An Overview of Eastern Research Group's Approach to TO-15A/NATTS TAD rev4

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Presentation Overview

- Method Overview
- Method Detection Limit
- Canister Certification
- Instrument Calibration
- Analyte Qualifiers/Database Management
- Conclusions

TO-15A / TAD rev. 4 Method Overview

- Released in September 2019
  - Based on TO-15 method
  - Incorporation of Current Technologies
- Lower Method Detection Limits to accurately reflect ambient level analysis (0.5 ppbV -> 20 pptV)
  - Outlining collection and analysis of ***<u>trace level</u>*** toxics (20 to 5000 pptV)
- Special Consideration for Reproducibility
  - Increase in quality control samples and tighter criteria
  - Canister and Sampler Certification

NATTS TAD vs TO-15A

- ERG is required by client to follow the NATTS Technical Assistance Document rev4
  - Released specifically with ambient monitoring in mind
  - Released following the release of TO-15A
  - Largely the same criteria

Table 1.2-1. Analytes of Principle Interest for the NATTS Program

HAP	Analyte Class and Collection and Analysis Method	Tier	10^{-6} Cancer Risk Concentration (µg/m³)	Noncancer Risk [Hazard Quotient = 0.1] Concentration (µg/m³)
acrolein	VOC byTO-15A	I (UATS)	NA	0.002
tetrachloroethylene	VOC byTO-15A	I (UATS)	3.8 [a]	4 [a]
benzene	VOC byTO-15A	I (UATS)	0.13	3
carbon tetrachloride	VOC byTO-15A	I (UATS)	0.17	10
chloroform	VOC byTO-15A	I (UATS)	NA	9.8
trichloroethylene	VOC byTO-15A	I (UATS)	0.21 [a]	0.2 [a]
1,3-butadiene	VOC byTO-15A	I (UATS)	0.03	0.2
vinyl chloride	VOC byTO-15A	I (UATS)	0.11	10
acetonitrile	VOC byTO-15A	II	NA	6
acrylonitrile	VOC byTO-15A	II (UATS)	0.015	2
bromoform	VOC byTO-15A	II	0.91	NA
carbon disulfide	VOC byTO-15A	II	NA	70
chlorobenzene	VOC byTO-15A	II	100	NA
chloroprene	VOC byTO-15A	II	NA	0.7
p-dichlorobenzene	VOC byTO-15A	II	0.091	80
cis-1,3-dichloropropene	VOC byTO-15A	II (UATS)	0.3	2
trans-1,3-dichloropropene	VOC byTO-15A	II (UATS)	0.3	2
ethyl acrylate	VOC byTO-15A	II	0.071	NA
ethyl benzene	VOC byTO-15A	II	NA	100
ethylene oxide	VOC byTO-15A	I	0.0002	NA
hexachloro-1,3-butadiene	VOC byTO-15A	II	0.0022	9
methyl ethyl ketone	VOC byTO-15A	II	NA	500
methyl isobutyl ketone	VOC byTO-15A	II	NA	300
methyl methacrylate	VOC byTO-15A	II	NA	70
methyl tert-butyl ether	VOC byTO-15A	II	3.8	300
methylene chloride	VOC byTO-15A	II (UATS)	2.1	100
styrene	VOC byTO-15A	II	NA	100
1,1,2,2-tetrachloroethane	VOC byTO-15A	II (UATS)	0.017	NA
toluene	VOC byTO-15A	II	NA	40
1,1,2-trichloroethane	VOC byTO-15A	II	0.063	40
1,2,4-trichlorobenzene	VOC byTO-15A	II	NA	20
m&p-xylenes	VOC byTO-15A	II	NA	10
o-xylene	VOC byTO-15A	II	NA	10

Tier 1 Compounds - MDL

- ERG MDLs from current Systems
  - Determined by highest of Spike and Blank data
  - Intended to capture sample matrix effects

Tier 1 Compound MDL (pptV)	
Vinyl Chloride	5.1
1,3-Butadiene	22.0
Ethylene Oxide	25.5
Acrolein	82.6
Chloroform	13.4
Benzene	10.1
Carbon Tetrachloride	7.5
Trichloroethylene	6.8
Tetrachloroethylene	8.6

Description of the MDL process

- TO-15A MDL methodology in Section 17 includes:
  - Low level spiked samples
  - Collection of blank data
  - Year-round MDL samples
- NATTS TAD has similar requirements

Compound name	MDLsp (pptV)	MDLb (pptV)	Method	Selected MDL
Vinyl chloride	5.1	2.6	MDLsp	5.1
1,3-Butadiene	22.0	2.4	MDLsp	22.0
Ethylene Oxide	25.5	0.0	MDLsp	25.5
Acrolein	82.6	64.6	MDLsp	82.6
Chloroform	13.4	3.4	MDLsp	13.4
Benzene	9.1	10.1	MDLb	10.1
Carbon Tetrachloride	7.5	2.6	MDLsp	7.5
Trichloroethylene	4.0	6.8	MDLb	6.8
Tetrachloroethylene	8.6	4.0	MDLsp	8.6

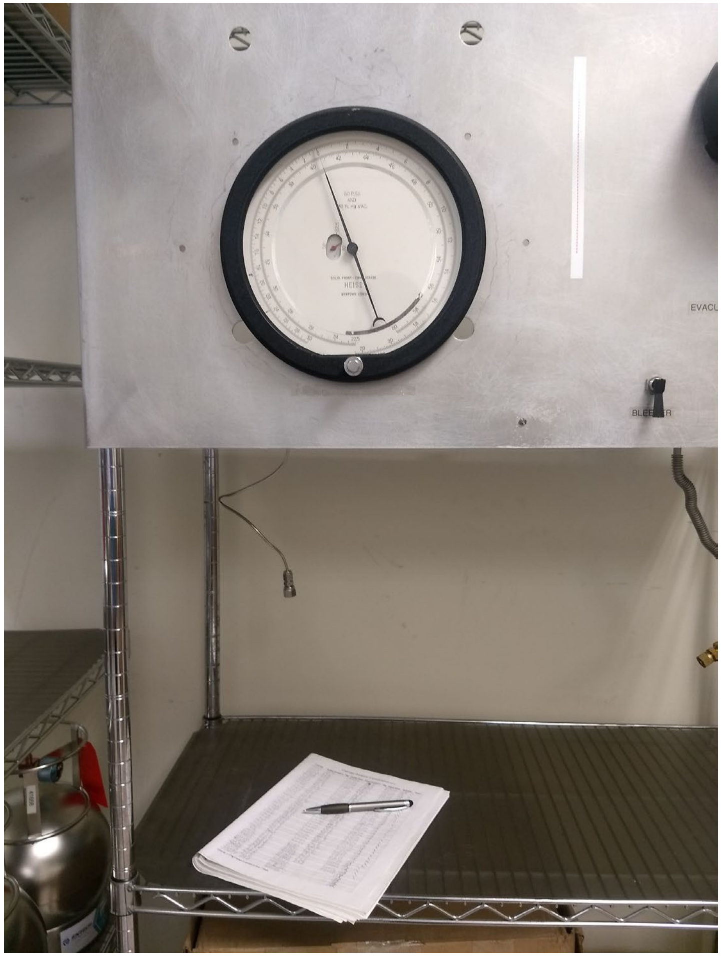
Canister Certification

- ERG follows **NATTS TAD** requirements
- **Leak Check**
  - TAD Criteria – <5% volume over 7 days and ~20% sample leak over 30 days
  - Layman's Terms: <0.1psi/day
- **Zero-Air Challenge** - held 30 days (hold time)
  - TAD Criteria – <3xMDL or **30** pptV, whichever is lower
- **Known-Standard Challenge** - held 30 days (hold time)
  - TAD Criteria – (<±30.1% Nominal Recovery)

Considerable extra work to accomplish these goals!

Canister Leak Check

- Leak check performed on high-accuracy Heise gauges
  - Evacuate/Pressurize canister
  - Record an initial reading
  - Hold for “several” days
  - Record a final reading
- Criteria: <0.1 psi/day (0.69kPa/day)
  - ERG: 93.6% Pass Rate



Canister Zero-Air Challenge

Procedure:

1. Canisters are cleaned and evacuated
2. Filled with humidified zero-air
3. Held for 30 days (Hold Time)
4. Analyzed against blank criteria (30pptV or 3xMDL)
5. Failures flagged accordingly

Canister Zero-Air Challenge

194 Cans Tested in Total

↓

All Compound Failures Listed

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85% TAD Failure
17% >5xMDL Failure

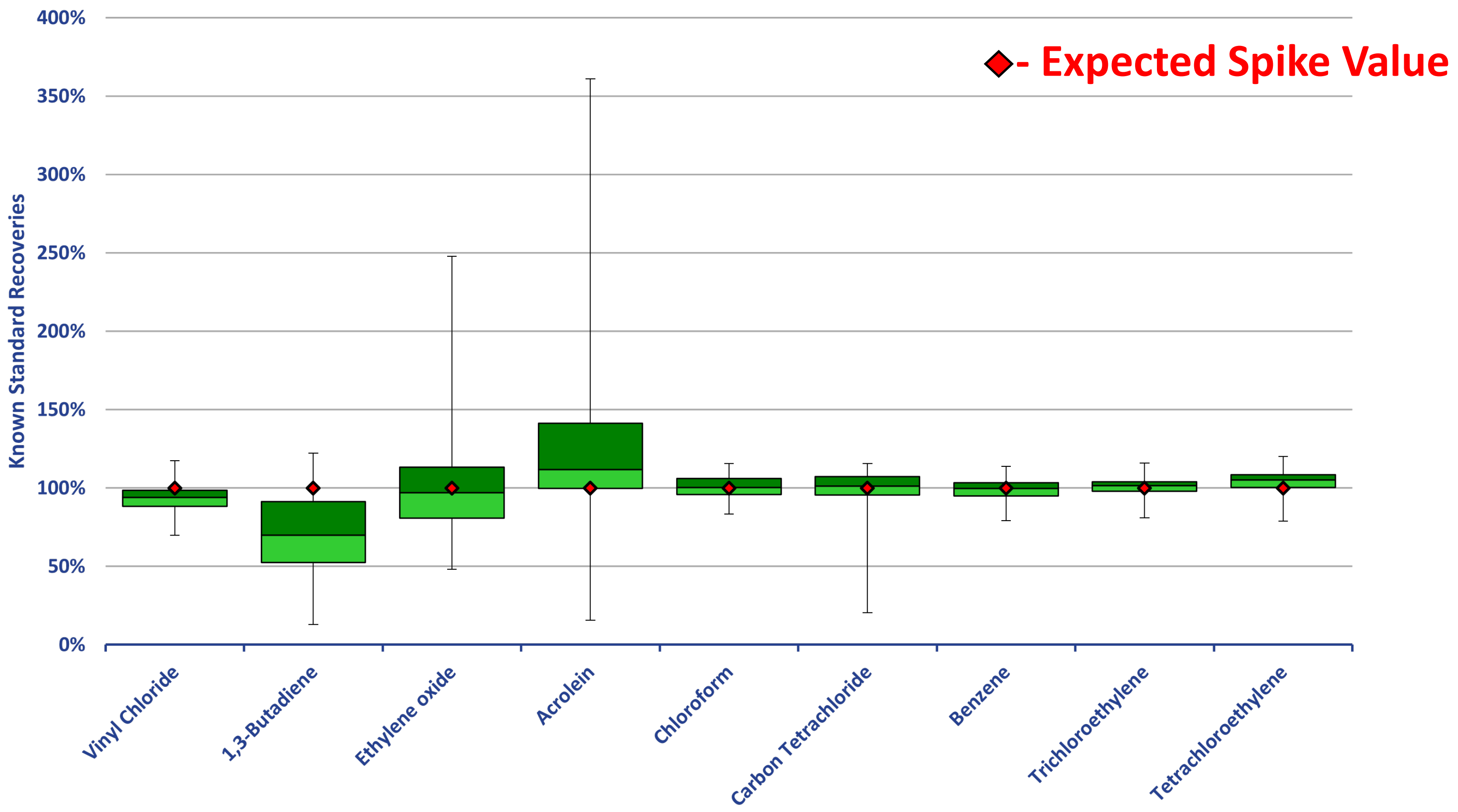
Compound	% Failing TAD	%Failing >5xMDL	Compound tier
Acrolein	80%	7%	1
Ethylene oxide	40%	8%	1
Acetonitrile	15%	2%	2
Toluene	10%	4%	2
Chloromethane	10%	2%	-
Dichloromethane	10%	2%	2
Carbon Disulfide	9%	1%	2
Chloroethane	8%	2%	-
Methyl Methacrylate	7%	0%	2
Dichlorodifluoromethane	3%	2%	-
Trichlorofluoromethane	1%	1%	-
n-Octane	1%	1%	-
Carbon Tetrachloride	1%	1%	1
Benzene	1%	1%	1
Dichlorotetrafluoroethane	1%	0%	-
Trichlorotrifluoroethane	1%	0%	-
Methyl Isobutyl Ketone	1%	0%	2

Canister Known-Standard Challenge

Procedure:

1. Canisters are cleaned and evacuated
2. Filled with low level spike (~300 pptV)
3. Held for 30 days (Hold Time)
4. Analyzed against nominal criteria (<±30.1% Recovery)
5. Failures flagged accordingly

Canister Known-Standard Challenge



Instrument Calibration

- New Calibration Guidelines:
  - MUCH lower bottom points – Calibrations from zero!
  - Biasing towards trace level analysis
  - Flexibility in curve types – Quadratics + Linear fit now!
  - Nominal Recoveries determine success!
- New Calibration Methodology:
  - Individual Standards Method: 1 canister = 1 cal point
  - Effective Dilution Method: Utilization of concentrator for dilution

Instrument Calibration Types

Benzene – AVG RF			
Cal Point	Nominal Recovery	Nominal Concentration	Spike Concentration
1	N/A	N/A	0.000
2	-2.9%	0.020	0.021
3	-0.1%	0.052	0.052
4	3.5%	0.108	0.104
5	6.6%	0.278	0.261
6	-3.3%	1.010	1.044
7	-1.6%	2.055	2.088
8	-2.3%	5.100	5.220

Benzene – Quadratic (Unforced)			
Cal Point	Nominal Recovery	Nominal Concentration	Spike Concentration
1	N/A	-0.002	0.000
2	-22.4%	0.016	0.021
3	-6.6%	0.049	0.052
4	1.3%	0.106	0.104
5	7.1%	0.280	0.261
6	-1.6%	1.027	1.044
7	0.4%	2.096	2.088
8	0.0%	5.219	5.220

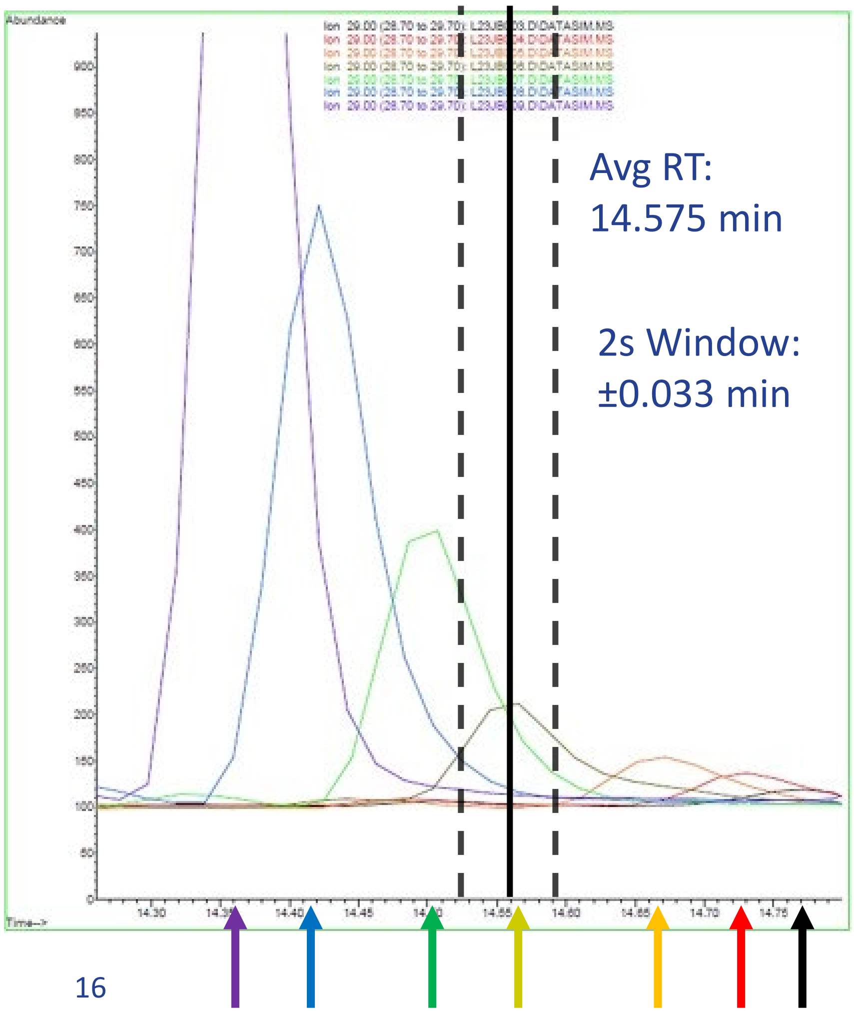
Continuing / Initial Calibration Verification

- CCV criteria is the same
  - <±30.1% recovery
  - Nominals now instead of AVG RF vs CCRF
- Closing CCV is now required in all sequences and recommended every 10 samples

Not overly difficult ***IF*** system is performing well

ERG

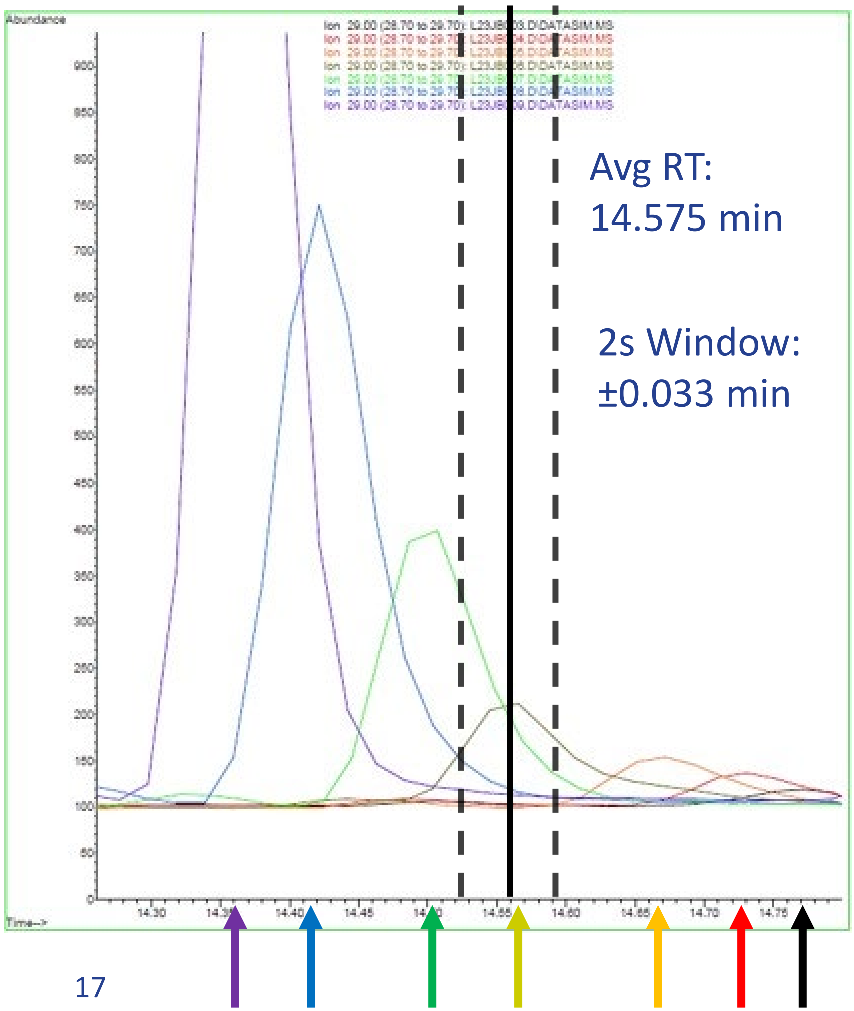
Retention Time – Polar Compound Peak Shifting

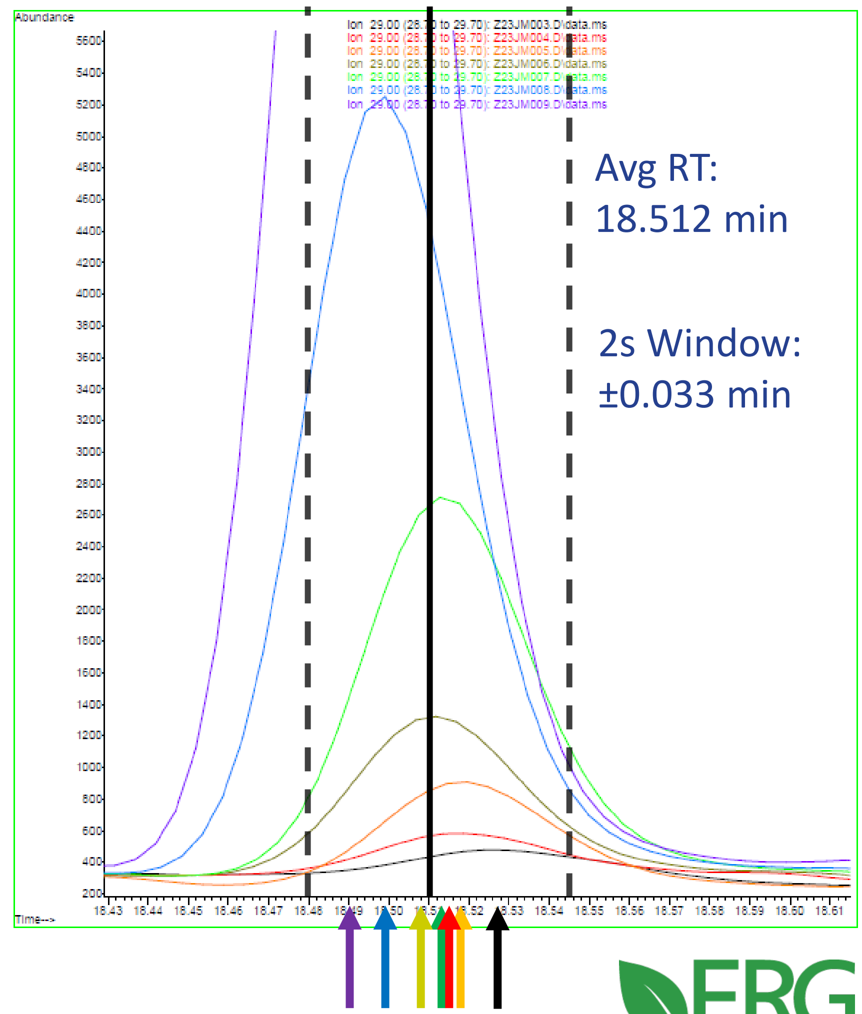


- Polar compounds can shift beyond the 2s RT windows
- Difficulty when non-target compounds appear in the window
- Requires experienced analyst to identify compounds at unknown concentration

ERG

Retention Time – Polar Compound Peak Shifting





Analyte Qualifiers

Compound Name
Vinyl chloride
1,3-Butadiene
Ethylene Oxide
Acrolein
Chloroform
Benzene
Carbon Tetrachloride
Trichloroethylene
Tetrachloroethylene

What About AQS?

Compound Name	Canister Certification	Sampler Certification	Canister Cleaning	Sequence QC	Analytical	All Together
Vinyl chloride						
1,3-Butadiene	CF, LL			LK		CF, LK, LL
Ethylene Oxide	CF, LK	SB, LL		FB		CF, SB, LK, LL, FB
Acrolein	CF, LK		QB-03			QB-03, CF, LK
Chloroform					CE	CE
Benzene					D	D
Carbon Tetrachloride						
Trichloroethylene		SB, LK		QB-01		LK, SB, QB-01
Tetrachloroethylene						

Conclusion

- Canister certification and canister quality seem to impact every aspect of trace level analysis
- Canister certification and blanks are the major issues that ERG has had – spiking has helped to highlight problems with certain canisters
- Data management tools are required for accurate qualification

Canister quality determines analysis quality!

More effort for each sample!

NATTS Audit Results

TO-15 NATTS PT Audit Samples – %Difference from mean of Participating NATTS Labs

(criteria: <±25% Difference)

Pollutant	Qtr 1, 2023	Qtr 2, 2023	Qtr 3, 2023	Qtr 4, 2023	Qtr 1, 2024
1,1,2,2-Tetrachloroethane	-2.1	15.4	-2.4	10.0	-4.1
1,2-Dibromoethane	-2.9	-14.4	-1.7	6.2	-3.2
1,2-Dichloroethane	2.0	5.6	4.5	11.2	4.8
1,2-Dichloropropane	6.7	4.9	-4.5	11.7	-1.8
1,3-Butadiene	21.7	-7.3	0.6	3.8	7.2
cis-1,3-Dichloropropene	3.2	-4.0	-8.1	11.1	-1.6
trans-1,3-Dichloropropene	-5.2	-17.1	-17.3	6.6	-3.0
Acrolein	-21.3	4.0	-3.8	-0.3	10.6
Benzene	9.7	2.1	-1.2	0.0	1.0
Carbon Tetrachloride	17.3	15.0	13.4	5.3	-1.8
Chloroform	7.8	11.9	9.2	11.3	9.5
Dichloromethane	2.1	12.5	7.4	10.3	-2.7
Ethylene Oxide	-3.5	18.3	-3.6	0.9	-6.3
Tetrachloroethylene	3.1	-0.4	5.8	13.2	8.8
Trichloroethylene	8.6	9.0	8.6	8.6	7.4
Vinyl chloride	13.2	-4.3	7.3	11.2	5.8

Questions

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