LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

LLNL-TR-408180

Analysis of Ethanolamines: Validation of Semi-Volatile Analysis by HPLC-MS/MS by EPA Method MS888

Janel Owens, Alexander Vu, Carolyn Koester

October 27, 2008

Disclaimer

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

Analysis of Ethanolamines: Validation of Semi-Volatile Analysis by HPLC-MS/MS by EPA Method MS888

Janel Owens, Alexander Vu, and Carolyn Koester
Lawrence Livermore National Laboratory
7000 East Ave, L-091
Livermore, CA 94550
owens33@llnl.gov; koester1@llnl.gov;
(925) 422-8914 (JO) and (925) 422-6888 (CK)

TECHNICAL REPORT

LLNL-TR-#####

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

Overview and Objectives

The Environmental Protection Agency's (EPA) Region 5 Chicago Regional Laboratory (CRL) developed a method titled *Analysis of Diethanolamine, Triethanolamine, n-Methyldiethanolamine, and n-Ethyldiethanolamine in Water by Single Reaction Monitoring Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS): EPA Method MS888*. 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 *EPA Method MS888* for analysis of the listed ethanolamines 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 *EPA Method MS888* can be determined.

LLNL Verification of Procedures

Task 1: Verification of Instrument Conditions

For this study, a Waters Micromass Quattro *micro* API triple quadrupole mass spectrometer (Serial Number QAA594) coupled to a Waters 2795 liquid chromatograph was utilized for analysis. To verify instrument conditions, individual standards of diethanolamine (CAS # 111-42-2), triethanolamine (CAS # 102-71-6), n-methyldiethanolamine (CAS # 105-59-9), and n-ethyldiethanolamine (CAS # 139-87-7), and the surrogate compound diethanolamine-d8 (CAS # 103691-51-6) were prepared at concentrations of approximately 100 µg/mL in water/acetonitrile/200 mM ammonium acetate prepared in water (60/30/10, v/v/v). These individual standards were infused at 20 µL/min using an external Harvard Syringe Pump (Model 22 (Harvard Apparatus, Holliston, MA) and ionized in positive ion mode electrospray ionization (ESI). The initial tune file used for validating the ionization of each ethanolamine was as described in the *EPA Method MS888* SOP (**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 1**.

All ions previously identified in the *EPA Method MS888* SOP were confirmed and the following transitions from parent to product ion are listed in **Table 2** and **Figure 1**.

Table 1: Optimization of Tune File Parameters

Parameter	***EPA MS888* Parameters**	**LLNL Parameters**
Capillary voltage, kV	0.5	**2**
Cone voltage, V	25 for all analytes	Variable
Extractor, V	2	2
RF lens, V	0.2	0.2
Source Temp, °C	120	120
Desolvation Temp, °C	300	300
Desolvation gas, L/h	500	**400**
Cone gas, L/h	25	25
Low mass resolution 1	14.5	14.5
High mass resolution 1	14.5	14.5
Ion energy 1	0.5	**1**
Entrance energy, eV	-1	-1
Collision energy, eV	Variable	Variable
Exit energy, eV	2	2
Low mass resolution 2	15	15
High mass resolution 2	15	15
Ion energy 2	0.5	**1.5**
Multiplier	650	650
Inter-channel delay, s	0.02	0.02
Inter-scan delay, s	0.1	0.1
Repeats	1	1
Span, Da	0	0
Dwell, s	0.1	0.1

*Entries indicated by bold text were changed from initially described parameters.

Table 2: Confirmation of parent and product ions and optimization of cone voltage and collision energies for all analytes

		Analyte				Surrogate
	Parameter	Diethanolamine	Triethanolamine	n-Methyldiethanolamine	n-Ethyldiethanolamine	Diethanolamine-d8
EPA MS888 Parameters	Parent ion, m/z	106	150.2	120.1	134.2	114
	Product ion, m/z	87.8	132.1	101.9	116	95.8
	Cone voltage, V	25	25	25	25	25
	Collision energy, eV	11	14	13	13	12
LLNL Parameters	Parent ion, m/z	105.88	150.05	119.96	134.07	113.97
	Product ion, m/z	87.78	132.02	101.83	115.95	95.9
	Cone voltage, V	20	15	25	25	20
	Collision energy, eV	13	13	12	11	12

Table 3: Gradient Program for HPLC Mobile Phases

Time (min)	Flow (µL/min)	% A	% B	% C
0	400	95	0	5
1	400	95	0	5
2	400	90	0	10
4	300	90	0	10
10	300	60	30	10
13	300	60	30	10
15	300	40	50	10
18	300	30	60	10
20	300	30	60	10
25	300	95	0	5
27	300	95	0	5

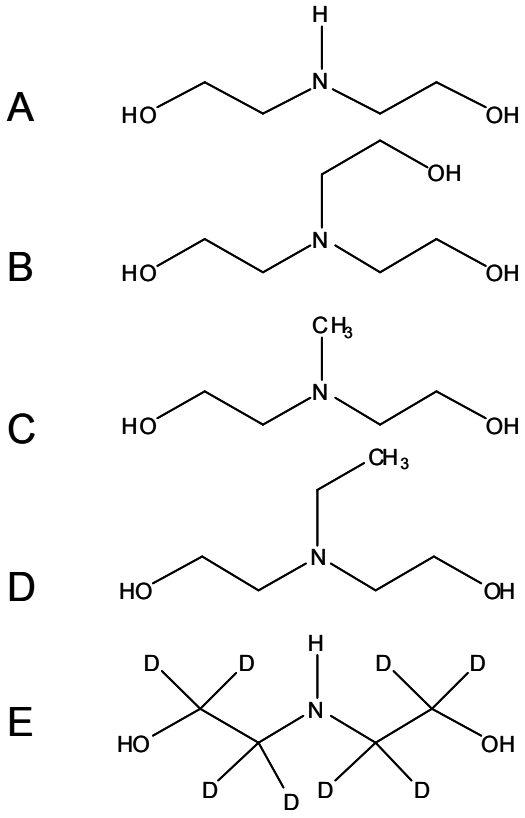
A: Acetonitrile
B: Water
C: 200 mM ammonium acetate in water

Table 4: Binary Gradient Program for HPLC Mobile Phases

Time (min)	Flow (µL/min)	% A	% B
0	400	100	0
1	400	100	0
2	400	94.7	5.3
4	300	94.7	5.3
10	300	63.2	36.8
13	300	63.2	36.8
15	300	42.1	57.9
18	300	31.6	68.4
20	300	31.6	68.4
25	300	100	0
27	300	100	0

A: 15 mM ammonium acetate in acetonitrile/water (95/5)
B: 15 mM ammonium acetate in water

Figure 1: Structures of analytes (A – D) and surrogate (E) with parent and product ions.



Diethanolamine: MW = 105.14 g/mol
m/z 105.88 $[M+H]^+$ ⟶ *m/z* 87.78

Triethanolamine: MW = 149.19 g/mol
m/z 150.05 $[M+H]^+$ ⟶ *m/z* 132.02

n-Methyldiethanolamine: MW = 119.16 g/mol
m/z 119.96 $[M+H]^+$ ⟶ *m/z* 101.83

n-Ethyldiethanolamine: MW = 133.19 g/mol
m/z 134.07 $[M+H]^+$ ⟶ *m/z* 115.95

Diethanolamine-d8: MW = 113.14 g/mol
m/z 113.97 $[M+H]^+$ ⟶ *m/z* 95.90

After optimization of tune file parameters, the chromatography was optimized. A HILIC Silica analytical column (100 x 2.1 mm i.d., 3 µm; Waters Corp., Milford, MA) was utilized for separations of the analyte and surrogate. The mobile phase conditions described in *EPA Method MS888* SOP were initially used (**Table 3**). The column compartment was maintained at 30 °C, autosampler at 15 °C, and the column equilibration time was 2 minutes between each sample. However, using these conditions, the retention times were highly variable. The binary gradient program (**Table 4**) was then adopted with a 3 min column equilibration time between each sample. Under these conditions, the stabilization of the retention times improved (**Table 5**).

Table 5: Comparison of retention times (RT) among all standards and samples and between groups for all analytes

	All standards and samples			Standards only			Reagent Water			Surface Water		
Analyte	Mean RT	RSD, %	Range	Mean RT	RSD, %	Range	Mean RT	RSD, %	Range	Mean RT	RSD, %	Range
Diethanolamine	9.99	2.04	9.61 - 10.25	10.01	1.15	9.75 - 10.08	10.02	2.47	9.61 - 10.23	9.93	1.77	9.66 - 10.25
Triethanolamine	4.99	2.39	4.76 - 5.17	5.09	0.32	5.07 - 5.12	4.95	2.26	4.76 - 5.12	5.03	2.58	4.79 - 5.17
n-Methyl diethanolamine	8.63	1.82	8.37 - 8.86	8.70	1.56	8.37 - 8.79	8.56	1.90	8.37 - 8.86	8.69	1.29	8.49 - 8.87
n-Ethyl diethanolamine	8.07	2.15	7.91 - 8.43	7.98	0.42	7.95 - 8.04	8.00	1.31	7.91 - 8.40	8.35	1.12	8.20 - 8.43
Diethanolamine-d8	10.18	2.46	9.80 - 10.57	10.35	1.13	10.10 - 10.47	10.09	2.79	9.80 - 10.55	10.25	1.61	9.95 - 10.57

Table 6: Calibration Curve Data for Ethanolamines

Analyte	**LOD, ppb (S/N)**	**LOQ, ppb (S/N)**	**Low standard**	**High standard**	**R2**
Diethanolamine	12.5 ppb (7.10)	25 ppb (10.54)	Level 1, 25 ppb	Level 7, 500 ppb	0.9932
Triethanolamine	12.5 ppb (3.46)	25 ppb (6.14)	Level 1, 25 ppb	Level 6, 500 ppb	0.9904
N-Methyldiethanolamine	5 ppb (3.39)	25 ppb (28.60)	Level 1, 25 ppb	Level 7, 500 ppb	0.9933
N-Ethyldiethanolamine	12.5 ppb (4.43)	25 ppb (8.39)	Level 1, 25 ppb	Level 7, 500 ppb	0.9983
Diethanolamine-d8	5 ppb (20.72)	25 ppb (42.23)	Level 1, 25 ppb	Level 7, 500 ppb	0.9974

Task 2: Determination of calibration curve data

Analytical standards were prepared according to the *EPA Method MS888* SOP. The concentration of the analytes and surrogate ranged from 5 ppb (µg/L) to 500 ppb. The low and high calibration levels that were included in the curve are shown in **Table 6**, along with signal to noise (S/N) data. The limit of detection (LOD) data is provided as well. Briefly, the signal to noise (S/N) at 25 ppb was greater than 10 (the limit of quantitation) for all analytes with the exceptions of n-ethyldiethanolamine (S/N at 25 ppb = 8.39) and triethanolamine (S/N at 25 ppb = 6.14). The S/N for the surrogate diethanolamine-d8 at the 25 ppb standard was 42.28.

All calibration curves were quadratic with 1/x weighting; and a minimum of six standards were included in each calibration curve. Standards run during the sequence set, between surface and reagent water samples, were also included in the calibration curve, with the exception of triethanolamine. The two Level 4 standards run at the end of the sample list (see **Appendix 1**) suffered from poor chromatography, and reduced the r^2 value of the curve to less than 0.99 when included. Thus, they were excluded from the curve. The level 6 standard was excluded from the n-ethyldiethanolamine calibration curve because it had a relative deviation from the target greater than 20%. Finally, the Level 7 standard was not included in the triethanolamine calibration curve because it formed an asymptotic curve.

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 (25 ppb, 50 ppb, 200 ppb, and 425 ppb) and duplicate samples of surface water at these same fortification levels. Example chromatograms of each analyte in a standard, reagent water, and surface water at 200 ppb are

shown in **Figure 2**. The results of the precision and bias study are shown in **Table 7** (reagent water) and **Table 8** (surface water).

The recovery of diethanolamine in reagent water ranged from 55.8 % (at 25 ppb) to 77.5% (at 425 ppb) with a relative standard deviation (RSD) of 13.8 % or less. These values are in good agreement with the **Quality Control Acceptance Criteria** (Table 2, *EPA Method MS888* SOP) where the values range from 63 to 123% for reagent water and 86 to 146% for surface water. In the duplicate surface water samples analyzed by LLNL, the recoveries ranged from 89% (at 25 ppb) to 133.5% (at 425 ppb), which again indicates good agreement with the values established in Table 2 of *EPA Method MS888* SOP. The relative percent difference between duplicate samples was 9.0% or less.

Triethanolamine recoveries ranged from 48.0% (at 425 ppb) to 149.0% (at 200 ppb) in reagent water. The range of recovery for reagent water in *EPA Method MS888* SOP for this analyte is 54% to 114%. The recoveries of triethanolamine were generally not very precise, with RSD ranging from 5.8% (at 50 ppb) to 29.3% (at 200 ppb). In surface water samples, the recovery of triethanolamine ranged from 78.5% (at 425 ppb) to 220.5% (at 200 ppb), compared to 42 to 102% in *EPA Method MS888* SOP. The relative percent difference between the duplicate samples ranged from 6.4% (at 425 ppb) to 95.4% (at 25 ppb). This analyte was tricky to analyze because of its early elution (RT = 4.99 min) and unstable baseline.

N-Ethyldiethanolamine recoveries ranged from 37.0% (at 25 ppb) to 71.5% (at 200 ppb) with an RSD of 14.8% or less. Peak shape for reagent water samples was very clean and sharp. The range of recoveries in reagent water (Table 2, *MS888* SOP) for this analyte is 73 to 133%, so these reported results are much lower than previous work. In surface water samples, the recovery was even lower, ranging from 0% (at 25 ppb) to 18% (at 200 ppb), compared to the

range of 31% to 91% reported in the *MS888* SOP. The relative percent difference between duplicates was 35.3% (at 50 ppb) to 7.4% (at 425 ppb). Peak shape of n-ethyldiethanolamine in surface water was very broad and suffered from peak splitting (**Figure 2**).

The recoveries of n-methyldiethanolamine in reagent water ranged from 57.8% (at 25 ppb) to 72.5% (at 200 ppb), with RSD of 12.8% or less. These recoveries compared well to the range listed in Table 2 of the SOP (62% to 122%). In surface water, the recoveries ranged from 89.5% (at 425 ppb) to 122% (at 25 ppb). The relative percent difference between samples of 5.7% or less, indicating good precision. These recoveries compared well to the SOP values, which ranged from 20 to 120%.

Finally, the recoveries of the surrogate diethanolamine-D_8, spiked into all samples for a final concentration of 200 ppb, were established. In reagent water, the recovery ranged from 64% (for the 425 ppb sample set) to 84% (for the 50 ppb sample set). The RSD was 15.9% or less. The recovery range listed in the SOP is 75 to 135%, so these reported recoveries are comparable. In surface water samples, the recoveries ranged from 98% (for the 425 ppb sample set) to 132% (for the 50 ppb sample set). The relative percent difference between duplicates was 6.1% or less. These recoveries compare well to the reported range of 95 to 155% (SOP, Table 2).

Instrument ID: Waters Quattro *micro* API (S/N QAA594) with Waters 2795 HPLC
Surface Water Description: Collected from South Bay Aqueduct (drinking water from Sierra Nevada mountains to San Diego, CA)
Date of Analysis: 09/25/08

Data Reporting Form 4a. (Ethanolamines) Precision and Bias 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)
Diethanolamine	25	0	0	314.5	74	345.1	81	362.8	85	297.3	70	77.5	8.7
Triethanolamine	25	0	0	170.4	40	220	52	219.2	52	202.2	48	48.0	11.8
N-Ethyldiethanolamine	25	0	0	286.1	67	256.2	60	266	63	215	51	60.3	11.3
N-Methyldiethanolamine	25	0	0	295.8	70	296.8	70	297.7	70	266.3	63	68.3	5.1
bis(2-Hydroxyethyl)-D_8-amine	200	200	79.4	120	60	132.8	66	134.2	67	126.7	63	64.0	4.9

		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)
Diethanolamine	50	0	0	145.5	73	161.9	81	121.1	61	167.1	84	74.8	13.7
Triethanolamine	50	0	0	264.3	132	317.2	159	202.3	101	408.6	204	149.0	29.3
N-Ethyldiethanolamine	50	0	0	132.1	66	155.4	78	119.8	60	163.3	82	71.5	14.3
N-Methyldiethanolamine	50	0	0	148.4	74	157.8	79	118.9	59	155	78	72.5	12.8
bis(2-Hydroxyethyl)-D_8-amine	200	200	99.8	132.7	66	163.1	82	135.7	68	184	92	77.0	15.9

		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)
Diethanolamine	200	0	0	29.1	58	32.5	65	27	54	35.7	71	62.0	12.1
Triethanolamine	200	0	0	33.9	68	33.4	67	36.8	74	37.6	75	71.0	5.7
N-Ethyldiethanolamine	200	0	0	24.4	49	32.7	65	ND		29.9	60	58.0	14.1
N-Methyldiethanolamine	200	0	0	28.3	57	34	68	27.9	56	35.4	71	63.0	12.1
bis(2-Hydroxyethyl)-D_8-amine	200	200	148.3	166.6	83	175.6	88	147.6	74	182.1	91	84.0	8.9

		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)
Diethanolamine	425	0	0	15.2	61	12.8	51	13.1	52	14.8	59	55.8	9.0
Triethanolamine	425	0	0	17.8	71	12.1	48	15.2	61	17.8	71	62.8	17.4
N-Ethyldiethanolamine	425	0	0	9.9	40	8.4	34	7.7	31	10.8	43	37.0	14.8
N-Methyldiethanolamine	425	0	0	14.7	59	12.8	51	13.8	55	16.5	66	57.8	11.1
bis(2-Hydroxyethyl)-D_8-amine	200	200	126.1	136.8	68	132	66	126.3	63	139.2	70	66.8	4.5

Table 7: Results of precision and bias study in replicates of reagent water spiked at 425 ppb, 200 ppb, 50 ppb, and 25 ppb.

Laboratory: LLNL
Instrument ID: Waters Quattro *micro* API triple quadrupole MS (QAA594) with 2795 HPLC
Surface Water Description: South Bay Aqueduct water (drinking water from Sierra Nevada mountains to San Diego, CA)
Date of Analysis: 9/25/2008

Data Reporting Form 4b. (Ethanolamines) 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)
Diethanolamine	25	0	0	556	131	577.6	136	133.5	3.7
Triethanolamine	25	0	0	325.1	76	345.4	81	78.5	6.4
N-Ethyldiethanolamine	25	0	0	56	13	58.3	14	13.5	7.4
N-Methyldiethanolamine	25	0	0	378.4	89	381.1	90	89.5	1.1
bis(2-Hydroxyethyl)-D_8-amine	200	200	250.7	199.8	100	192.4	96	98	4.1

		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)
Diethanolamine	50	0	0	202.1	101	216.7	108	104.5	6.7
Triethanolamine	50	0	0	409	205	472.1	236	220.5	14.1
N-Ethyldiethanolamine	50	0	0	33.4	17	38.6	19	18	11.1
N-Methyldiethanolamine	50	0	0	206.2	103	217.2	109	106	5.7
bis(2-Hydroxyethyl)-D_8-amine	200	200	274.1	220.1	110	219.2	110	110	0

		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)
Diethanolamine	200	0	0	46.1	92	45.5	91	91.5	1.1
Triethanolamine	200	0	0	75.4	151	69.4	139	145	8.3
N-Ethyldiethanolamine	200	0	0	7.2	14	10.1	20	17	35.3
N-Methyldiethanolamine	200	0	0	54.9	116	60.2	120	118	3.4
bis(2-Hydroxyethyl)-D_8-amine	200	200	279.4	256.8	128	272.7	136	132	6.1

		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)
Diethanolamine	425	0	0	21.2	85	23.2	93	89	9
Triethanolamine	425	0	0	18.7	75	53.1	212	143.5	95.4
N-Ethyldiethanolamine	425	0	0	0	0	0	0	0	-
N-Methyldiethanolamine	425	0	0	30.1	120	30.8	123	121.5	2.5
bis(2-Hydroxyethyl)-D_8-amine	200	200	244.4	260.2	130	263.7	132	131	0.76

Table 8: Results of precision and bias study in duplicates of surface water spiked at 425 ppb, 200 ppb, 50 ppb, and 25 ppb.

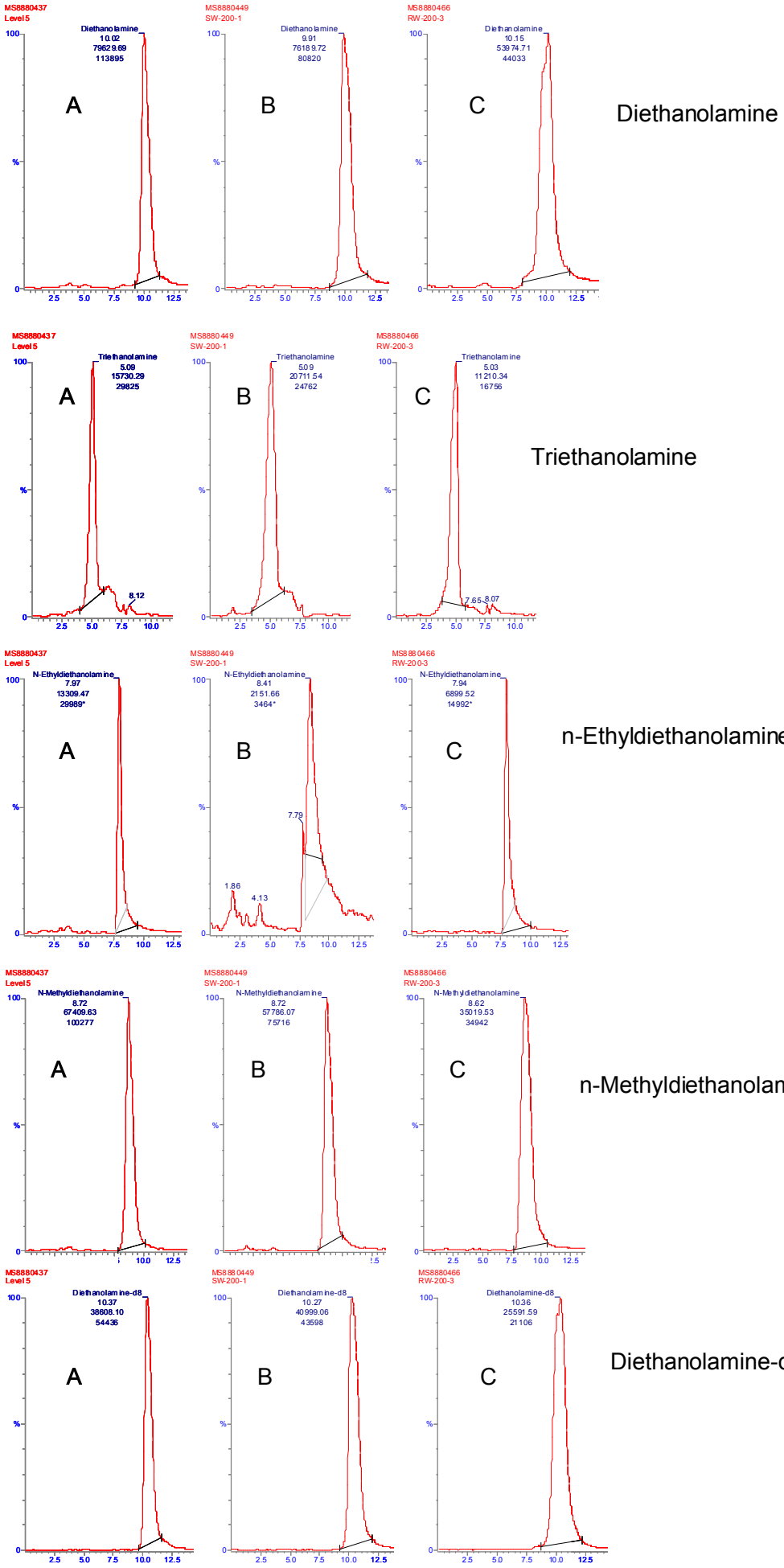


Figure 2: Example chromatograms of the four analytes and the surrogate in A) standard of 250 ppb; B) Surface water at 200 ppb; and C) Reagent water at 200 ppb.

Appendix 1: Sequence list

MassLynx - Sample List

Sample List: C:\MassLynx\MS666.PRO\SampleDB\092508.SPL
Printed: Monday, October 06, 2008 12:39:17 PM

	File Name	File Text	MS File	Inlet File	Bottle	Inject Volume	Sample Type	Conc A
1	MS8880426	Blank	MS888av	MS888AV	3:	25.000000	Blank	---
2	MS8880427	Level 7; EPA-STDS-3-111-2	MS888av	MS888AV	3:2	25.000000	Standard	500
3	MS8880428	Level 6; EPA-STDS-3-114-1	MS888av	MS888AV	3:3	25.000000	Standard	350
4	MS8880429	Level 5; EPA-STDS-3-114-2	MS888av	MS888AV	3:4	25.000000	Standard	250
5	MS8880430	Level 4; EPA-STDS-3-114-3	MS888av	MS888AV	3:5	25.000000	Standard	150
6	MS8880431	Level 3; EPA-STDS-3-115-1	MS888av	MS888AV	3:6	25.000000	Standard	75
7	MS8880432	Level 2; EPA-STDS-3-115-2	MS888av	MS888AV	3:7	25.000000	Standard	50
8	MS8880433	Level 1; EPA-STDS-3-115-3	MS888av	MS888AV	3:8	25.000000	Standard	25
9	MS8880434	Blank	MS888av	MS888AV	3:1	25.000000	Blank	---
10	MS8880435	Level 7; EPA-STDS-3-111-2	MS888av	MS888AV	3:2	25.000000	Standard	500
11	MS8880436	Level 6; EPA-STDS-3-114-1	MS888av	MS888AV	3:3	25.000000	Standard	350
12	MS8880437	Level 5; EPA-STDS-3-114-2	MS888av	MS888AV	3:4	25.000000	Standard	250
13	MS8880438	Level 4; EPA-STDS-3-114-3	MS888av	MS888AV	3:5	25.000000	Standard	150
14	MS8880439	Level 3; EPA-STDS-3-115-1	MS888av	MS888AV	3:6	25.000000	Standard	75
15	MS8880440	Level 2; EPA-STDS-3-115-2	MS888av	MS888AV	3:7	25.000000	Standard	50
16	MS8880441	Level 1; EPA-STDS-3-115-3	MS888av	MS888AV	3:8	25.000000	Standard	25
17	MS8880442	12.5 ppb; EPA-STDS-3-116-1	MS888av	MS888AV	3:9	25.000000	Standard	12.5
18	MS8880443	5 ppb; EPA-STDS-3-116-2	MS888av	MS888AV	3:10	25.000000	Standard	5
19	MS8880444	Blank	MS888av	MS888AV	3:1	25.000000	Blank	---
20	MS8880445	SWB-1	MS888av	MS888AV	3:11	25.000000	Analyte	---
21	MS8880446	SW-425-1	MS888av	MS888AV	3:12	25.000000	Analyte	---
22	MS8880447	SW-425-2	MS888av	MS888AV	3:13	25.000000	Analyte	---
23	MS8880448	SWB-2	MS888av	MS888AV	3:14	25.000000	Analyte	---
24	MS8880449	SW-200-1	MS888av	MS888AV	3:15	25.000000	Analyte	---
25	MS8880450	SW-200-2	MS888av	MS888AV	3:16	25.000000	Analyte	---
26	MS8880451	SWB-3	MS888av	MS888AV	3:17	25.000000	Analyte	---
27	MS8880452	SW-50-1	MS888av	MS888AV	3:18	25.000000	Analyte	---
28	MS8880453	SW-50-2	MS888av	MS888AV	3:19	25.000000	Analyte	---
29	MS8880454	SWB-4	MS888av	MS888AV	3:20	25.000000	Analyte	---
30	MS8880455	SW-25-1	MS888av	MS888AV	3:21	25.000000	Analyte	---
31	MS8880456	SW-25-1	MS888av	MS888AV	3:22	25.000000	Analyte	---
32	MS8880457	Blank	MS888av	MS888AV	3:1	25.000000	Analyte	---
33	MS8880458	RWB-1	MS888av	MS888AV	3:23	25.000000	Analyte	---
34	MS8880459	RW-425-1	MS888av	MS888AV	3:24	25.000000	Analyte	---
35	MS8880460	RW-425-2	MS888av	MS888AV	3:25	25.000000	Analyte	---
36	MS8880461	RW-425-3	MS888av	MS888AV	3:26	25.000000	Analyte	---
37	MS8880462	RW-425-4	MS888av	MS888AV	3:27	25.000000	Analyte	---
38	MS8880463	RWB-3	MS888av	MS888AV	3:28	25.000000	Analyte	---
39	MS8880464	RW-200-1	MS888av	MS888AV	3:29	25.000000	Analyte	---
40	MS8880465	RW-200-2	MS888av	MS888AV	3:30	25.000000	Analyte	---
41	MS8880466	RW-200-3	MS888av	MS888AV	3:31	25.000000	Analyte	---
42	MS8880467	RW-200-4	MS888av	MS888AV	3:32	25.000000	Analyte	---
43	MS8880468	RWB-2	MS888av	MS888AV	3:33	25.000000	Analyte	---
44	MS8880469	RW-50-1	MS888av	MS888AV	3:34	25.000000	Analyte	---
45	MS8880470	RW-50-2	MS888av	MS888AV	3:35	25.000000	Analyte	---
46	MS8880471	RW-50-3	MS888av	MS888AV	3:36	25.000000	Analyte	---
47	MS8880472	RW-50-4	MS888av	MS888AV	3:37	25.000000	Analyte	---
48	MS8880473	RWB-1	MS888av	MS888AV	3:38	25.000000	Analyte	---
49	MS8880474	RW-25-1	MS888av	MS888AV	3:39	25.000000	Analyte	---
50	MS8880475	RW-25-2	MS888av	MS888AV	3:40	25.000000	Analyte	---
51	MS8880476	RW-25-3	MS888av	MS888AV	3:41	25.000000	Analyte	---
52	MS8880477	RW-25-4	MS888av	MS888AV	3:42	25.000000	Analyte	---
53	MS8880478	Blank	MS888av	MS888AV	3:1	25.000000	Analyte	---
54	MS8880479	Level 4	MS888av	MS888AV	3:5	25.000000	Standard	150
55	MS8880480	SW-425-1 dil	MS888av	MS888AV	3:43	25.000000	Analyte	---
56	MS8880481	SW-425-2 dil	MS888av	MS888AV	3:44	25.000000	Analyte	---
57	MS8880482	Blank	MS888av	MS888AV	3:1	25.000000	Blank	---
58	MS8880483	RW-425-1 dil	MS888av	MS888AV	3:45	25.000000	Analyte	---
59	MS8880484	RW-425-2 dil	MS888av	MS888AV	3:46	25.000000	Analyte	---
60	MS8880485	RW-425-3 dil	MS888av	MS888AV	3:47	25.000000	Analyte	---
61	MS8880486	RW-425-4-dil	MS888av	MS888AV	3:48	25.000000	Analyte	---
62	MS8880487	Level 4	MS888av	MS888AV	3:5	25.000000	Standard	150