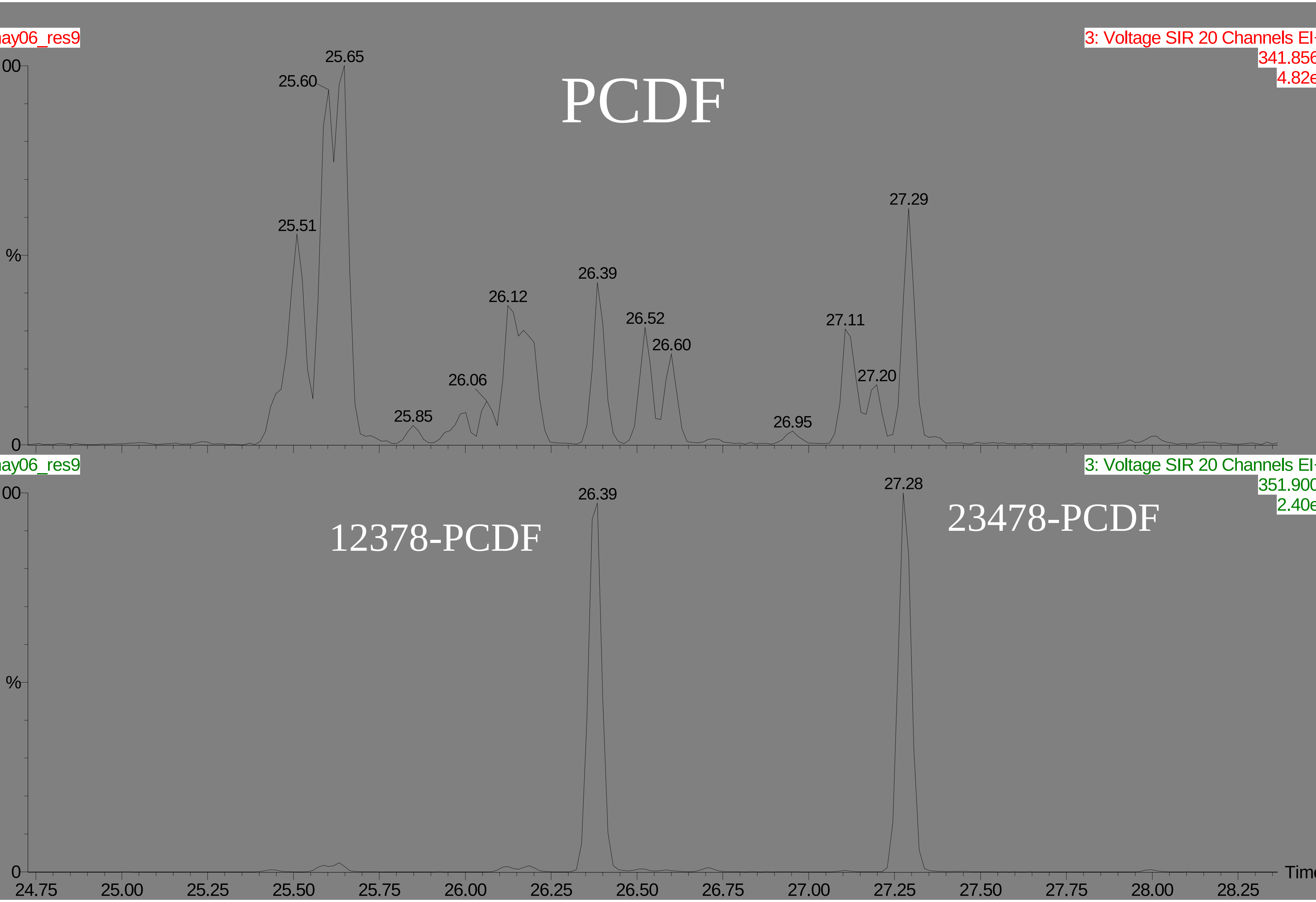


Table II - 2,3,7,8-TCDD (pg/g)

	5% phenyl	X-225®	Rtx-Dioxin2®	Certified Value
WMS-01	21	23	14	17.7±5.6
EC-2 (DX-1)	240	n/a	284	263(± 53)
Sediment	8.5	8.1	9	6
Flyash	5.6	6.7	4.4	5
Flyash-2	<3	3.1	4.4	4.0



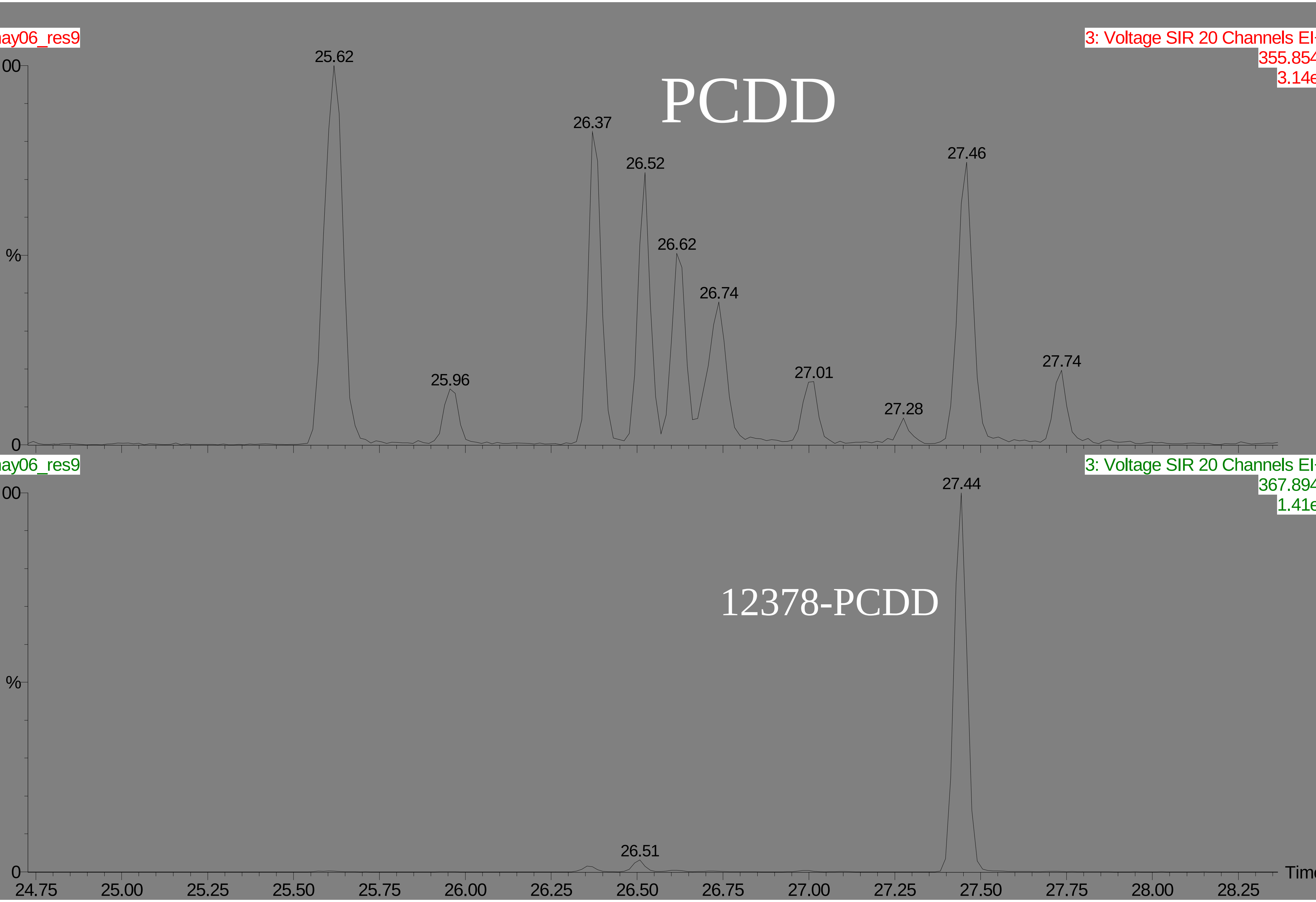
PCDF
12378-PCDF
23478-PCDF
ay06_res9
3: Voltage SIR 20 Channels EI
341.856
4.82e
351.900
2.40e
25.65
25.60
25.51
25.85
26.06
26.12
26.39
26.52
26.60
26.95
27.11
27.20
27.29
27.28
%
0
24.75
25.00
25.25
25.50
25.75
26.00
26.25
26.50
26.75
27.00
27.25
27.50
27.75
28.00
28.25
Tim

Table III - 1,2,3,7,8-PCDF (pg/g)

	5% phenyl	Rtx-Dioxin2®	Certified Value
WMS-01	13	11	12.6 ± 5
EC-2(DX-1)	33	30	39 ± 14
Sediment	42	40	49
Flyash	72	72	73
Flyash-2	86	68	70

Table IV- 2,3,4,7,8-PCDF (pg/g)

	5%phenyl	Rtx-Dioxin2®	Certified Value
WMS-01	26	15	18.5 ± 6.1
EC-2(DX-1)	63	55	62 ± 32
Sediment	23	18	21
Flyash	170	140	120
Flyash-2	160	130	110



ay06_res9
3: Voltage SIR 20 Channels EI
355.854
3.14e
PCDD
25.62
26.37
26.52
27.46
26.62
26.74
27.74
25.96
27.01
27.28
100
%
0
ay06_res9
3: Voltage SIR 20 Channels EI
367.894
1.41e
27.44
12378-PCDD
26.51
24.75
25.00
25.25
25.50
25.75
26.00
26.25
26.50
26.75
27.00
27.25
27.50
27.75
28.00
28.25
Time

HxCDF ion channel in Flyash sample

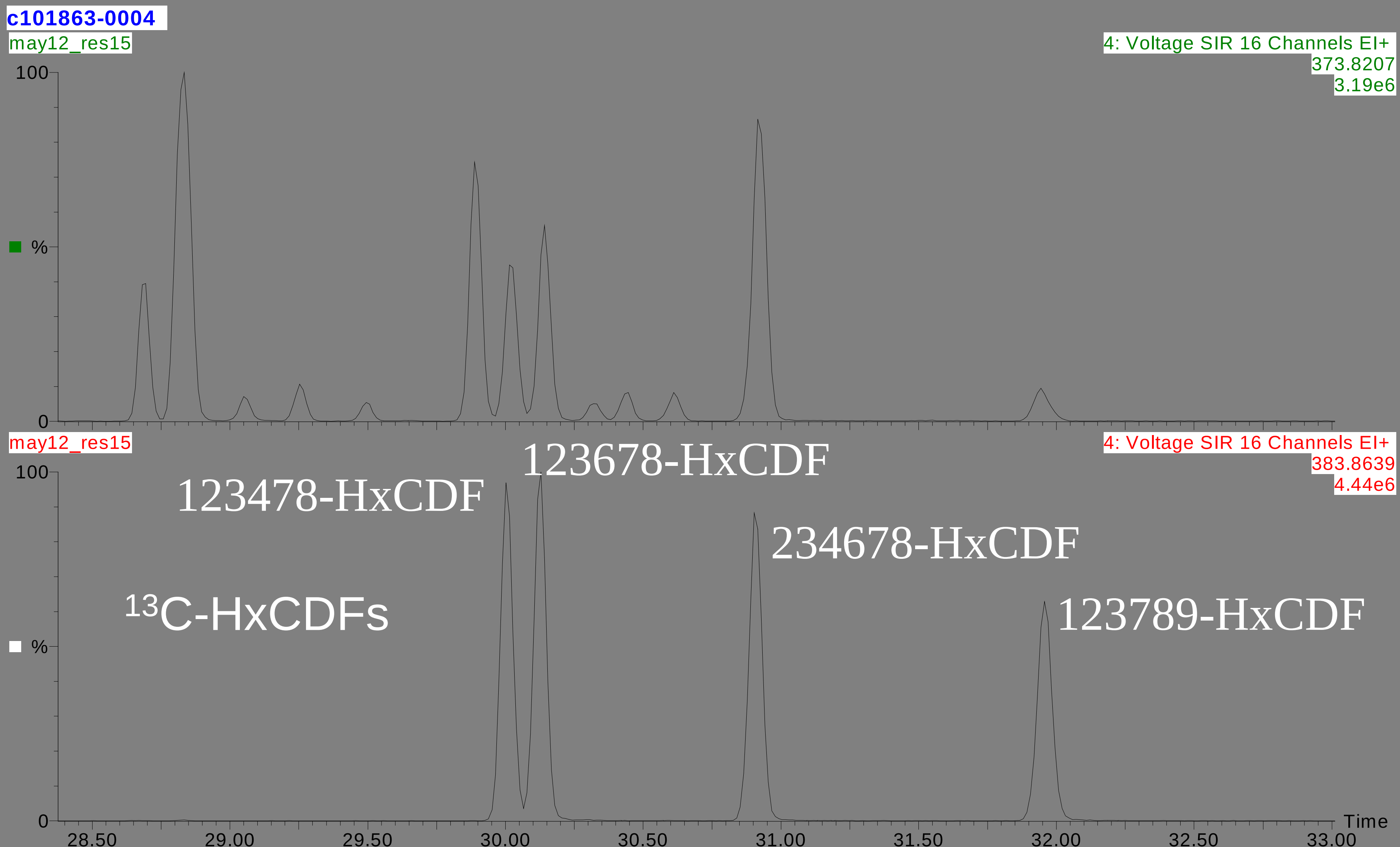


Table V - 1,2,3,4,7,8-HxCDF (pg/g)

	5% phenyl	**Rtx-Dioxin2®**	**Certified Value**
WMS-01	80	50	67 ± 24
EC-2 (DX-1)	780	630	714 (± 276)
Sediment	290	210	230
Flyash	570	200	190
Flyash-2	520	190	180

HxCDD ion channel for sediment

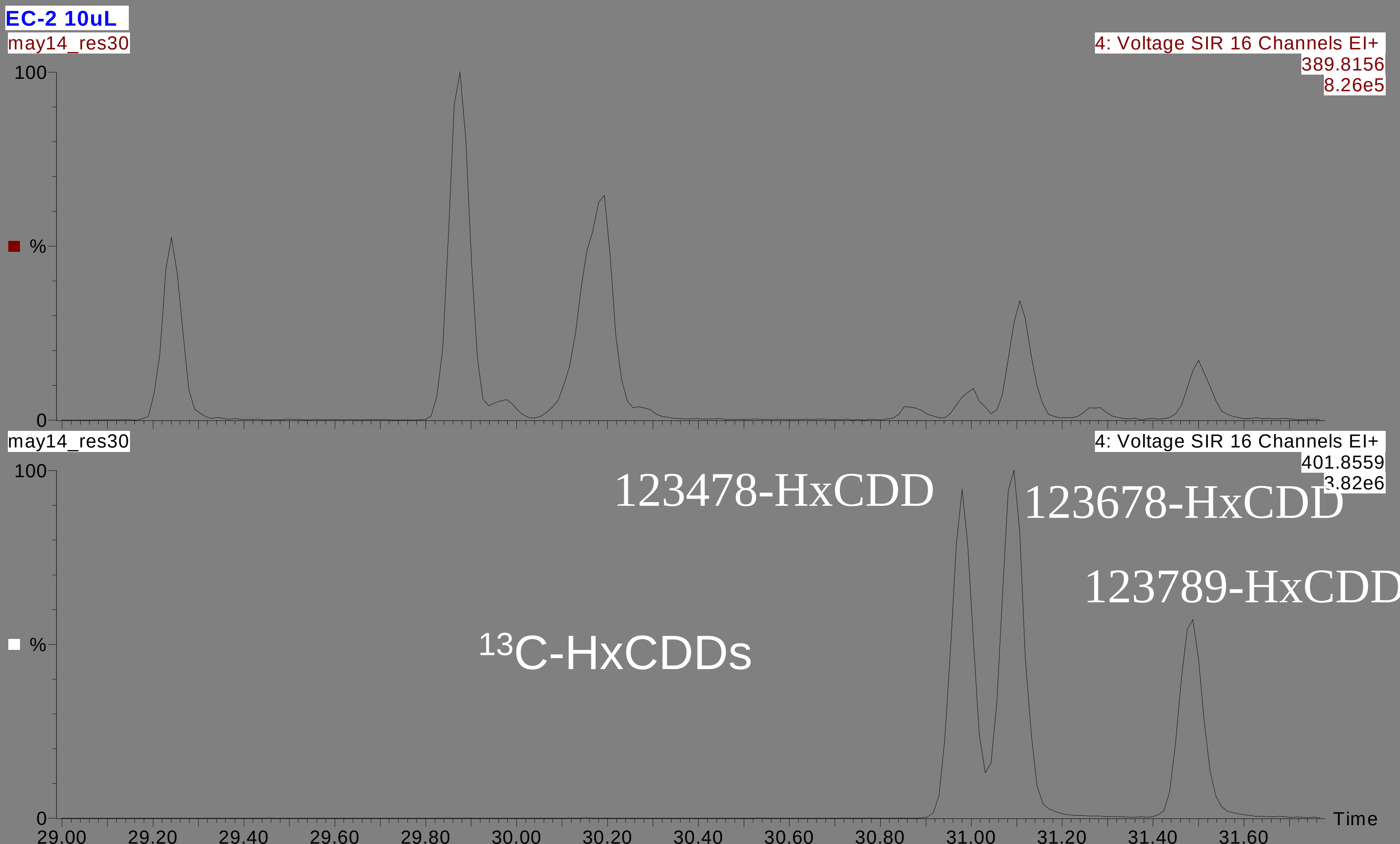
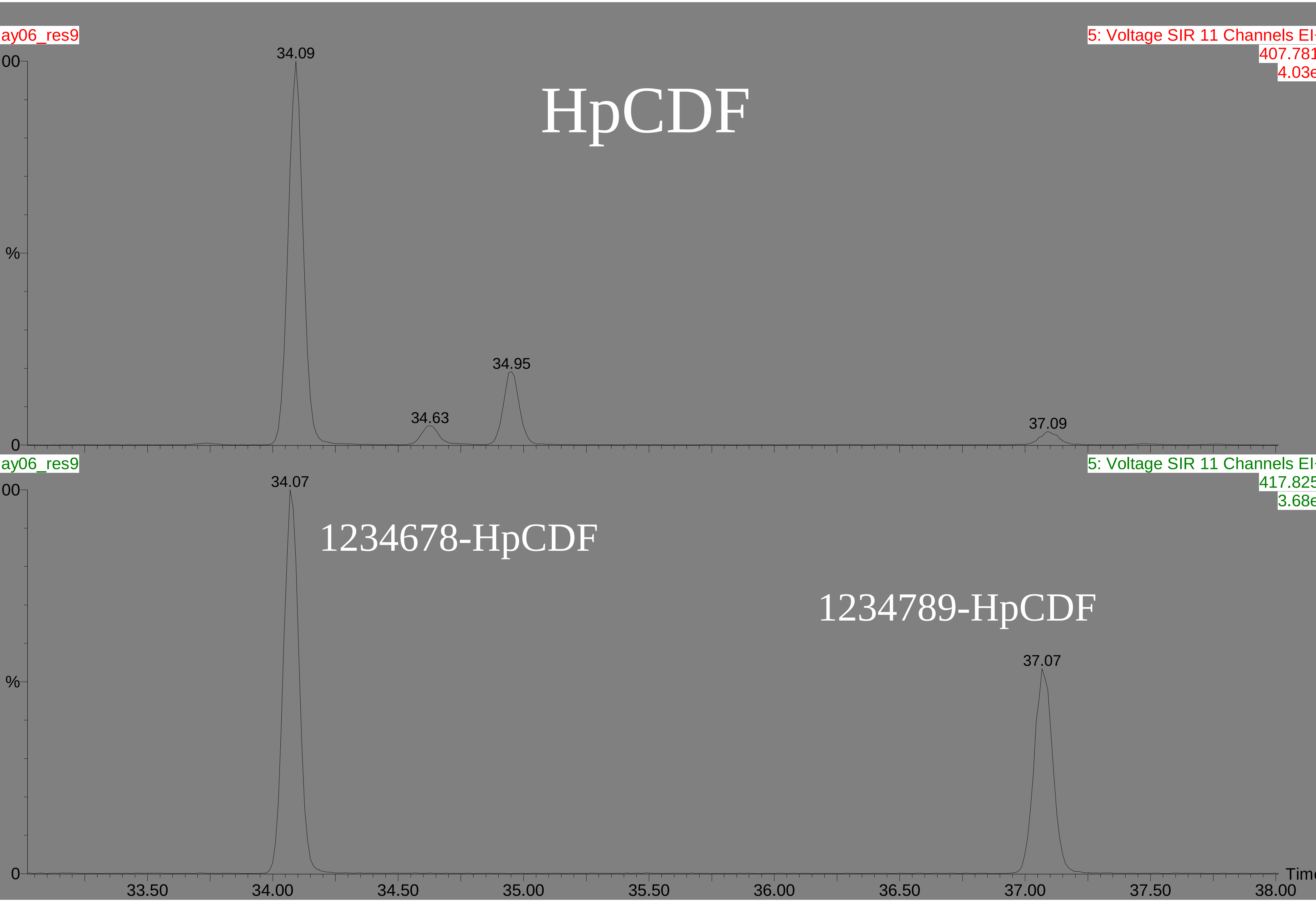
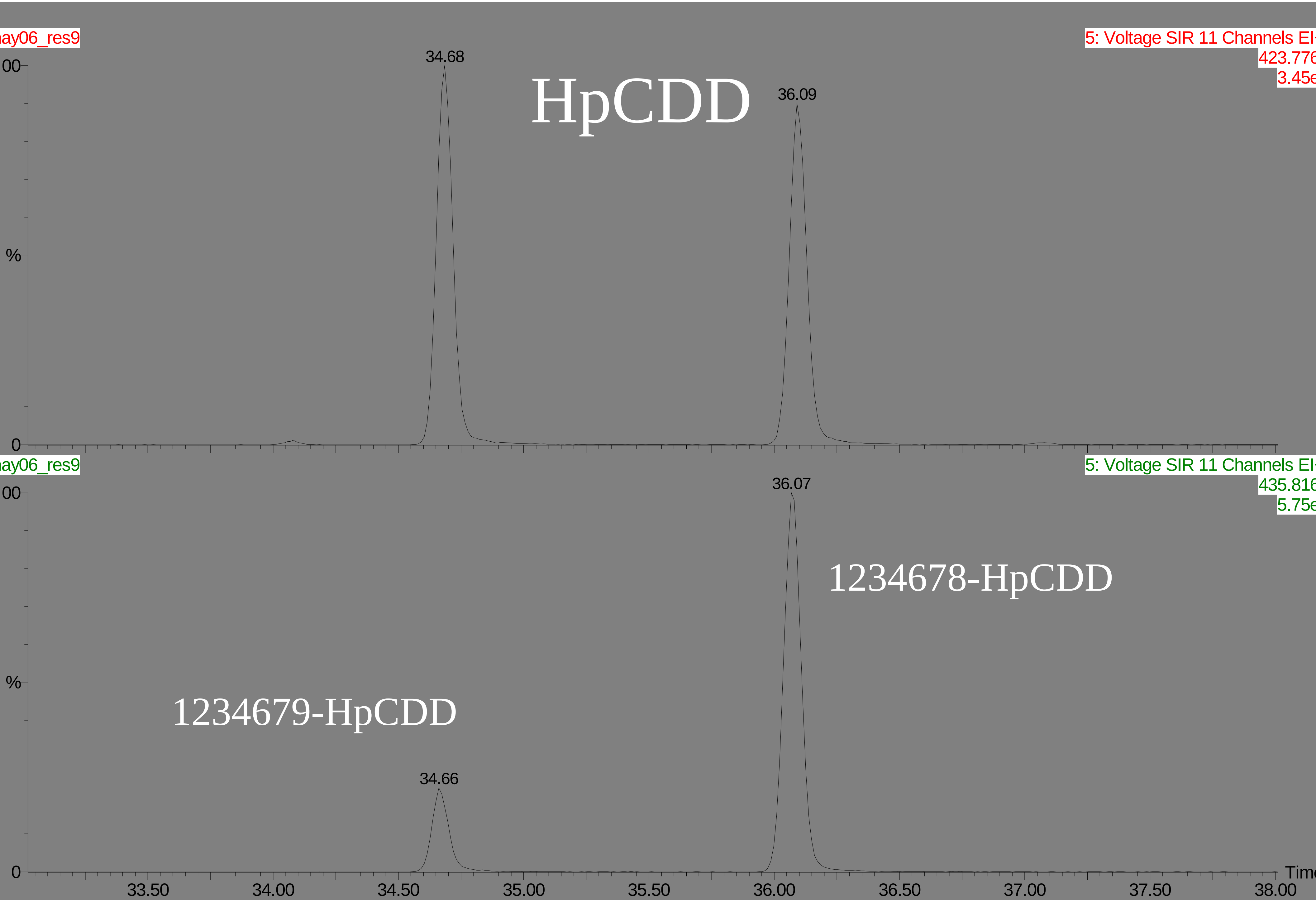


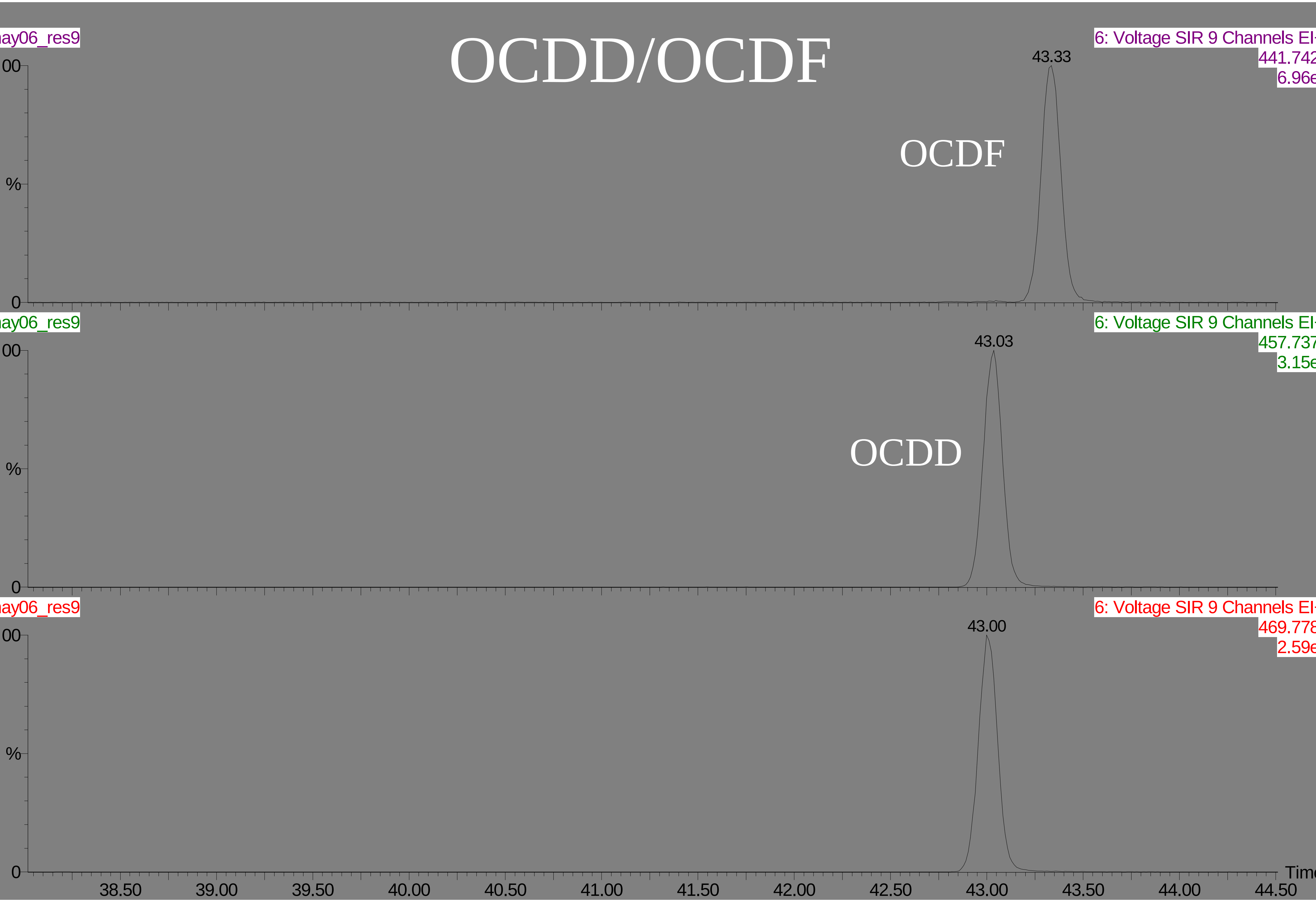
Table VI - 1,2,3,7,8,9-HxCDD (pg/g)

	5% phenyl	Rtx-Dioxin2®	Certified Value
WMS-01	27	29	17.3 ± 8
EC-2 (DX-1)	65	38	53 (± 24)
Sediment	5	6.3	3
Flyash	40	38	40
Flyash-2	39	29	33


ay06_res9
5: Voltage SIR 11 Channels EI
407.781
4.03e
HpCDF
34.09
34.63
34.95
37.09
100
%
0
ay06_res9
5: Voltage SIR 11 Channels EI
417.825
3.68e
34.07
1234678-HpCDF
1234789-HpCDF
37.07
100
%
0
33.50
34.00
34.50
35.00
35.50
36.00
36.50
37.00
37.50
38.00
Time



ay06_res9
5: Voltage SIR 11 Channels EI
423.776
3.45e
HpCDD
34.68
36.09
100
%
0
ay06_res9
5: Voltage SIR 11 Channels EI
435.816
5.75e
36.07
1234678-HpCDD
1234679-HpCDD
34.66
33.50
34.00
34.50
35.00
35.50
36.00
36.50
37.00
37.50
38.00
Time


OCDD/OCDF
OCDF
OCDD
ay06_res9
6: Voltage SIR 9 Channels EI
441.742
6.96e
43.33
457.737
3.15e
43.03
469.778
2.59e
43.00
00
%
0
Time
38.50
39.00
39.50
40.00
40.50
41.00
41.50
42.00
42.50
43.00
43.50
44.00
44.50

Rtx-Dioxin2 Capillary Column

- Proprietary backbone stabilized polysiloxane designed for toxic dioxin and furan analysis by GC-HRMS
- 340 maximum operating temperature in standard fused silica tubing
- Can be used as secondary confirmation column for Rtx-Dioxin, or other primary columns like 5% diphenyl phases
- Can function as single column for stand-alone dioxin and furan analysis – and has been accredited for use as such
  - Clive Robinson ALS Environmental –Queensland Australia
- Chromatographically separates the chlorinated diphenylethers from the furans – especially important in biota matrices
- Columns available:
  - Cat # 10758 - 60 M X 0.25 mm i.d. X 0.25 um d.f.
  - Cat # 10759 - 40 M X 0.18 mm i.d. X 0.18 um d.f.