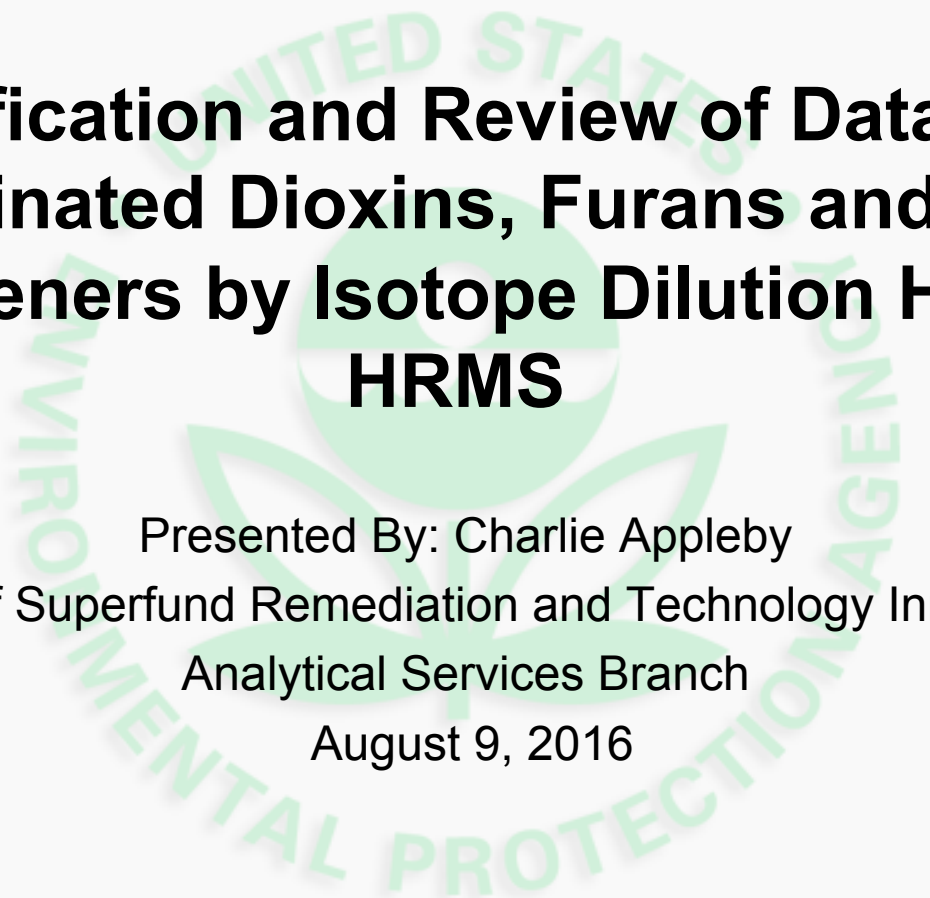




Verification and Review of Data for Chlorinated Dioxins, Furans and PCB Congeners by Isotope Dilution HRGC/ HRMS

Presented By: Charlie Appleby
Office of Superfund Remediation and Technology Innovation
Analytical Services Branch
August 9, 2016

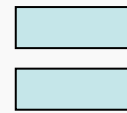
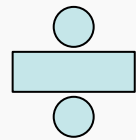


Agenda



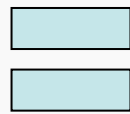
- Overview
 - What is Isotope Dilution, HRGC/HRMS?
 - Preparing for the Review, laboratory documentation,
 - Step by step process
 - Documenting the Review
 - Follow-up Actions
- Themes:
 - Sample and Data Integrity
 - Data Quality Elements

Isotope Dilution

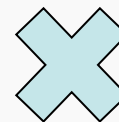


C

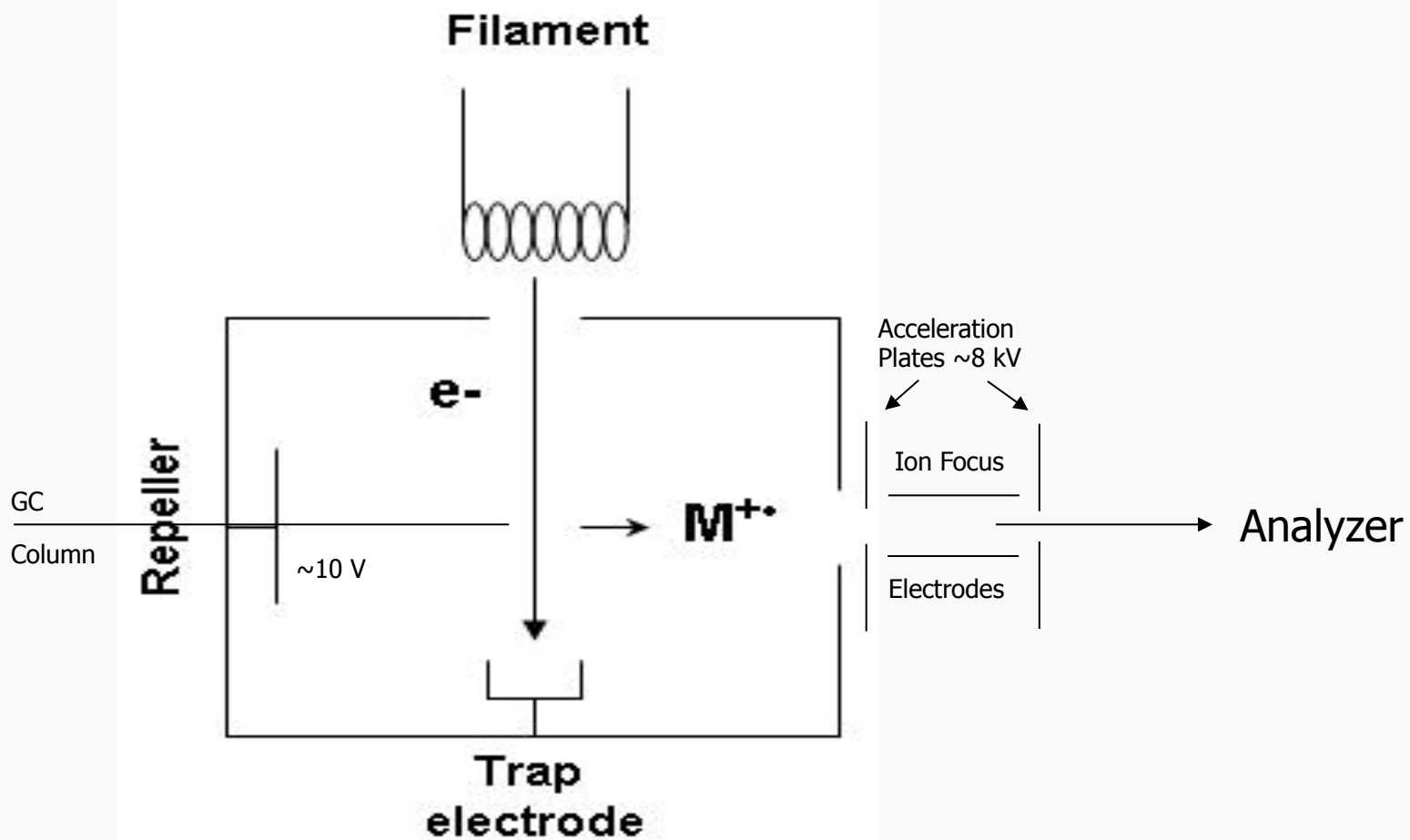
N



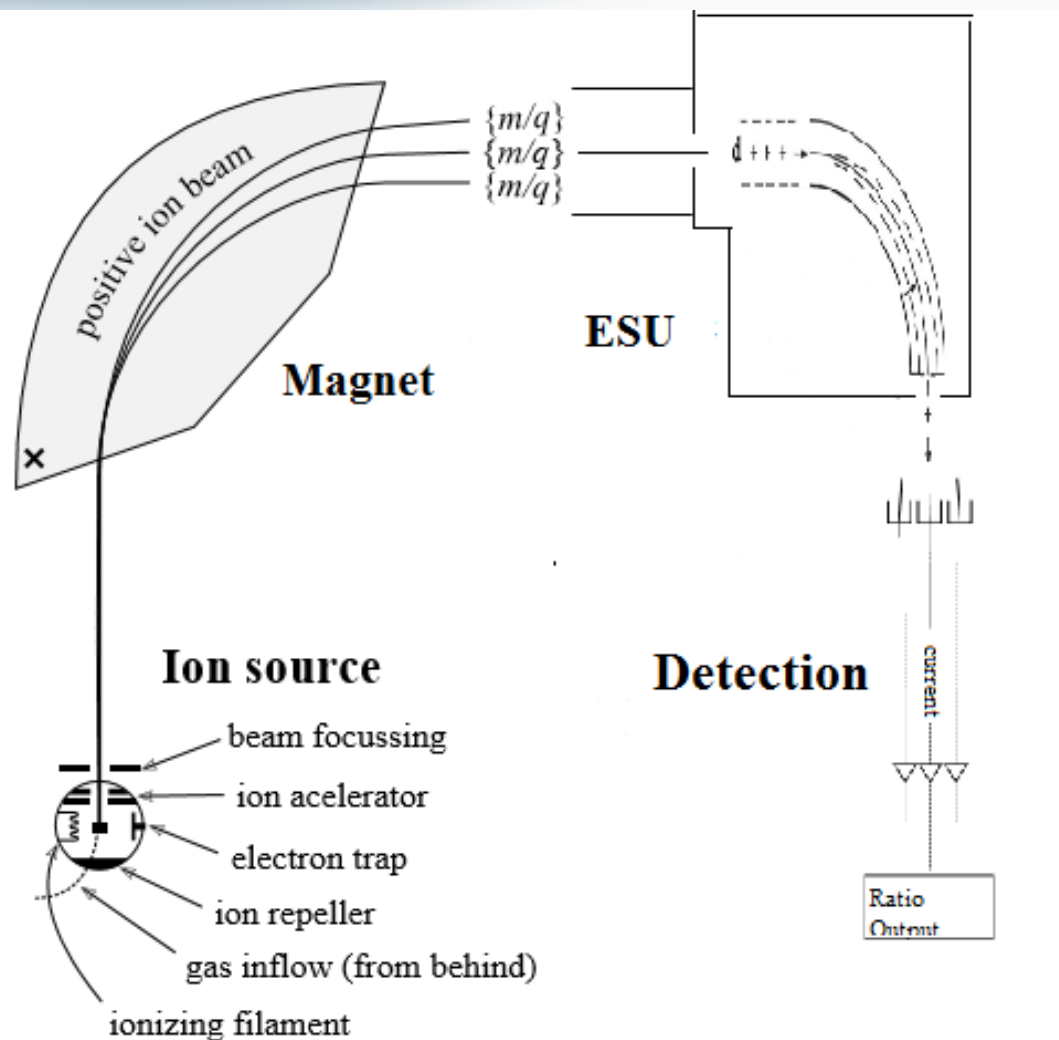
C



Electron Impact Ion Source



Magnetic Sector Mass Spectrometer



Summary: Critical Aspects of System



- Provide stable, reproducible performance
- Provide means to isolate and detect analytes of concern
 - Chromatographic
 - Ion formation
 - Mass resolution
- Meet or exceed sensitivity requirements

Initial Data Package Review



- Perform evidentiary or contract compliance audit
- Read Case Narrative and correspondence
- Review chain-of-custody
- Review QC summary forms, if present
- Review preservation and storage conditions
- Review sample analytical sequence information

Case Narrative Outline



- Sample Receipt and Storage
- Sample Preparation
- Analysis
- Reporting Conventions
- QA/QC Summary
- Analysis Discussion
- Sample Calculations
- Signed Statement

Initial Data Package Review



- **RRF Equation**

$$RRF = \frac{(A_{s1} + A_{s2}) C_{IS}}{(A_{IS1} + A_{IS2}) C_s}$$

- **Sample Concentration Equations**

$$C_n = \frac{(A_{s1} + A_{s2}) C_{IS}}{(A_{IS1} + A_{IS2}) RRF_n * \text{Vol or Mass}}$$

$$EDL = \frac{2.5 * H_x * Q_{IS}}{H_{IS} * W * RRF_n}$$

- **Internal Standard Recovery**

$$C_n = \frac{(A_{IS1} + A_{IS2}) Q_{RS}}{(A_{RS1} + A_{RS2}) RRF_{IS}}$$

$$\% \text{Recovery} = \frac{C_{IS} * 100}{\text{Amount Spiked}}$$

Preservation / Holding Time



Evaluation	Sample Type	Criteria Exceedance	Action	
			Detected Compounds	Non-Detected Compounds
Technical Holding Time	Aqueous/Soil	>1 year	J	UJ or R
	Fish, Tissue	>1 year	Use professional judgment	
Storage Temperature	Aqueous/Soil	>4°C shipment and storage	J	UJ
	Fish, Tissue	>4°C shipment and <-10°C storage	J	UJ
Preservation	Aqueous	Cl ₂ but no Thiosulfate	J	R
		pH not adjusted when required	J	UJ
Sample Extract Improperly Stored	All types	>35 days <1 year	J	UJ
		>1 year	J	UJ or R

Initial Data Package Review



	<u>PAGE NOS.</u>		<u>CHECK</u>	
	<u>FROM</u>	<u>TO</u>	<u>LAB</u>	<u>EPA</u>
1. <u>Inventory Sheet</u> (DC-2) (Do not number)				
2. <u>SDG Narrative</u>	1	2	✓	
3. <u>Traffic Report</u>	3	8	✓	
4. <u>CDD/CDF Data</u>				
a. Sample Data				
Sample Data Summary (FORM I-HR CDD-1)	9	28	✓	
Toxicity Equivalence Summary (FORM I-HR CDD-2)				
Second Column confirmation Summary (FORM I-HR CDD-3)	29		✓	
TEF Adjusted Concentration Mammal/Fish/Bird (FORM I-HR CDD-4)	30	49	✓	

System Performance



- Data Elements
 - Lab Name, Case Num, SDG Num, Contract
 - Inventory Sheet
 - SDG Narrative
 - Traffic Reports
 - Sample Data
 - Calibration Data
 - Summary and Raw QC Data
 - Miscellaneous Data

Initial Data Package Review

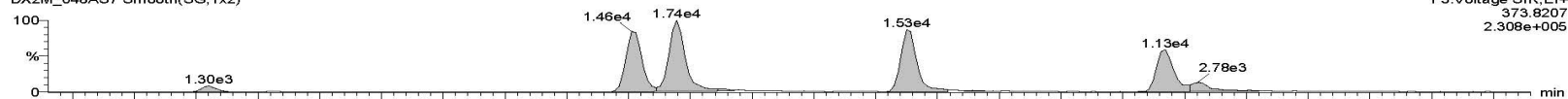


Dataset:

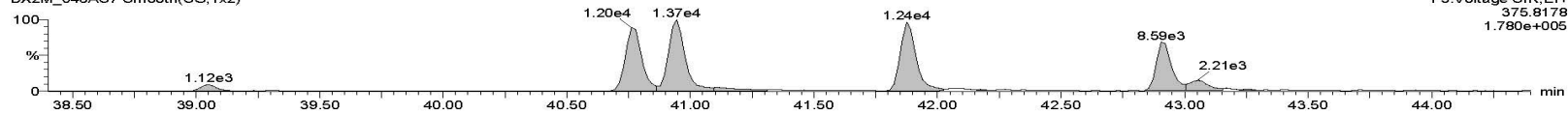
Name: DX2M_048AS7, Date: 26-Mar-2012, Time: 18:51:07, ID: DX036B-CAL,,CS101, Description: 1,,1.0uL CS-1

Total Hexa-Furans

DX2M_048AS7 Smooth(SG,1x2)

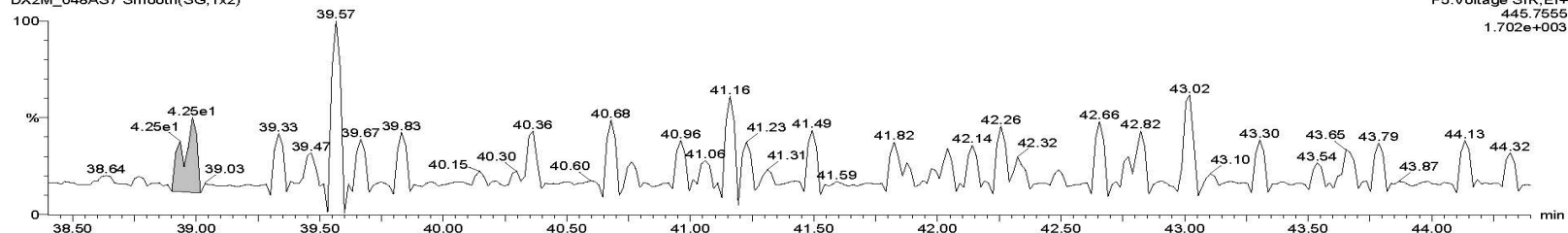


DX2M_048AS7 Smooth(SG,1x2)



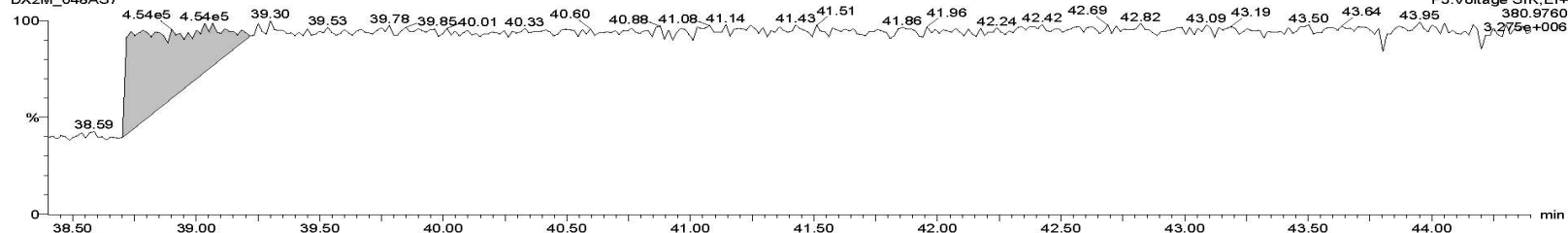
Octa DPE

DX2M_048AS7 Smooth(SG,1x2)



Hexa Lock

DX2M_048AS7



Initial Data Package Review



ANALYTICAL SEQUENCE SUMMARY HIGH RESOLUTION

Lab Name: Contract:
 Lab Code: Case No.: TO No.: SDG No.: 193
 GC Column: DB-5 ID: 0.25 (mm) Instrument ID: E-HMS-04
 Init. Calib. Date(s): 05/03/2012
 Initial Calib. Times: 05:17am

The Analytical Sequence of standards, samples, blanks, and Laboratory Control Samples (LCs) is as follows:

EPA SampleNo.	Lab Sample ID	Lab File ID	Date Analyzed	Time Analyzed
PFK				05:06:21
Window Define		8230	6-JUL-12	05:14:35
CCAL CS3		8231	6-JUL-12	06:10:10
DLCS-	00313-01	8232	6-JUL-12	07:18:59
DLCS-	00313-02	8233	6-JUL-12	08:09:46
XXXXXXXXXX	XXXXXXXXXX	8234	6-JUL-12	09:00:56
XXXXXXXXXX	XXXXXXXXXX	8235	6-JUL-12	09:52:12
DFBLK-	00313-01	8236	6-JUL-12	11:11:40
XXXXXXXXXX	XXXXXXXXXX	8237	6-JUL-12	12:02:09
238	00584-002	8238	6-JUL-12	12:53:25
240	00584-003	8239	6-JUL-12	13:44:34
Window Define		8240	6-JUL-12	14:38:40
CCAL CS3		8241	6-JUL-12	15:27:23
PFK				15:32:06

System Performance

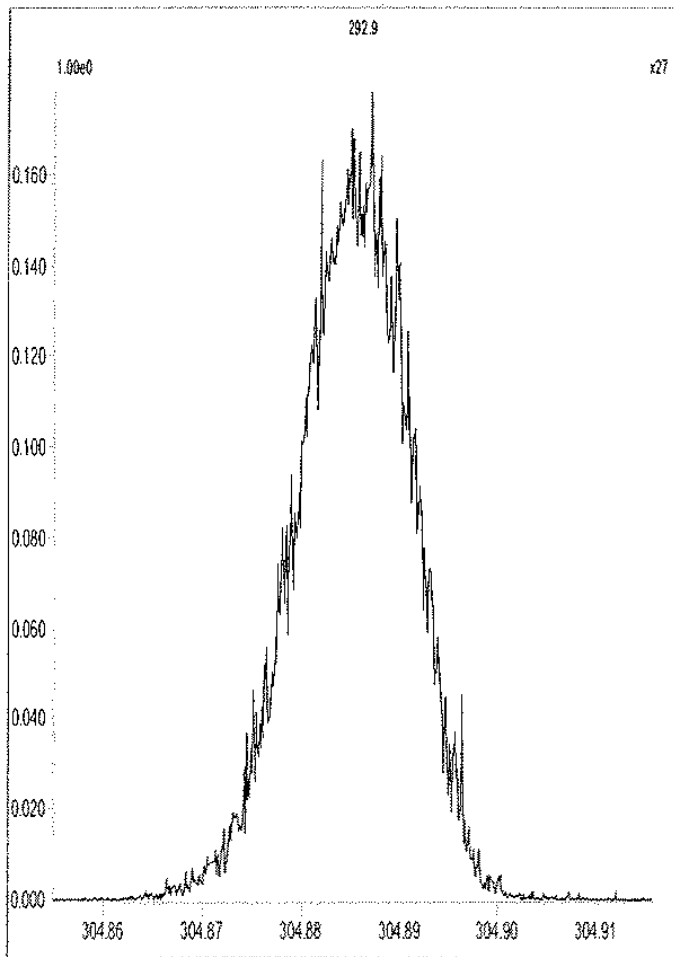


- Verify Mass Calibration and Resolution
 - Range of masses (should match descriptor)
 - Accurate masses of selected reference standard ions
 - Peak Matching Experiment
 - Documentation generated during PFK scan, not saved

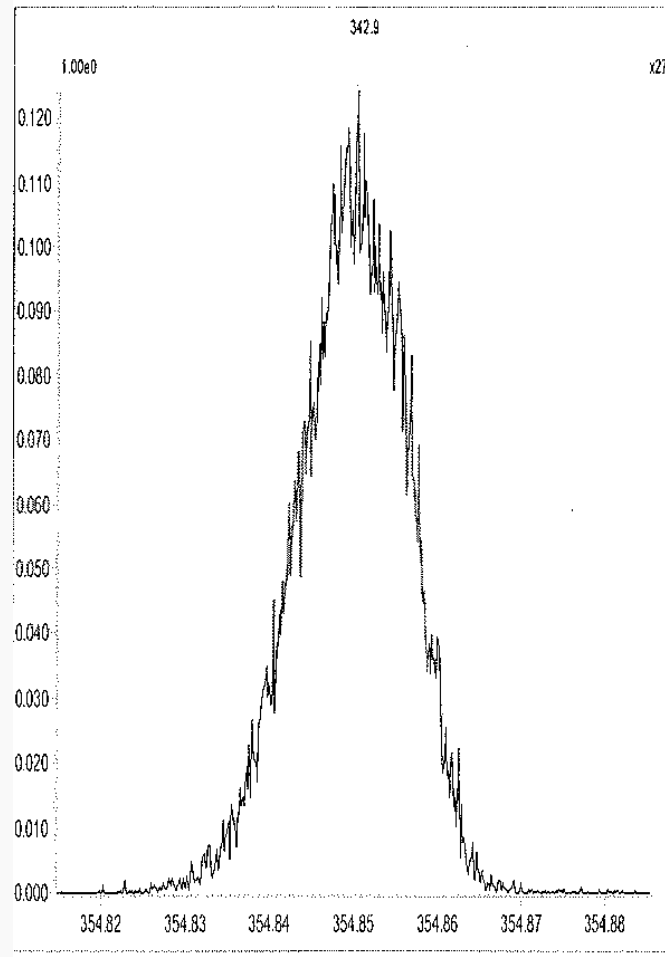
System Performance



M 304.9824 R 12019



M 354.9792 R 12889



August 9, 2016

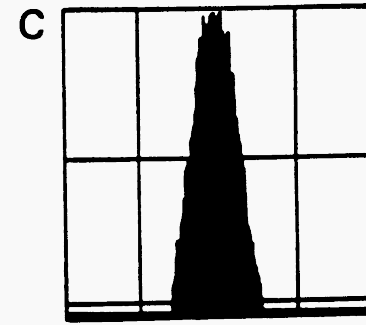
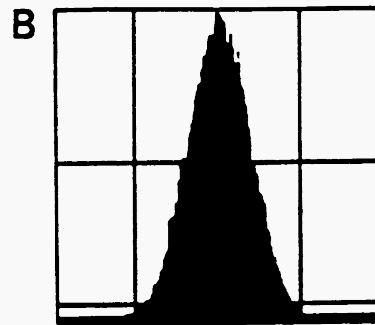
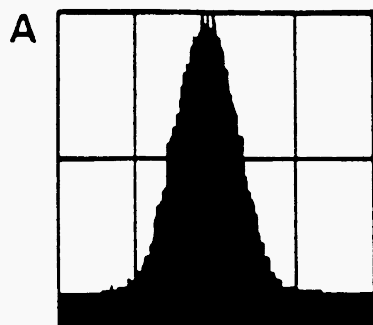
U.S. Environmental Protection Agency

16

System Performance



PEAK PROFILE DISPLAYS DEMONSTRATING THE EFFECT OF THE DETECTOR ZERO ON THE MEASURED RESOLVING POWER



System Performance



Criteria	Action	
	Detected Associated Compounds	Non-Detected Associated Compounds
Mass Spectrometer resolution of $\geq 10,000$ is not demonstrated	R or professional judgment	No qualification
Inability of the mass spectrometer to identify the upper mass fragment	R or professional judgment	R or professional judgment

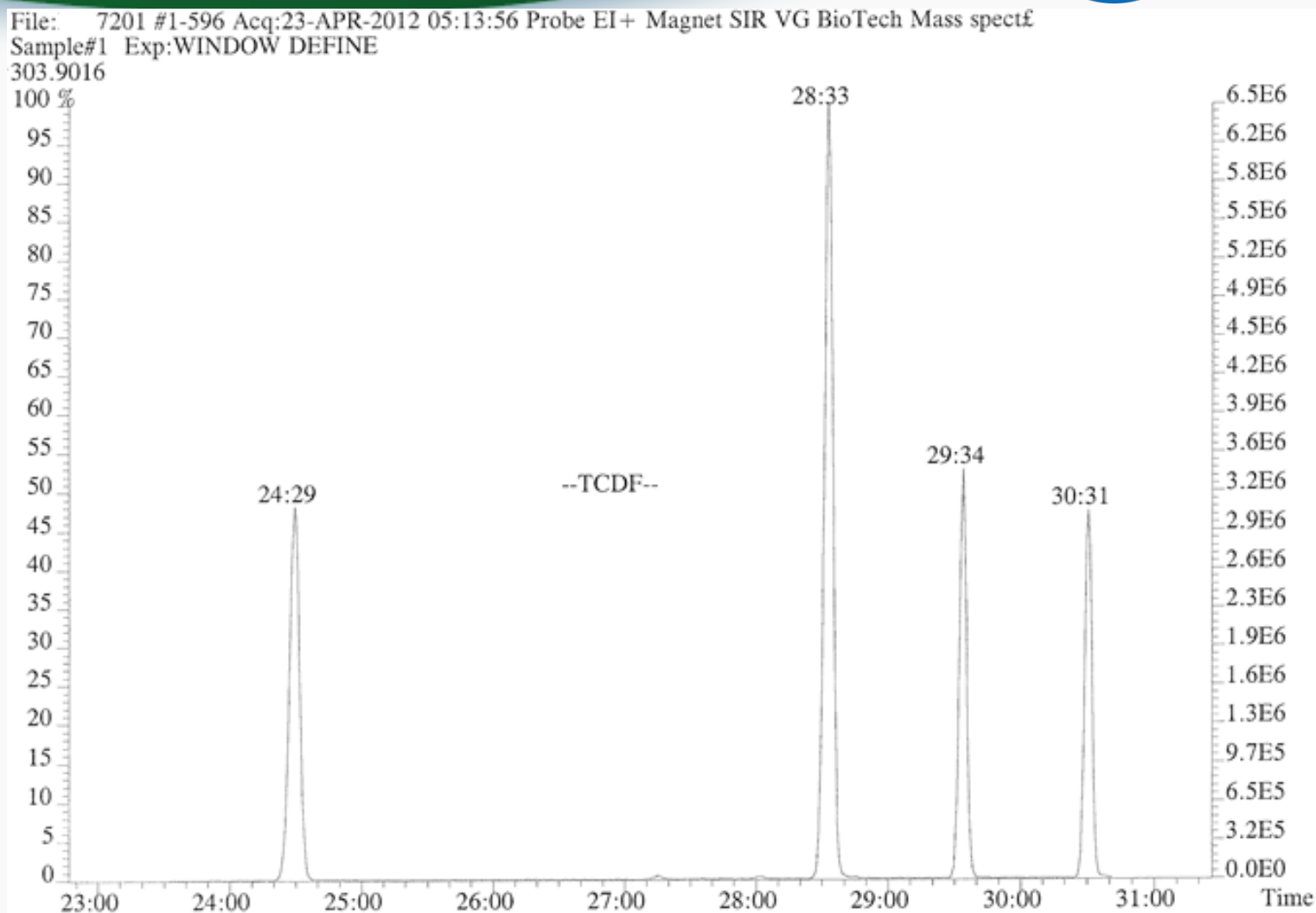
System Performance

Window Defining Mixture (WDM)

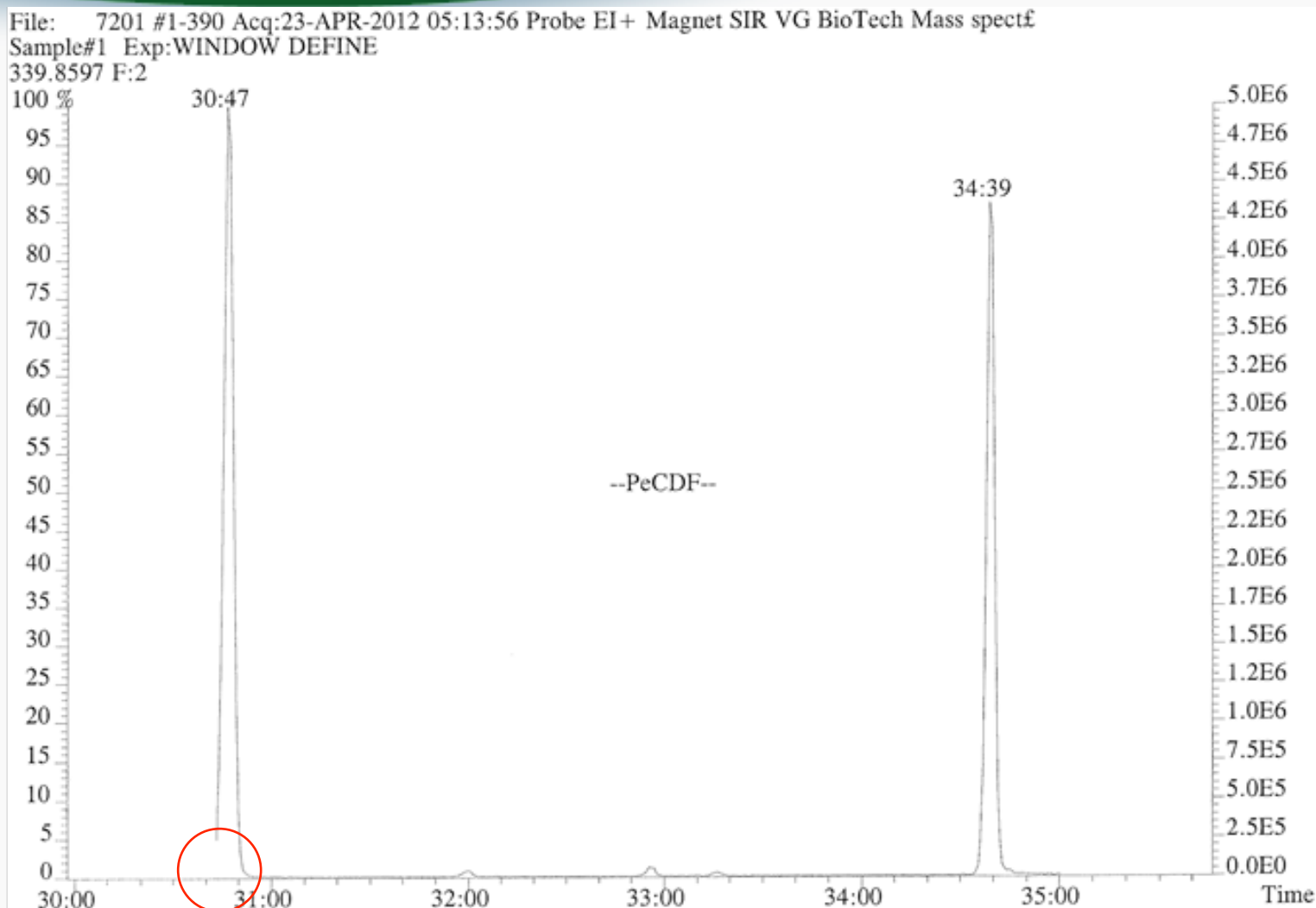


- Verify WDM Analyzed After PFK but Before Calibration.
 - First / Last of descriptor must elute within window
 - Tetra / penta descriptors
 - CBC Descriptors
- Verify GC Resolution with ISC
 - May be combined with WDM
- If Lab Uses a Different GC column,
 - Must define (and meet) criteria
 - Provide tabular information in Narrative

System Performance Window Defining Mixture (WDM)



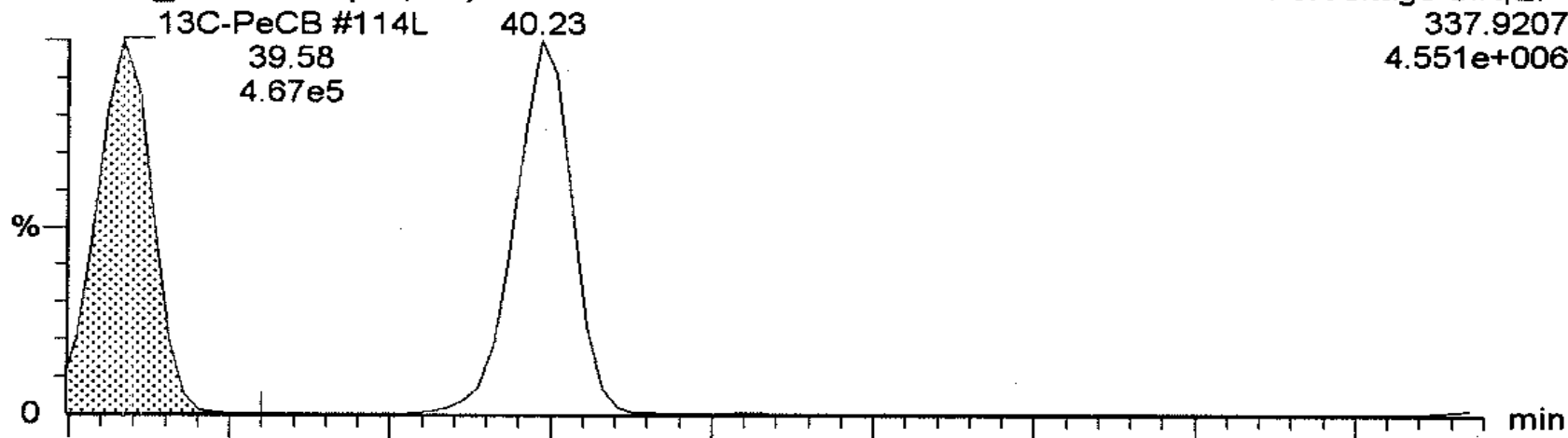
System Performance Window Defining Mixture (WDM)



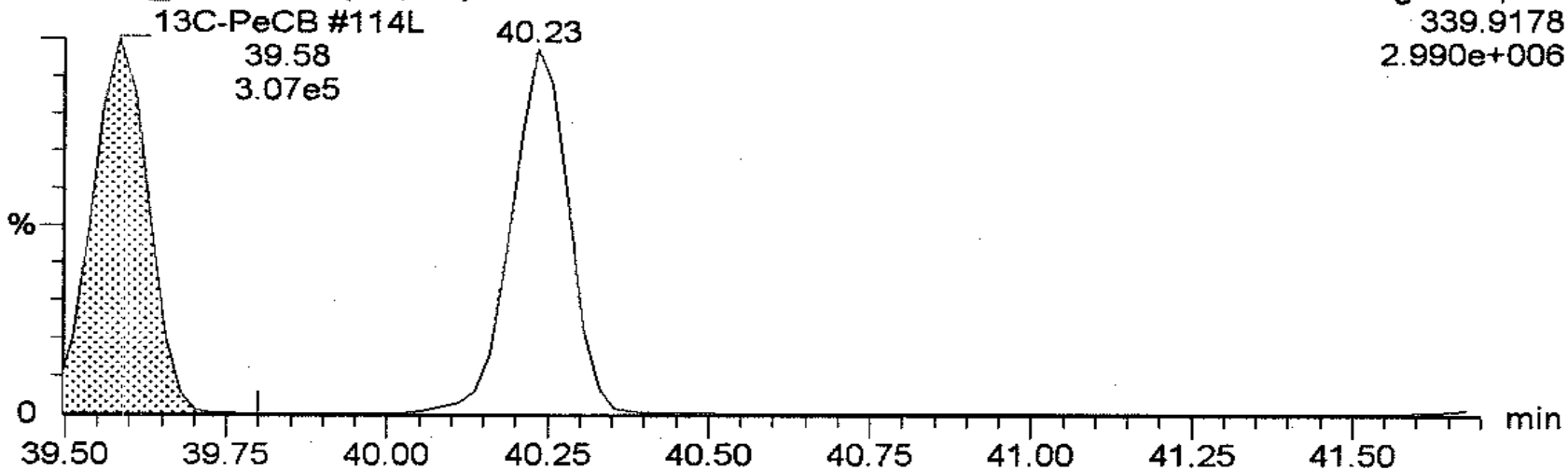
System Performance Window Defining Mixture (WDM)



M05233M1_03 Smooth(Mn,1x1)



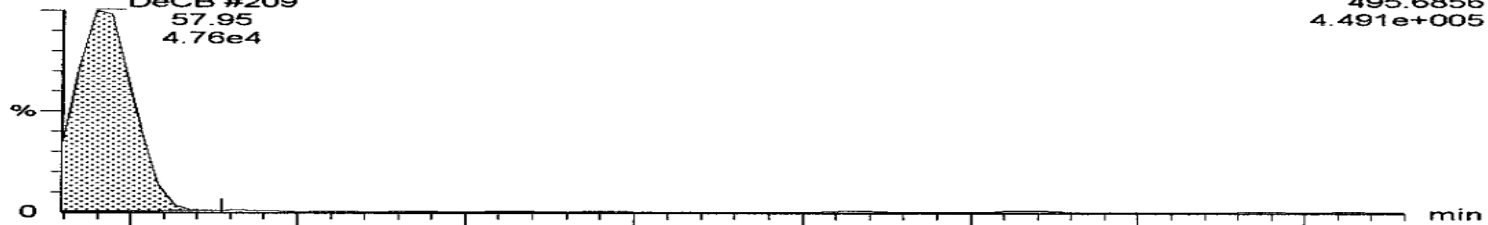
M05233M1_03 Smooth(Mn,1x1)



System Performance Window Defining Mixture (WDM)

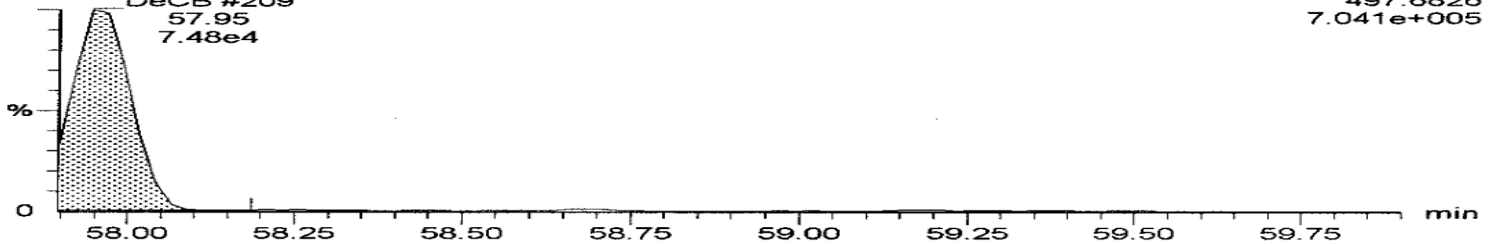


M05223M1_07 Smooth(Mn,1x1)
DeCB #209
57.95
4.76e4



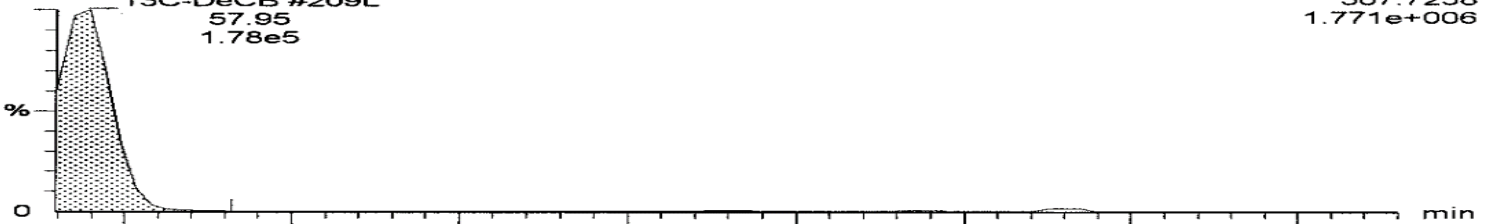
F6: Voltage SIR, EI+
495.6856
4.491e+005

M05223M1_07 Smooth(Mn,1x1)
DeCB #209
57.95
7.48e4



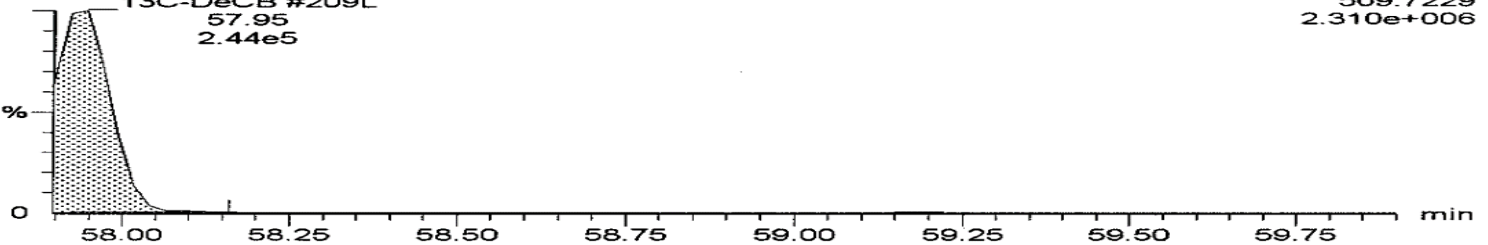
F6: Voltage SIR, EI+
497.6826
7.041e+005

M05223M1_07 Smooth(Mn,1x1)
13C-DeCB #209L
57.95
1.78e5



F6: Voltage SIR, EI+
507.7258
1.771e+006

M05223M1_07 Smooth(Mn,1x1)
13C-DeCB #209L
57.95
2.44e5



F6: Voltage SIR, EI+
509.7229
2.310e+006

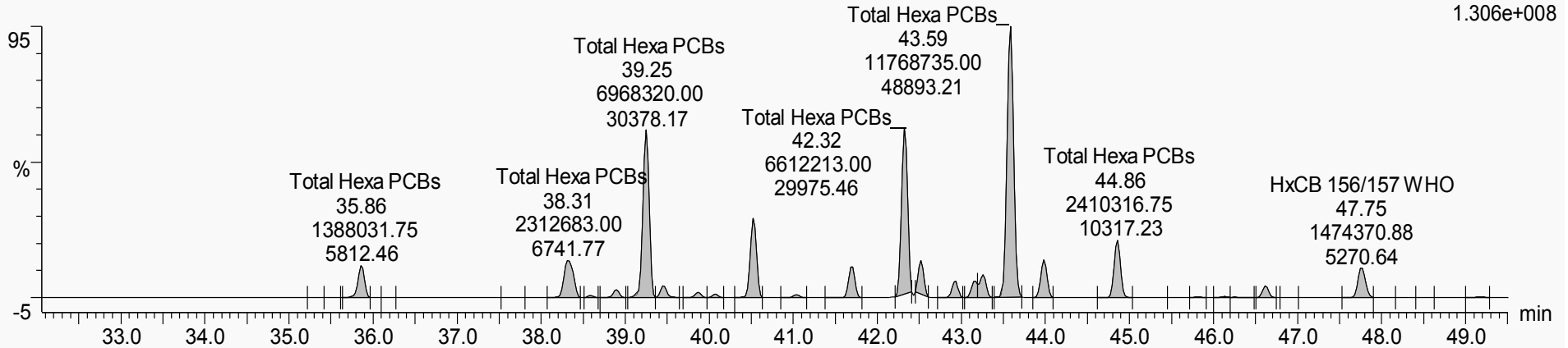
System Performance Window Defining Mixture (WDM)



Total Hexa PCBs

112712_BPC_12M658688_3879132_5x Smooth(SG,1x2)

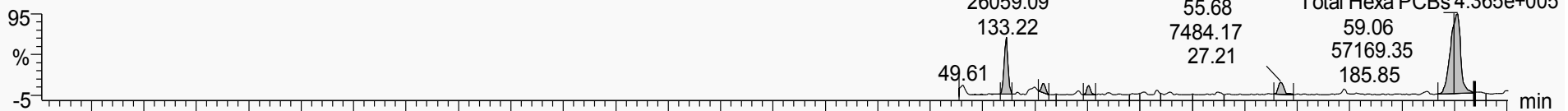
F3:Voltage SIR,EI+
359.8415
1.306e+008



Total Hexa PCBs

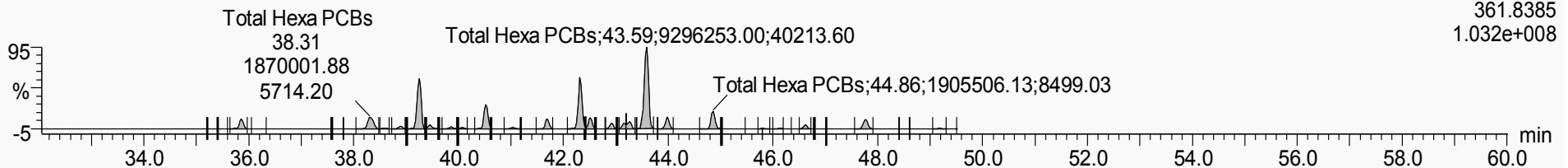
112712_BPC_12M658688_3879132_5x Smooth(SG,1x2)

F4:Voltage SIR,EI+
359.8415
4.365e+005



112712_BPC_12M658688_3879132_5x Smooth(SG,1x2)

F3:Voltage SIR,EI+
361.8385
1.032e+008



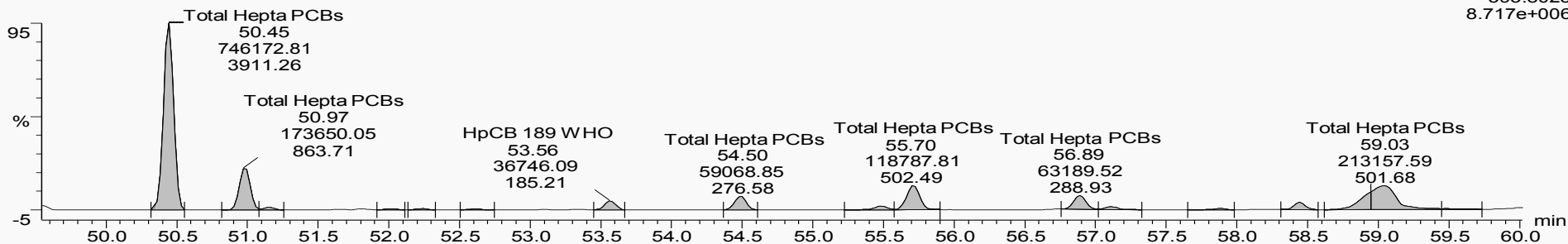
System Performance Window Defining Mixture (WDM)



Total Hepta PCBs

112712_BPC_12M658688_3879132_5x Smooth(SG,1x2)

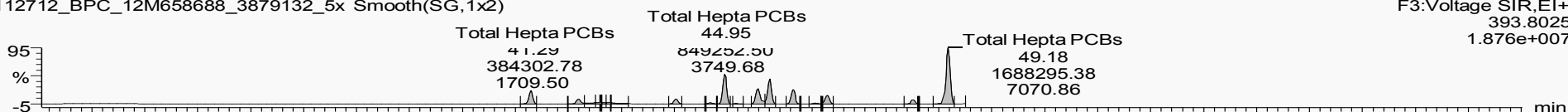
F4:Voltage SIR,EI+
393.8025
8.717e+006



Total Hepta PCBs

112712_BPC_12M658688_3879132_5x Smooth(SG,1x2)

F3:Voltage SIR,EI+
393.8025
1.876e+007



112712_BPC_12M658688_3879132_5x Smooth(SG,1x2)

F4:Voltage SIR,EI+
395.7995
8.264e+006

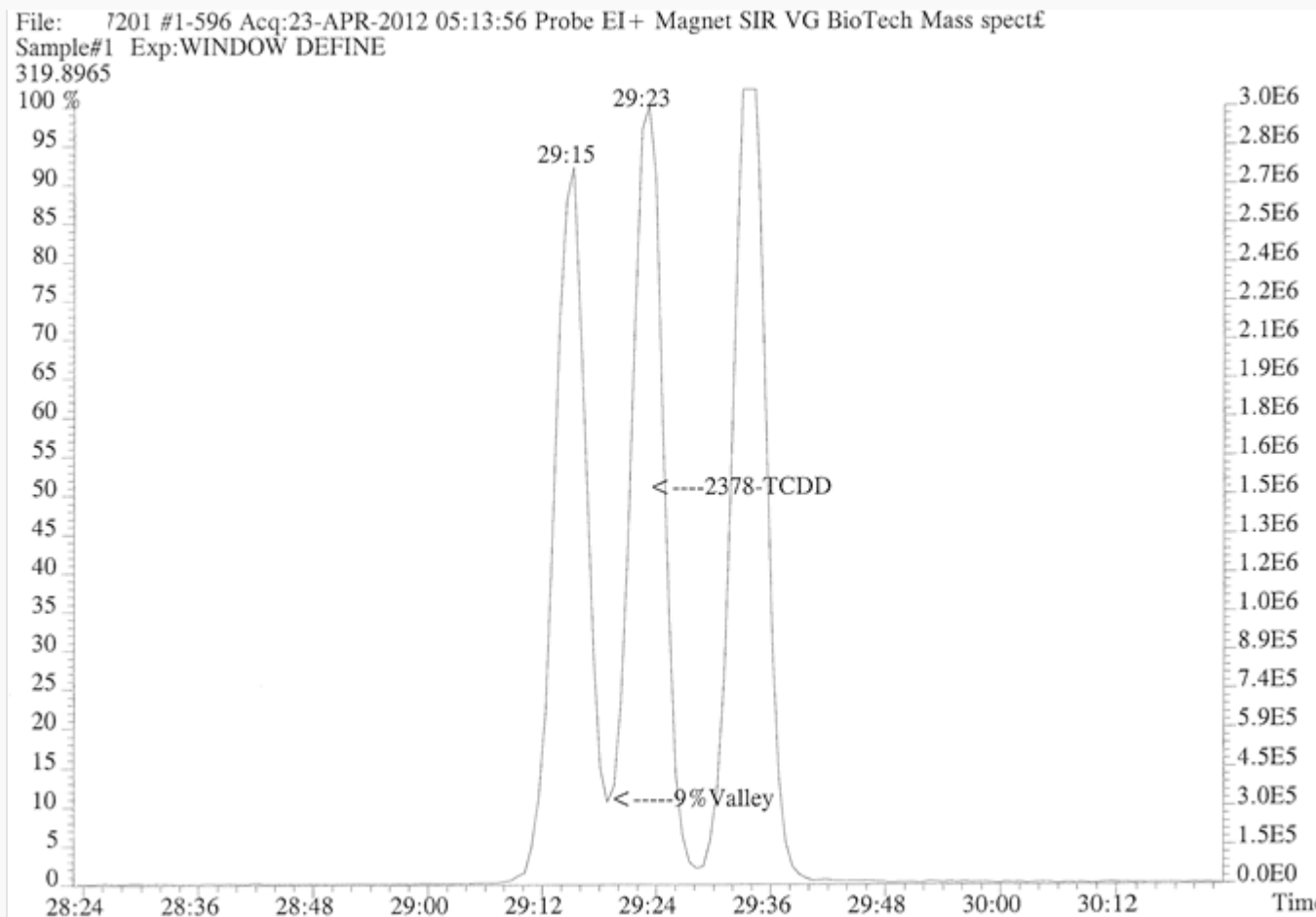


System Performance Window Defining Mixture (WDM)

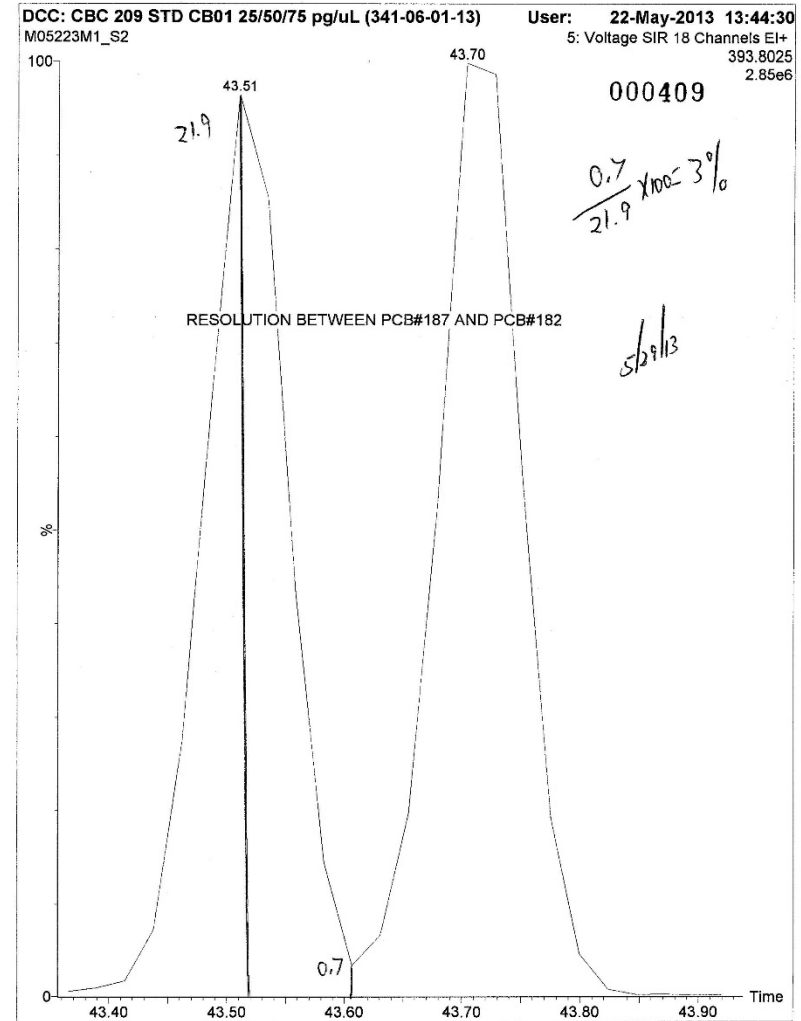
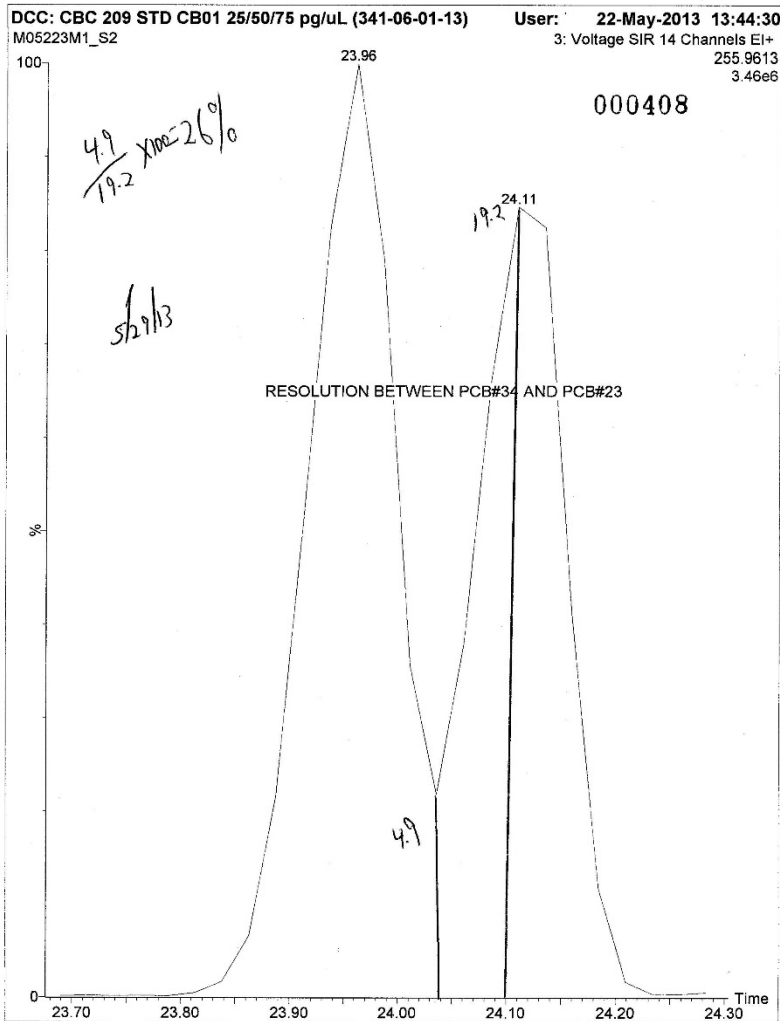


Congener	Retention Time First Eluting	Retention Time Last Eluting
TCDF	24:29	30:31
TCDD	26:17	30:29
PeCDF	30:47	34:39
PeCDD	32:09	34:30
HxCDF	35:31	37:50
HxCDD	36:02	37:31
HpCDF	39:13	40:31
HpCDD	39:27	40:06
% Valley 2378-TCDD:	9 %	

System Performance Window Defining Mixture (WDM)



System Performance Window Defining Mixture (WDM)



System Performance



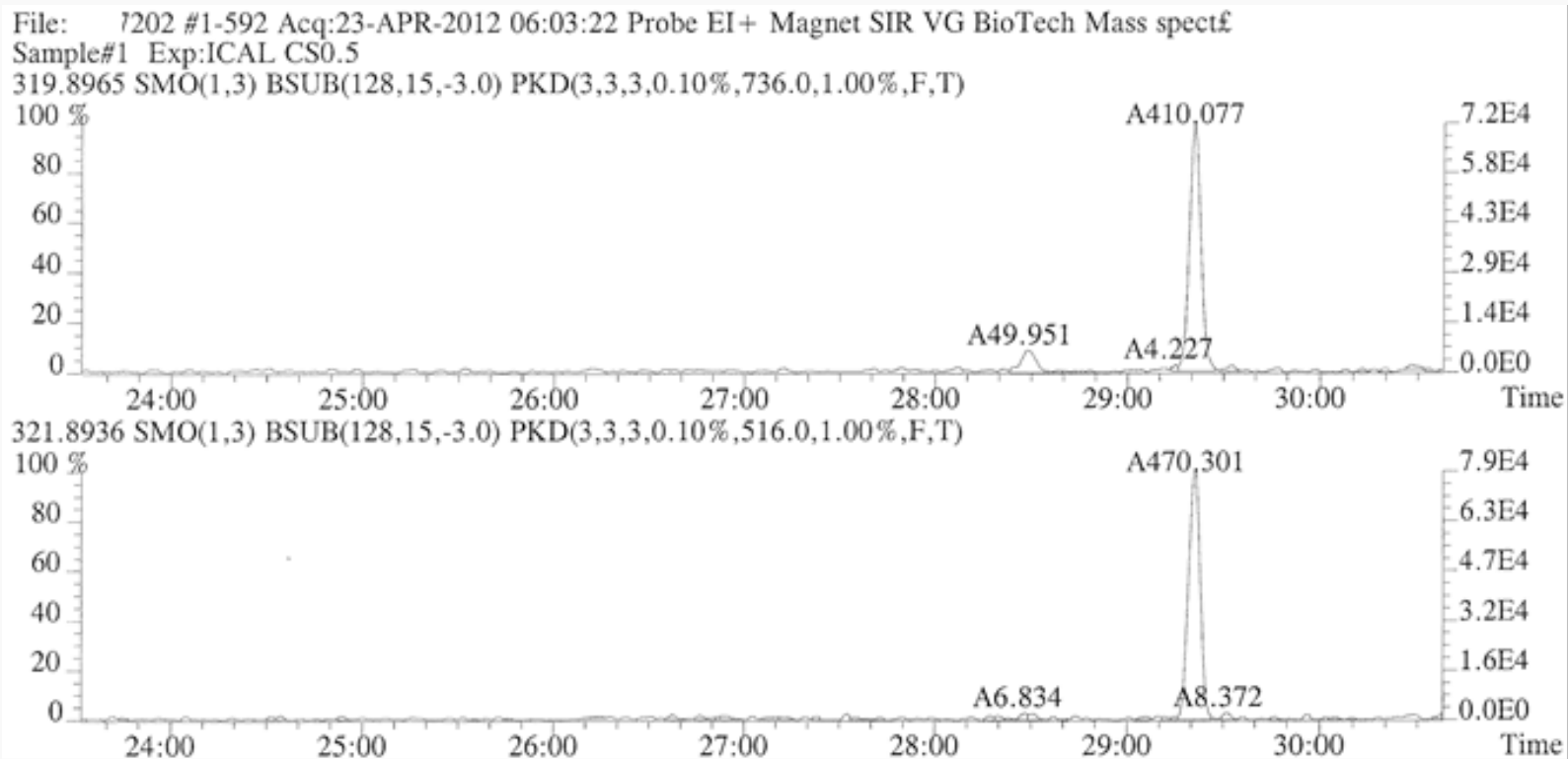
Criteria	Action ¹	
	Detected Associated Compounds	Non-Detected Associated Compounds
WDM fails, or WDM adjustments are not made, or WDM is not reported, <u>and</u> Calibration standard performance is acceptable	J-Homologue Totals Only	UJ-Homologue Totals Only
WDM fails, and WDM adjustments are not made, and Calibration standards indicate a problem in detecting 2,3,7,8-substituted congeners because of gross errors in the scan descriptor times	R	R
ISC fails (GC Resolution (% Valley) of >25%), or ISC adjustments are not made	J all tetra – hexa-congeners	Not qualified
ISC fails, or ISC adjustments are not made, and Calibration standards or samples indicate a problem in resolving 2,3,7,8-substituted congeners	R	R
RT changes >15 seconds or RRT changes not within the values in Table A.3	Use professional judgment for qualification of target analytes; qualify homologue totals as estimated (J, UJ).	

Initial Calibration Data

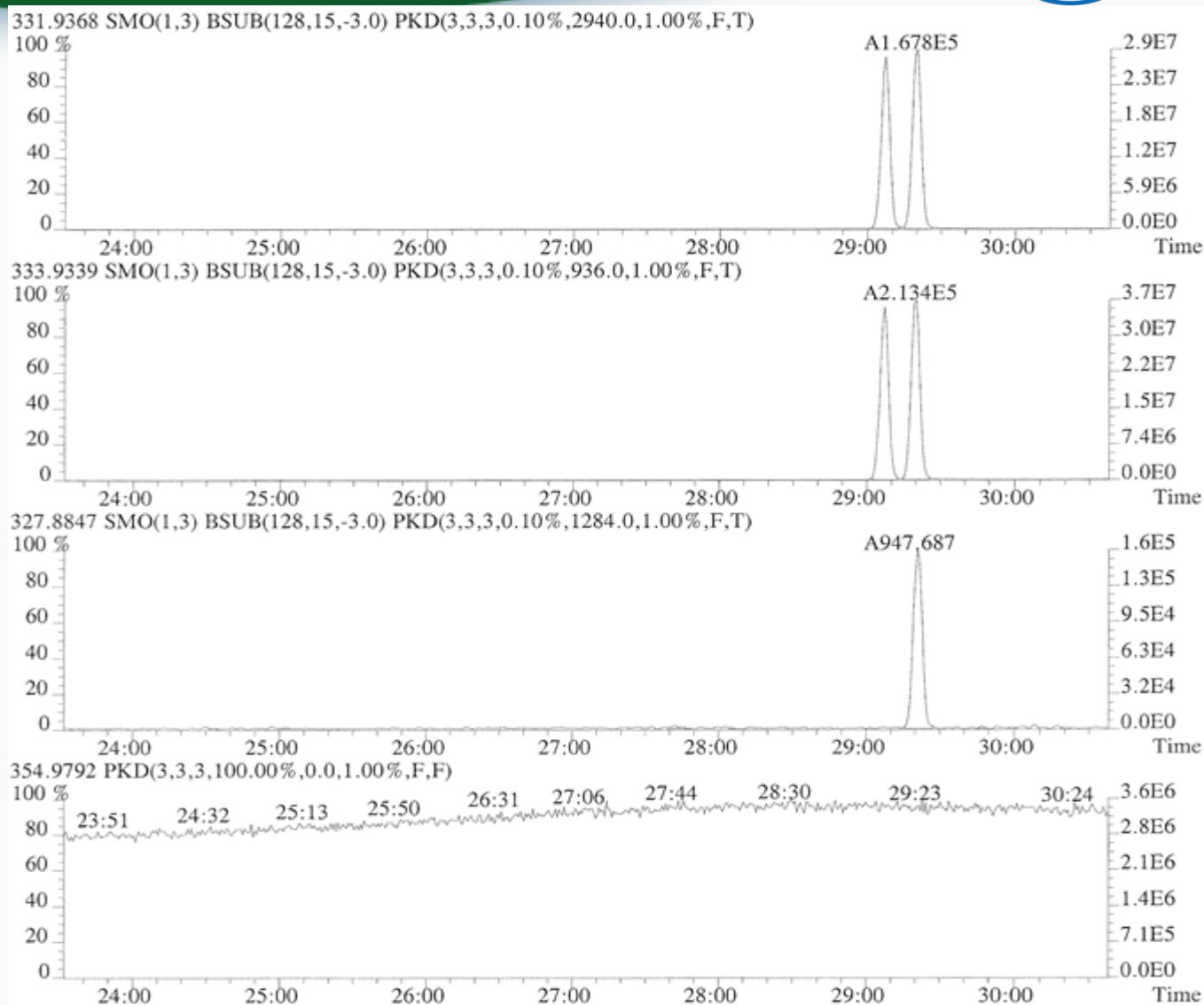


- Review initial calibration levels and frequency, checking % RSD or linearity
- Verify calculations for initial calibration
- Verify sensitivity (i.e. examine low standard)

Initial Calibration Data



Initial Calibration Data



Initial Calibration Data



Target Analytes	SELECTED IONS	ION ABUNDANCE RATIO						FLAG	ION RATIO QC LIMITS
		CS0.5	CS1	CS2	CS3	CS4	CS5		
2,3,7,8-TCDF	304/306	0.77	0.72	0.76	0.77	0.79	0.79		0.65-0.89
1,2,3,7,8-PeCDF	340/342	1.51	1.59	1.53	1.56	1.56	1.57		0.65-0.89
2,3,4,7,8-PeCDF	340/342	1.51	1.55	1.56	1.55	1.57	1.56		1.32-1.78
1,2,3,4,7,8-HxCDF	374/376	1.24	1.24	1.31	1.30	1.27	1.26		1.32-1.78
1,2,3,6,7,8-HxCDF	374/376	1.23	1.23	1.21	1.22	1.29	1.28		1.32-1.78
2,3,4,6,7,8-HxCDF	374/376	1.24	1.19	1.25	1.25	1.26	1.28		1.05-1.43
1,2,3,7,8,9-HxCDF	374/376	1.30	1.27	1.25	1.25	1.27	1.27		1.05-1.43
1,2,3,4,6,7,8-HpCDF	408/410	1.04	1.03	1.03	1.03	1.04	1.04		1.05-1.43
1,2,3,4,7,8,9-HpCDF	408/410	1.09	1.03	1.03	1.05	1.04	1.04		1.05-1.43
OCDF	442/444	0.89	0.91	0.91	0.90	0.91	0.91		1.05-1.43
2,3,7,8-TCDD	320/322	0.87	0.76	0.76	0.76	0.78	0.77		1.05-1.43
1,2,3,7,8-PeCDD	356/358	1.53	1.59	1.53	1.57	1.56	1.55		1.05-1.43
1,2,3,4,7,8-HxCDD	390/392	1.22	1.21	1.24	1.24	1.24	1.21		0.88-1.20
1,2,3,6,7,8-HxCDD	390/392	1.18	1.23	1.26	1.27	1.24	1.24		0.88-1.20
1,2,3,7,8,9-HxCDD	390/392	1.31	1.23	1.22	1.24	1.24	1.23		0.88-1.20
1,2,3,4,6,7,8-HpCDD	424/426	1.00	1.02	1.04	1.04	1.04	1.04		0.76-1.02
OCDD	458/460	0.92	0.89	0.88	0.90	0.89	0.89		0.76-1.02
13C-2,3,7,8-TCDF	316/318	0.77	0.78	0.77	0.77	0.77	0.77		0.65-0.89
13C-1,2,3,7,8-PeCDF	352/354	1.56	1.57	1.55	1.56	1.56	1.56		1.32-1.78
13C-2,3,4,7,8-PeCDF	352/354	1.57	1.57	1.56	1.56	1.55	1.57		1.05-1.43
13C-1,2,3,4,7,8-HxCDF	384/385	0.52	0.53	0.54	0.54	0.52	0.52		1.05-1.43
13C-1,2,3,6,7,8-HxCDF	384/385	0.53	0.51	0.51	0.50	0.52	0.52		0.88-1.20
13C-2,3,4,6,7,8-HxCDF	384/385	0.52	0.52	0.52	0.52	0.52	0.52		0.76-1.02
13C-1,2,3,7,8,9-HxCDF	384/385	0.52	0.52	0.52	0.52	0.52	0.52		0.65-0.89
13C-1,2,3,4,6,7,8-CDF	418/420	0.45	0.45	0.45	0.45	0.44	0.45		1.32-1.78
13C-1,2,3,4,7,8,9-CDF	418/420	0.45	0.45	0.45	0.45	0.45	0.45		1.32-1.78
13C-2,3,7,8-TCDD	332/334	0.79	0.78	0.78	0.79	0.78	0.79		0.43-0.59
13C-1,2,3,7,8-PeCDD	368/370	1.58	1.58	1.57	1.58	1.56	1.56		0.43-0.59
13C-1,2,3,4,7,8-HxCDD	402/404	1.26	1.25	1.26	1.26	1.24	1.24		0.43-0.59
13C-1,2,3,6,7,8-HxCDD	402/404	1.25	1.26	1.25	1.25	1.24	1.25		0.43-0.59
13C-1,2,3,4,6,7,8-CDD	436/438	1.06	1.06	1.05	1.04	1.04	1.05		0.37-0.51
13C-OCDD	470/472	0.90	0.90	0.89	0.90	0.89	0.89		0.37-0.51

Initial Calibration Data



6DFA6
CDD/CDF INITIAL CALIBRATION RESPONSE FACTOR SUMMARY
HIGH RESOLUTION

Lab Name: - Contract No.:
 Lab Code: Case No.: TO No.: SDG No.: 193
 GC Column: DB-5 ID: 0.25(mm) Instrument ID: E-HRMS-03
 Init. Calib. Date(s): 04/23/12
 Init. Calib. Time.: 05:13

RR/RRF

Target Analytes	RR/RRF						MEAN		QC LIMITS
	CS0.5	CS1	CS2	CS3	CS4	CS5	RR/RRF	%RSD	
2,3,7,8-TCDD	0.92	0.99	0.99	0.96	1.01	1.01	0.98	3.29	+/-20%
2,3,7,8-TCDF	0.93	0.94	0.93	0.91	0.93	0.93	0.93	0.96	+/-20%
1,2,3,7,8-PeCDF	0.96	1.02	1.02	0.93	1.04	1.04	1.00	4.37	+/-20%
1,2,3,7,8-PeCDD	0.85	0.92	0.91	0.92	0.94	0.94	0.91	3.60	+/-20%
2,3,4,7,8-PeCDF	0.90	0.96	0.96	1.00	0.97	0.98	0.96	3.40	+/-20%
1,2,3,4,7,8-HxCDF	1.16	1.26	1.26	1.19	1.25	1.21	1.22	3.41	+/-20%
1,2,3,6,7,8-HxCDF	1.09	1.14	1.16	1.15	1.15	1.14	1.14	2.08	+/-20%
1,2,3,4,7,8-HxCDD	0.93	0.99	1.02	1.06	1.01	1.00	1.00	4.40	+/-20%
1,2,3,6,7,8-HxCDD	0.95	1.03	1.01	0.88	1.01	1.00	0.98	5.84	+/-20%
1,2,3,7,8,9-HxCDD	1.01	1.05	1.04	1.04	1.05	1.05	1.04	1.62	+/-20%
2,3,4,6,7,8-HxCDF	1.09	1.18	1.16	1.12	1.16	1.12	1.14	3.13	+/-20%
1,2,3,7,8,9-HxCDF	1.13	1.20	1.18	1.13	1.19	1.16	1.16	2.56	+/-20%
1,2,3,4,6,7,8-HpCDF	1.33	1.44	1.41	1.34	1.43	1.41	1.39	3.46	+/-20%
1,2,3,4,6,7,8-HpCDD	0.95	1.02	1.02	0.97	1.03	1.02	1.00	3.14	+/-20%
1,2,3,4,7,8,9-HpCDF	1.28	1.34	1.33	1.37	1.36	1.34	1.33	2.38	+/-20%
OCDD	1.00	1.08	1.06	0.99	1.09	1.11	1.05	4.75	+/-20%
OCDF	1.19	1.23	1.24	1.09	1.29	1.32	1.23	6.52	+/-20%

Initial Calibration Data



Name	RT-1	Resp 1	Resp 2	Ratio	Meet	Mod?	RRT
2,3,7,8-TCDF	28:31	1.117e+03	1.557e+03	0.72	yes	no	1.001
1,2,3,7,8-PeCDF	32:55	7.190e+03	4.529e+03	1.59	yes	no	1.001
2,3,4,7,8-PeCDF	33:39	6.413e+03	4.148e+03	1.55	yes	no	1.000
1,2,3,4,7,8-HxCDF	36:29	5.746e+03	4.635e+03	1.24	yes	no	1.000
1,2,3,6,7,8-HxCDF	36:35	5.979e+03	4.867e+03	1.23	yes	no	1.000
2,3,4,6,7,8-HxCDF	37:04	5.534e+03	4.663e+03	1.19	yes	no	1.000
1,2,3,7,8,9-HxCDF	37:46	5.168e+03	4.077e+03	1.27	yes	no	1.000
1,2,3,4,6,7,8-HpCDF	39:12	4.787e+03	4.657e+03	1.03	yes	no	1.000
1,2,3,4,7,8,9-HpCDF	40:30	3.775e+03	3.673e+03	1.03	yes	no	1.000
OCDF	43:15	5.272e+03	5.801e+03	0.91	yes	no	1.004
2,3,7,8-TCDD	29:22	9.344e+02	1.233e+03	0.76	yes	no	1.001
1,2,3,7,8-PeCDD	34:01	4.866e+03	3.062e+03	1.59	yes	no	1.001
1,2,3,4,7,8-HxCDD	37:10	4.053e+03	3.339e+03	1.21	yes	no	1.000
1,2,3,6,7,8-HxCDD	37:15	4.085e+03	3.329e+03	1.23	yes	no	1.000
1,2,3,7,8,9-HxCDD	37:32	4.271e+03	3.460e+03	1.23	yes	no	1.008
1,2,3,4,6,7,8-HpCDD	40:05	3.271e+03	3.210e+03	1.02	yes	no	1.000
OCDD	43:05	4.582e+03	5.162e+03	0.89	yes	no	1.000
13C-2,3,7,8-TCDF	28:30	2.487e+05	3.208e+05	0.78	yes	no	0.978
13C-1,2,3,7,8-PeCDF	32:54	2.802e+05	1.781e+05	1.57	yes	no	1.129
13C-2,3,4,7,8-PeCDF	33:38	2.685e+05	1.710e+05	1.57	yes	no	1.154
13C-1,2,3,4,7,8-HxCDF	36:28	1.146e+05	2.150e+05	0.53	yes	no	0.972
13C-1,2,3,6,7,8-HxCDF	36:34	1.273e+05	2.519e+05	0.51	yes	no	0.975
13C-2,3,4,6,7,8-HxCDF	37:03	1.186e+05	2.259e+05	0.52	yes	no	0.988
13C-1,2,3,7,8,9-HxCDF	37:45	1.049e+05	2.031e+05	0.52	yes	no	1.006
13C-1,2,3,4,6,7,8-HpCDF	39:11	8.125e+04	1.803e+05	0.45	yes	no	1.044
13C-1,2,3,4,7,8,9-HpCDF	40:29	6.924e+04	1.534e+05	0.45	yes	no	1.079
13C-2,3,7,8-TCDD	29:21	1.925e+05	2.452e+05	0.78	yes	no	1.007
13C-1,2,3,7,8-PeCDD	33:59	2.112e+05	1.339e+05	1.58	yes	no	1.166
13C-1,2,3,4,7,8-HxCDD	37:10	1.659e+05	1.324e+05	1.25	yes	no	0.991
13C-1,2,3,6,7,8-HxCDD	37:14	1.611e+05	1.279e+05	1.26	yes	no	0.992
13C-1,2,3,4,6,7,8-HpCDD	40:04	1.303e+05	1.234e+05	1.06	yes	no	1.068
13C-OCDD	43:05	1.715e+05	1.900e+05	0.90	yes	no	1.148
13C-1,2,3,4-TCDD	29:08	1.964e+05	2.473e+05	0.79	yes	no	*
13C-1,2,3,7,8,9-HxCDD	37:31	1.735e+05	1.389e+05	1.25	yes	no	*
37Cl-2,3,7,8-TCDD	29:22	2.319e+03			no		1.008

Initial Calibration Data



Name	Signal 1	Noise 1	S/N Rat.1	Signal 2	Noise 2	S/N Rat.2
2,3,7,8-TCDF	1.87e+05	3.80e+02	4.9e+02	2.61e+05	5.68e+02	4.6e+02
1,2,3,7,8-PeCDF	1.42e+06	4.16e+02	3.4e+03	8.89e+05	1.24e+03	7.2e+02
2,3,4,7,8-PeCDF	1.26e+06	4.16e+02	3.0e+03	8.28e+05	1.24e+03	6.7e+02
1,2,3,4,7,8-HxCDF	1.25e+06	7.20e+02	1.7e+03	9.88e+05	3.80e+02	2.6e+03
1,2,3,6,7,8-HxCDF	1.30e+06	7.20e+02	1.8e+03	1.05e+06	3.80e+02	2.8e+03
2,3,4,6,7,8-HxCDF	1.21e+06	7.20e+02	1.7e+03	1.03e+06	3.80e+02	2.7e+03
1,2,3,7,8,9-HxCDF	1.09e+06	7.20e+02	1.5e+03	8.47e+05	3.80e+02	2.2e+03
1,2,3,4,6,7,8-HpCDF	1.03e+06	1.59e+03	6.5e+02	9.98e+05	1.26e+03	7.9e+02
1,2,3,4,7,8,9-HpCDF	7.28e+05	1.59e+03	4.6e+02	7.20e+05	1.26e+03	5.7e+02
OCDF	8.52e+05	4.40e+02	1.9e+03	9.60e+05	5.48e+02	1.8e+03
2,3,7,8-TCDD	1.63e+05	5.60e+02	2.9e+02	2.04e+05	3.80e+02	5.4e+02
1,2,3,7,8-PeCDD	9.68e+05	5.44e+02	1.8e+03	6.20e+05	2.52e+02	2.5e+03
1,2,3,4,7,8-HxCDD	9.05e+05	6.60e+02	1.4e+03	7.43e+05	6.68e+02	1.1e+03
1,2,3,6,7,8-HxCDD	9.02e+05	6.60e+02	1.4e+03	7.41e+05	6.68e+02	1.1e+03
1,2,3,7,8,9-HxCDD	9.01e+05	6.60e+02	1.4e+03	7.35e+05	6.68e+02	1.1e+03
1,2,3,4,6,7,8-HpCDD	6.40e+05	4.24e+02	1.5e+03	6.44e+05	2.80e+02	2.3e+03
OCDD	7.86e+05	3.84e+02	2.0e+03	8.58e+05	2.68e+02	3.2e+03
13C-2,3,7,8-TCDF	4.13e+07	3.98e+03	1.0e+04	5.32e+07	9.12e+02	5.8e+04
13C-1,2,3,7,8-PeCDF	5.44e+07	2.88e+02	1.9e+05	3.47e+07	4.60e+02	7.5e+04
13C-2,3,4,7,8-PeCDF	5.39e+07	2.88e+02	1.9e+05	3.42e+07	4.60e+02	7.4e+04
13C-1,2,3,4,7,8-HxCDF	2.45e+07	4.80e+02	5.1e+04	4.72e+07	1.12e+03	4.2e+04
13C-1,2,3,6,7,8-HxCDF	2.76e+07	4.80e+02	5.7e+04	5.26e+07	1.12e+03	4.7e+04
13C-2,3,4,6,7,8-HxCDF	2.58e+07	4.80e+02	5.4e+04	4.90e+07	1.12e+03	4.4e+04
13C-1,2,3,7,8,9-HxCDF	2.22e+07	4.80e+02	4.6e+04	4.24e+07	1.12e+03	3.8e+04
13C-1,2,3,4,6,7,8-HpCDF	1.73e+07	5.04e+03	3.4e+03	3.80e+07	7.10e+03	5.4e+03
13C-1,2,3,4,7,8,9-HpCDF	1.34e+07	5.04e+03	2.6e+03	2.96e+07	7.10e+03	4.2e+03
13C-2,3,7,8-TCDD	3.35e+07	3.08e+03	1.1e+04	4.25e+07	1.37e+03	3.1e+04
13C-1,2,3,7,8-PeCDD	4.20e+07	4.48e+02	9.4e+04	2.67e+07	3.48e+02	7.7e+04
13C-1,2,3,4,7,8-HxCDD	3.70e+07	2.38e+03	1.6e+04	2.95e+07	1.45e+03	2.0e+04
13C-1,2,3,6,7,8-HxCDD	3.44e+07	2.38e+03	1.4e+04	2.75e+07	1.45e+03	1.9e+04
13C-1,2,3,4,6,7,8-HpCDD	2.58e+07	1.24e+03	2.1e+04	2.46e+07	6.84e+02	3.6e+04
13C-OCDD	2.87e+07	5.72e+02	5.0e+04	3.19e+07	5.28e+02	6.0e+04
13C-1,2,3,4-TCDD	3.48e+07	3.08e+03	1.1e+04	4.39e+07	1.37e+03	3.2e+04
13C-1,2,3,7,8,9-HxCDD	3.73e+07	2.38e+03	1.6e+04	3.00e+07	1.45e+03	2.1e+04
37Cl-2,3,7,8-TCDD	3.90e+05	8.68e+02	4.5e+02			

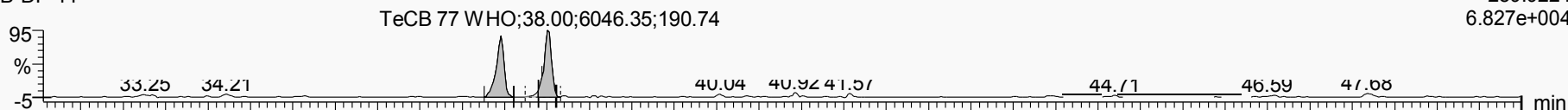
Initial Calibration Data



TeCB 81 WHO

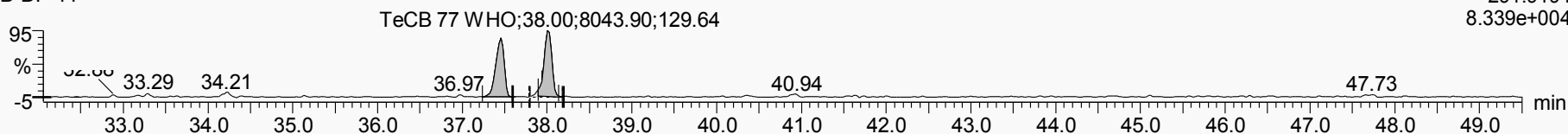
112512_BPC_CS1 Smooth(SG,1x2)
B-DF-44

F3:Voltage SIR,EI+
289.9224
6.827e+004



112512_BPC_CS1 Smooth(SG,1x2)
B-DF-44

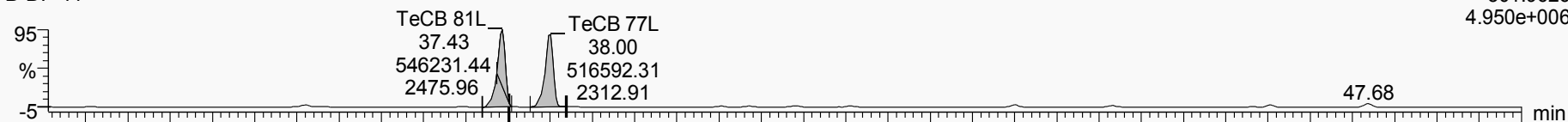
F3:Voltage SIR,EI+
291.9194
8.339e+004



TeCB 81L

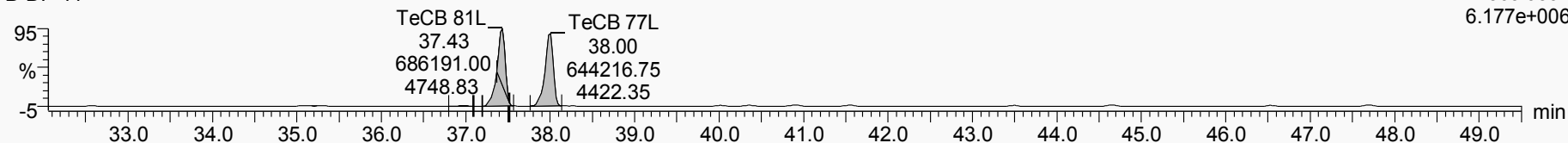
112512_BPC_CS1 Smooth(SG,1x2)
B-DF-44

F3:Voltage SIR,EI+
301.9626
4.950e+006



112512_BPC_CS1 Smooth(SG,1x2)
B-DF-44

F3:Voltage SIR,EI+
303.9597
6.177e+006

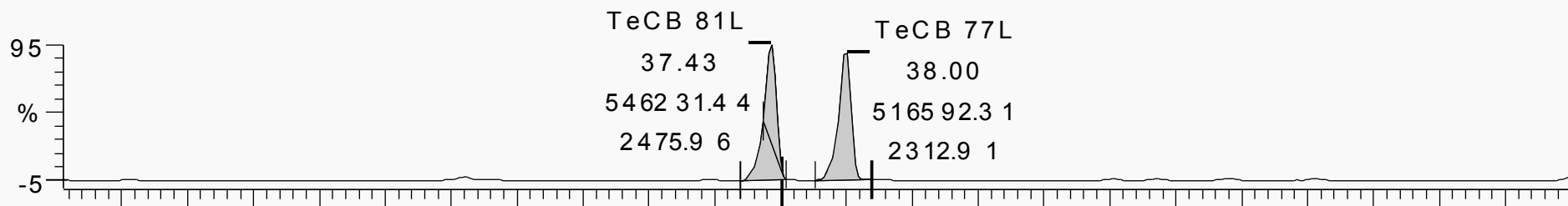


Initial Calibration Data

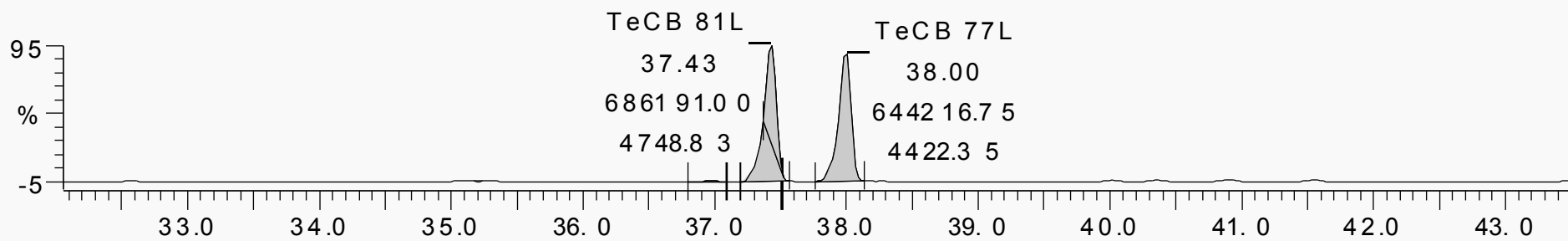


TeCB 81L

1125 12_B PC_CS1 Smooth (SG, 1x2)
B-DF-44



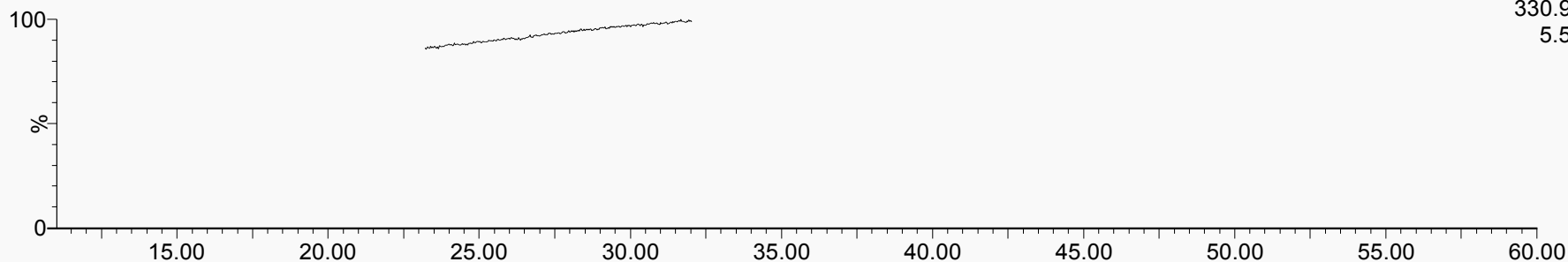
1125 12_B PC_CS1 Smooth (SG, 1x2)
B-DF-44



Initial Calibration Data

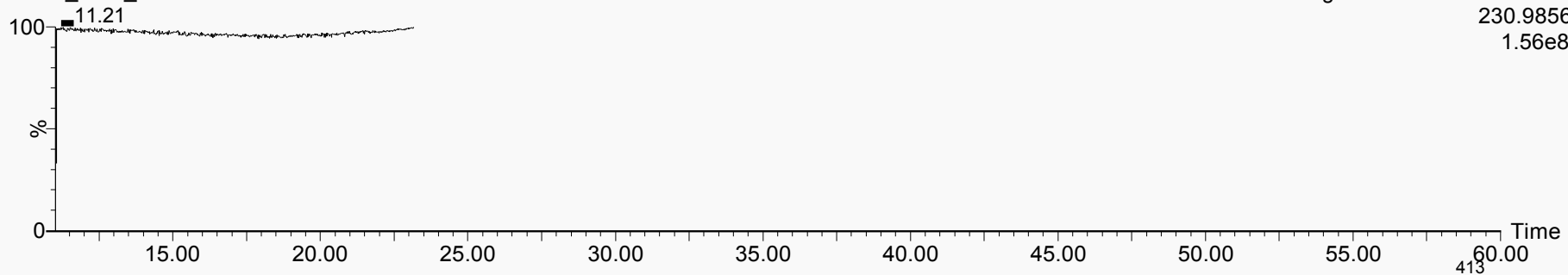


112512_BPC_CS1



2: Voltage SIR 19 Channels EI+
330.9792
5.57e7

112512_BPC_CS1



1: Voltage SIR 16 Channels EI+
230.9856
1.56e8

Initial Calibration Data



Criteria	Action	
	Detected Compounds	Non-Detected Compounds
Initial calibrations are not performed	R	R
Initial calibration not at proper frequency	J	UJ
Ion Abundance Ratio out	R or professional judgment	R or professional judgment
GC Resolution (% Valley) >25%	J	UJ
Linearity : RRF %RSDs; RR %RSDs out	J	UJ
Sensitivity <10:1 S/N ratio for all SICPs	J	R or professional judgment
RTs outside criteria	R	R

Continuing Calibration Data



- Review daily beginning and ending continuing calibration verification standard performance
 - Usually measured in % difference
 - Check S/N
 - Check Relative Retention Times
- Check calculations for verification standards
- Verify that system has adequate stability
 - Absolute RT criteria
 - RRT criteria
 - Ion abundance ratio criteria

Continuing Calibration Data



Target Analytes	SELECTED IONS	RR/RRF	MEAN RR/RRF	%D	%D FLAG	ION RATIO	ION RATIO FLAG	ION RATIO QC LIMITS
2,3,7,8-TCDD	320/322	0.99	0.98	1.36		0.76		0.65-0.89
2,3,7,8-TCDF	304/306	0.91	0.93	-2.46		0.76		0.65-0.89
1,2,3,7,8-PeCDF	340/342	0.96	1.00	-4.42		1.54		1.32-1.78
1,2,3,7,8-PeCDD	356/358	0.96	0.91	4.73		1.57		1.32-1.78
2,3,4,7,8-PeCDF	340/342	1.02	0.96	5.66		1.51		1.32-1.78
1,2,3,4,7,8-HxCDF	374/376	1.19	1.22	-2.71		1.20		1.05-1.43
1,2,3,6,7,8-HxCDF	374/376	1.19	1.14	4.82		1.20		1.05-1.43
1,2,3,4,7,8-HxCDD	390/392	1.11	1.00	11.22		1.28		1.05-1.43
1,2,3,6,7,8-HxCDD	390/392	0.91	0.98	-6.82		1.24		1.05-1.43
1,2,3,7,8,9-HxCDD	390/392	1.08	1.04	4.03		1.26		1.05-1.43
2,3,4,6,7,8-HxCDF	374/376	1.14	1.14	-0.24		1.19		1.05-1.43
1,2,3,7,8,9-HxCDF	374/376	1.15	1.16	-1.14		1.23		1.05-1.43
1,2,3,4,6,7,8-HpCDF	408/410	1.38	1.39	-1.03		1.01		0.88-1.20
1,2,3,4,6,7,8-HpCDD	424/426	1.00	1.00	0.06		1.05		0.88-1.20
1,2,3,4,7,8,9-HpCDF	408/410	1.39	1.33	4.37		1.01		0.88-1.20
OCDD	458/460	0.98	1.05	-6.75		0.88		0.76-1.02
OCDF	442/444	1.19	1.23	-3.17		0.89		0.76-1.02
Labeled Compounds								
13C-2,3,7,8-TCDD	332/334	1.04	1.00	4.17		0.79		0.65-0.89
13C-1,2,3,7,8-PeCDD	368/370	0.93	0.82	13.37		1.57		1.32-1.78
13C-1,2,3,4,7,8-HxCDD	402/404	0.92	0.93	-0.97		1.27		1.05-1.43
13C-1,2,3,6,7,8-HxCDD	402/404	1.00	0.94	6.22		1.28		1.05-1.43
13C-1,2,3,4,6,7,8-HpCDD	424/426	0.89	0.82	8.74		1.06		0.88-1.20
13C-OCDD	470/472	0.76	0.59	27.94		0.90		0.76-1.02
13C-2,3,7,8-TCDF	316/318	1.36	1.28	6.04		0.78		0.65-0.89
13C-1,2,3,7,8-PeCDF	352/354	1.28	1.10	16.34		1.57		1.32-1.78
13C-2,3,4,7,8-PeCDF	352/354	1.21	1.07	13.99		1.57		1.32-1.78
13C-1,2,3,4,7,8-HxCDF	384/386	1.11	1.06	4.53		0.52		0.43-0.59
13C-1,2,3,6,7,8-HxCDF	384/386	1.18	1.19	-0.75		0.52		0.43-0.59
13C-2,3,4,6,7,8-HxCDF	384/386	1.14	1.10	3.75		0.52		0.43-0.59
13C-1,2,3,7,8,9-HxCDF	384/386	1.07	0.98	8.86		0.53		0.43-0.59
13C-1,2,3,4,6,7,8-HpCDF	418/420	0.92	0.84	9.95		0.45		0.37-0.51
13C-1,2,3,4,7,8,9-HpCDF	418/420	0.79	0.71	12.05		0.44		0.37-0.51

Continuing Calibration Data



Target Analytes	RRT	RT
2,3,7,8-TCDD	1.001	29:11
2,3,7,8-TCDF	1.001	28:19
1,2,3,7,8-PeCDF	1.001	32:47
1,2,3,7,8-PeCDD	1.000	33:53
2,3,4,7,8-PeCDF	1.000	33:31
1,2,3,4,7,8-HxCDF	1.000	36:23
1,2,3,6,7,8-HxCDF	1.000	36:29
1,2,3,4,7,8-HxCDD	1.000	37:05
1,2,3,6,7,8-HxCDD	1.000	37:09
1,2,3,7,8,9-HxCDD	1.008	37:26
2,3,4,6,7,8-HxCDF	1.000	36:57
1,2,3,7,8,9-HxCDF	1.000	37:40
1,2,3,4,6,7,8-HpCDF	1.000	39:07
1,2,3,4,6,7,8-HpCDD	1.000	40:00
1,2,3,4,7,8,9-HpCDF	1.000	40:23
OCDD	1.000	43:01
OCDF	1.004	43:10
Labeled Compounds		
13C-2,3,7,8-TCDD	1.007	29:10
13C-1,2,3,7,8-PeCDD	1.170	33:52
13C-1,2,3,4,7,8-HxCDD	0.990	37:04
13C-1,2,3,6,7,8-HxCDD	0.992	37:09
13C-1,2,3,4,6,7,8-HpCDD	1.068	39:59
13C-OCDD	1.149	43:00
13C-2,3,7,8-TCDF	0.978	28:18
13C-1,2,3,7,8-PeCDF	1.132	32:46
13C-2,3,4,7,8-PeCDF	1.158	33:31
13C-1,2,3,4,7,8-HxCDF	0.972	36:22
13C-1,2,3,6,7,8-HxCDF	0.974	36:28
13C-2,3,4,6,7,8-HxCDF	0.987	36:57
13C-1,2,3,7,8,9-HxCDF	1.006	37:39
13C-1,2,3,4,6,7,8-HpCDF	1.045	39:06
13C-1,2,3,4,7,8,9-HpCDF	1.079	40:23
CLEAN-UP		
37Cl-2,3,7,8-TCDD	NA	29:11
Internal Standards		
13C-1,2,3,4-TCDD	NA	28:57
13C-1,2,3,7,8,9-HxCDD	NA	37:26

Continuing Calibration Data



CL No.	Labeled Congener	Mean RRT	RRT (CS3)	Q	RRT QC Limit
4	PCB-77L	1.34724	1.3476		1.3513-1.3629
4	PCB-81L	1.32704	1.3274		1.3287-1.3403
5	PCB-105L	1.17692	1.1768		1.1808-1.1900
5	PCB-114L	1.15864	1.1588		1.1590-1.1683
5	PCB-118L	1.14326	1.1433		1.1424-1.1516
5	PCB-123L	1.13384	1.134		1.1331-1.1424
5	PCB-126L	1.26494	1.2649		1.2700-1.2792
6	PCB-156L/157L	1.0961	1.0962		1.0981-1.1003
6	PCB-167L	1.0694	1.0695		1.0664-1.0739
6	PCB-169L	1.17066	1.1707		1.1738-1.1761
7	PCB-189L	0.96226	0.9621		0.9587-0.9645
Labeled Cleanup Standard					
3	PCB-28L	0.9319	0.9328		0.9209-0.9324
5	PCB-111L	1.07736	1.0776		1.0730-1.0823
7	PCB-178L	1.0104	1.0106		1.0052-1.0127

Continuing Calibration Data



Calibration Verification Criteria	Action	
	Detected Compounds	Non-Detected Compounds
Ion abundance ratios not within $\pm 15\%$ window	J	R
Absolute RT of $^{13}\text{C}_{12}$ -1,2,3,4-TCDD >25 minutes on DB-5 column, or >15 minutes on DB-225 (or equivalent) column	Use professional judgment	
Internal standards in the calibration verification not within 15 seconds of the RT in the initial calibration	Use professional judgment for qualification of target analytes; qualify homologues as estimated (J, UJ).	
RRTs in the calibration verification not within the limits defined in Table A.3	Use professional judgment	
Sensitivity: S/N <10 for all compounds	J	R
%D for RRs not within $\pm 25\%$, %D for RRFs not within $\pm 35\%$	J	UJ
RT changes >15 seconds or RRT changes not within the values in Table A.3	Use professional judgment for qualification of target analytes; qualify homologue totals as estimated (J, UJ).	
Relative ion abundance criteria is not within windows in CS3 (12-hour) standard	J	UJ

Blank Data



- Examine method blank data for:
 - Appropriate frequency
 - Presence of target analytes
 - Presence of interferences
- Check instrument blanks for evidence of carry-over of high-level contaminants.
- Evaluate blank performance relative to data quality needs.

Blank Data



4DF - FORM IV-HR CDD
 CDD/CDF METHOD BLANK SUMMARY
 HIGH RESOLUTION

EPA Sample No.

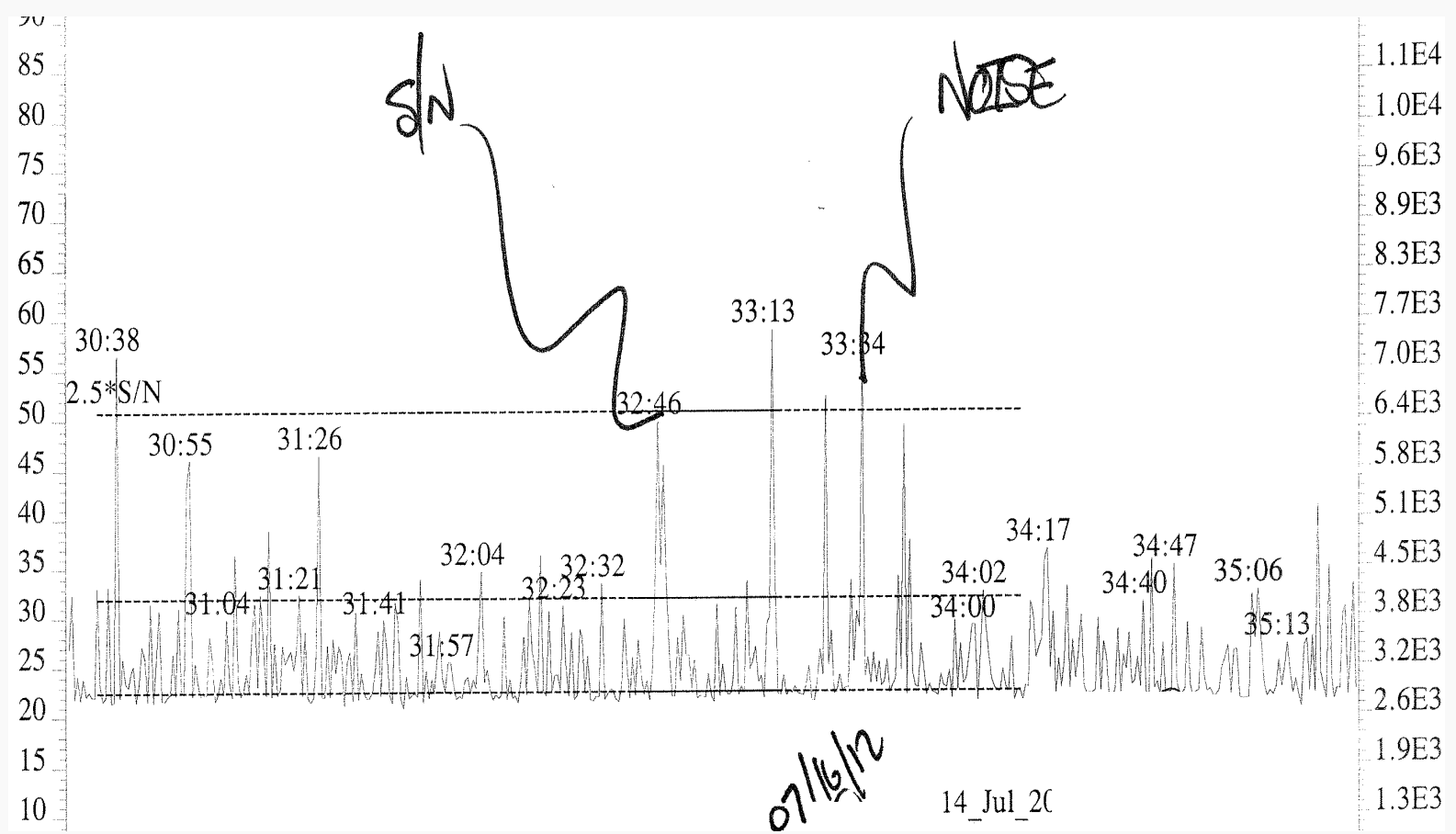
DFBLK

Lab Name: _____
 Lab Code: _____ Case No.: _____
 Matrix: (Soil/Water/Ash/Tissue/Oil) _____ Soil
 Sample wt/vol: _____ 10.554 (g/mL) _____ g
 Water Sample Prep: _____ (SEPF/SPE)
 GC Column: _____ DB-5 ID: _____ 0.25 (mm)
 Instrument ID: _____ E-HRMS-03

Contract: _____ W001071
 TO No.: _____ SDG No.: _____ 193
 Lab Sample ID: _____ 00341-01
 Lab File ID: _____ 8291
 Date Received: _____
 Date Extracted: _____ 06/12/2012
 Date Analyzed: _____ 06/19/2012

EPA Sample No.	Lab Sample ID	Lab File ID	Date Analyzed
DFBLK	00341-01	8291	06/19/2012
DLCS	00341-02	8292	06/19/2012
DLCS	00341-03	8293	06/19/2012
193	00584-001	8294	06/19/2012

Blank Data

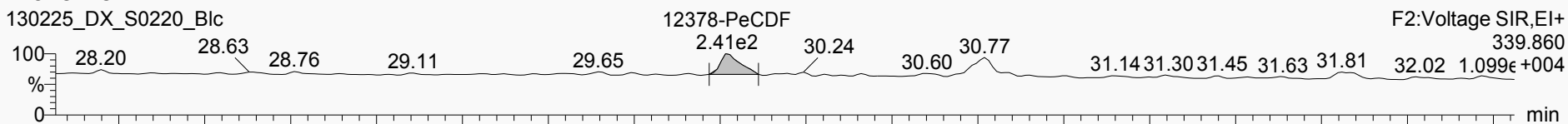


Blank Data

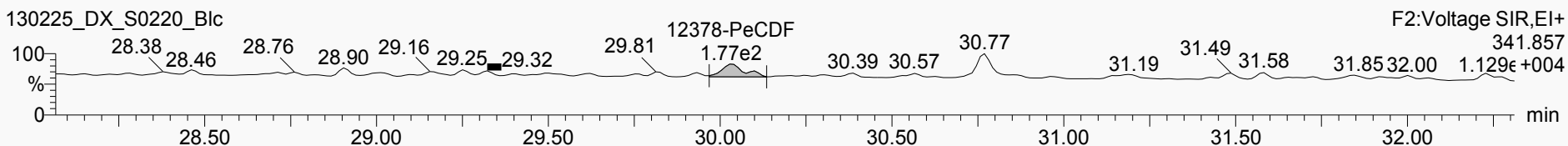


12378-PeCDF

130225_DX_S0220_Blc



130225_DX_S0220_Blc



Method Blank



Method Blank Result	Sample Result	Action
< < CRQL or EDL	Not detected	No qualification
	\geq CRQL or EDL and \gg Blank Result	No qualification or use professional judgment to avoid false pos. or neg. (see E.2.b above)
\geq CRQL or EDL	Not detected	No qualification
	\geq CRQL or EDL and $<$ Blank Result	U*
	$>$ CRQL or EDL and \geq Blank Result	J or use professional judgment
Gross contamination	Positive	R

Laboratory Control Spike



- Examine LCS, or On-Going Precision and Recovery (OPR) data for:
 - Appropriate frequency
 - Recovery of target analytes
 - Presence of interferences
 - Appropriate matrices

Laboratory Control Spike



Laboratory Control Sample Performance Criteria	Action	
	Detected Associated Compounds	Non-Detected Associated Compounds
%R > Upper Acceptance Limit	J	No qualification
% R >10% but < Lower Acceptance Limit	J	UJ
% R <10%	J	R
LCS performed but not at required frequency	J	Use professional judgment
LCS not performed	J	Use professional judgment

Sample Data

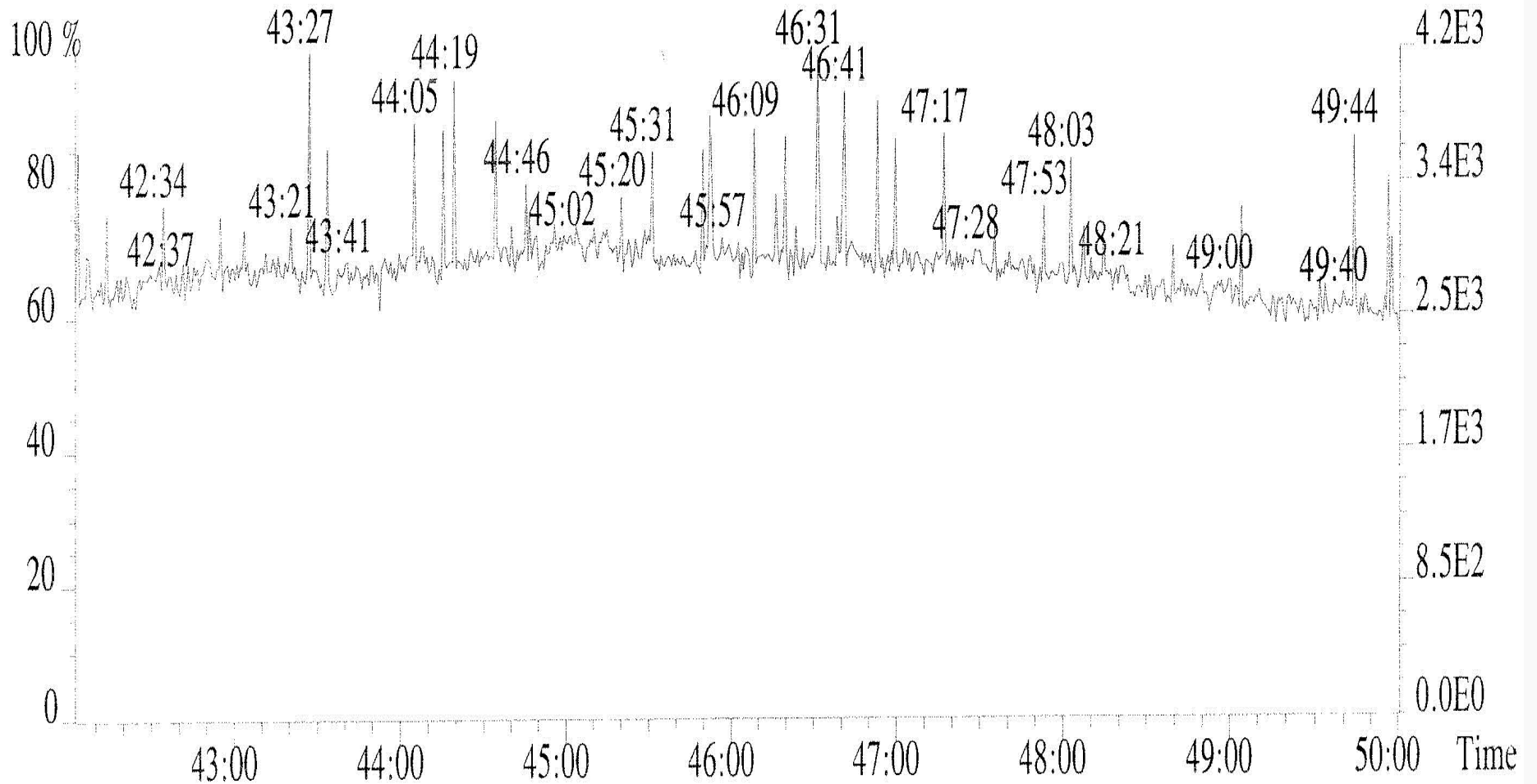


- Review sample extraction and analysis run logs, reporting forms, processed data and raw data.
- Examine sample data for:
 - reported analytes as well as non-detects
 - chromatography
 - retention time match
 - ion ratios
 - both ions meeting S/N criteria
 - abnormal labeled compound recovery
 - diphenyl ether interference
 - lock mass stability
- Verify calculations of sample results.
- Check for transcription errors.

System Performance



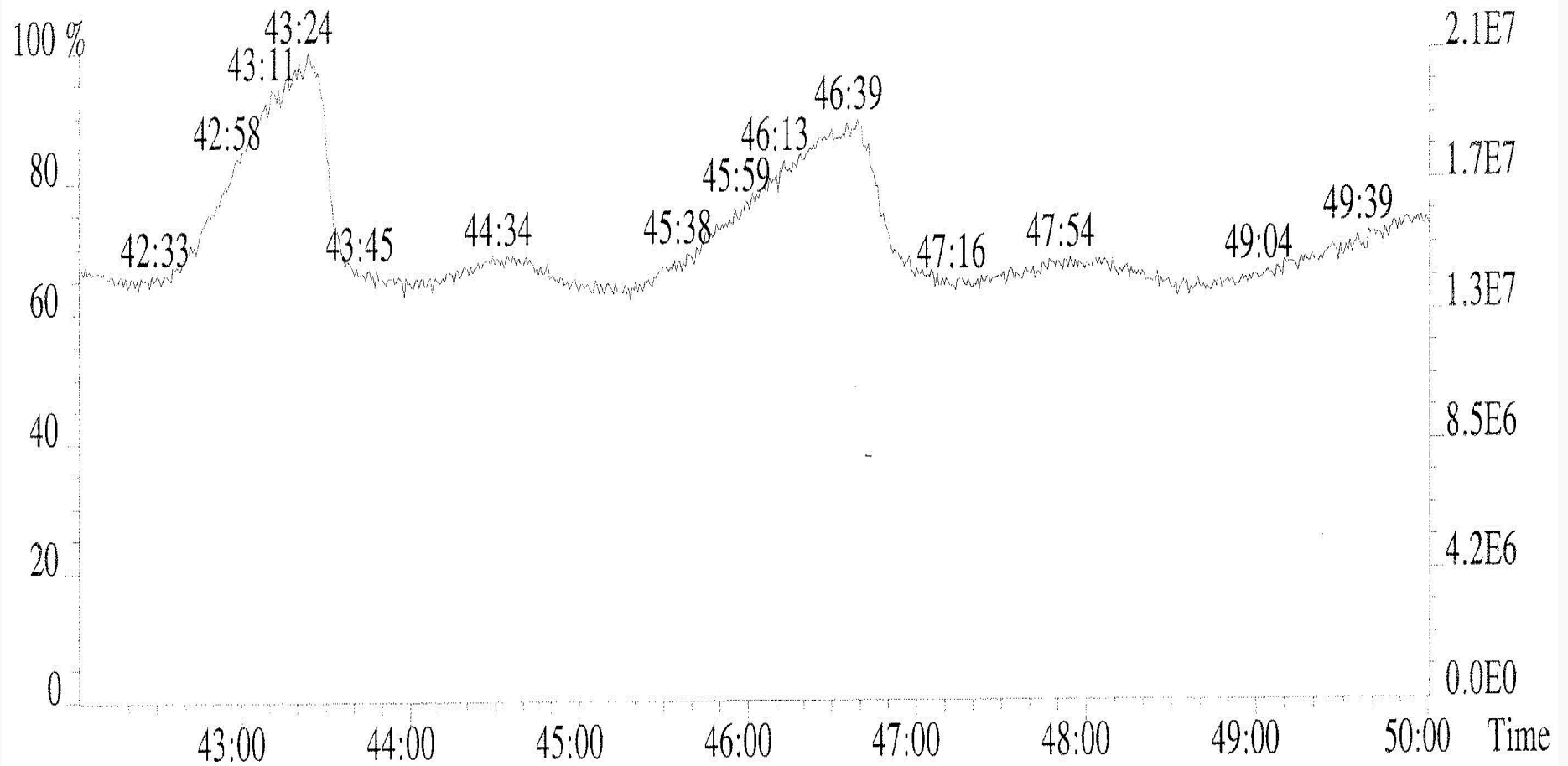
513.6775 F:5 PKD(5,3,5,100.00%,0.0,1.00%,F,F)



System Performance



442.9728 F:5 PKD(3,3,3,100.00%,0.0,0.40%,F,F)



Final Evaluation of Data



- Note all deviations from the method and all QC deficiencies
- Evaluate the impact on all data and on individual samples
- Apply data qualifiers as appropriate
- Write up your findings in a data review narrative.



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