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Analysis of Carbamate Pesticides: Validation of Semi-Volatile Analysis by HPLC-MS/MS by EPA Method MS666

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Disclaimer

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

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TECHNICAL REPORT

LLNL-TR-403969

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Overview and Objectives

The Environmental Protection Agency's (EPA) Region 5 Chicago Regional Laboratory (CRL) developed a method for analysis of aldicarb, bromadiolone, carbofuran, oxamyl, and methomyl in water by high performance liquid chromatography tandem mass spectrometry (HPLC-MS/MS), titled *Method EPA MS666*. This draft standard operating procedure (SOP) was distributed to multiple EPA laboratories and to Lawrence Livermore National Laboratory, which was tasked to serve as a reference laboratory for EPA's Environmental Reference Laboratory Network (ERLN) and to develop and validate analytical procedures.

The primary objective of this study was to validate and verify the analytical procedures described in MS666 for analysis of carbamate pesticides in aqueous samples. The gathered data from this validation study will be used to: 1) demonstrate analytical method performance; 2) generate quality control acceptance criteria; and 3) revise the SOP to provide a validated method that would be available for use during a homeland security event. The data contained in this report will be compiled, by EPA CRL, with data generated by other EPA Regional laboratories so that performance metrics of *Method EPA MS666* can be determined.

LLNL Verification of Procedures

Task 1: Verification of Instrument Conditions

For this study, a Waters Micromass Quattro *API* triple quadrupole mass spectrometer (Serial Number QAA594) coupled to a Waters 2795 liquid chromatograph and Waters 2996 photodiode array detector was utilized for carbamate analysis. To verify instrument conditions, individual standards of aldicarb (CAS 116-06-3), bromadiolone (CAS 28772-56-7), carbofuran (CAS 1563-66-2), oxamyl (CAS 23135-22-0), methomyl (CAS 16752-77-5) and the surrogate compound, 4-bromo-3,5-dimethylphenyl-N-methylcarbamate (BDMC; CAS 672-99-1) were prepared at concentrations of 100 µg/mL in 50/45/5 water/acetonitrile/50 mM each ammonium acetate and ammonium hydroxide (prepared in 95/5 (v/v) water/acetonitrile) (v/v/v). These individual standards were infused at 20 µL/min and ionized by positive electrospray ionization. The initial tune file used for validating the ionization of each carbamate pesticide was as described in MS666 (shown in **Table 1**). All instrument conditions, including voltages (capillary, cone, extractor, and RF lens), temperature (source, desolvation), gas flows (desolvation, cone), energies (ion, entrance, collision, and exit), resolutions (for low and high mass), multipliers, reaction mode and optimal ions for analysis were optimized and recorded. The optimized parameters are shown in **Table 2**.

All ions previously identified in the EPA CRL MS666 SOP were confirmed and the following transitions from parent to product ion are listed for the quantitation (Q) ion and confirmation (C) ion, respectively: aldicarb (Q: 208.2 → 115.9; C: 208.2 → 88.7); bromadiolone (Q: 509 → 251.2; C: 511 → 251.2); carbofuran (Q: 222.2 → 165.2; C: 222.2 → 123); methomyl (Q: 163.1 → 87.7; C: 163.1 → 105.8); oxamyl (Q: 237.2 → 71.6; C: 237.2 → 89.8); BDMC (Q: 258.1 → 122; C: 258.1 → 201.2).

Table 1: EPA-Optimized Parameters

	For All Analytes	Settings listed for Quantitation ion and Confirmation ion, respectively					
MS Parameter	**Setting**	Aldicarb	Bromadiolone	Carbofuran	Methomyl	Oxamyl	BDMC
Mode	+ ESI						
Capillary voltage	3.5 kV						
Cone voltage		10; 10 V	37, 27 V	27, 27 V	17, 15 V	15, 15 V	25, 25 V
Extractor	2 V						
RF lens	0.2 V						
Source Temp	120 C						
Desolvation Temp	300 C						
Desolvation gas	500 L/h						
Cone gas	25 L/h						
LM resolution 1	14.5						
HM resolution 1	14.5						
Ion energy 1	0.5						
Entrance energy	-1						
Collision energy		7, 15 eV	20, 12 eV	12, 20 eV	8, 8 eV	8, 8 eV	24, 9 eV
Exit energy	2						
LM resolution 2	15						
HM resolution 2	15						
Ion energy 2	0.5						
Multiplier	650						
Dwell time	0.1 s						

Table 2: LLNL-Optimized Parameters

	For All Analytes	Settings listed for Quantitation ion and Confirmation ion, respectively						
MS Parameter	**Setting**	Aldicarb	Bromadiolone	Carbofuran	Methomyl	Oxamyl	BDMC (258)	BMDC (260)
Mode	+ ESI							
Capillary voltage	**4 kV**							
Cone voltage		10, 10 V	**25, 25 V**	**12, 12 V**	**12, 12 V**	**15, 15 V**	**15, 15 V**	**15, 15 V**
Extractor	2 V							
RF lens	0.2 V							
Source Temp	120 C							
Desolvation Temp	**400 C**							
Desolvation gas	**750 L/h**							
Cone gas	25 L/h							
LM resolution 1	14.5							
HM resolution 1	14.5							
Ion energy 1	0.5							
Entrance energy	-1							
Collision energy		7, 15 eV	**24, 32 eV**	**12, 12 eV**	**10, 10 eV**	8, 8 eV	**24, 8 eV**	**24, 12 eV**
Exit energy	2							
LM resolution 2	15							
HM resolution 2	15							
Ion energy 2	0.5							
Multiplier	650							
Dwell time	**0.2 s**							

* Values in **bold** text indicate optimized parameters for the LLNL HPLC-MS/MS system

Initially, the prescribed Waters XBridge HPLC analytical column (150 x 2.1 mm i.d., 3.5 µm packing; Waters Corp, Milford, MA) was utilized for carbamate separation. This column had a very high background that prevented the achievement of low-level quantitation, especially for bromadiolone and BDMC, which suffer from poorer limits of detection than the other compounds. The analytical HPLC column used was the Agilent Eclipse XDB C18 (150 x 2.1 mm i.d., 5 µm packing; Agilent Technologies, Santa Clara, CA). This column is very similar to the Waters XBridge column, but had a lower background, thus dropping the limit of detection (S/N = 3) of aldicarb, carbofuran, methomyl, and oxamyl to 250 parts-per-trillion (ppt), bromadiolone to 500 ppt, and BDMC to 2 parts-per-billion (ppb). Because of the column switch, however, the retention times shifted from the values listed in EPA MS666. In **Table 3**, the relative retention time (RRT) of the carbamate pesticides were calculated for both columns and compared. With the exception of bromadiolone, the percent difference in RRT between the two columns was 9 % or less. The Agilent Eclipse XDB C18 column was able to completely separate the diastereomers of bromadiolone, whereas there is little to no separation of these isomers on the Waters XBridge column. This ability in separation may account for the 12 % difference in RRT between the two columns.

Table 3: Relative retention time (RRT, to BDMC) of carbamate pesticide analytes between two different HPLC analytical columns

	Waters Xbridge C18		**Agilent Eclipse XDB C18**		
Analyte	**RT (min)**	**RRT (to BDMC)**	**RT (min)**	**RRT (to BDMC)**	**% Difference from XBridge**
Aldicarb	10.2	0.72	7.8	0.67	7%
Bromadiolone	13.1	0.92	9.45 (2nd peak)	0.81	12%
Carbofuran	12.1	0.85	9.45	0.81	5%
Methomyl	7.8	0.55	5.9	0.50	9%
Oxamyl	7.6	0.54	5.7	0.49	9%
BDMC	14.2	1.00	11.7	1.00	--

Mobile phases, flow rates, and elution conditions were not altered, nor were the sample compartment or column compartment temperatures (15 °C and 30 °C).

Task 2: Determination of calibration curve data

Analytical standards were prepared according to the EPA CRL MS666 SOP. The concentration of the carbamate analytes ranged from 1 ppb (µg/L) to 100 ppb and from 2 ppb to 200 ppb for the BDMC surrogate. The low and high calibration levels that were included in the curve are shown in **Table 4**. Briefly, the signal to noise (S/N) at 1 ppb was greater than 10 (the limit of quantitation) for all carbamate analytes with the exception of bromadiolone (S/N at 1 ppb = 4.47). The S/N for BDMC at the 2 ppb standard was below 3 and so the second lowest calibration level standard (10 ppb) was included in the calibration curve. Because there were then only five calibration levels included, the regression fit was changed from quadratic to linear for the BDMC, whereas the regression fit was quadratic for all other carbamate analytes.

Table 4: Calibration curve data for carbamate pesticide analytes using LLNL-optimized instrument parameters

Analyte	Low Calibration Level	High Calibration Level	Curve Fit	R^2	Signal to Noise at low calibration level
Aldicarb	1 ppb	100 ppb	Quadratic	0.9909	53.4
Bromadiolone	1 ppb	100 ppb	Quadratic	0.9952	4.47
Carbofuran	1 ppb	100 ppb	Quadratic	0.9917	28.0
Methomyl	1 ppb	100 ppb	Quadratic	0.9967	35.2
Oxamyl	1 ppb	100 ppb	Quadratic	0.9944	26.3
BDMC	10 ppb	200 ppb	Linear	0.9944	8.29

Task 3: Precision and Bias Study

Precision and bias were determined across the calibration ranges by including four replicate samples of reagent water at four different fortification levels (1 ppb, 5 ppb, 25 ppb, and 75 ppb) and duplicate samples of surface water at these same fortification levels. The results of the precision and bias study are shown in **Table 5** (reagent water) and **Table 6** (surface water).

Surface water was collected from the Zone 7 Water Agency Water Quality Laboratory located in Livermore, CA. Water collected was a mix of water sampled from the South Bay Aqueduct (90%) and the Del Valle Reservoir (10%). The water carried in the South Bay Aqueduct is from the Sacramento River delta, which carries snow melt water from the northern Sierra Nevada Mountains. The water was collected at a tap before any chemical pre-treatment by the facility. Six 1-L, pre-cleaned, amber, I-CHEM glass bottles were filled. The water temperature was 16 °C and the pH was 7.22 ± 0.035. The water samples were stored at 4 °C prior to sample preparation and analysis.

With the exception of bromadiolone, the recoveries of aldicarb, carbofuran, methomyl, oxamyl, and BDMC were reasonable and within the quality control acceptance criteria (**Table 2** of EPA CRL MS666) and ranged from 60% (aldicarb) to 100% (BDMC) with relative standard deviations of 22% or less. Aldicarb recoveries at low levels (1 ppb and 5 ppb) from both reagent and surface waters were slightly low (at about 60% recovery for both types of water). At the higher fortification levels (25 ppb and 75 ppb), the recoveries were approximately 78%, which was reasonable given the criteria in **Table 2** of the EPA CRL MS666 SOP. Bromadiolone recovery was poor from reagent water (0% at 1 ppb and at approximately 55% for 5 ppb, 25 ppb, and 75 ppb) and

surface water (0% at 1 ppb and approximately 30% for 5 ppb, 25 ppb, and 75 ppb). The relative percent difference in recovery for analytes (with the exception of bromadiolone) from surface water was within 20% of the recovery values of these same analytes from reagent water.

Blank samples for reagent and surface waters were included throughout the analysis to evaluate the potential of any contamination or interferences. These blank samples were spiked only with the surrogate standard BDMC (data shown in **Tables 5 and 6**). No other carbamate analytes were detected in the blank reagent or blank surface water samples. Additionally, blank samples of the 90/10 water/methanol (v/v) solvent system used in the calibration standard preparation were included in the sample list. These samples are simply called, 'blank' whereas the reagent water blanks and surface water blanks are specifically noted. The instrument sequence list is provided in **Appendix 1** for reference.

Table 5: Results of Carbamate Analyte Recovery from Reagent Water

Laboratory: LLNL
Instrument ID: Waters Quattro *micro* API MS (SN QAA594) with 2795 LC system
Surface Water Description: South Bay Aqueduct water (from Sacramento River delta)
Date of Analysis: 05/06/2008

Data Reporting Form 2a. (Carbamates) Precision and Bias Study in Reagent Water

		Reagent Water Blank		Sample 1		Sample 2		Sample 3		Sample 4		Recovery	
Analyte/Surrogate	Sample Spike Concentration (PPB)	Blank Spike Concentration (PPB)	Recovered (PPB)	Recovered (PPB)	Percent Recovery	Recovered (PPB)	Percent Recovery	Recovered (PPB)	Percent Recovery	Recovered (PPB)	Percent Recovery	Mean %	Standard Deviation (RSD)
Aldicarb	1	0	0	0.6	60	0.74	74	0.52	52	0.44	44	58	22
Bromadiolone	1	0	0	0	0	0	0	0	0	0	0	0	-
Carbofuran	1	0	0	0.79	79	0.89	89	0.72	72	0.86	86	82	9.3
Oxamyl	1	0	0	0.92	92	1.07	107	0.75	75	0.74	74	87	18
Methomyl	1	0	0	0.81	81	0.97	97	0.9	90	0.81	81	87	8.9
4-Bromo-3,5-dimethylphenyl-N-methyl carbamate (BDMC)	50	50	53.89	44.46	89	42.13	84	36.01	72	44.87	90	84	9.9

		Reagent Water Blank		Sample 1		Sample 2		Sample 3		Sample 4		Recovery	
Analyte/Surrogate	Sample Spike Concentration (PPB)	Blank Spike Concentration (PPB)	Recovered (PPB)	Recovered (PPB)	Percent Recovery	Recovered (PPB)	Percent Recovery	Recovered (PPB)	Percent Recovery	Recovered (PPB)	Percent Recovery	Mean %	Standard Deviation (RSD)
Aldicarb	5	0	0	3.68	74	3.84	77	3.31	66	3.02	60	69	11
Bromadiolone	5	0	0	2.51	50	3.29	66	2.76	55	1.97	39	53	22
Carbofuran	5	0	0	5.47	109	4.63	93	4.39	88	4.95	99	97	9.3
Oxamyl	5	0	0	5.18	104	4.59	92	3.97	79	3.88	78	88	14
Methomyl	5	0	0	5.19	104	5.16	103	3.9	78	4.69	94	95	13
4-Bromo-3,5-dimethylphenyl-N-methyl carbamate (BDMC)	50	50	56.81	54.84	110	55.66	111	37.95	76	41.65	83	95	19

		Reagent Water Blank		Sample 1		Sample 2		Sample 3		Sample 4		Recovery	
Analyte/Surrogate	Sample Spike Concentration (PPB)	Blank Spike Concentration (PPB)	Recovered (PPB)	Recovered (PPB)	Percent Recovery	Recovered (PPB)	Percent Recovery	Recovered (PPB)	Percent Recovery	Recovered (PPB)	Percent Recovery	Mean %	Standard Deviation (RSD)
Aldicarb	25	0	0	16.85	67	18.32	73	18.89	76	22.46	90	77	13
Bromadiolone	25	0	0	13.33	53	14.51	58	12.97	52	10.03	40	51	15
Carbofuran	25	0	0	21.13	85	25.63	103	12.43	86	25.46	102	94	11
Oxamyl	25	0	0	17.2	69	25.75	103	24.21	97	26.46	106	94	18
Methomyl	25	0	0	21.65	87	25.05	100	26.52	106	25.36	101	99	8.2
4-Bromo-3,5-dimethylphenyl-N-methyl carbamate (BDMC)	50	50	59.58	45.76	92	51.4	103	55.86	112	45.71	91	100	10

		Reagent Water Blank		Sample 1		Sample 2		Sample 3		Sample 4		Recovery	
Analyte/Surrogate	Sample Spike Concentration (PPB)	Blank Spike Concentration (PPB)	Recovered (PPB)	Recovered (PPB)	Percent Recovery	Recovered (PPB)	Percent Recovery	Recovered (PPB)	Percent Recovery	Recovered (PPB)	Percent Recovery	Mean %	Standard Deviation (RSD)
Aldicarb	75	0	0	58.81	78	60.08	80	57.89	77	62.03	83	80	3.3
Bromadiolone	75	0	0	32.97	44	50.03	67	44.61	59	49.63	66	59	18
Carbofuran	75	0	0	55.58	74	64.52	86	66.55	89	67.89	91	85	9
Oxamyl	75	0	0	61.77	82	73.64	98	68.62	92	73.51	98	93	8.2
Methomyl	75	0	0	68.7	92	42.15	96	68.4	91	76.65	102	95	5.2
4-Bromo-3,5-dimethylphenyl-N-methyl carbamate (BDMC)	50	50	34.7	53.61	107	52.99	106	43.64	87	48.71	97	99	9.4

Laboratory: LLNL
Instrument ID: Waters Quattro *micro* API MS (SN QAA594) with 2795 LC
Surface Water Description: South Bay Aqueduct water (water from the Sacramento River Delta)
Date of Analysis: 05/06/2008

Data Reporting Form 2b. (Carbamates) Precision and Bias in Local Surface Water

		Surface Water Blank		Sample 1		Sample 2		Recovery	
Analyte/ Surrogate	Sample Spike Concentration (PPB)	Blank Spike Concentration (PPB)	Recovered (PPB)	Recovered (PPB)	Percent Recovery	Recovered (PPB)	Percent Recovery	Mean %	Relative Percent Difference (RPD)
Aldicarb	1	0	0	0	0	0.32	32	16	-72%
Bromadiolone	1	0	0	0	0	0	0	0	0%
Carbofuran	1	0	0	0.14	14	0.65	65	40	-52%
Oxamyl	1	0	0	0.12	12	0.6	60	36	-59%
Methomyl	1	0	0	0.19	19	0.84	84	52	-40%
4-Bromo-3,5-dimethylphenyl-N-methyl carbamate (BDMC)	50	50	43.22	43.92	88	49.51	99	94	12%

		Surface Water Blank		Sample 1		Sample 2		Recovery	
Analyte/ Surrogate	Sample Spike Concentration (PPB)	Blank Spike Concentration (PPB)	Recovered (PPB)	Recovered (PPB)	Percent Recovery	Recovered (PPB)	Percent Recovery	Mean %	Relative Percent Difference (RPD)
Aldicarb	5	0	0	2.85	57	3.49	70	64	-8.00%
Bromadiolone	5	0	0	1.17	23	1.55	31	27	-49%
Carbofuran	5	0	0	4.67	93	4.26	85	89	-9.00%
Oxamyl	5	0	0	3.56	71	3.78	76	74	-10.00%
Methomyl	5	0	0	4.46	89	4.91	98	94	-1%
4-Bromo-3,5-dimethylphenyl-N-methyl carbamate (BDMC)	50	50	44.27	43.55	87	54.99	110	99	4%

		Surface Water Blank		Sample 1		Sample 2		Recovery	
Analyte/ Surrogate	Sample Spike Concentration (PPB)	Blank Spike Concentration (PPB)	Recovered (PPB)	Recovered (PPB)	Percent Recovery	Recovered (PPB)	Percent Recovery	Mean %	Relative Percent Difference (RPD)
Aldicarb	25	0	0	21.69	87	17.82	71	79	3%
Bromadiolone	25	0	0	6.88	28	8.37	33	31	-40%
Carbofuran	25	0	0	23.61	94	21.38	86	90	-4%
Oxamyl	25	0	0	19.98	80	17.98	72	76	-19%
Methomyl	25	0	0	23.35	93	22.42	90	92	-7%
4-Bromo-3,5-dimethylphenyl-N-methyl carbamate (BDMC)	50	50	43.53	51.28	103	39.36	79	91	-9%

		Surface Water Blank		Sample 1		Sample 2		Recovery	
Analyte/ Surrogate	Sample Spike Concentration (PPB)	Blank Spike Concentration (PPB)	Recovered (PPB)	Recovered (PPB)	Percent Recovery	Recovered (PPB)	Percent Recovery	Mean %	Relative Percent Difference (RPD)
Aldicarb	75	0	0	58.76	78	58	77	78	-3%
Bromadiolone	75	0	0	17.12	23	22.75	30	27	-55%
Carbofuran	75	0	0	63.4	85	59.83	80	83	-3%
Oxamyl	75	0	0	53.02	71	54.68	73	72	-22%
Methomyl	75	0	0	56.59	75	62.94	84	80	-17%
4-Bromo-3,5-dimethylphenyl-N-methyl carbamate (BDMC)	50	50	35.24	45.59	91	42.88	86	89	-11%

Table 6: Results of Carbamate Analyte Recovery from Surface Water

Appendix 1: Sample List

Sample List: 050608data
Saved under: C:\MassLynx\Janel\MS666.PRO\SampleDB\
MS Method: MS666m
Inlet File: MS666
Tune File: Carbamates.ipr
Injection Volume: 100 uL

No.	File Name	Text and Sample ID	Bottle	Sample Type
1	MS6660314	Blank	2:10	Blank
2	MS6660315	Level 6; EPA-STDS-2-79-2	2:1	Standard
3	MS6660316	Level 5; EPA-STDS-2-82-1	2:2	Standard
4	MS6660317	Level 4; EPA-STDS-2-82-2	2:3	Standard
5	MS6660318	Level 3; EPA-STDS-2-83-1	2:4	Standard
6	MS6660319	Level 2; EPA-STDS-2-83-2	2:5	Standard
7	MS6660320	Level 1; EPA-STDS-2-84-1	2:6	Standard
8	MS6660321	0.5 ppb; EPA-STDS-2-84-2	2:7	Standard
9	MS6660322	0.25 ppb; EPA-STDS-2-85-1	2:8	Standard
10	MS6660323	Blank	2:10	Blank
11	MS6660324	Lab Control 1; EPA-STDS-2-80-13	2:11	Analyte
12	MS6660325	Lab Control 2; EPA-STDS-2-80-14	2:12	Analyte
13	MS6660326	Reagent water blank (RWB) 1; EPA-STDS-2-80-1	2:13	Analyte
14	MS6660327	Reagent water (RW) + 1 ppb, 1; EPA-STDS-2-80-5	2:14	Analyte
15	MS6660328	RW + 1 ppb, 2; EPA-STDS-2-80-6	2:15	Analyte
16	MS6660329	RW + 1 ppb, 3; EPA-STDS-2-80-7	2:16	Analyte
17	MS6660330	RW + 1 ppb, 4; EPA-STDS-2-80-8	2:17	Analyte
18	MS6660331	RWB 2; EPA-STDS-2-80-2	2:18	Analyte
19	MS6660332	RW + 5 ppb, 1; EPA-STDS-2-80-9	2:19	Analyte
20	MS6660333	RW + 5 ppb, 2; EPA-STDS-2-80-10	2:20	Analyte
21	MS6660334	RW + 5 ppb, 3; EPA-STDS-2-80-11	2:21	Analyte
22	MS6660335	RW + 5 ppb, 4; EPA-STDS-2-80-12	2:22	Analyte
23	MS6660336	RWB 3; EPA-STDS-2-80-3	2:23	Analyte
24	MS6660337	RW + 25 ppb, 1; EPA-STDS-2-80-13	2:24	Analyte
25	MS6660338	RW + 25 ppb, 2; EPA-STDS-2-80-14	2:25	Analyte
26	MS6660339	RW + 25 ppb, 3; EPA-STDS-2-80-15	2:26	Analyte
27	MS6660340	RW + 25 ppb, 4; EPA-STDS-2-80-16	2:27	Analyte
28	MS6660341	RWB 4; EPA-STDS-2-80-4	2:28	Analyte
29	MS6660342	RW + 75 ppb, 1; EPA-STDS-2-80-17	2:29	Analyte
30	MS6660343	RW + 75 ppb, 2; EPA-STDS-2-80-18	2:30	Analyte
31	MS6660344	RW + 75 ppb, 3; EPA-STDS-2-80-19	2:31	Analyte
32	MS6660345	RW + 75 ppb, 4; EPA-STDS-2-80-20	2:32	Analyte
33	MS6660346	Blank	2:33	Blank
34	MS6660347	Surface water blank (SWB) 1; EPA-STDS-2-81-1	2:34	Analyte
35	MS6660348	SW + 1 ppb, 1; EPA-STDS-2-81-5	2:35	Analyte
36	MS6660349	SW + 1 ppb, 2; EPA-STDS-2-81-6	2:36	Analyte
37	MS6660350	SWB 2; EPA-STDS-2-81-2	2:37	Analyte
38	MS6660351	SW + 5 ppb, 1; EPA-STDS-2-81-7	2:38	Analyte
39	MS6660352	SW + 5 ppb, 2; EPA-STDS-2-81-8	2:39	Analyte
40	MS6660353	SWB 3; EPA-STDS-2-81-3	2:40	Analyte
41	MS6660354	SW + 25 ppb, 1; EPA-STDS-2-81-9	2:41	Analyte
42	MS6660355	SW + 25 ppb, 2; EPA-STDS-2-81-10	2:42	Analyte
43	MS6660356	SWB 4; EPA-STDS-2-81-4	2:43	Analyte
44	MS6660357	SW + 75 ppb, 1; EPA-STDS-2-81-11	2:44	Analyte
45	MS6660358	SW + 75 ppb, 2; EPA-STDS-2-81-12	2:45	Analyte
46	MS6660359	Blank	2:10	Blank
47	MS6660360	Matrix Spike 1; EPA-STDS-2-81-9	2:46	Analyte
48	MS6660361	Matrix Spike 2; EPA-STDS-2-81-10	2:47	Analyte
49	MS6660362	Level 3; EPA-STDS-2-83-1	2:4	Standard