NATTS Technical Assistance Document Revision 4 – VOCs Sampling and Analysis

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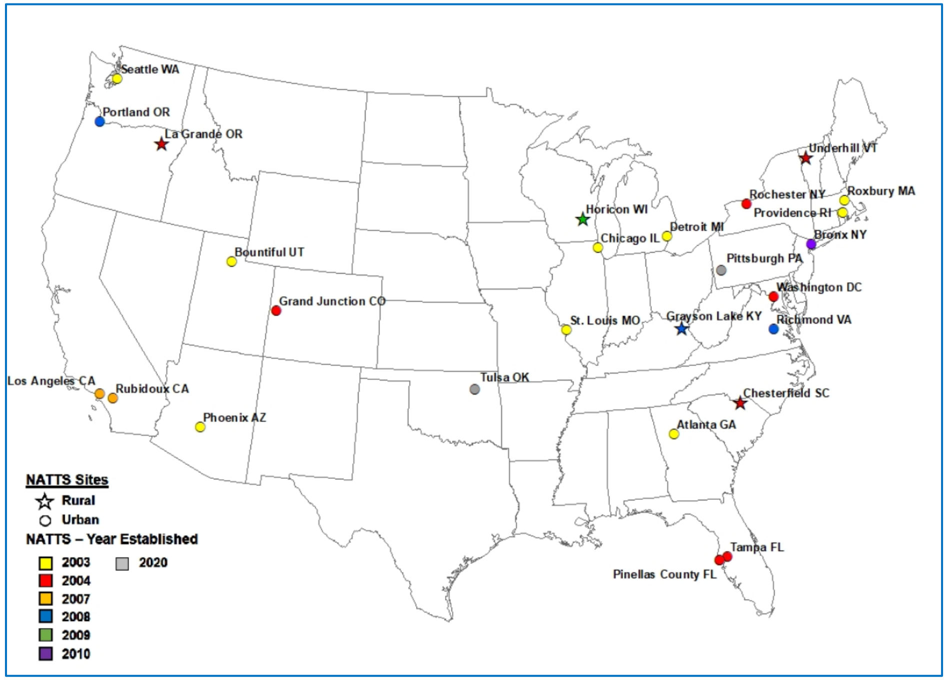
Audience

- NATTS monitoring agencies
- Analytical support laboratories (ASLs)
- Air toxics monitoring agencies
- EPA Regional staff overseeing air toxics monitoring

Presumes attendees are familiar with the guidance in the NATTS Technical Assistance Document (TAD) Revision 3

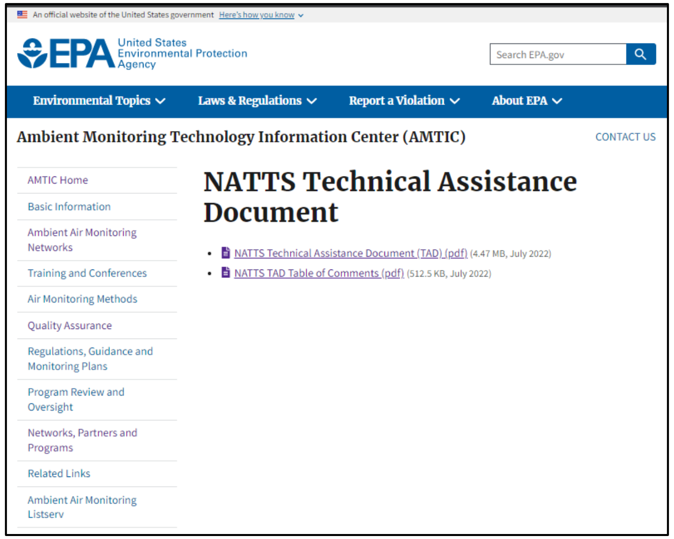


Agenda

- NATTS TAD Revision Rationale
  - Doris Chen & Greg Noah – EPA OAQPS
- TAD Revision 4 Development
- NATTS Implementation of TO-15A In TAD Rev 4
- Notable changes to VOCs measurements
- Question and Answer
  - Please submit questions via the chat

TAD Revision 4 - Development

- The NATTS Technical Assistance Document Revision 4 was recently published in early August 2022
  - https://www.epa.gov/amtic/natts-technical-assistance-document
- For the revision:
  - EPA was aware there were known needed changes:
    - Include new analytes
    - Address updated instrumentation and method guidance (e.g., TO-15A)
    - Address ambiguities and discrepancies in TAD Revision 3
  - EPA sought NATTS and air toxics monitoring stakeholder input on the revision and considered input for inclusion (see link above)
  - EPA assembled a small workgroup of EPA and SLT monitoring agency staff to review and adjudicate comments



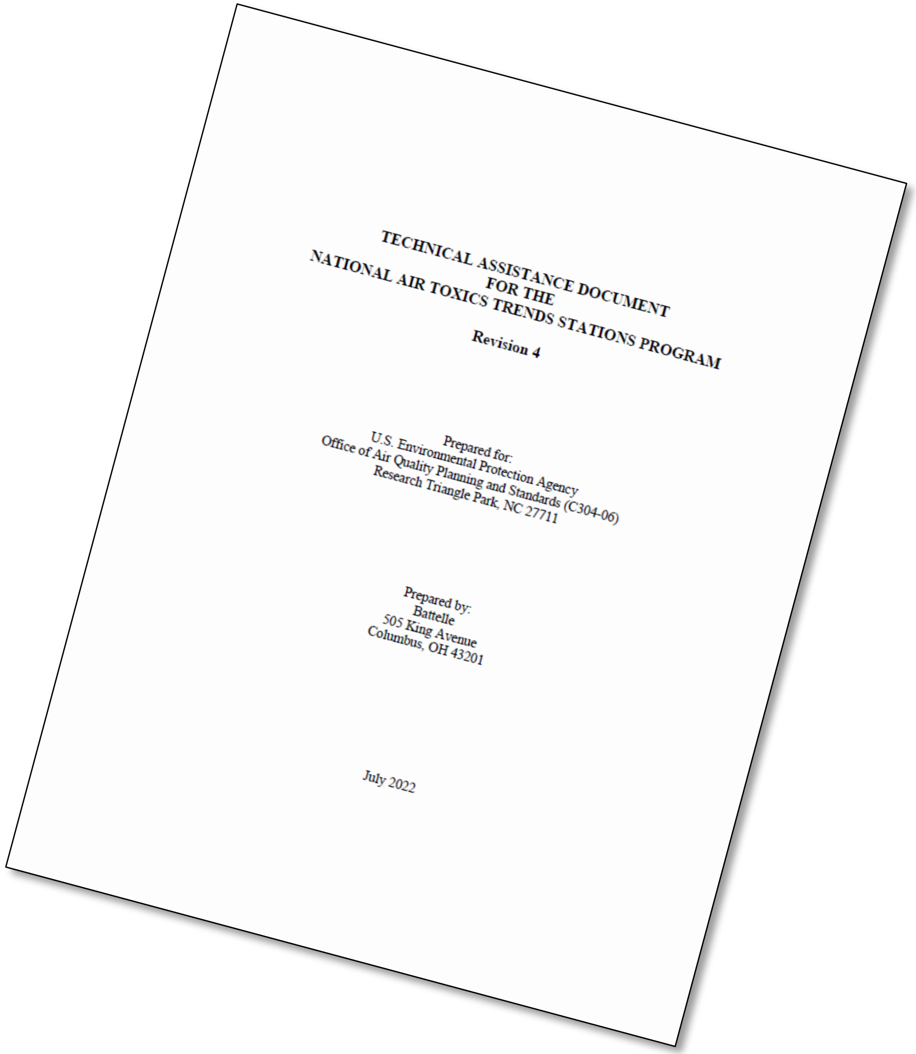
Ambient Monitoring Technology Information Center (AMTIC)

NATTS Technical Assistance Document

- NATTS Technical Assistance Document (TAD) (pdf) (4.47 MB, July 2022)
- NATTS TAD Table of Comments (pdf) (512.5 KB, July 2022)

TAD Revision 4 - Implementation

- NATTS monitoring agencies and analytical support laboratories (ASLs) are expected to be compliant with the Technical Assistance Document Revision 4 by August 2023



TECHNICAL ASSISTANCE DOCUMENT
FOR THE
NATIONAL AIR TOXICS TRENDS STATIONS PROGRAM

Revision 4

Prepared for:
U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards (C304-06)
Research Triangle Park, NC 27711

Prepared by:
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July 2022

Notable Changes for TAD Revision 4 - VOCs

- TO-15A was revised to adjust for measuring lower concentrations (0.5 ppbv reduced to 0.02 ppbv)
- Many updates to TO-15A were common to TAD Rev 3; however, there are additional updates in TAD Rev 4:
  - Canister background acceptance criteria lowered
  - Entire measurement system cleanliness considered
  - Instrumentation improvements
  - MDL procedure updates
  - Sampling flow rate and ending sample pressure determinations
- New Tier I analyte

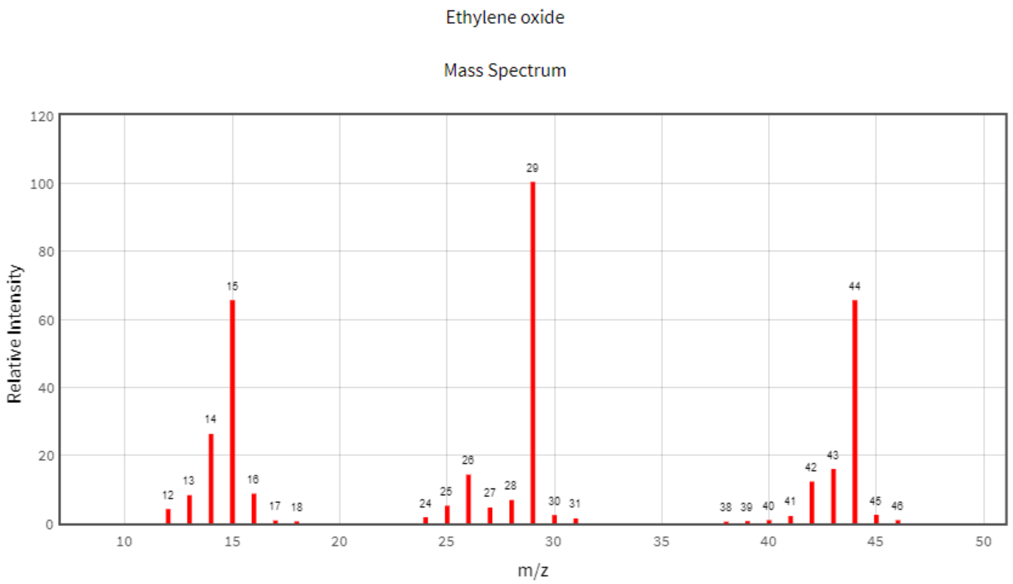
New
and
Improved!

Notable Changes for TAD Revision 4 – VOCs (cont’d)

- Focuses on cleanliness and characterization of entire measurement system
  - Sampling media (canisters)
  - Sampling units
  - Diluent gases
  - Cleaning components
- Clarifies use of zero air and ultra-high purity nitrogen
- Update to precision assessment

Newly Added VOCs Analyte

- New Tier I Required Analyte: Ethylene Oxide (EtO)
- Toxicologically important
- Three challenges to accurately measure EtO
  - Standard gas stability (degradation)
  - Analytical separation (coelutions)
  - Canister growth (enhancement)



https://webbook.nist.gov/chemistry/

Clean Reagent Gases

Clean reagent gases are specified

- Ultra-high purity (UHP) nitrogen limited to:
    - Canister cleaning
    - Standards dilution
    - Method blank
    - Sample dilution
- Hydrocarbon-free (HCF) zero air specified for:
    - Canister qualification
    - Sampling unit qualification
- Recommended to analyze reagent gases to ensure sufficiently clean
    - Each target analyte ≤ 0.03 ppbv or 3xMDL, whichever is lower

VOCs Sampling

Updated Aspects of VOCs Sampling

- Media preparation - canister cleaning
- VOCs samplers are to be qualified before field deployment
  - Zero challenge
  - Known standard challenge
- Canisters are to be qualified before use
  - Leak check
  - Zero challenge (~30 days)
  - Known standard challenge (~30 days)
- Flow characteristics established
  - Subambient sampling - critical not to exceed constant flow range
  - Pressurized sampling - not to exceed 3 psig (~18 psia)

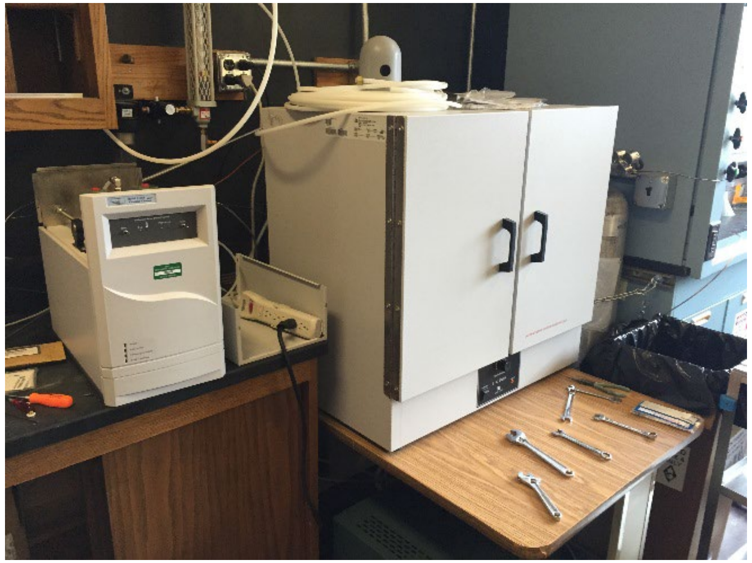
Media Preparation - Canister Cleaning

General recommendations

- Pre-evacuation before connection to cleaning system
- Stainless steel construction, minimal internal volume, oil-free pumps
- Use heat
  - Approximately 70°C (no benefit to exceed 80°C)
  - Heat entire canister and valve evenly
- Purge gas as clean as possible (avoid introducing contaminants during cleaning)
  - Each target compound preferably < 0.02 ppbv
  - Minimal interferences (e.g., non-target compounds such as hydrocarbons)
- Zero air or nitrogen per canister manufacturer recommendations
  - Do not heat silicon ceramic-lined canisters above 80°C to avoid damaging lining
- Humidify purge gas (40 to 60% RH) – aids in scavenging VOCs from interior surfaces
- Five or more cycles of pressurization/evacuation (more typically more effective)
- Final evacuation to ≤ 50 mTorr
- Do not hold at high vacuum – allows diffusion of contaminants back into canisters

Media Preparation - Canister Cleaning (cont'd)

- One batch blank canister to represent 8 or fewer canisters
  - Random
  - Highest overall concentration
  - Highest concentration of specific analytes (e.g., high MW)
  - Composite (TAD Section 4.2.4.2.4)
  - Analyzing all is best practice
- Correct measured concentrations in the batch blank(s) to standard ambient pressure (14.7 psia) (next slide)
- Measurements < 0.03 ppbv or 3xMDL, whichever is lower, corrected to standard atmospheric pressure (1 ata [atmosphere absolute] = 14.7 psia)



Canister Cleaning Criteria – Correction to 1 ata

Correction to standard atmospheric pressure best approximates impact to collected samples

- Measure batch blank canister absolute pressure (P_b)
- Multiply the canister cleanliness criterion (C_{bstd}) by the standard absolute atmospheric pressure P_{std} and divide by the measured absolute pressure (P_b)
- Example:
    - P_b = 20.2 psia
    - C_{bstd} benzene = 0.03 ppbv
    - P_{std} = 14.7 psia
    - 0.03 ppbv · 14.7 psia/20.2 psia = **0.022 ppbv**

$$C_{bcorr} = C_{bstd} \cdot \frac{P_{std}}{P_b}$$

Canister Qualification

Qualify canisters before deployed and every 3 years thereafter

- Leak check
  - Performed over several days by evacuating (~5 psia) or pressurizing (~25 psia)
  - Ensures leak rate is < 0.1 psi/day
- Bias checks
  - Fill canisters with test gas to best mimic ambient air
  - Zero challenge (~30 days)
    - Humidified (40-60% RH) zero air
    - All target compounds ≤ 0.03 ppbv or 3xMDL, preferably < 0.020 ppbv
    - Measurements corrected to 1 ata (next slide)
  - Known standard challenge (~30 days)
    - Humidified (40-60% RH) standard in zero air at (~0.1 to 0.5 ppbv)
    - Concentrations within ±30% of theoretical nominal

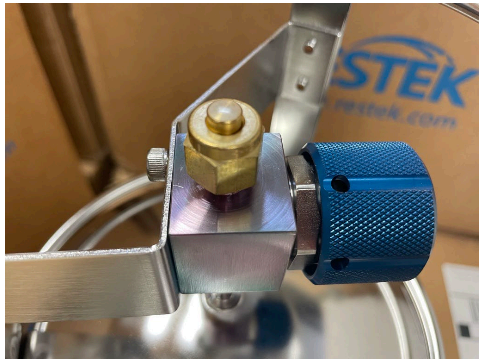
Canister Qualification – Correction to 1 ata

Canister pressure impacts dilution of contaminants

- Correct measurements to standard ambient pressure of 1 ata (14.7 psia)
  - Measure concentration in canister (C_{zmeas})
  - Measure canister absolute pressure with calibrated gauge (P_{can})
  - Multiply C_{zmeas} by P_{can} and divide by EPA standard pressure (P_{stp})
- Example:
  - P_{can} = 17.8 psia
  - C_{zmeas} benzene = 0.011 ppbv
  - P_{stp} = 14.7 psia
  - 0.011 ppbv · 17.8 psia/14.7 psia = **0.013 ppbv**

$$C_{zcorr} = \frac{C_{zmeas} \cdot P_{can}}{P_{stp}}$$

Canister Handling and Maintenance



Keep particulate matter out of the canister!

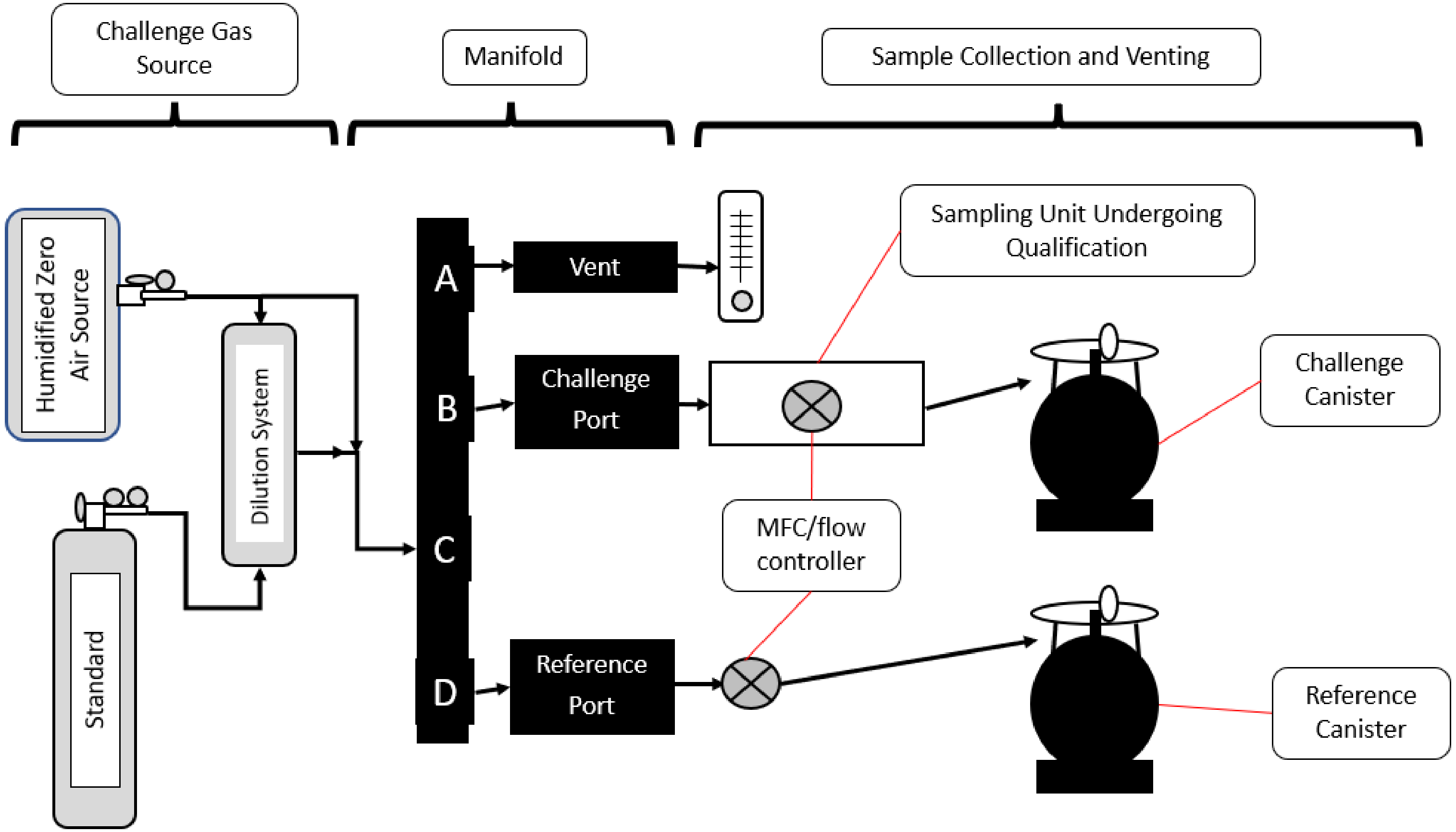
- Install stainless steel particulate filter on sampling unit
- Always install a cap on the canister when valve opening is not connected
- Do not overheat canister (> 80°C), especially when filled with zero air or ambient air – damages lining
- Handle canisters gently
  - Avoids causing leaks in valve connection
  - Avoids damage to canister interior wetted surfaces
- Do not use a wrench on the valve
- Only use a wrench on the fittings after hand tightening

Sampling Unit Qualification

Perform maintenance and calibration before qualification

- Flow rate calibration/adjustment
- Particulate filter replacement
- Bias check
  - Provide test gas to the sampler to best resemble ambient air
  - Collect reference sample upstream and challenge sample through sampler
  - Results of challenge sample are relative to the reference sample
  - Zero challenge
    - Humidified (40-60% RH) zero air
    - All target compounds ≤ 0.03 ppbv or 3xMDL, preferably < 0.020 ppbv after correction for reference sample
  - Known standard challenge
    - Humidified (40-60% RH) standard in zero air at (0.1 to 0.5 ppbv)
    - Concentrations within ±15% of reference sample

Sampling Unit Qualification



Canister Qualification Data Impact

Treat affected compounds from affected canisters accordingly:

Zero Qualification:

- Values exceed 0.03 ppbv or 3-fold MDL – Tier I and non-Tier I treated identically:
  - Qualify as LK (estimated and high bias)
  - Qualify as CF (canister bias check exceeds criteria)
- Values exceed 5x-MDL:
  - Tier I – invalidate associated data as EC (fails critical criterion)
  - Non-Tier I – qualify as above (LK and CF)

Known Standard Qualification:

- Values exceed ±30% of theoretical nominal – Tier I and non-Tier I treated identically :
  - Recovery < 70% qualify as LL (estimated and low bias) and CF
  - Recovery > 130% qualify as LK and CF

Sampler Qualification Data Impact

Treat affected compounds from affected samplers accordingly:

Zero Qualification:

- Values exceed 0.03 ppbv or 3-fold MDL – Tier I and non-Tier I treated identically:
  - Qualify as LK (estimated and high bias)
  - Qualify as SB (sampler bias check exceeds criteria)
- Values exceed 5x-MDL:
  - Tier I – invalidate associated data as EC (fails critical criterion)
  - Non-Tier I – qualify as above (LK and SB)

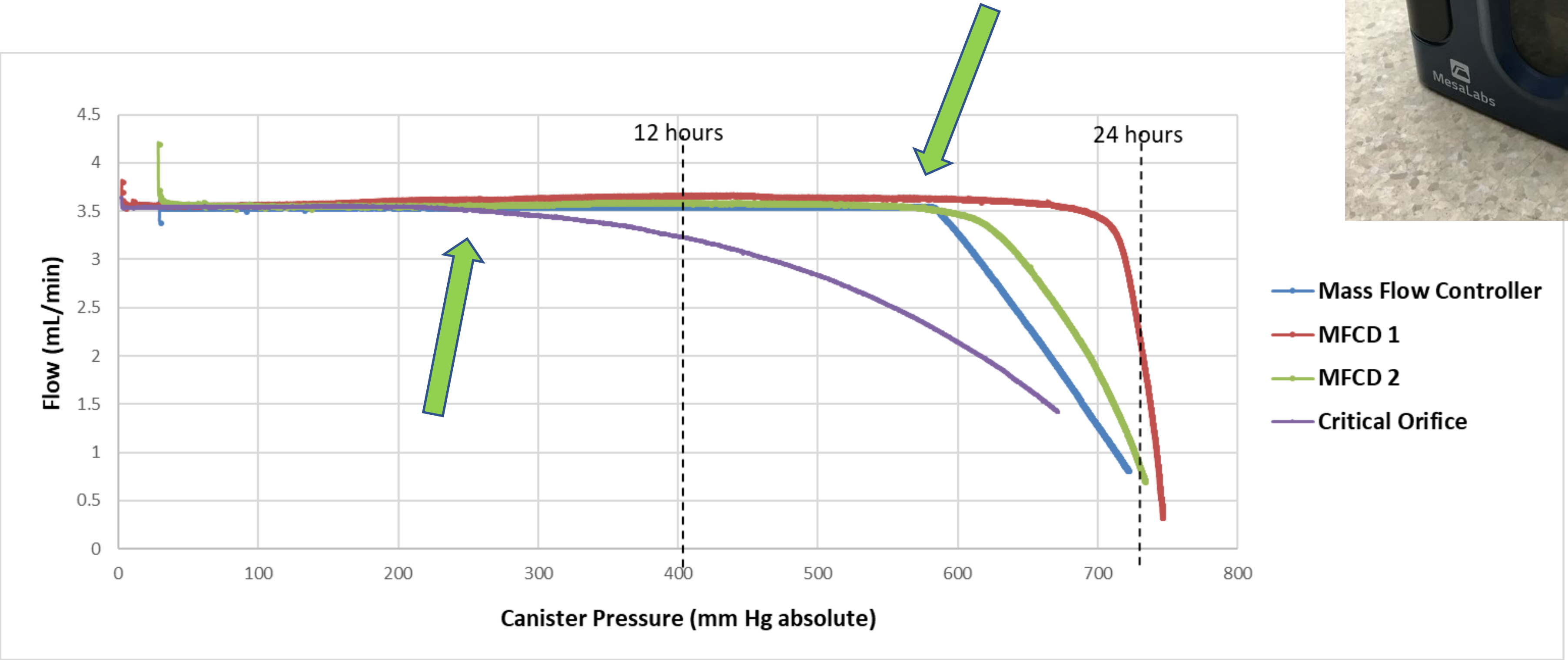
Known Standard Qualification:

- Values exceed ±15% of reference sample – Tier I and non-Tier I treated identically :
  - Recovery < 85% qualify as LL (estimated and low bias) and SB
  - Recovery > 115% qualify as LK and SB

Sampling Unit Flow Rate Establishment

Flow rate is critical to ensure temporally representative sample

Must be constant over 24 hours



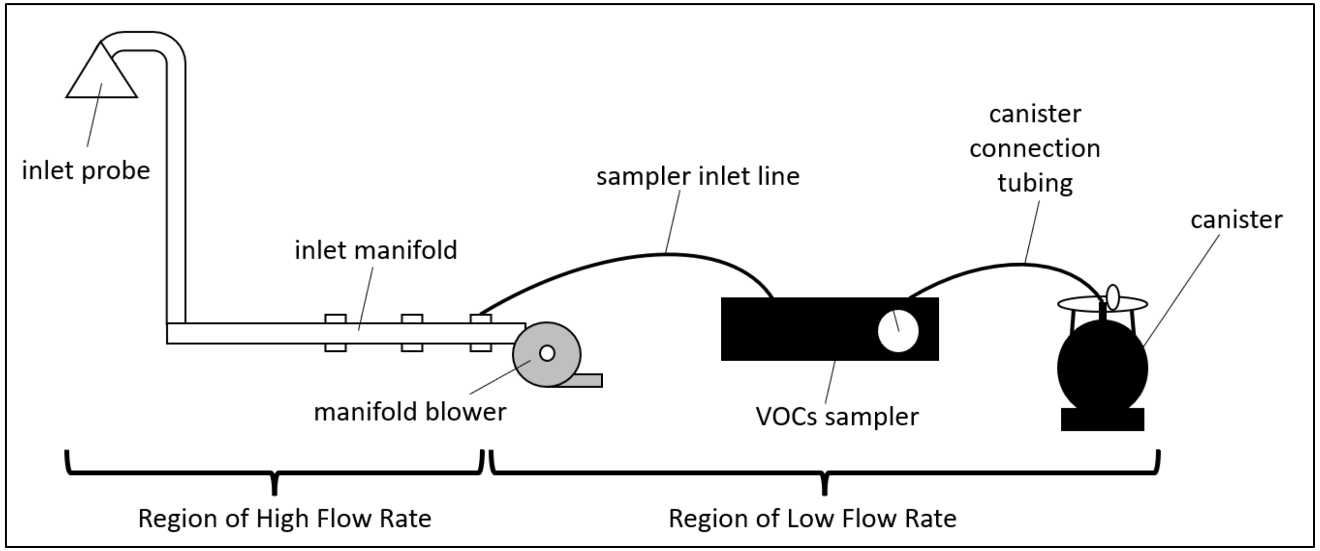
Sampling Unit Flow Rate Establishment

- Flow rates are not critical to concentration measurement (whole air method)
- Subambient sampling *typically* uses the canister vacuum to drive flow (2-3 mL/minute)
    - Must not exceed pressure differential where flow rate is constant (where flow rate decreases by not more than 15%)
    - Sampling ending pressure (i.e., vacuum) is to be determined experimentally for subambient sampling methods
        - Flow rate set to achieve 90% of this final pressure
- Pressurized sampling requires a pump (~ 5 mL/minute)
    - Flow rate should result in a canister pressure of ≤ 3 psig
    - Reduces likelihood of condensation and the complications to precision on replicate analysis

Residence Time Clarification

Previous TAD indicated to minimize residence time

- Residence time will be ≤ 20 seconds to sampling unit inlet
  - If exceeds or is not determined, qualify associated data as SX
- Flow rates are very low ~ 2.5 to 5 mL/minute
  - Likely requires helper pump unless sampling unit has higher draw



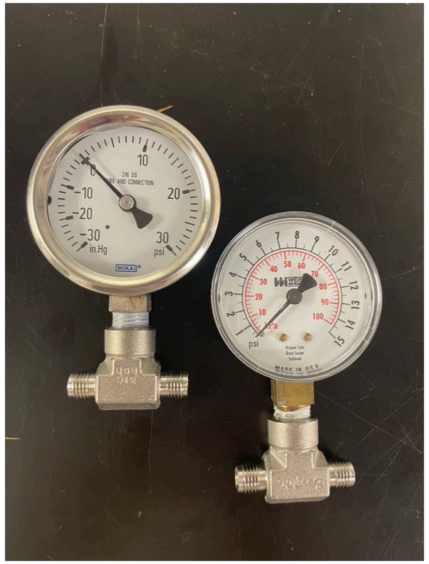
Starting Canister Pressure Threshold

Canister must be sufficiently evacuated

- Prevents sample dilution/contamination with unknown gas
- Starting canister pressure should not exceed 50 mTorr or 0.0067 kPa
- Evacuated canister pressure
  - Should not exceed 5% of desired ending canister pressure
  - *Must* not exceed 10% of desired ending canister pressure (invalidate as AA)
- For example:

		5%		**10%**	
sampling type	**typical ending pressure (psia)**	**psia**	**inHg vacuum**	**psia**	**inHg vacuum**
pressurized	18 psia	0.90	28.1	1.8	26.3
subambient	11 psia	0.55	28.8	1.1	27.7

Sample Retrieval Pressure Requirements



Canister pressures measured on sample retrieval with calibrated gauge

- Canisters should not be at ambient pressure
  - Subambient pressure sampling - leaked – invalidate data as AA (pressure out of limits)
  - Pressurized sampling
    - Incomplete collection – verify sampling period 23 to 25 hours
    - Leaked – qualify data as LJ (estimated)
- Pressurized samples
  - If pressure is > ambient laboratory pressure – no qualification needed
- Subambient samples
  - Cannot exceed 90% of the pressure where flow rate ceases to be constant
    – invalidate data as AA (pressure out of limits)

VOCs Analysis

Canister Sample Receipt

Must have COC

Measure pressure on receipt with calibrated gauge

- Within ±0.5 psia of the retrieval pressure
- Correction permitted for temperature differences (4.2.5)
    - 10°C difference will result in a 0.5 psia pressure change
- For subambient sample receipt pressure compared to retrieval pressure
    - Difference of 0.5 to 1.5 psia – qualify as LJ (estimated) (error in TAD Rev 4 text)
    - Difference > 1.5 psia – invalidate as AA (sample pressure out of limits)

VOCs Stock Standards

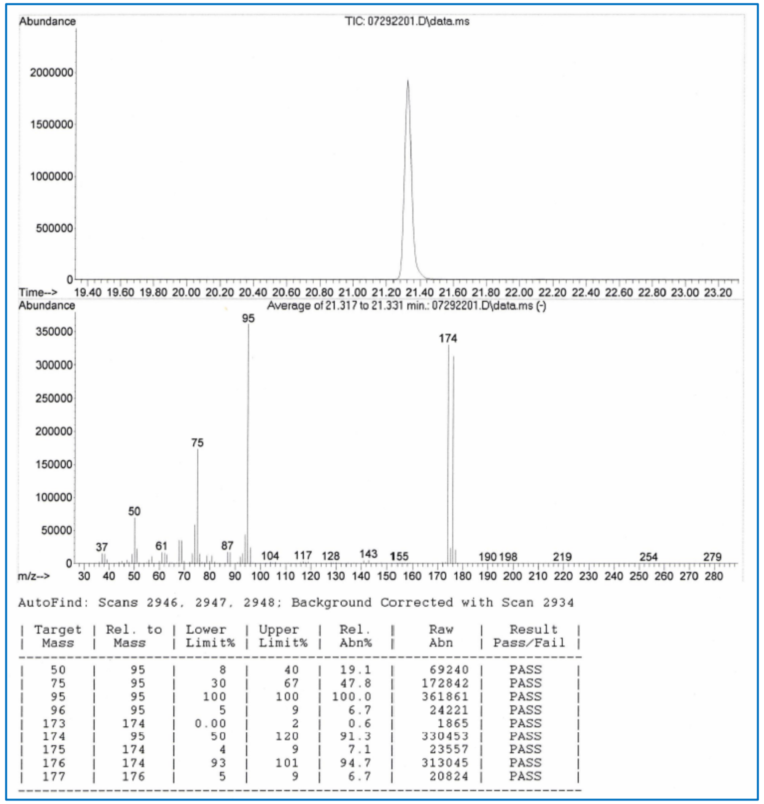
- Purchase from reputable provider
- Select concentrations that are readily diluted to desired working concentrations
- Use certified concentrations in calculations, not requested concentration
  - E.g., requested concentration = 250 ppbv, certified concentration = 244 ppbv
- Recommend annual recertification (not practical for lecture cylinders)
- If using expired standard and standard is recertified:
  - No qualification if recertification value is within 10% of initial value
  - If value is < 90% of initial, qualify affected compounds as LK (estimated, high bias)
  - If value is > 110% of initial, qualify affected compounds as LL (estimated, low bias)
  - If value is < 80% or > 120%, invalidate as EC (exceeds critical criterion)

VOCs Working Standards Preparation

- Dilute one or more stock standard gases using calibrated dilution equipment
- Practice proper cylinder connection hygiene
- Dynamic dilution
  - Verify flow controller is set for metered gas (e.g., air, nitrogen)
  - Calibrate flow controllers to be within 2% of certified flow transfer standard
  - Recommend passivation period of minimally 30 minutes
- Static dilution
  - Calibrate pressure transducers according to manufacturer tolerance

GC/MS Tuning and Instrument Readiness

- Prior to initial calibration (ICAL):
  - System bake-out
  - Ramp GC oven program
  - Perform an air/water check (also before daily analysis)
  - GC/MS tuning (also before daily analysis)
    - Use BFB tuning (not required - applies to quadrupole and ion trap MS), or
    - Follow manufacturer instructions/criteria for tuning
  - Instrument blank (IB) (also before daily analysis)
  - Method blank (MB) (also before daily analysis)
  - Autosampler leak check (ensures canister connections are leak-free)



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AutoFind: Scans 2946, 2947, 2948; Background Corrected with Scan 2934

| Target | Rel. to | Lower  | Upper  |  Rel.  |    Raw    |   Result  |
|  Mass  |  Mass   | Limit% | Limit% |  Abn%  |    Abn    | Pass/Fail |
-------------------------------------------------------------------------
|   50   |    95   |      8 |     40 |   19.1 |     69240 |   PASS    |
|   75   |    95   |     30 |     67 |   47.8 |    172842 |   PASS    |
|   95   |    95   |    100 |    100 |  100.0 |    361861 |   PASS    |
|   96   |    95   |      5 |      9 |    6.7 |     24221 |   PASS    |
|  173   |   174   |   0.00 |      2 |    0.6 |      1865 |   PASS    |
|  174   |    95   |     50 |    120 |   91.3 |    330453 |   PASS    |
|  175   |   174   |      4 |      9 |    7.1 |     23557 |   PASS    |
|  176   |   174   |     93 |    101 |   94.7 |    313045 |   PASS    |
|  177   |   176   |      5 |      9 |    6.7 |     20824 |   PASS    |
-------------------------------------------------------------------------
```

Initial Calibration

- ICAL required
  - Initially
  - When continuing calibration verification (CCV) fails (due to calibration drift)
  - After instrument maintenance that changes the calibration response
    - Preconcentrator trap replacement
    - Column replacement
    - Cleaning MS source
  - When internal standard (IS) response is out of specification (not due to matrix)
- Minimum of five calibration concentration levels, more recommended
  - Minimum of eight if employing quadratic regression modeling
- Should cover approximate normal measurement range, as practical
  - Approximately 20 to 5000 pptv

Initial Calibration (cont'd)

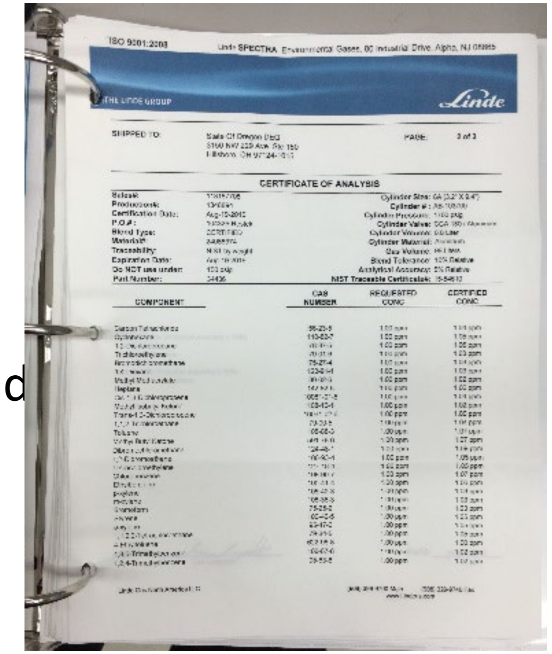
- Established by analysis of known concentration standards
- Individual standards method
  - Each concentration level has a dedicated canister
  - Does not expose the preconcentrator to differing amounts of water
- Effective dilution method
  - Preconcentrator trap experiences different level of penetration into sorbent
  - Analysts should demonstrate linearity of volume delivery using individual standards method first

Initial Calibration - Example

- Establish a calibration curve with the following 7 concentrations:
  - 25, 50, 100, 200, 500, 2000, 5000 pptv
  - 500 cc is the normal analysis volume
- Individual standards method
  - Each concentration level in its own canister
  - Analyze 500 cc of each
- Effective dilution method
  - Strongly recommend minimum of two canisters at different concentration levels
  - Proportional different volumes analyzed to provide effective concentrations
    - Prepare 250 pptv and 5000 pptv canisters

standard concentration (ppbv)	**volume analyzed (cc) from 250 pptv canister**	**volume analyzed (cc) from 5000 pptv canister**
25	50	NA
50	100	NA
100	200	NA
250	500	NA
500	NA	50
2000	NA	200
5000	NA	500

Initial Calibration (cont’d)



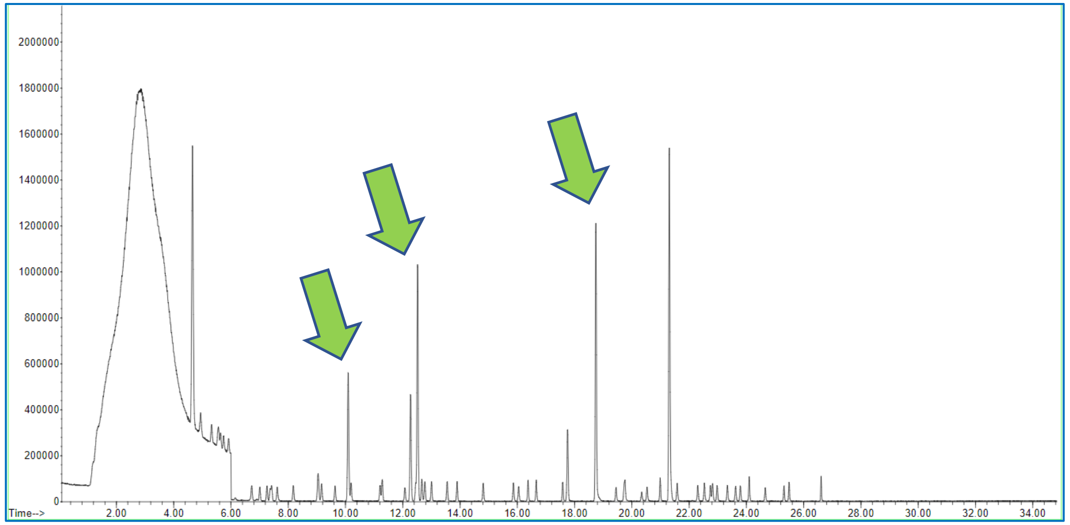
- Calibration curve modeling
  - Average relative response factor (RRF)
    - Assumes calibration curve goes through origin
    - Must be < 30% relative standard deviation for each compound
  - Linear least-squares regression
    - Correlation coefficient (r^2) ≥ 0.995
  - Quadratic least-squares regression
    - $r^2 \geq 0.995$
  - Instrument response for each calibration level is plugged into the calibration model
    - Each concentration level must be within ±30% of the theoretical nominal
  - Calibration levels cannot be excluded unless they are the lowest concentration
- Verify calibration with second source calibration verification (SSCV)
  - Must be within ±30% of theoretical nominal concentration

Routine Quality Control (QC)

- Continuing calibration verification (CCV)
  - Concentration in lower 1/3 of calibration curve range
  - Each day of analysis once ICAL is established (before samples)
  - Recommended after each 10 analyses
  - Concludes (brackets) each daily analytical sequence
  - Must be within ±30% of theoretical nominal concentration
- Blanks - must be ≤ 0.03 ppbv or 3xMDL, whichever is lower
  - Instrument blank (not required, but strongly recommended)
    - No gas is sampled, injection of carrier gas from desorbed trap
  - Method blank – required each day of analysis
  - Dilution blank – required with each ICAL
    - Demonstrates gas employed for preparing standards is sufficiently clean
- Replicate analysis – precision covered on subsequent slide

Internal Standards (ISs)

- Each injection is to have minimally one IS
- Deuterated homologues or non-typical natural compounds that behave chemically like target VOCs
- Recommend three ISs roughly covering the molecular weight range
  - 1,4-difluorobenzene
  - d5-chlorobenzene
  - Bromochloromethane
- IS concentration should provide a peak response roughly equal to a VOC in the highest calibration standard level

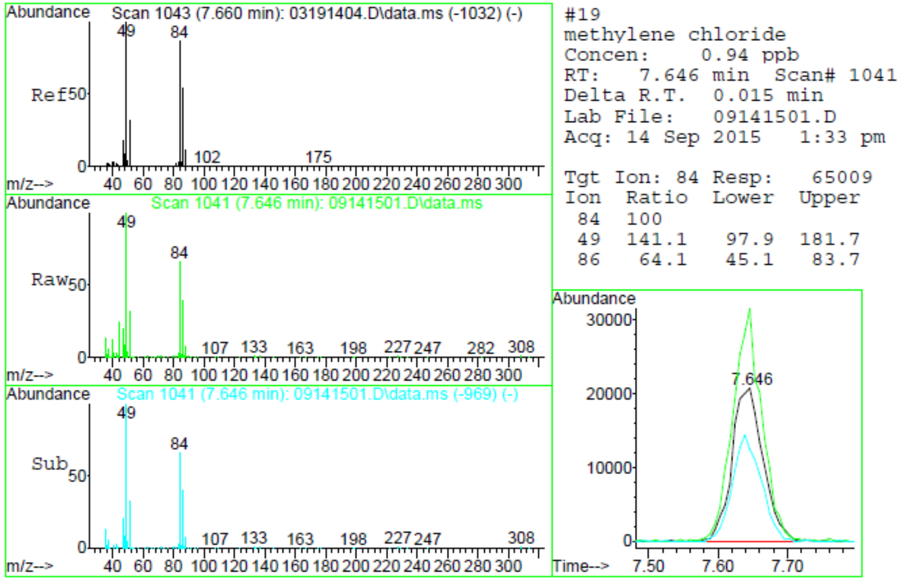


Analyte Identification

Positive identification requires meeting four criteria

1. Peak retention time (RT) within 2 seconds of ICAL average RT
2. Relative abundance of at least one qualifier ion within 30% of the relative abundance of the ICAL average
   - Low limit should never be zero
3. Signal-to-noise ratio (S:N) > 3:1, preferably > 5:1 for target and qualifier ion
4. Target and qualifier ion peaks co-maximized (within one scan)

Analytes may be positively identified by an experienced analyst when any of these four criteria is not met. Rationale for such positive identification should be documented and reported data should be appropriately qualified.



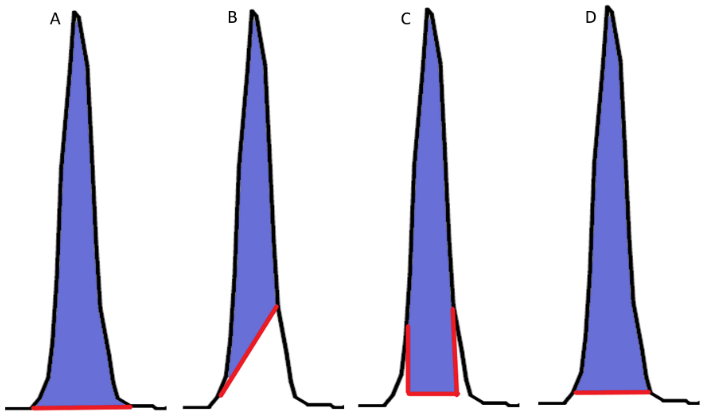
```
#19
methylene chloride
Concen:     0.94 ppb
RT:    7.646 min  Scan# 1041
Delta R.T.  0.015 min
Lab File:   09141501.D
Acq: 14 Sep 2015   1:33 pm

Tgt Ion: 84 Resp:   65009
Ion  Ratio  Lower  Upper
 84  100
 49  141.1   97.9  181.7
 86   64.1   45.1   83.7
```

Peak Integration

Integration of chromatographic peaks should be:

- Technically justifiable
  - Not adjusted to meet acceptance criteria
- Optimized through automation in software
  - Minimizes manual intervention and increases consistency
- Consistent among standards, QC samples, and ambient samples
- Manually changed when needed, with justification
- Reviewed by a peer for suitability



Refer to Appendix D for guidance

Method Detection Limits (MDLs)

We will discuss MDLs in-depth in the subsequent TAD Revision 4 webinar

- Tier I VOC determined MDLs must be less than the values listed in Table 4.1-1 (note EtO was lowered)
- Employ the typical variety of (qualified) canisters in the fleet for determining MDLs
- All method steps for routine analysis must be followed
  - Analysis volume same as normal analysis volume
  - Typical sample dilution steps
  - Include routine method blank data from different canisters (should not include numerous analyses of same blank canister)
  - Must use HCF zero air for spiked sample preparation

Tier I VOC	**MDL MQO (ppbv)**
Acrolein	0.039
Benzene	0.041
1,3-Butadiene	0.050
Carbon tetrachloride	0.027
Chloroform	0.10
Ethylene oxide	0.030
Tetrachloroethylene	0.025
Trichloroethylene	0.037
Vinyl chloride	0.043

VOCs Data Handling

Routine QC Criteria

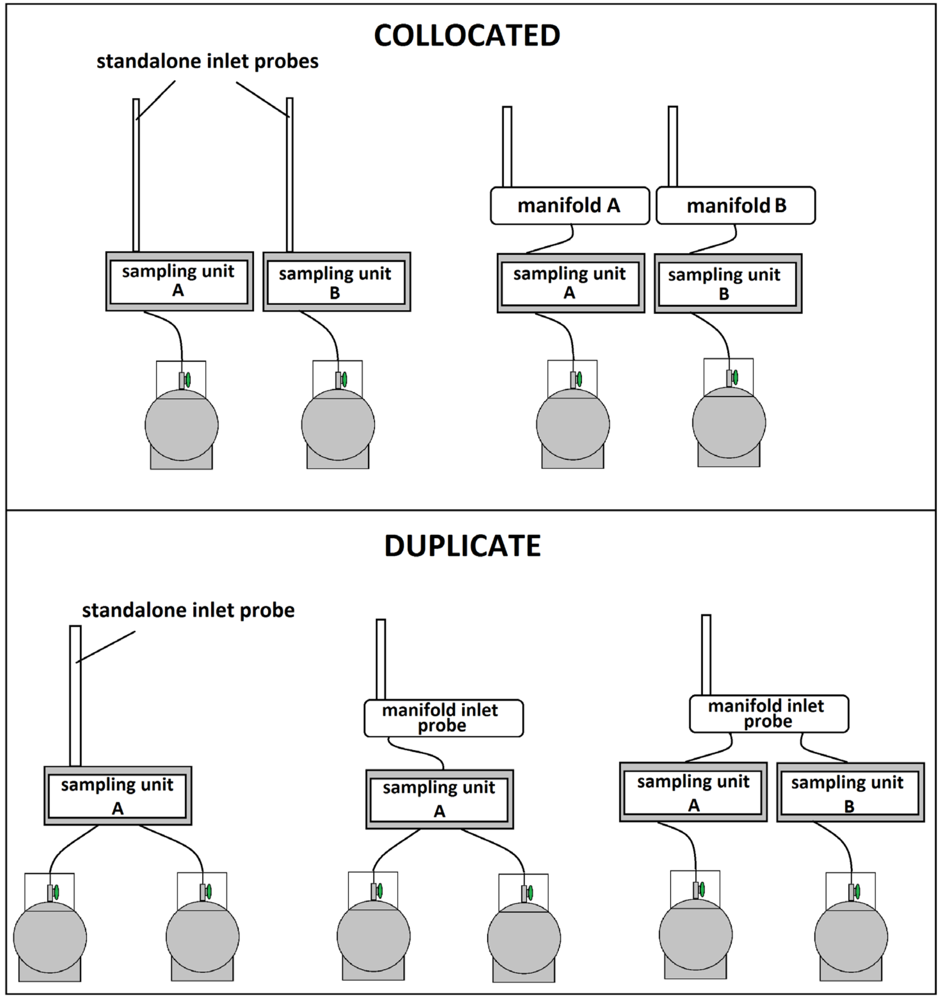
For Tier I VOCs with failing QC criteria for the ICAL, SSCV, or CCV, the data should not be reported, samples should be reanalyzed with passing QC, and the acceptable data reported

- When samples cannot be reanalyzed with passing QC, data for Tier I VOCs will be invalidated as EC (failure of critical criterion)
- Non-Tier VOCs data can be qualified as listed in Section 7.1
- Data are not invalidated for criteria exceedances for blanks or precision analyses
  - Refer to Section 7.1 for data qualification guidance

Precision Evaluation

Collocated, Duplicate, and Replicate Analyses – definitions remain unchanged

- Collocated – primary and collocated must have separate inlet probes to ambient air
- Duplicate – primary and duplicate share inlet probe to ambient air (may have separate sampling instruments)
- Replicate – second discrete analysis from the same canister



Precision Evaluation

Precision evaluated as relative percent difference (RPD)

RPD = absolute difference divided by average as a percentage

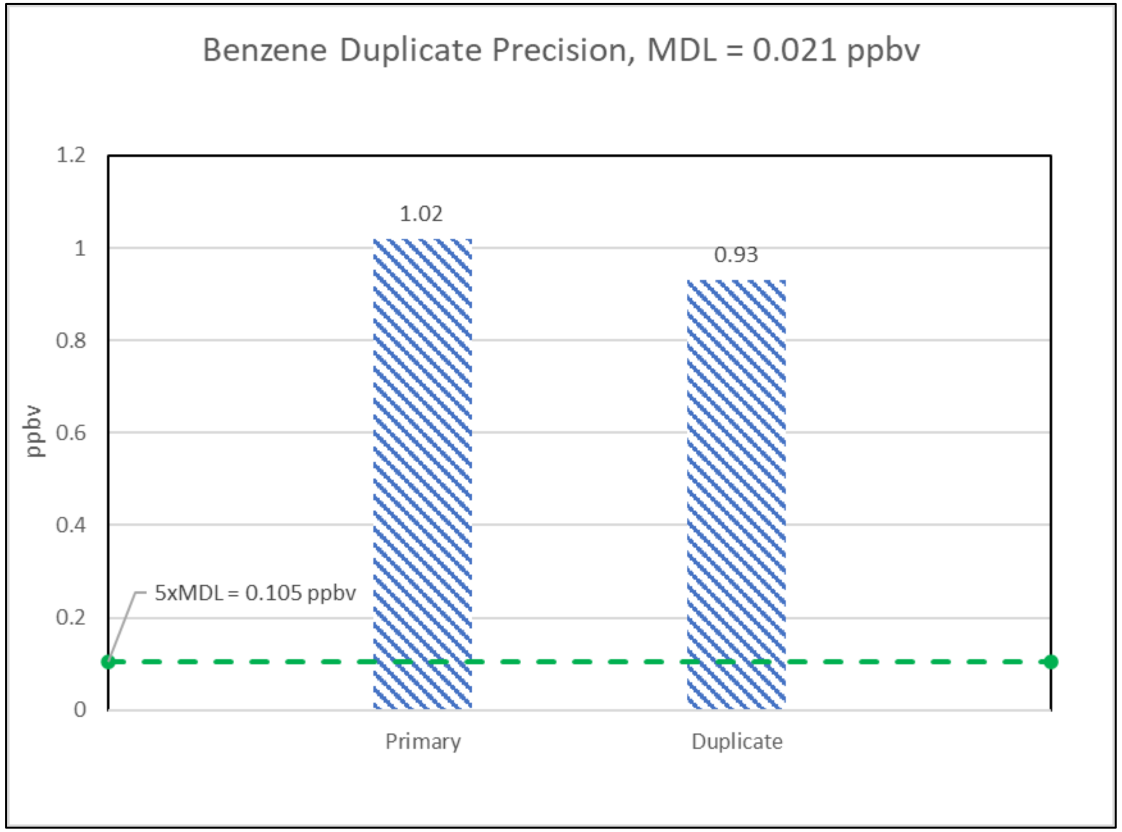
- Not needed when both measurements are < 5xMDL
  - For TAD Rev 3, when either was < 5xMDL, no evaluation was needed
  - This overlooked clearly discrepant precision measurements
- Evaluation is needed when one or both precision measurements is above the 5xMDL threshold
  - Straightforward when both measurements are > 5xMDL
  - Substitution needed when only one measurement is > 5xMDL
- RPD must be < 25.1%

Precision Evaluation

SCENARIO 1

Both benzene precision measurements are > 5xMDL

- Visually reasonable
- Primary = 1.02 ppbv
- Duplicate = 0.93 ppbv
- 5xMDL = 0.105 ppbv
  - MDL = 0.021 ppbv
- RPD = 9.2% (meets precision criteria)

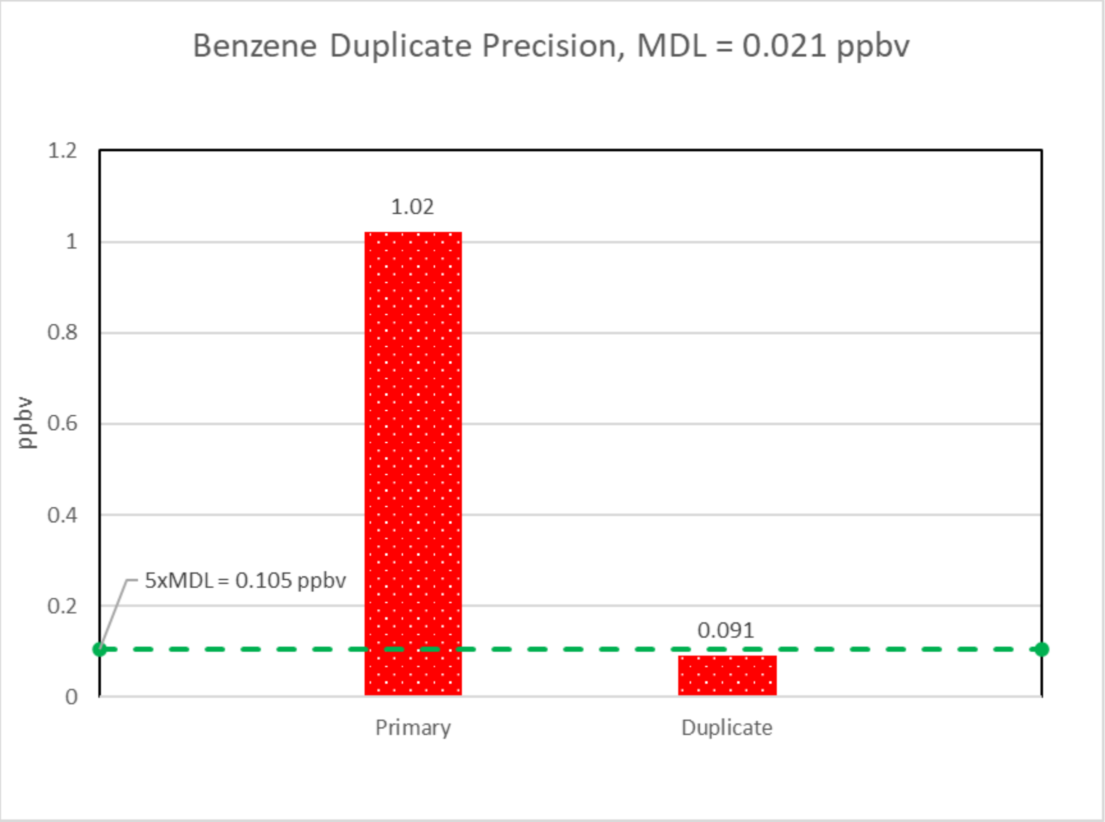


Precision Evaluation

SCENARIO 2

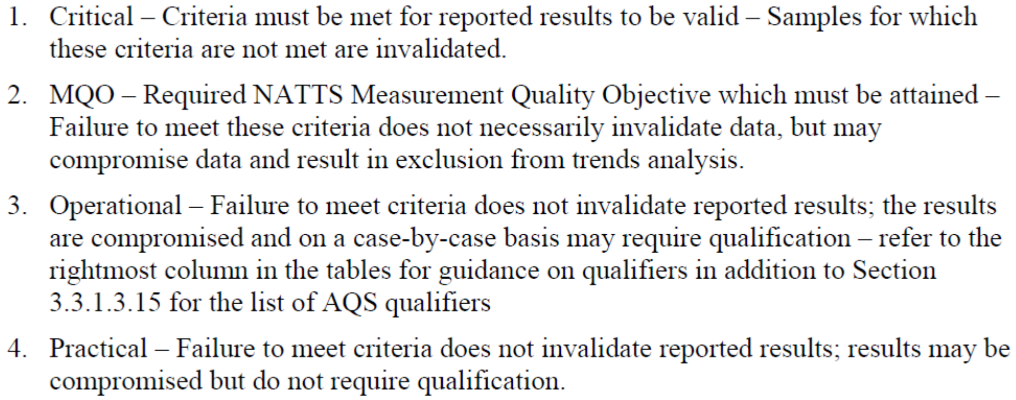
Only one precision measurement is > 5xMDL (assessment wasn't required under TAD Rev 3)

- Clearly discrepant
- Primary = 1.02 ppbv
- Duplicate = 0.091 ppbv
- 5xMDL = 0.105 ppbv
  - MDL = 0.021 ppbv
- RPD = 167%
- Substitute the 5xMDL value (0.105 ppbv) for the duplicate value
  - RPD = 163%, far exceeds the precision criterion

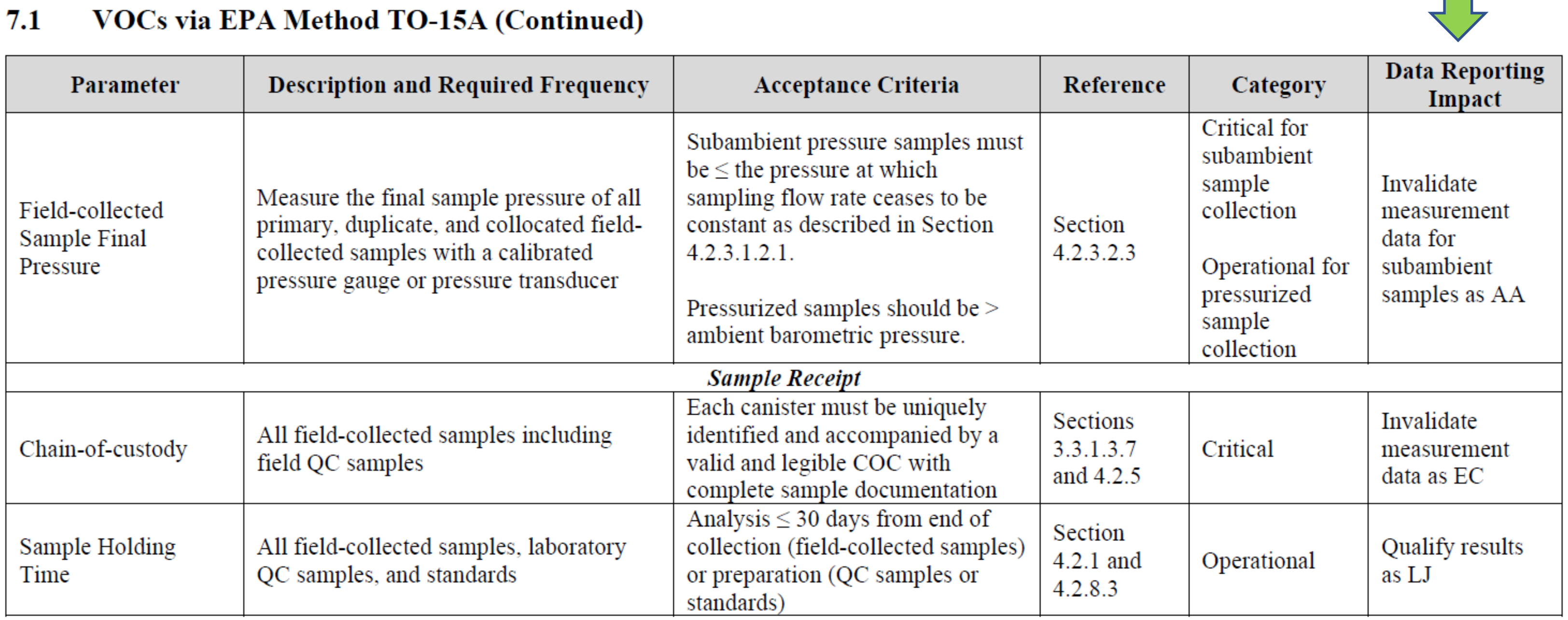


Validation Tables

- Section 7.1
- Column added for data reporting impact
- Aspects are detailed in text describing rationale
- Will cover additional details in next TAD webinar



1. Critical – Criteria must be met for reported results to be valid – Samples for which these criteria are not met are invalidated.
2. MQO – Required NATTS Measurement Quality Objective which must be attained – Failure to meet these criteria does not necessarily invalidate data, but may compromise data and result in exclusion from trends analysis.
3. Operational – Failure to meet criteria does not invalidate reported results; the results are compromised and on a case-by-case basis may require qualification – refer to the rightmost column in the tables for guidance on qualifiers in addition to Section 3.3.1.3.15 for the list of AQS qualifiers
4. Practical – Failure to meet criteria does not invalidate reported results; results may be compromised but do not require qualification.



7.1 VOCs via EPA Method TO-15A (Continued)

Parameter	Description and Required Frequency	Acceptance Criteria	Reference	Category	Data Reporting Impact
Field-collected Sample Final Pressure	Measure the final sample pressure of all primary, duplicate, and collocated field-collected samples with a calibrated pressure gauge or pressure transducer	Subambient pressure samples must be ≤ the pressure at which sampling flow rate ceases to be constant as described in Section 4.2.3.1.2.1. Pressurized samples should be > ambient barometric pressure.	Section 4.2.3.2.3	Critical for subambient sample collection Operational for pressurized sample collection	Invalidate measurement data for subambient samples as AA
		Sample Receipt			
Chain-of-custody	All field-collected samples including field QC samples	Each canister must be uniquely identified and accompanied by a valid and legible COC with complete sample documentation	Sections 3.3.1.3.7 and 4.2.5	Critical	Invalidate measurement data as EC
Sample Holding Time	All field-collected samples, laboratory QC samples, and standards	Analysis ≤ 30 days from end of collection (field-collected samples) or preparation (QC samples or standards)	Section 4.2.1 and 4.2.8.3	Operational	Qualify results as LJ

Ethylene Oxide

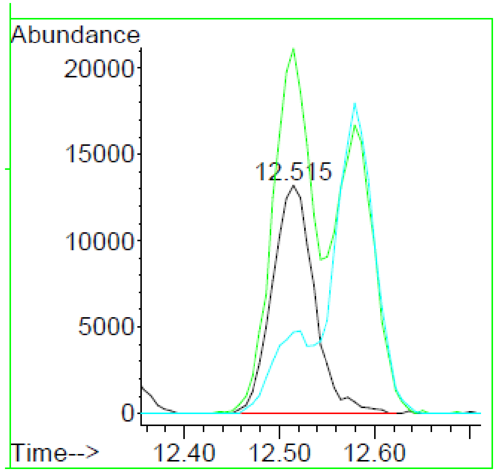
Ethylene Oxide Measurement Challenges

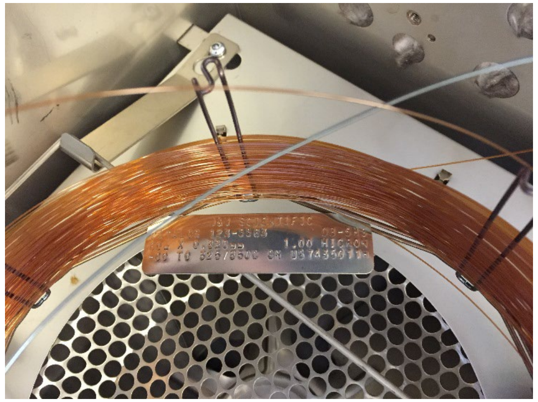
EtO measurements are complicated compared to well-behaved VOCs (e.g., benzene)

- Potential coelutions with other compounds or interferences that share the same m/z
- Stock standard gas stability
- Growth of EtO in canisters

Ethylene Oxide Coelutions

- Potential coelutions with other compounds or interferences that share the same m/z (assumes 70 mV EI impact MS) – 15, 29, 44
  - trans-2-butene (15, 29, 42, 43)
  - acetaldehyde (15, 29, 42, 43, 44)
  - methanol (15, 29)
  - 2,2-dimethylpropane (15, 29, 42, 43)
  - Others
- Verify GC/MS system is leak free – presence of water, CO_2 (m/z 44)
- Operate MS in SIM or SIM/SCAN mode to assess coeluting interferences
- Parameters to change
  - Oven temperature program (may need to use cryo cooling)
  - Column – longer (e.g., 100-m) or different stationary phase (increase polarity) – can impact elution order and performance of other VOCs
  - Adjust water management parameters – purge times and/or flow rates



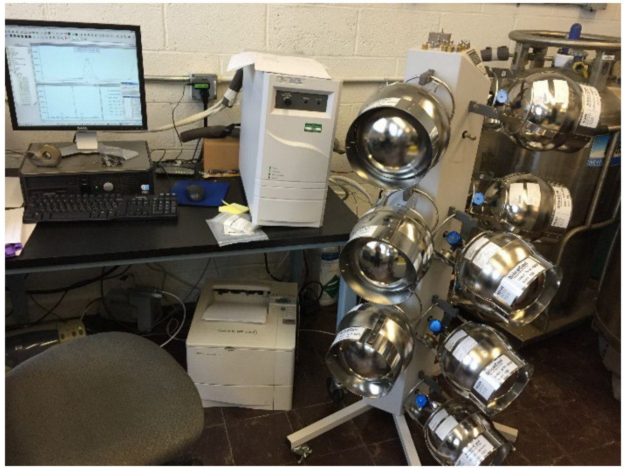


Ethylene Oxide Stock Standards

- EPA ORD studying gas concentration stability from different manufacturers and at different concentrations
- Second source standard is needed to verify standard concentrations are stable
- When primary (calibration) and second source (verification) standards show trending disagreement toward percent difference of 30%, this indicates a standard stability problem
    - If second source recovers high (> 130%) - primary standard implicated
    - If second source recovers low (< 70%) second source standard implicated

Ethylene Oxide - Canisters

- Growth of EtO in canisters
  - Concentration increases in oxygenated environments with humidity
    - HCF zero air
    - ambient air
  - Demonstrates similar behavior as acrolein and other oxygenated VOCs
  - Requires canister qualification to avoid high measurement bias
    - Cannot be performed with UHP nitrogen (inert)
  - EPA commissioning study to investigate
    - Impact of canister type (silicon-ceramic lined vs electropolished)
    - Canister conditions that correlate to EtO growth
    - Potential best practices for cleaning, remediation, and maintenance
  - Track canisters so their history is known
  - Designate canisters for ambient air use (sampling, calibration, QC)



Additional Resources

- EPA Method TO-15A
  https://www.epa.gov/sites/default/files/2019-12/documents/to-15a_vocs.pdf
- TO-15A webinar questions/responses – June 3, 2020
  https://www.epa.gov/sites/default/files/2020-08/documents/to-15a_webinar_june_3_2020_comment_table.pdf

Question and Answer

Please submit questions via the chat. Note that not all questions may be directly addressed within this webinar.
Questions and answers will be compiled into a document for distribution.

Thank you

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