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

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Analytical Services Branch
July 29, 2015

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


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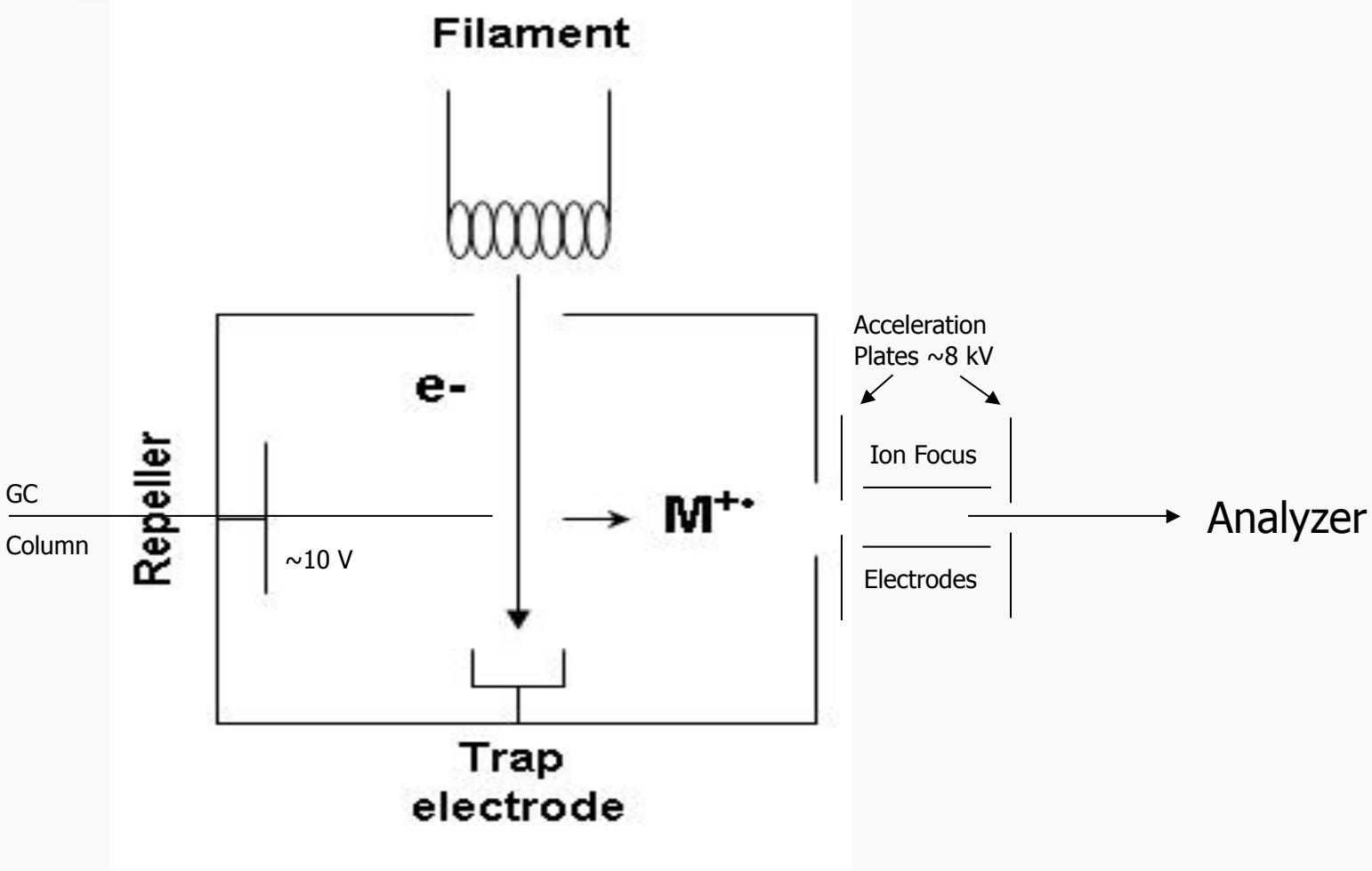
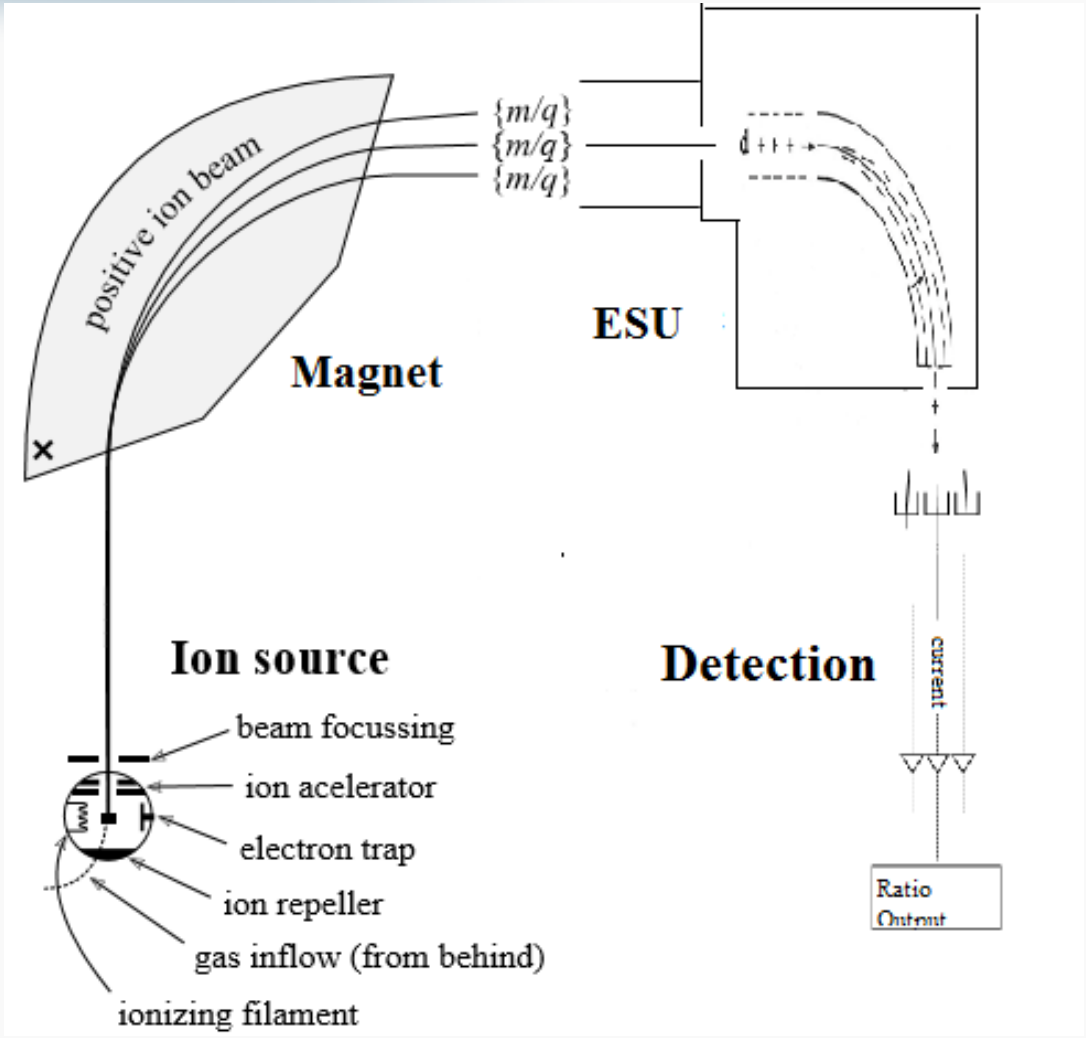
Electron Impact Ion Source



Magnetic Sector Mass Spectrometer



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

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

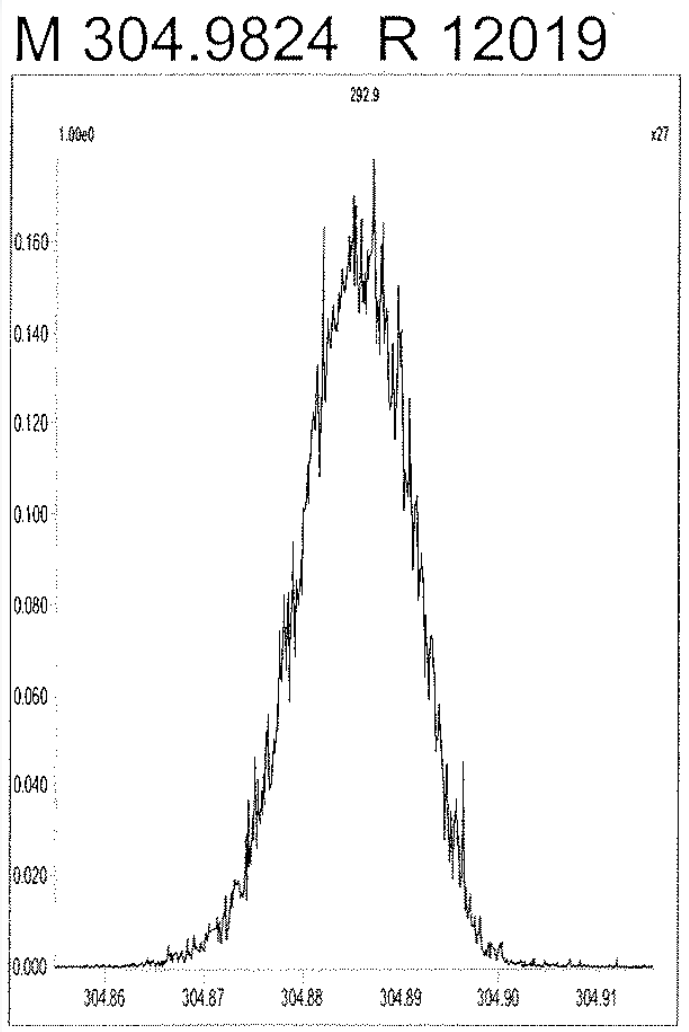
The Analytical Sequence of standards, samples, blanks, and Laboratory Control Samples(LCSs) is as follows:

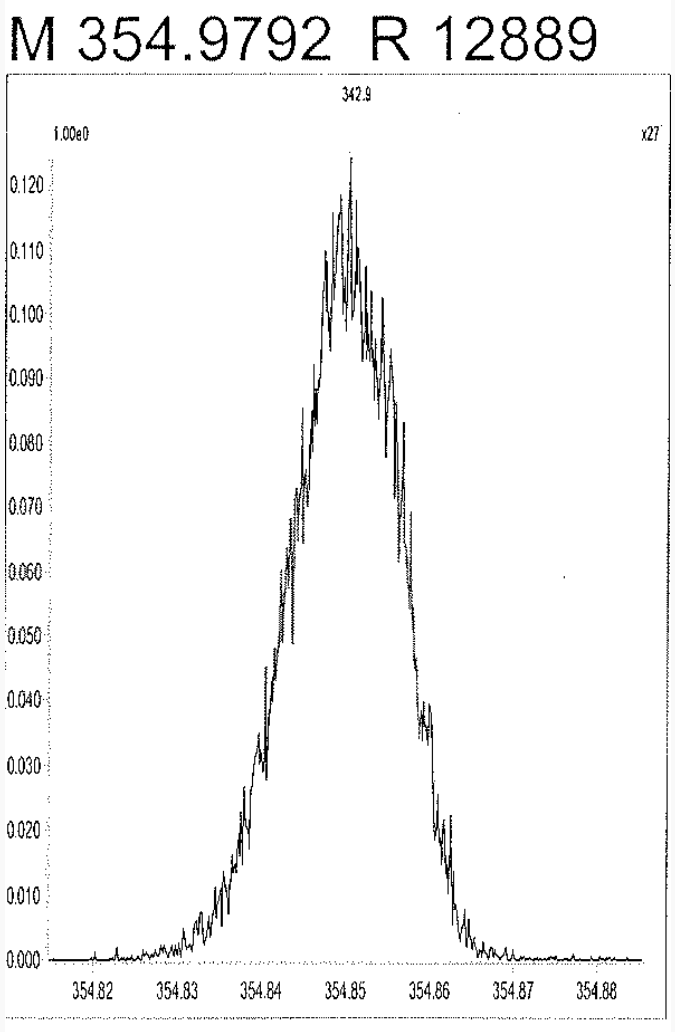
EPA SampleNo.	Lab Sample ID	Lab File ID	Date Analyzed	Time Analyzed
PFK				05:06:21
Window Define		8230	6-JUL-12	05:14:35
CCAL CS3		8231	6-JUL-12	06:10:10
DLCS-	00313-01	8232	6-JUL-12	07:18:59
DLCS-	00313-02	8233	6-JUL-12	08:09:46
XXXXXXXXX	XXXXXXXXXX	8234	6-JUL-12	09:00:56
XXXXXXXXX	XXXXXXXXXX	8235	6-JUL-12	09:52:12
DFBLK-	00313-01	8236	6-JUL-12	11:11:40
XXXXXXXXX	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

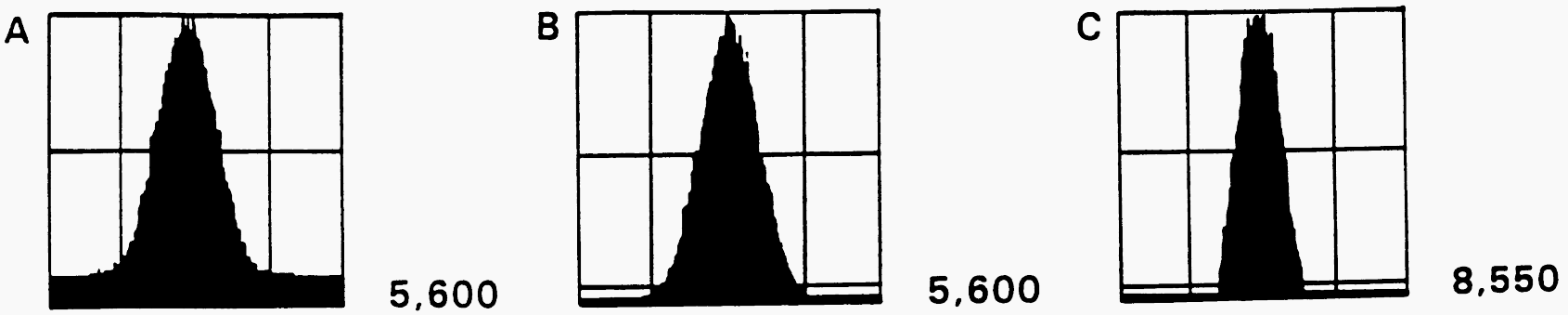
System Performance





System Performance

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



System Performance

Criteria	Action[1]	
	Detected Associated Compounds	Non-Detected Associated Compounds
Mass Spectrometer resolution of ≥ 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)

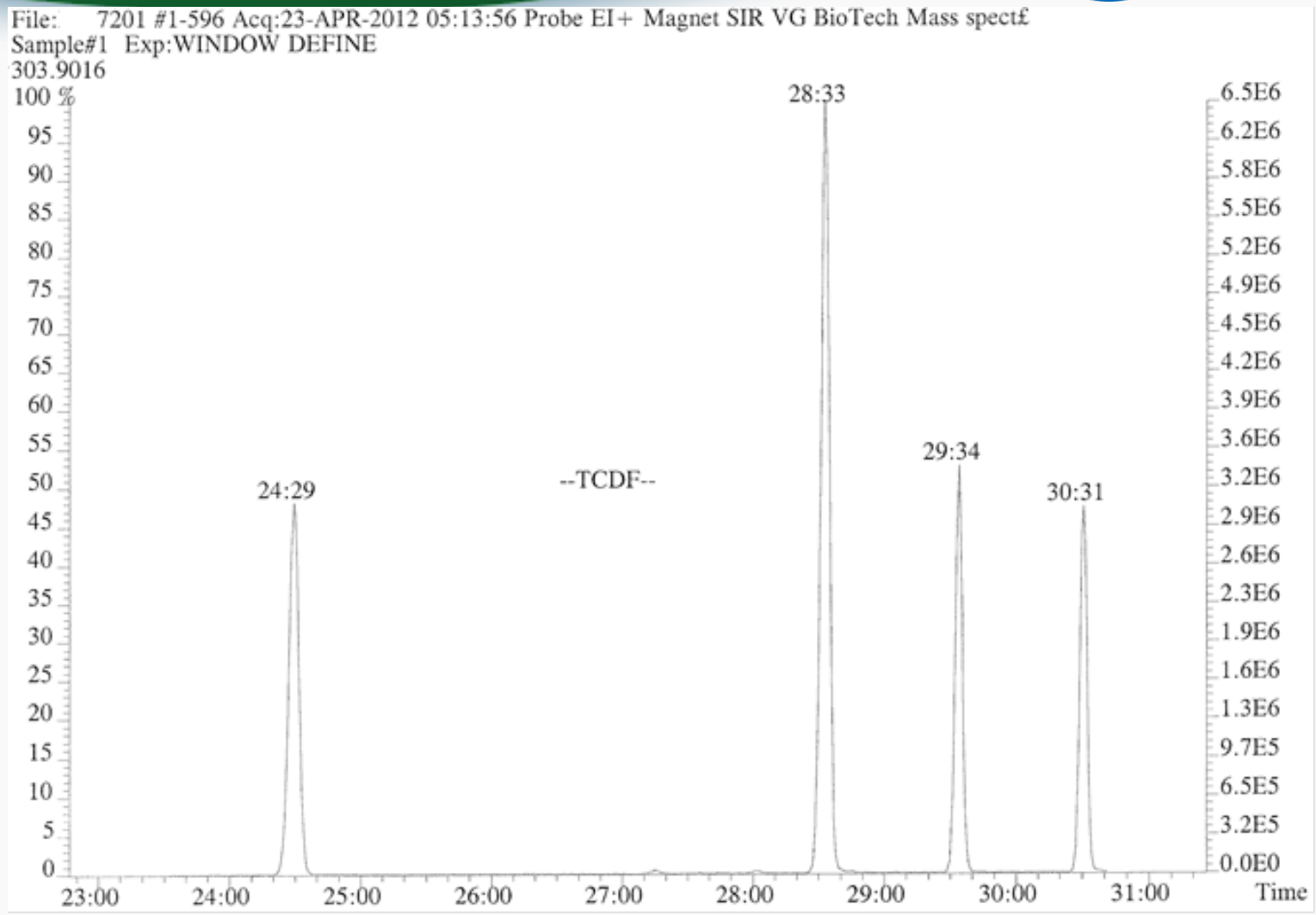
- Verify WDM Analyzed After PFK but Before Calibration.
  - First / Last of descriptor must elute within window
  - Tetra / penta descriptors
  - CBC Descriptors
- Verify GC Resolution with ISC
  - May be combined with WDM
- If Lab Uses a Different GC column,
  - Must define (and meet) criteria
  - Provide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

System Performance
Window Defining Mixture (WDM)

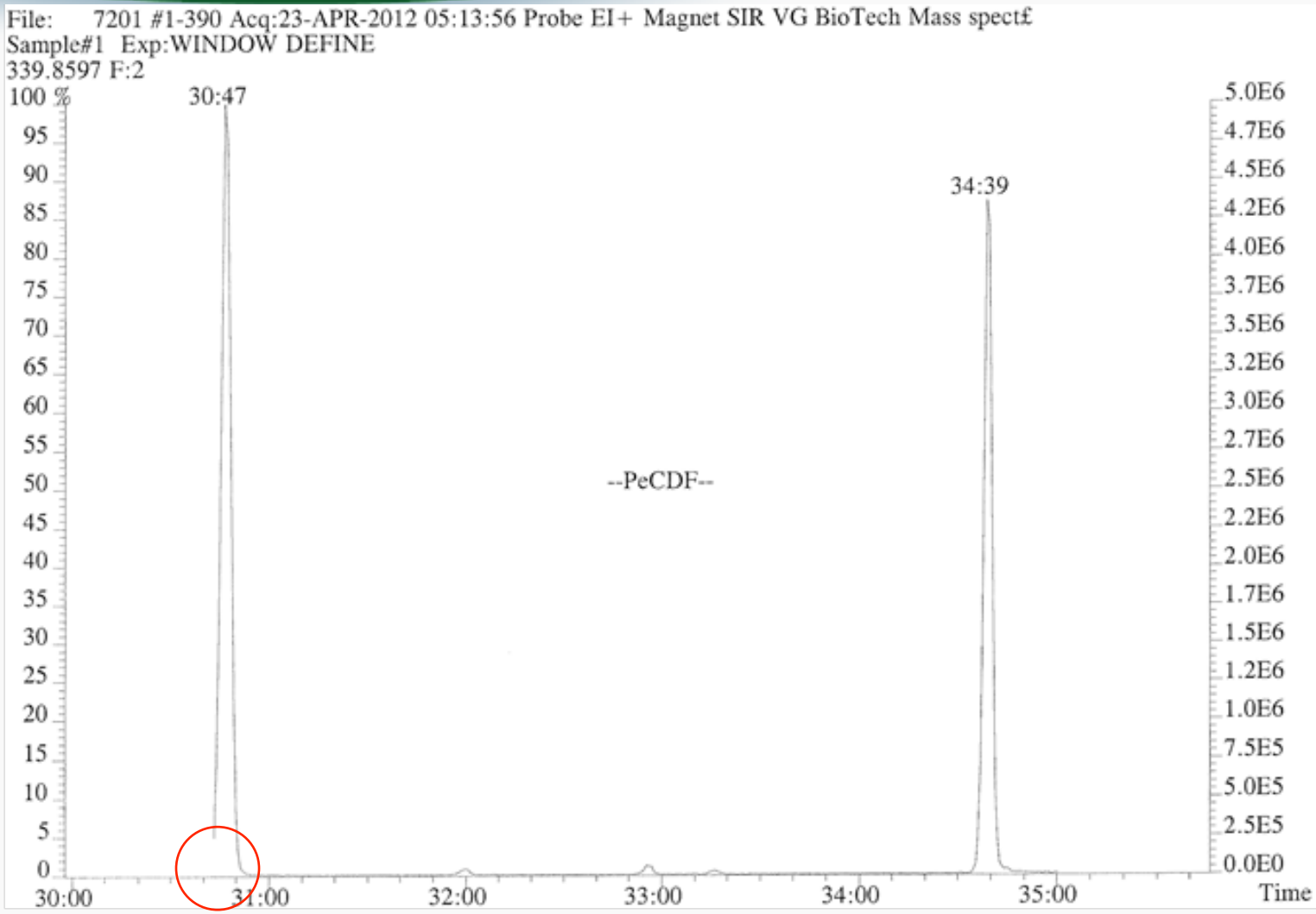
Congener	Retention Time First Eluting	Retention Time Last Eluting
TCDF	24:29	30:31
TCDD	26:17	30:29
PeCDF	30:47	34:39
PeCDD	32:09	34:30
HxCDF	35:31	37:50
HxCDD	36:02	37:31
HpCDF	39:13	40:31
HpCDD	39:27	40:06

% Valley 2378-TCDD: 9 %

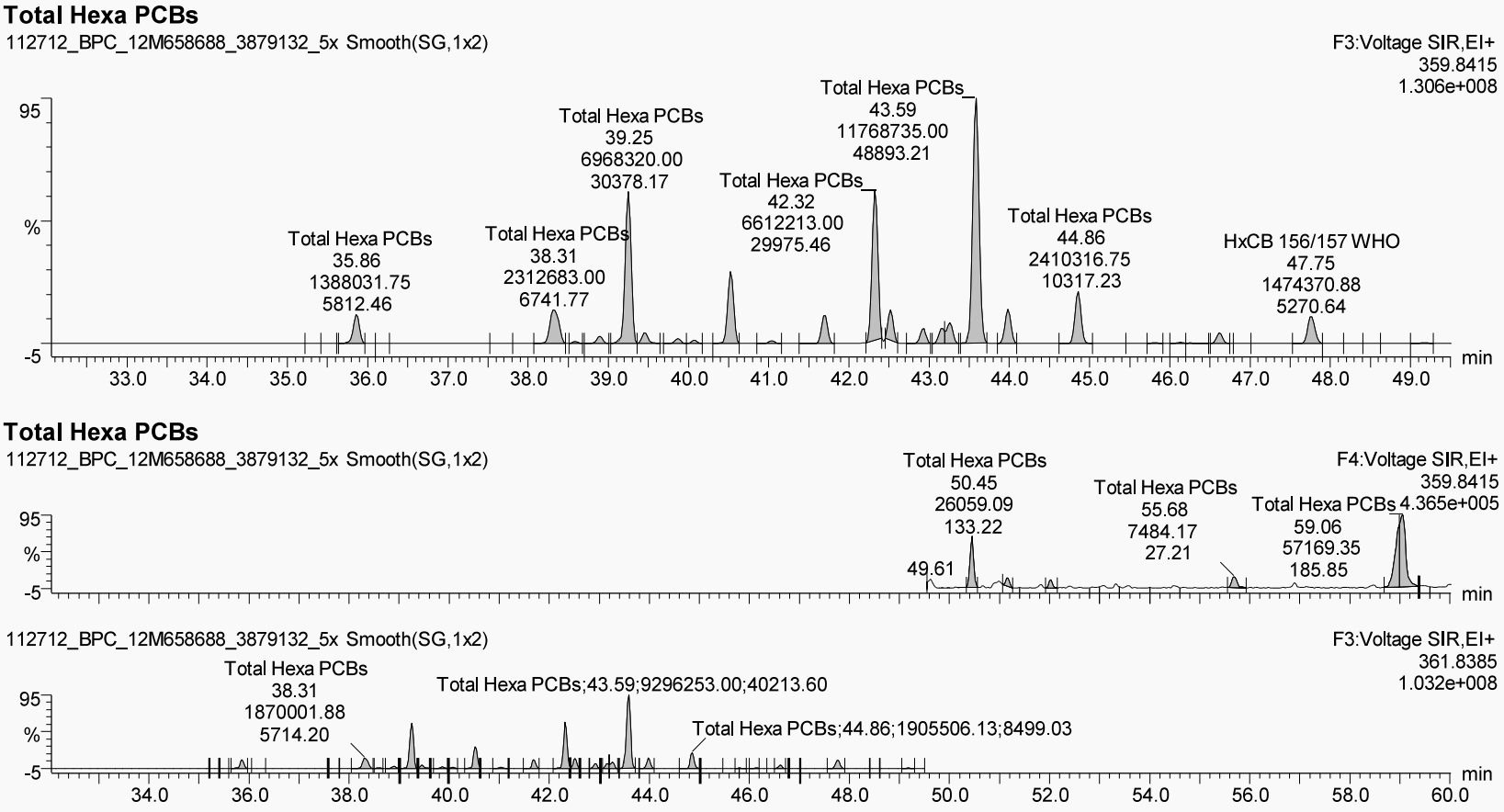
System Performance
Window Defining Mixture (WDM)



System Performance
Window Defining Mixture (WDM)

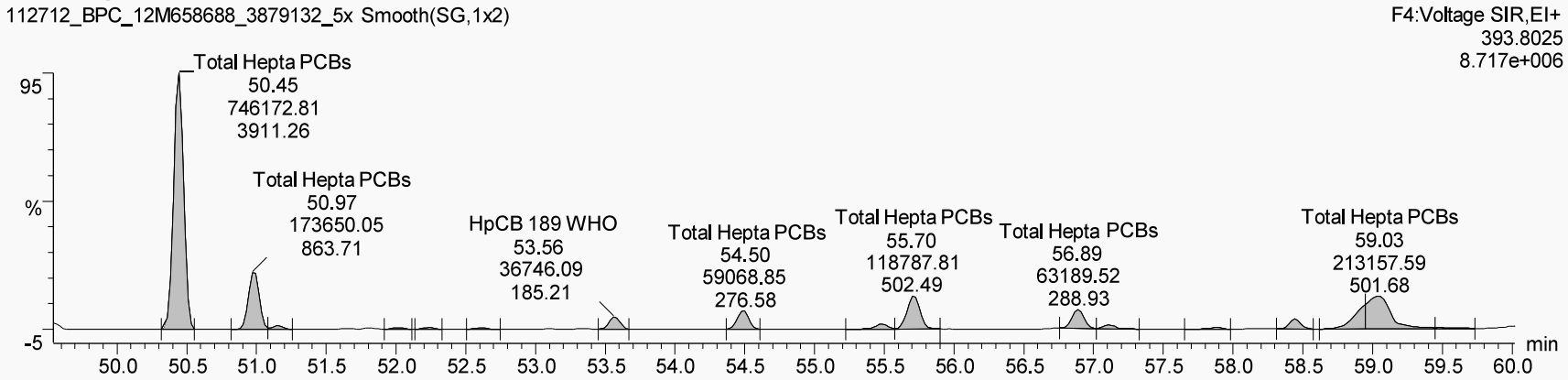


System Performance
Window Defining Mixture (WDM)

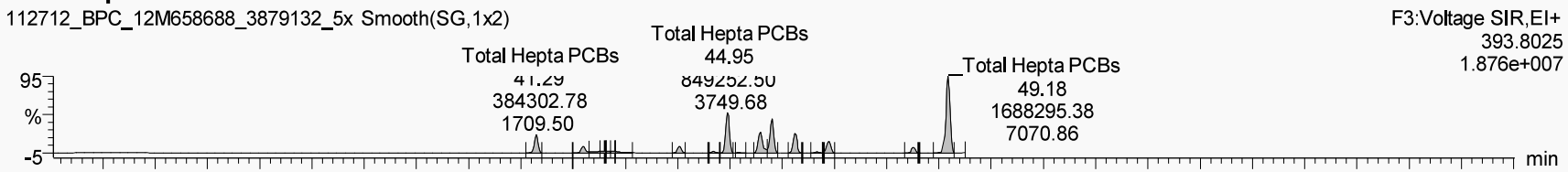


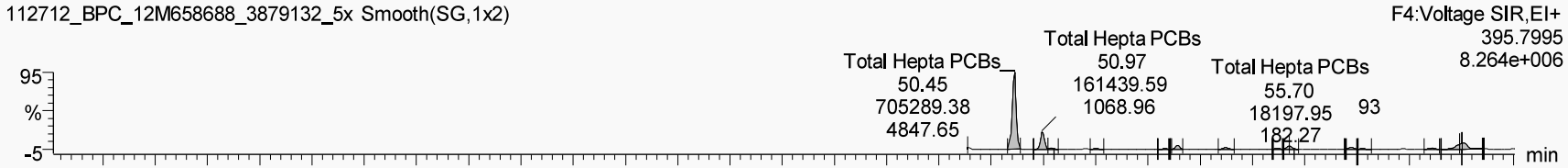
System Performance
Window Defining Mixture (WDM)

Total Hepta PCBs

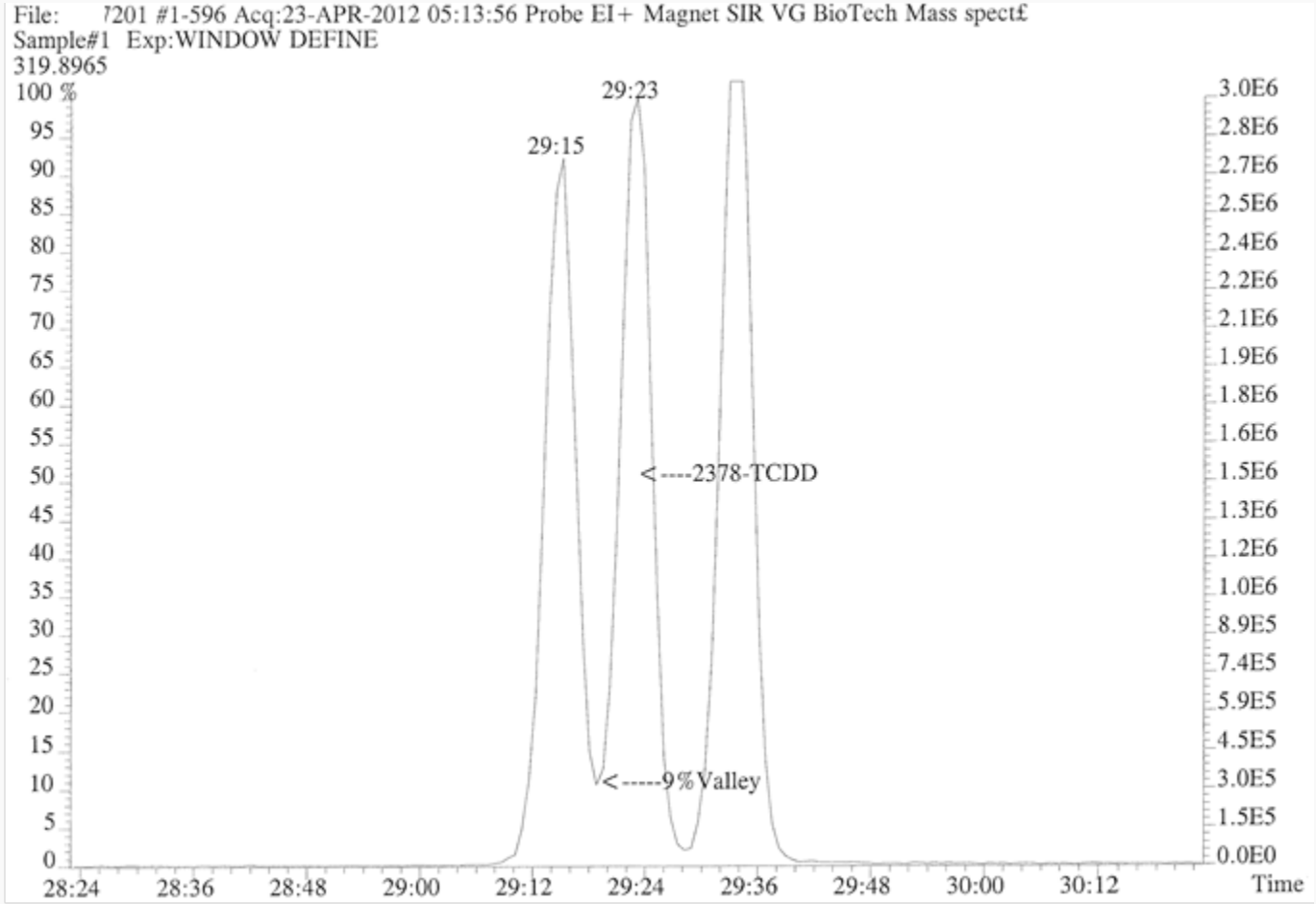


Total Hepta PCBs





System Performance
Window Defining Mixture (WDM)



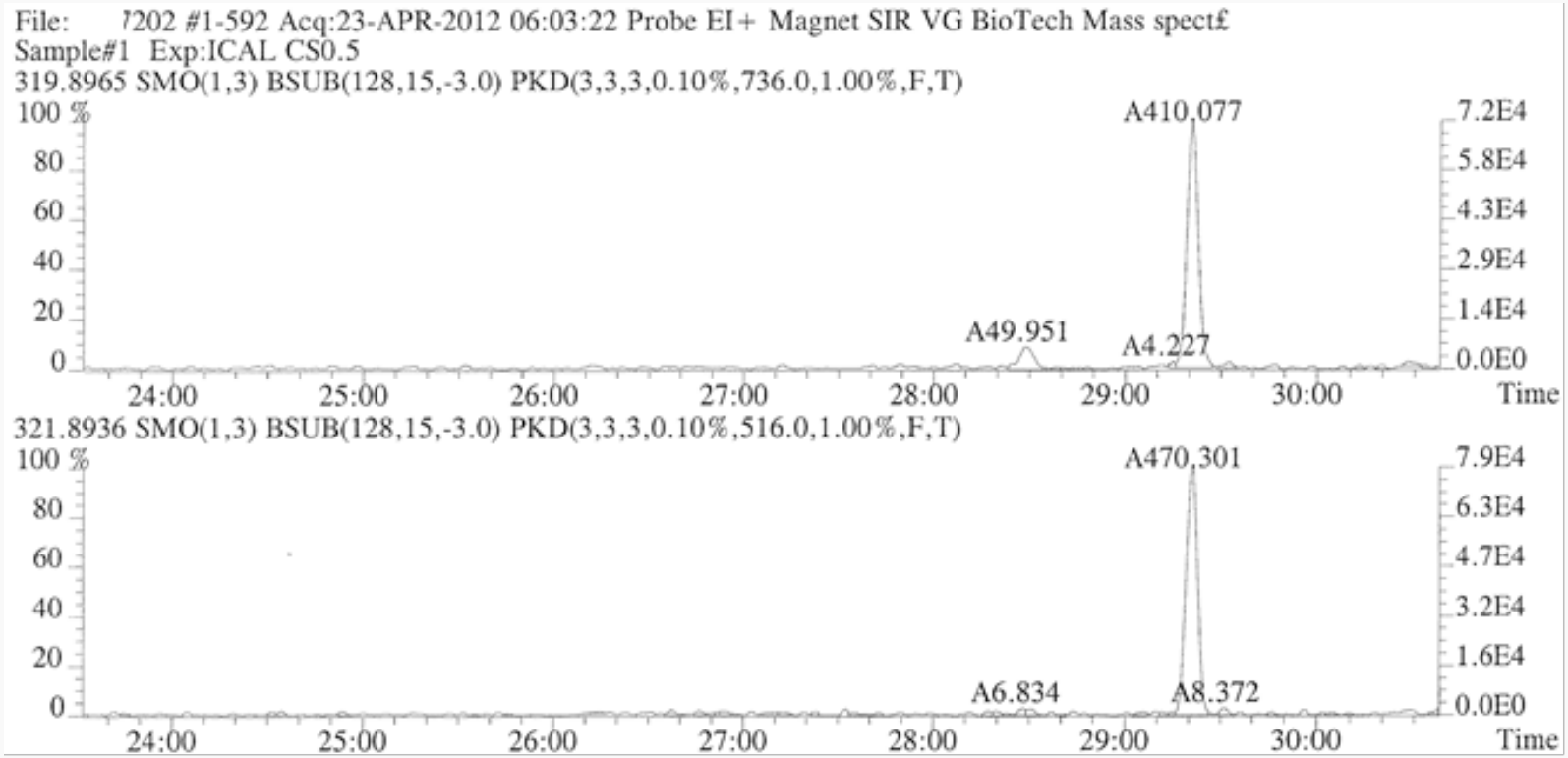
System Performance

Criteria	Action[1]	
	Detected Associated Compounds	Non-Detected Associated Compounds
WDM fails, or WDM adjustments are not made, or WDM is not reported, and 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).	

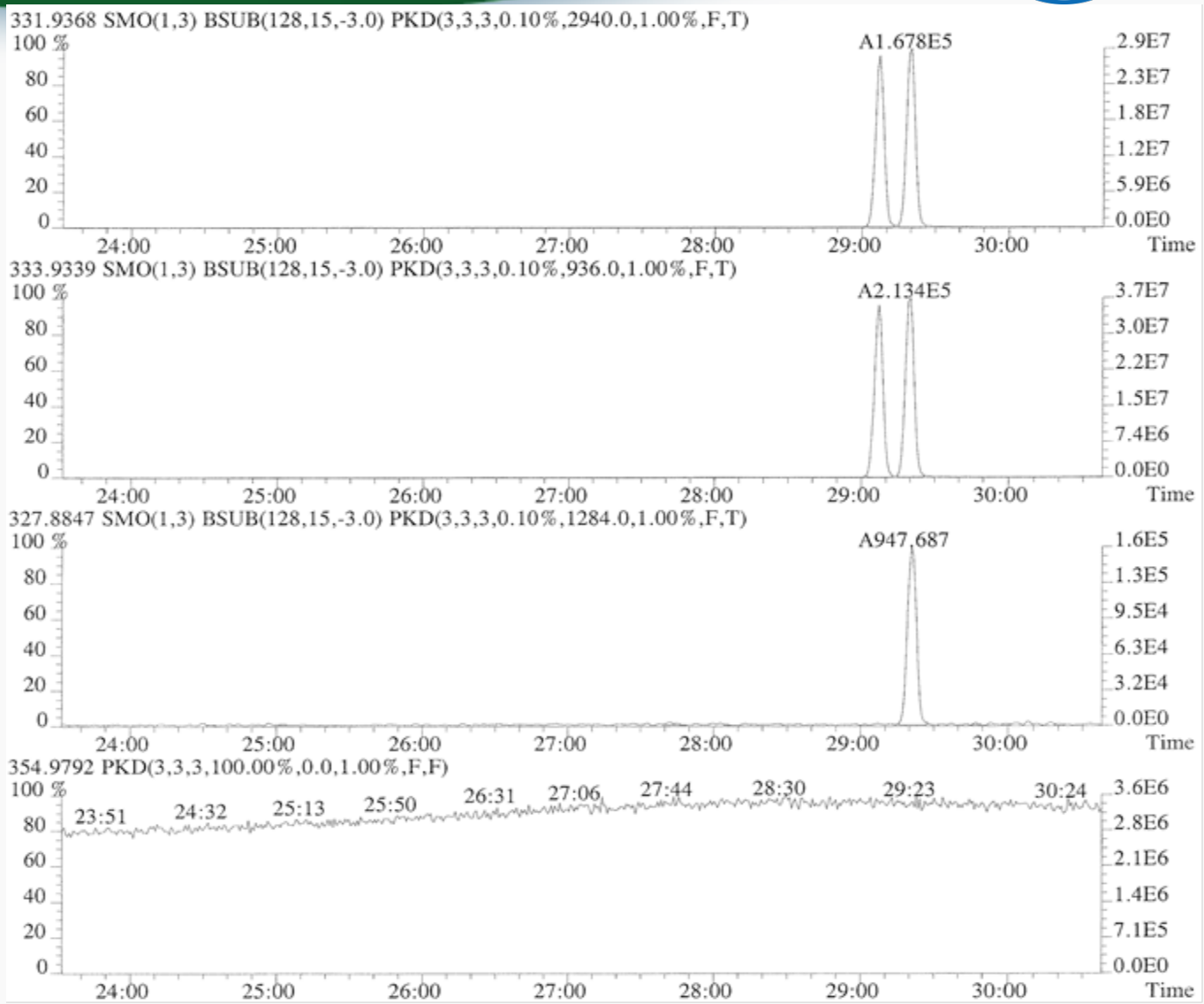
Initial Calibration Data

- 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 CS0.5	CS1	CS2	CS3	CS4	CS5	FLAG	ION RATIO QC lIMITS
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-Hx╗	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-Hx╗	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-Hx╗	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-Hx╗	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-╗	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-╗	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-Hx╗	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-Hx╗	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-╗	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						MEAN		
Target Analytes	CS0.5	CS1	CS2	CS3	CS4	CS5	RR/RRF	%RSD	QC LIMITS
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

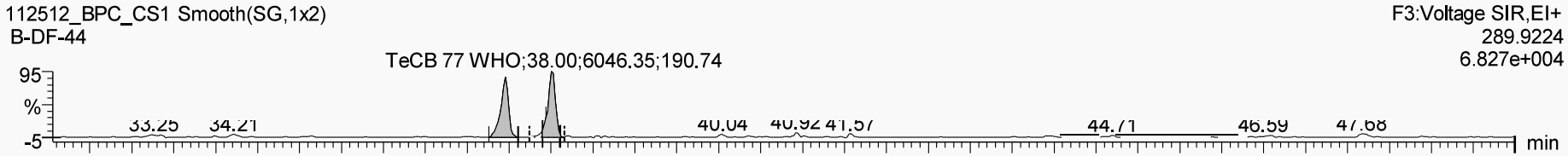
Name	RT-1	Resp 1	Resp 2	Ratio	Meet	Mod?	RRT
2,3,7,8-TCDF	28:31	1.117e+03	1.557e+03	0.72	yes	no	1.001
1,2,3,7,8-PeCDF	32:55	7.190e+03	4.529e+03	1.59	yes	no	1.001
2,3,4,7,8-PeCDF	33:39	6.413e+03	4.148e+03	1.55	yes	no	1.000
1,2,3,4,7,8-HxCDF	36:29	5.746e+03	4.635e+03	1.24	yes	no	1.000
1,2,3,6,7,8-HxCDF	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

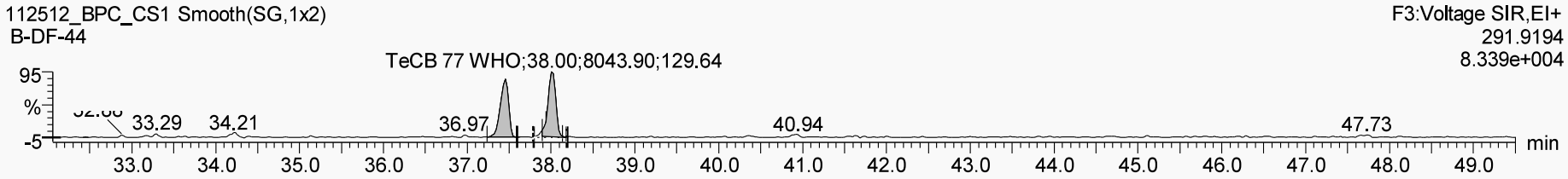
Initial Calibration Data

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			

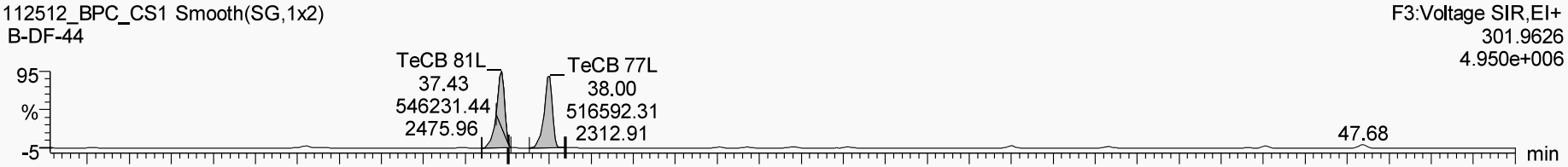
Initial Calibration Data

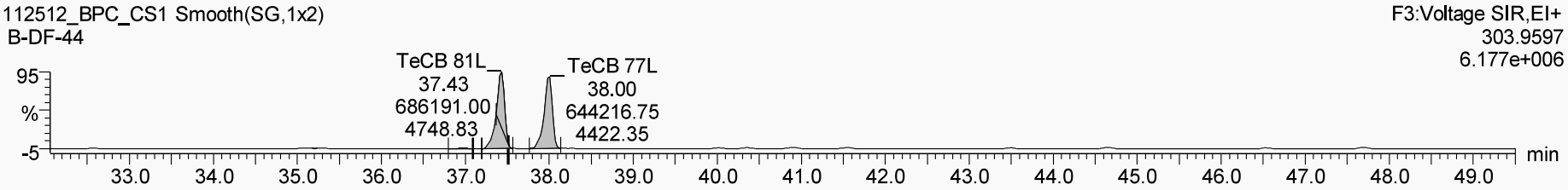
TeCB 81 WHO



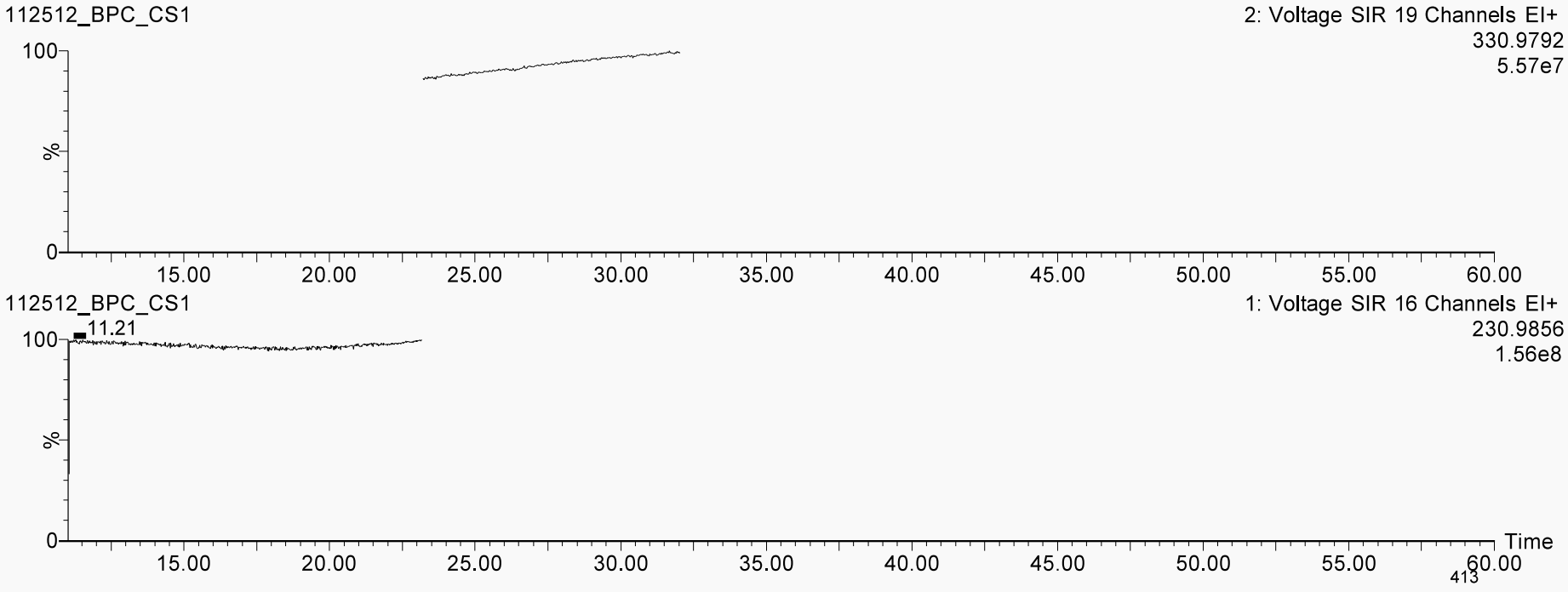


TeCB 81L





Initial Calibration Data



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 Compoubds								
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 Compoubds		
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 ± 15% window	J	R
Absolute RT of $^{13}C_{12}$-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 ± 25%, %D for RRFs not within ± 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

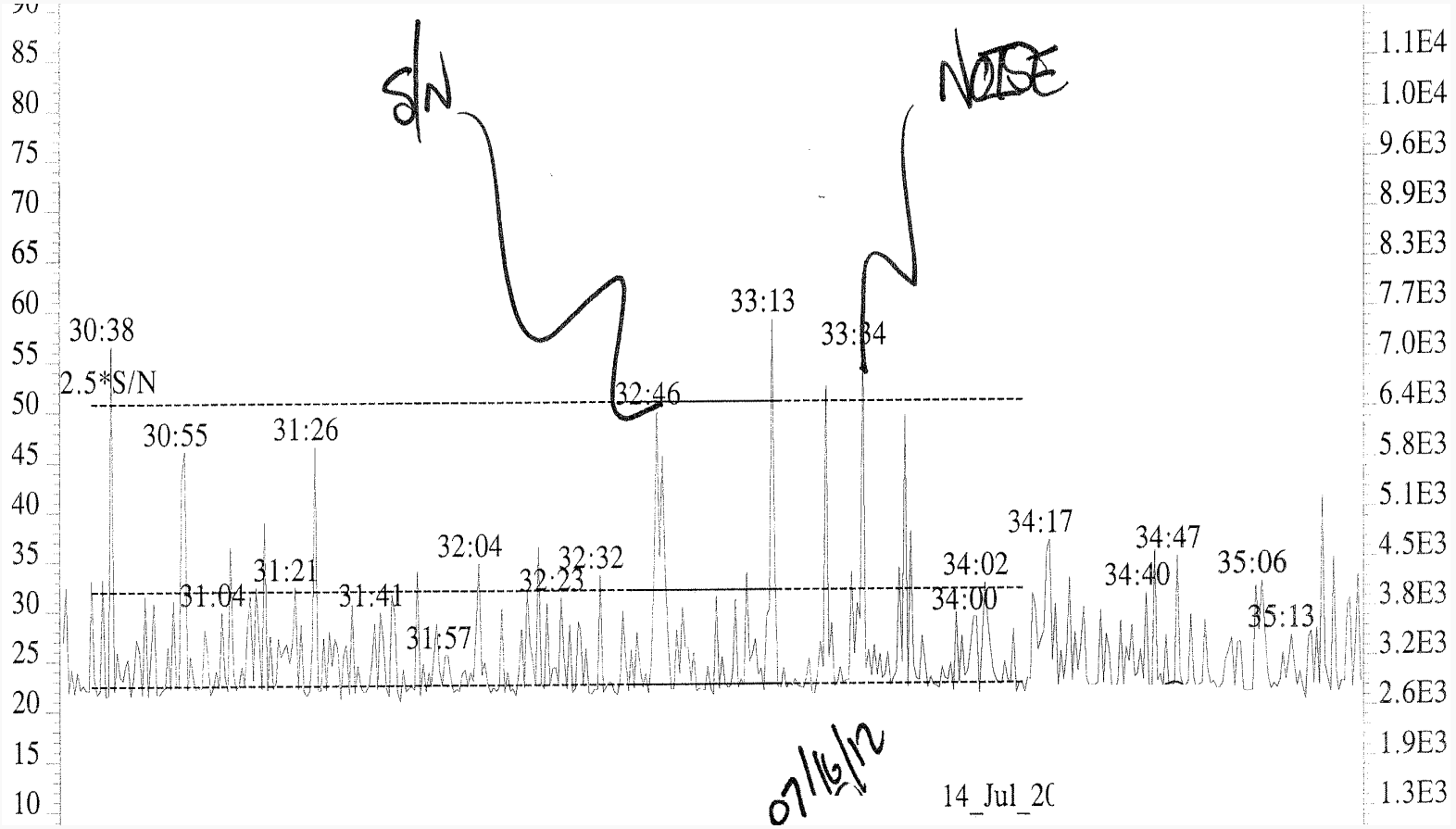
4DF - FORM IV-HR CDD
CDD/CDF METHOD BLANK SUMMARY
HIGH RESOLUTION

EPA Sample No.: DFBLK

Lab Name: _____ Contract: W001071
Lab Code: ___ Case No.: _____ TO No.: ___ SDG No.: 193
Matrix: (Soil/Water/Ash/Tissue/Oil) Soil Lab Sample ID: 00341-01
Sample wt/vol: 10.554 (g/mL) g Lab File ID: 8291
Water Sample Prep: _____ (SEPF/SPE) Date Received: _____
GC Column: DB-5 ID: 0.25 (mm) Date Extracted: 06/12/2012
Instrument ID: E-HRMS-03 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


S/N
NOISE
30:38
2.5*S/N
30:55
31:26
31:04
31:21
31:41
31:57
32:04
32:23
32:32
32:46
33:13
33:34
34:02
34:00
34:17
34:40
34:47
35:06
35:13
07/16/12
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90
85
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60
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50
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40
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30
25
20
15
10
1.1E4
1.0E4
9.6E3
8.9E3
8.3E3
7.7E3
7.0E3
6.4E3
5.8E3
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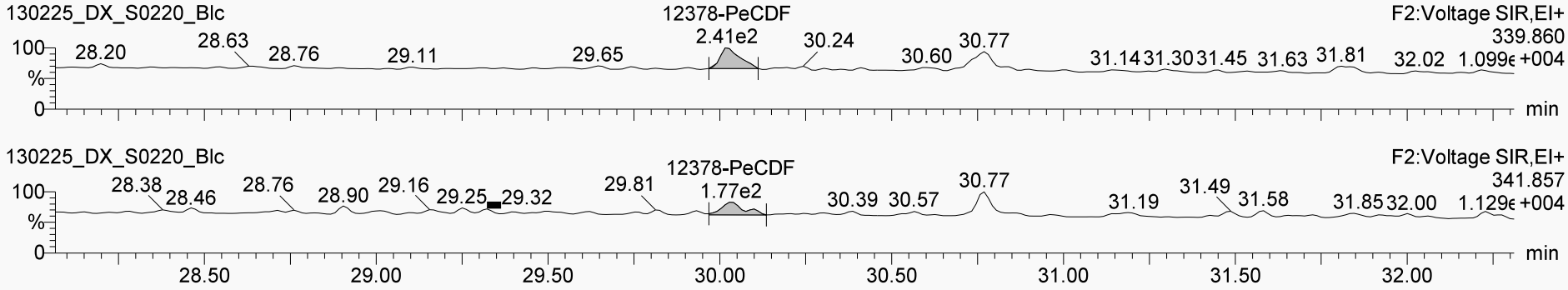
4.5E3
3.8E3
3.2E3
2.6E3
1.9E3
1.3E3

Blank Data

12378-PeCDF



Method Blank

Method Blank Result	Sample Result	Action
< < CRQL or EDL	Not detected	No qualification
	≥CRQL or EDL and >> Blank Result	No qualification or use professional judgment to avoid false pos. or neg. (see E.2.b above)
≥ CRQL or EDL	Not detected	No qualification
	≥CRQL or EDL and < Blank Result	U*
	> CRQL or EDL and ≥ 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

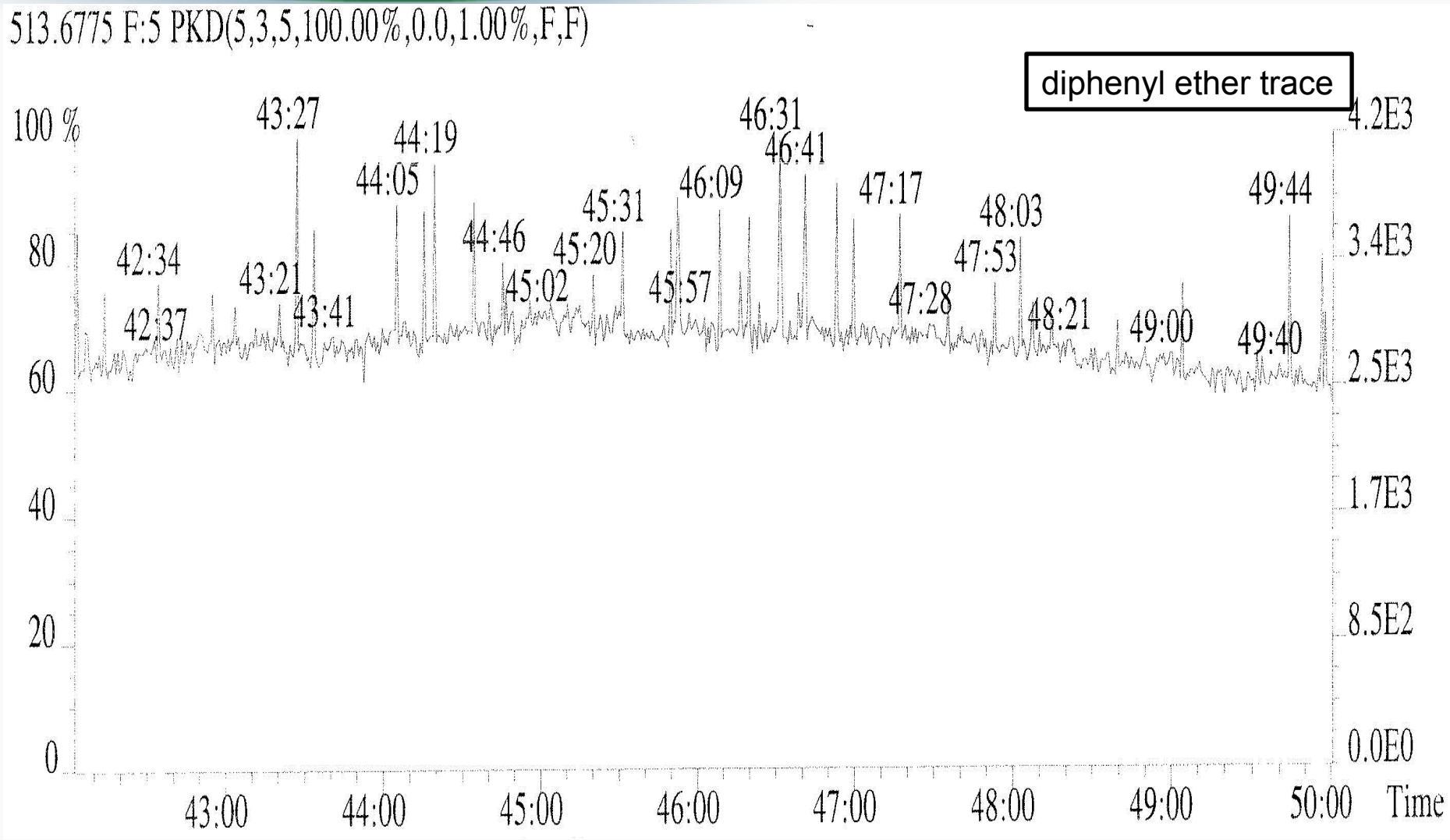
Laboratory Control Spike

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

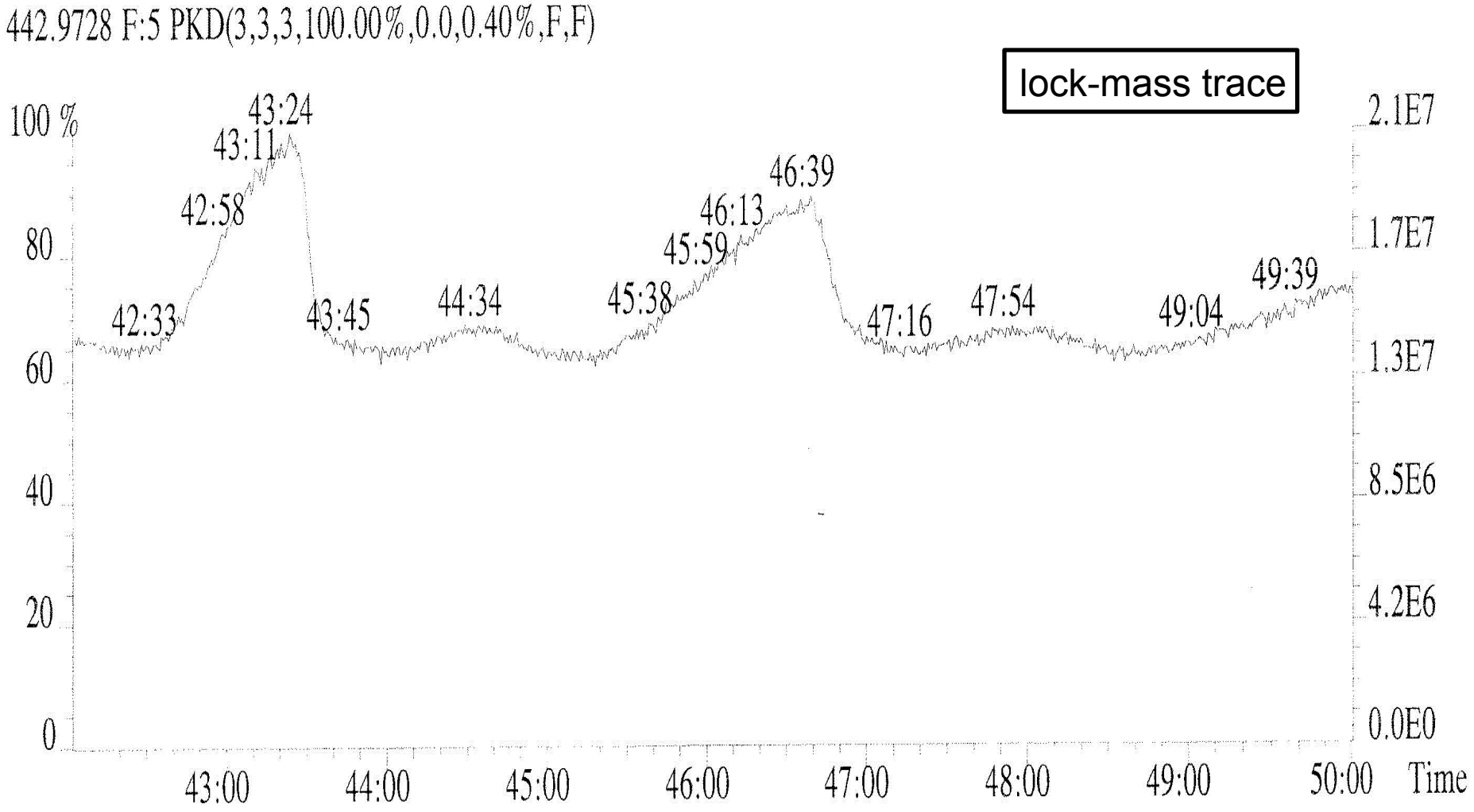
Sample Data

- 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



System Performance



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

Contact Information:

Charles Appleby
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