

# Determining MDLs for VOCs in Canisters to Meet NATTS Requirements

**Michael Liadis**

Pinellas County Air Quality Division

Clearwater, FL

2016 EPA National Ambient Air Monitoring Conference, St. Louis, MO



# Why give this presentation?

- ▶ Labs are not meeting minimum MDLs specified in the NATTS Work Plan or TAD
- ▶ Inconsistent procedures are being used among NATTS labs for determining MDLs

# References

- ▶ 2015 NATTS Work Plan
- ▶ 2009 NATTS Technical Assistance Document (TAD)
- ▶ 40 CFR Part 136, Appendix B

# 2015 NATTS Work Plan MDLs

Analyte	Section 3.1 Required MDLs ( $\mu\text{g}/\text{m}^3$ )	Required MDLs (ppbv)
Acrolein	0.09000	0.039
Benzene	0.13000	0.041
Butadiene, 1,3-	0.10000	0.045
Carbon Tetrachloride	0.17000	0.027
Chloroform	0.50000	0.102
Tetrachloroethylene	0.17000	0.025
Trichloroethylene	0.20000	0.037
Vinyl Chloride	0.11000	0.043

# NATTS TAD MDLs

**Table 1.1-1**

<b>Analyte</b>	<b>Target MDLs (<math>\mu\text{g}/\text{m}^3</math>)</b>	<b>Target MDLs (ppbv)</b>
1,3-Dichloropropene - cis	0.300	0.066
1,3-Dichloropropene - trans	0.300	0.066
Dichloromethane	2.100	0.604
1,1,2,2-Tetrachloroethane	0.0170	0.0025

**Table 4.1-4**

<b>Analyte</b>	<b>Target MDLs (<math>\mu\text{g}/\text{m}^3</math>)</b>	<b>Target MDLs (ppbv)</b>
1,2-Dibromoethane	0.060	0.008
1,2-Dichloroethane	0.040	0.010
1,2 Dichloropropane	0.050	0.011

# NATTS PT MDL Results VOCs

Quarter 1, 2016

## Work Plan Section 3.1

Analyte	Reported MDL by Laboratory (ppbv)																								
Acrolein	0.025	0.03	0.025	NR	0.007	0.028	0.074	0.07	NR	0.005	0.047	0.03	0.097	0.014	0.085	0.063	0.015	0.08	0.05	NR	NR	0.111	0.04	0.12	0.016
Benzene	0.003	0.008	0.003	0.02	0.03	0.018	0.019	0.03	0.07	0.001	0.036	0.039	0.023	0.008	0.085	0.19	0.005	0.04	0.14	0.036	0.013	0.012	0.04	0.021	0.002
1,3-Butadiene	0.004	0.008	0.004	0.02	0.005	0.005	0.04	0.03	NR	0.003	0.1	0.024	0.064	0.015	0.085	0.53	0.013	0.08	0.14	0.14	0.008	0.015	0.04	0.026	0.005
Carbon Tetrachloride	0.004	0.005	0.004	0.02	0.027	0.006	0.024	0.04	NR	0.001	0.036	0.033	0.03	0.009	0.085	0.16	0.006	0.02	0.14	0.06	0.004	0.011	0.01	0.016	0.005
Chloroform	0.003	0.007	0.003	0.02	0.006	0.005	0.018	0.03	0.08	0.002	0.042	0.058	0.013	0.006	0.085	0.13	0.006	0.05	0.11	0.04	0.003	0.012	0.05	0.012	0.004
Tetrachloroethylene	0.003	0.006	0.003	0.02	0.022	0.008	0.022	0.04	0.03	0.001	0.027	0.025	0.01	0.005	0.085	0.094	0.002	0.07	0.12	0.03	0.006	0.015	0.02	0.016	0.004
Trichloroethylene	0.002	0.007	0.002	0.02	0.027	0.008	0.021	0.03	0.06	0.001	0.036	0.041	0.051	0.004	0.085	0.094	0.004	0.05	0.15	0.02	0.008	0.003	0.05	0.016	0.004
Vinyl chloride	0.003	0.006	0.003	0.02	0.005	0.008	0.033	0.03	0.09	0.004	0.057	0.028	0.092	0.005	0.085	0.44	0.008	0.07	0.09	0.07	0.009	0.019	0.04	0.032	0.008

# NATTS PT MDL Results VOCs

Quarter 1, 2016

TAD Table 1.1-1

Analyte	Reported MDL by Laboratory (ppbv)																								
Dichloromethane	0.003	0.007	0.003	0.02	0.005	0.01	0.026	0.02	0.07	0.002	0.038	0.063	0.06	0.004	0.085	0.063	0.009	0.08	0.1	0.04	0.002	0.018	0.05	0.021	0.004
1,3-Dichloropropene - cis	0.003	0.007	0.003	0.02	0.01	0.009	0.023	0.03	0.03	0.002	0.027	0.069	0.029	0.013	0.085	0.094	0.004	0.04	0.1	0.04	NR	0.009	0.05	0.02	0.003
1,3-Dichloropropene - trans	0.004	0.008	0.004	0.02	0.01	0.009	0.036	0.05	0.05	0.002	0.018	0.034	0.021	0.018	0.085	0.13	0.004	0.03	0.1	0.11	NR	0.014	0.05	0.027	0.004
1,1,2,2-Tetrachloroethane	0.003	0.016	0.003	0.02	0.018	0.012	0.016	0.04	0.06	0.001	0.027	0.039	0.023	0.007	0.085	0.13	0.004	0.05	0.1	0.06	NR	NR	0.05	0.03	0.006

# NATTS PT MDL Results VOCs

Quarter 1, 2016

TAD Table 4.1-4

Analyte	Reported MDL by Laboratory (ppbv)																								
1,2-Dibromoethane	0.003	0.007	0.003	0.02	0.016	0.011	0.037	0.05	0.03	0.001	0.026	0.038	0.012	0.009	0.085	0.12	0.006	0.04	0.1	0.04	0.007	NR	0.05	0.021	0.003
1,2-Dichloroethane	0.003	0.008	0.003	0.02	0.02	0.009	0.026	0.03	0.1	0.002	0.033	0.068	0.017	0.003	0.085	0.28	0.007	0.04	0.14	0.1	0.004	NR	0.05	0.013	0.003
1,2-Dichloropropane	0.003	0.008	0.003	0.02	0.016	0.01	0.022	0.04	0.07	0.001	0.035	0.063	0.023	0.008	0.085	0.22	0.004	0.04	0.09	0.06	NR	NR	0.05	0.019	0.005



# Procedure to Determine MDLs

## 40 CFR Part 136 Appendix B

- ▶ Estimate MDL
- ▶ Prepare a standard between one and five times the estimated MDL (Spike value)
- ▶ Analyze a minimum of seven aliquots
- ▶ Calculate MDL
- ▶  $\text{MDL} < \text{spike value} \leq 10 \times \text{MDL}$ 
  - ▶ ex:  $0.003 < 0.030 \leq 0.030 = \text{pass}$
  - ▶ ex:  $0.002 < 0.030 \not\leq 0.020 = \text{fail}$

# Procedure to Determine MDLs 2009 NATTS TAD

- ▶ Prepare at least seven standards in individual canisters
- ▶ Analyzed over a minimum two-day period
- ▶ Analyze each canister at same volume equivalent to the sample volume

# Instrumentation and Conditions

- ▶ GC/MS: Agilent 6890/5975 using SIM
- ▶ Preconcentrator: Entech 7200
- ▶ Canister Type: Restek SiloCan and Entech Silonite
- ▶ Canister Pressure: 1150 mmHg (7.54 psig)
- ▶ Canister Humidity: 22% RH
- ▶ Canister Spike Value: 0.010 ppbv

# Results of MDL Study

Analyte	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	Trial 7	Trial 8	Trial 9	Trial 10	MDL ppbv	10x mdl	NATTS MQO or Target
	3/2	3/2	3/2	3/2	3/3	3/3	3/3	3/11	3/11	3/11			
	3725	3726	3728	3898	7678	6469	7679	9960	9961	9963			
Acrolein	0.012	0.017	0.015	0.013	0.015	0.014	0.014	0.017	0.018	0.015	0.005	0.050	0.039
Benzene	0.014	0.013	0.014	0.014	0.014	0.014	0.013	0.014	0.013	0.014	0.001	0.010	0.041
1,3-Butadiene	0.012	0.010	0.010	0.012	0.010	0.010	0.009	0.010	0.011	0.010	0.003	0.030	0.045
Carbontetrachloride	0.009	0.009	0.010	0.009	0.009	0.009	0.010	0.010	0.010	0.009	0.001	0.010	0.027
Chloroform	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.011	0.010	0.010	0.001	0.010	0.102
Tetrachloroethylene	0.012	0.012	0.012	0.012	0.012	0.012	0.011	0.014	0.012	0.012	0.002	0.020	0.025
Trichloroethylene	0.010	0.011	0.011	0.010	0.011	0.010	0.011	0.010	0.010	0.010	0.001	0.010	0.037
Vinyl chloride	0.008	0.011	0.009	0.009	0.010	0.009	0.008	0.012	0.009	0.010	0.004	0.040	0.043
1,3-Dichloropropene-cis	0.010	0.010	0.011	0.009	0.010	0.011	0.010	0.010	0.010	0.010	0.002	0.020	0.066
1,3-Dichloropropene-trans	0.010	0.011	0.011	0.009	0.011	0.010	0.010	0.011	0.010	0.010	0.002	0.020	0.066
Dichloromethane	0.022	0.022	0.022	0.021	0.022	0.023	0.022	0.024	0.022	0.023	0.002	0.020	0.604
1,1,2,2-Tetrachloroethane	0.012	0.011	0.011	0.012	0.011	0.011	0.011	0.012	0.012	0.011	0.001	0.010	0.0025
1,2-Dibromoethane	0.010	0.011	0.010	0.011	0.010	0.010	0.010	0.010	0.010	0.010	0.001	0.010	0.008
1,2-Dichloroethane	0.010	0.010	0.010	0.010	0.010	0.009	0.010	0.011	0.010	0.011	0.002	0.020	0.010
1,2-Dichloropropane	0.011	0.011	0.011	0.011	0.011	0.011	0.010	0.011	0.010	0.011	0.001	0.010	0.011

# Results of MDL Study

Analyte	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5	Trial 6	Trial 7	Trial 8	Trial 9	Trial 10	MDL	10x mdl	NATTS
	3/2	3/2	3/2	3/2	3/3	3/3	3/3	3/11	3/11	3/11	ppbv		MQO or
	3725	3726	3728	3898	7678	6469	7679	9960	9961	9963			Target
Acrolein											0.005	0.050	0.039
Benzene											0.001	0.010	0.041
1,3-Butadiene											0.003	0.030	0.045
Carbontetrachloride											0.001	0.010	0.027
Chloroform											0.001	0.010	0.102
Tetrachloroethylene											0.002	0.020	0.025
Trichloroethylene											0.001	0.010	0.037
Vinyl chloride											0.004	0.040	0.043
1,3-Dichloropropene-cis											0.002	0.020	0.066
1,3-Dichloropropene-trans											0.002	0.020	0.066
Dichloromethane											0.002	0.020	0.604
1,1,2,2-Tetrachloroethane											0.001	0.010	0.0025
1,2-Dibromoethane											0.001	0.010	0.008
1,2-Dichloroethane											0.002	0.020	0.010
1,2-Dichloropropane											0.001	0.010	0.011

✓ At least 7 individual canisters  
 ✓ Analyzed over two or more days  
 ✓ MDL less than Spike Value  
 ✓ Spike Value less than or equal to 10x MDL  
 ✓ Met NATTS MQO or Target MDL

# Canister Cleaning





# Standards Preparation



# Accuracy

Analyte	MEASURED	TRUE	%REC
Acrolein	0.014	0.010	140
Benzene	0.014	0.010	140
1,3-Butadiene	0.010	0.010	100
Carbontetrachloride	0.009	0.010	90
Chloroform	0.010	0.010	100
Tetrachloroethylene	0.012	0.010	120
Trichloroethylene	0.011	0.010	110
Vinyl chloride	0.009	0.010	90
1,3-Dichloropropene-cis	0.010	0.010	100
1,3-Dichloropropene-trans	0.010	0.010	100
Dichloromethane	0.022	0.010	220
1,1,2,2-Tetrachloroethane	0.011	0.010	110
1,2-Dibromoethane	0.010	0.010	100
1,2-Dichloroethane	0.010	0.010	100
1,2-Dichloropropane	0.011	0.010	110



# Conclusion

- ▶ Thorough canister cleaning, consistent standards preparation and sensitive lab equipment can help meet MQO and target MDLs
- ▶ It is possible to meet all the criteria in the TAD and 40 CFR for determining MDLs

# Questions?

## ► Contact:

Michael Liadis

Environmental Chemist

Pinellas County Air Quality Division

Phone: (727) 464-4695

[mliadis@Pinellascounty.org](mailto:mliadis@Pinellascounty.org)