EPA Method TO-15A: Important Updates for the NATTS Network and Ambient Air Measurements

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EPA Method TO-15A - Overview

https://www.nytimes.com/2018/08/20/opinion/trump-republican-truth-climate-change.html?action=click&pgtype=Homepage&clickSource=story-heading&module=opinion-c-col-left-region&region=opinion-c-col-left-region&WT.nav=opinion-c-col-left-region

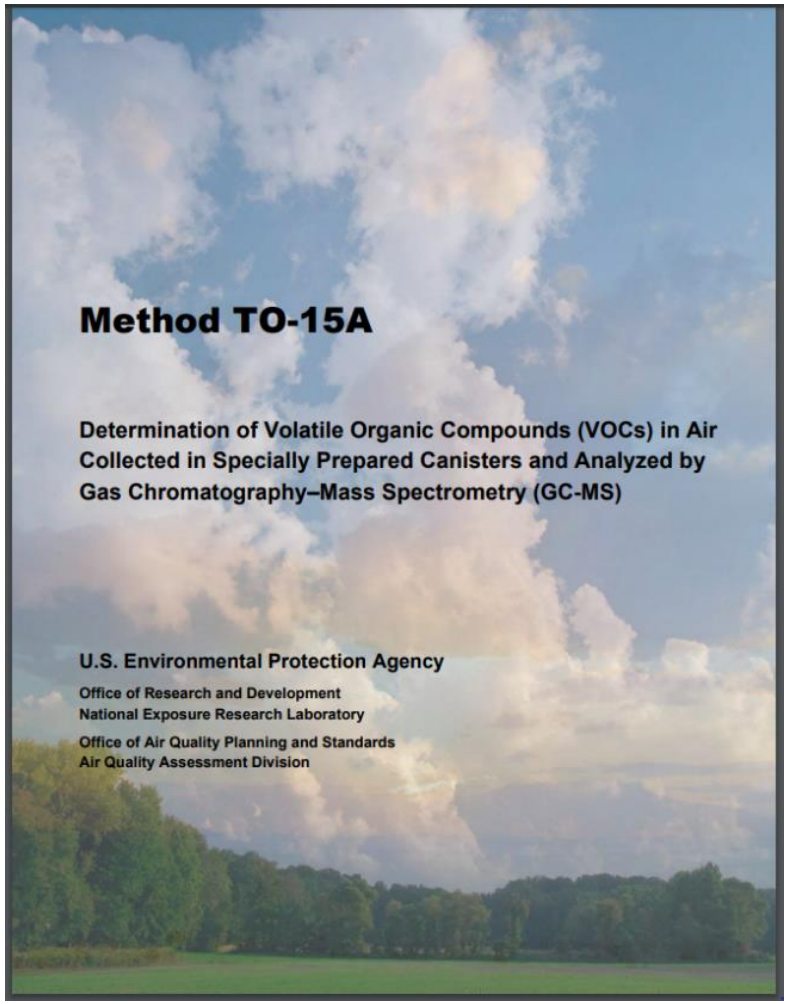
Updates Related to Ambient Air Measurements

- Standards, Reagents, and Gases
- Sampling and Equipment
- Canister Media, Cleaning, and Qualification
- Break/Questions
- Calibration Standards
- GC/MS Instrumentation
- Calibration, Analysis, and Data Interpretation
- Method Detection Limits
- Open Discussion/Questions

Disclaimer: Use of trade names does not indicate endorsement or guarantee fitness for purpose.

EPA Method TO-15A - Overview

- EPA Compendium TO-15A published September 2019
- https://www.epa.gov/amtic/compendium-methods-determination-toxic-organic-compounds-ambient-air
  - Summary table comparing criteria for TO-15A and NATTS TAD Revision 3 to be posted to AMTIC



Acknowledgements

- Authors
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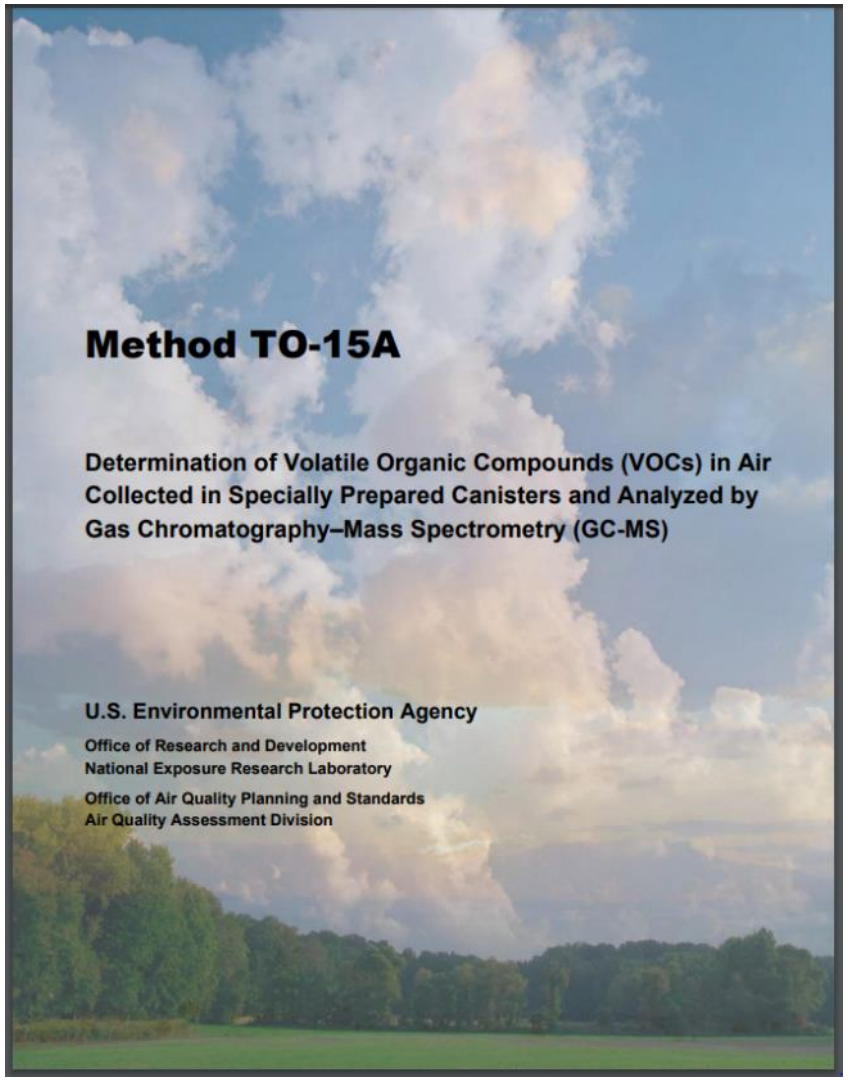
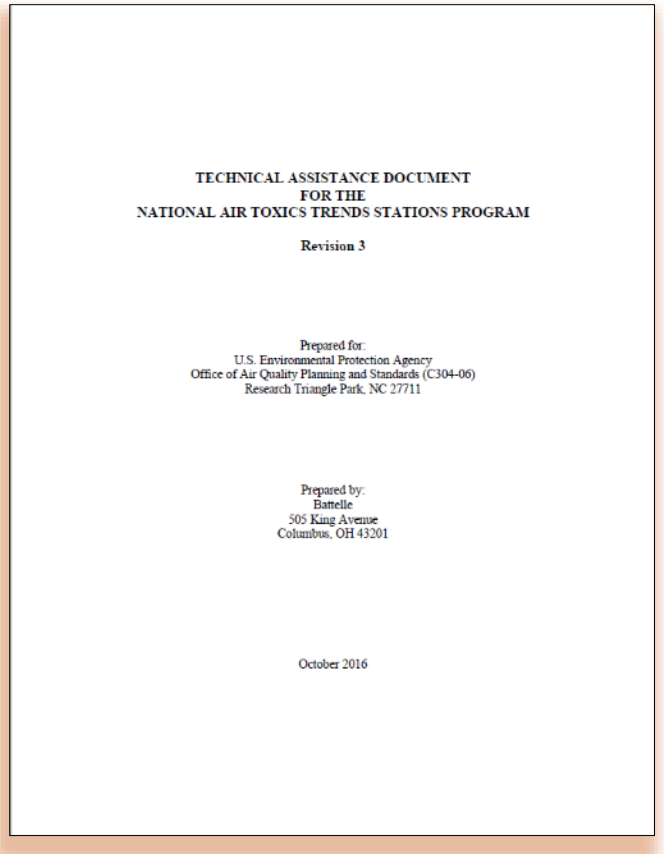
- User Community



EPA Method TO-15A - Overview

- EPA Office of Research and Development (ORD) led the development and rewrite of TO-15A
  - One of main goals of rewrite was to educate and inform Method users
  - Obsolete items removed and method wholly rewritten
  - Scope focus on ambient air
    - With some modification, also applies to source-level, vapor intrusion, exhaled breath, etc.
  - ORD and OAQPS communicated known needed updates
    - Many of the needed updates to Compendium Method TO-15 (1999) were included in NATTS TAD Revision 3 (October 2016)
      - *Further updates from NATTS TAD Revision 3 in comparison table*
  - Public comment period on 1999 document (TO-15)
  - Incorporated comments and aspects where supported by data and established methodology


TECHNICAL ASSISTANCE DOCUMENT
FOR THE
NATIONAL AIR TOXICS TRENDS STATIONS PROGRAM

Revision 3

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

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October 2016

EPA Method TO-15A - Overview

- Highlights of Major Updates from TO-15 (1999)
  - Canister Cleanliness Criteria – reflect need to measure lower concentrations due to decreasing concentrations of VOCs
  - Canister and Instrument Qualification
  - Humidity Guidance
  - Modern Preconcentration and Measurement Instrument Components
  - Calibration Standard Range and Regression Modeling
  - Quality Control Criteria
  - Qualitative Identification Criteria
  - Method Detection Limits (MDLs)

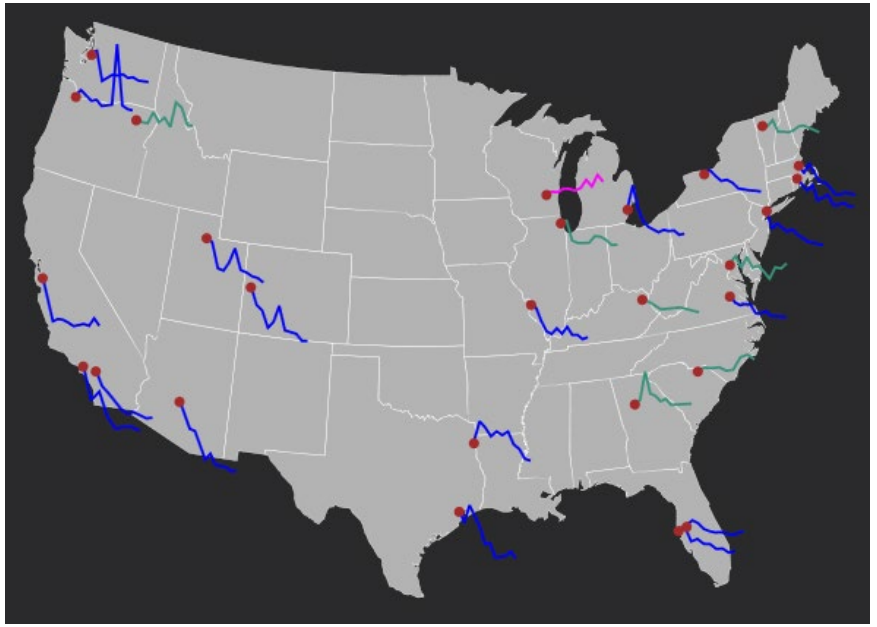


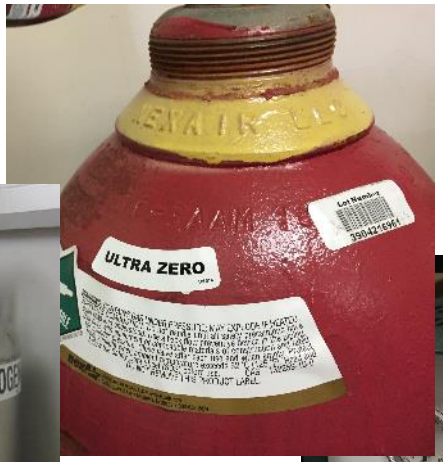
Image courtesy of: https://gispub.epa.gov/air/trendsreport/2016/

EPA Method TO-15A – Major Takeaways

- Need to measure lower (decreasing) ambient air concentrations requires minimizing and characterizing background levels of VOCs
- Canister media, sampling instruments, diluent and reagent gases, and analytical systems are interrelated and contamination or problems with any portion will compromise data
- Updated method defines characterization approaches and acceptance criteria of each portion of the method

Clean Gas and Diluent Gas

- < 20 pptv for each target volatile organic compound (VOC)
- Hydrocarbon free (HCF) Zero Air
  - Zero air generator
  - High pressure cylinders of “ultra” or “research-grade” zero air (< 0.05 ppm total hydrocarbons)
  - Hydrocarbon scrubber cartridges
  - Additional oxidation scrubbers
- Ultra-high purity (UHP) Nitrogen (N_2)
  - High pressure cylinders
  - Headspace from liquid N_2 dewar (LN2)
- UHP N_2 is not permitted for:
  - Challenge gases for canisters, sampling units, and instruments
  - Method detection limit spike sample standards
- Both HCF zero air or UHP N_2 are permitted for:
  - Calibration standard diluent gas
  - Canister cleaning purge gas
  - Canister cleaning blank gas
  - Sample diluent gas
  - Method blank



Water for Humidification

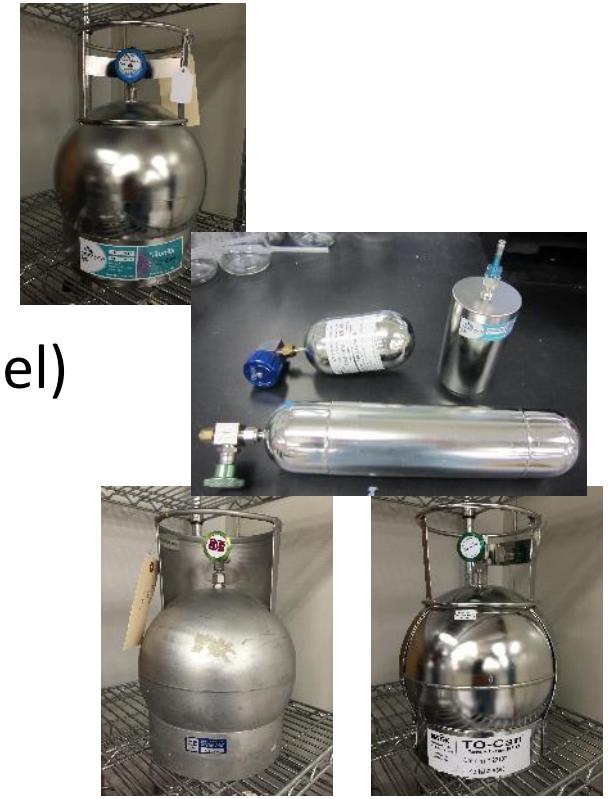
- ASTM Type I or HPLC-grade recommended
  - Resistivity > 18 MΩ·cm
- If contaminants are found:
  - Boil for 10 minutes
  - Sparge with UHP N_2 or He for 10 minutes
  - Store in sealed container

Vacuum/Pressure Gauges/Transducers

- Field use - accuracy ±0.25% full scale
  - Testing canister vacuum in the field
- NIST-traceable certified gauge
  - Range 0 to 30 psia and accuracy ±0.1% full scale
  - Maintain in laboratory and verify calibration of field gauges
  - Measure canister pressure on receipt
  - Measure static dilution pressures

Sampling Containers

- Stainless Steel Canisters (medium of choice)
  - Silicon-ceramic lined (e.g., Entech Silonite® or Restek Silco® Steel)
  - Electropolished (e.g., SUMMA passivated or Restek TO-Can®)
- Glass Bottles
  - Engineered and deactivated for VOCs collection
- Flexible (non-rigid) Containers
  - *Not included in scope of method*
  - Not suitable for NATTS network sampling
    - Tedlar® film bags
    - Mylar® or multi-layer films



https://www.entechinst.com/wp-content/uploads/2015/09/29-BV250AS_2019.png

Canister Cleaning

- Pre-evacuation recommended prior to connection to cleaning system
  - Evacuate to > 28 in Hg vacuum (oil-free rough pump)
  - Fill with clean purge gas
- Purge Gas (may be HCF zero air or UHP N_2)
  - Humidify to ~50%
  - Ensure purge gas is < 20 pptv for target VOCs
- Canisters should be heated (80°C) in oven
  - Ovens heat canister and valve uniformly
  - Jackets may not heat valve sufficiently
    - allows high boiling point VOCs to deposit/accumulate in valve
  - Heating bands create hot spots and may not sufficiently heat valve
  - Heating silicon ceramic lined canisters > 80°C not recommended with HCF zero air purge gas – damages lining integrity

Canister Cleaning (continued)

- Minimum 5 cycles of evacuation (> 28 in Hg vacuum) and pressurization (no more than 30 psig)
  - More cycles (e.g., 20 cycles) may be needed for effective cleaning
  - Automated cleaning systems permit additional unattended cycles
- Final evacuation to ≤ 50 mTorr
  - Back diffusion (migration of VOCs back into canisters) possible if left at high vacuum on system for extended period – perform additional cycle
- Canisters may be stored with pressurized purge gas and evacuated just prior to deployment

Canister Cleaning - Verification

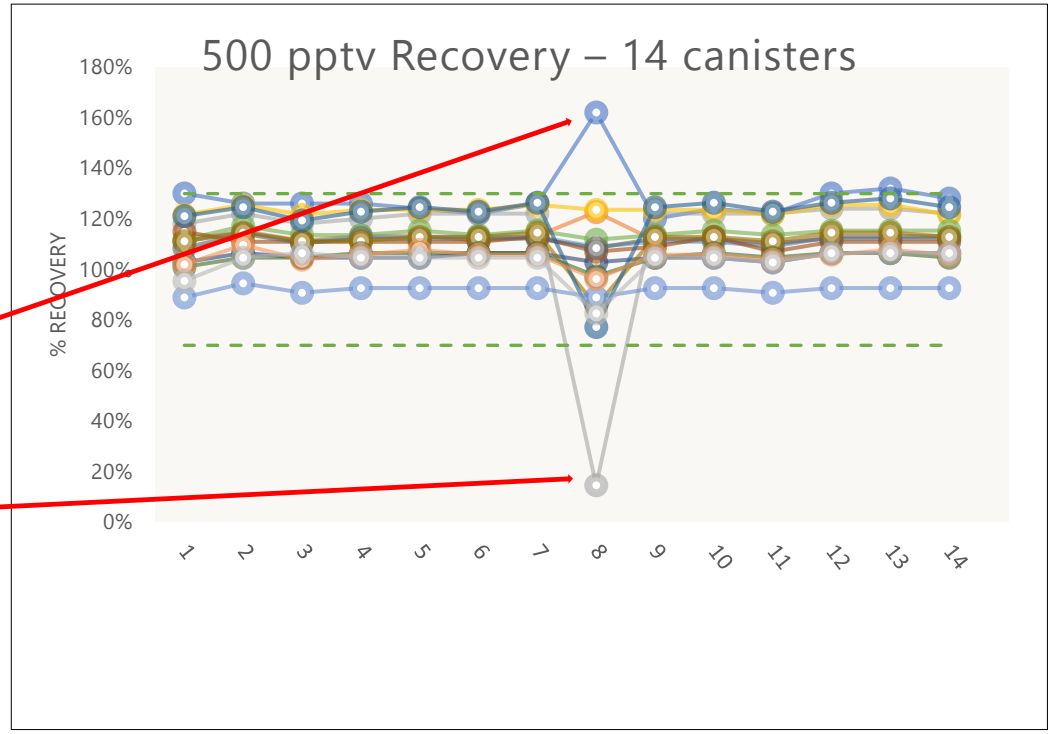
- Canister cleanliness batch defined as all canisters connected to manifold
- Prepare 1 verification blank for every 8 canisters cleaned
  - Recommend minimally 1/manifold
- Pressurize with clean humidified gas (HCF zero air or UHP N_2), allow to equilibrate for 24 hours
- Verification blanks must be < 20 pptv at ambient pressure
  - *NATTS TAD required < 200 pptv or 3xMDL, whichever was lower*

Canister Qualification

- Canister Leak Check (< 0.1 psi/day)
- Initially before use and every 3 years thereafter
- Humidified zero air (~40 to 50% RH) (UHP N_2 not permitted)
- Zero-air challenge
  - Initially 24 hours after filling
  - At a later timepoint - typical holding time (i.e., 30 days)
  - Results < 20 pptv (at ambient pressure) at initial and later timepoints
  - *NATTS TAD required < 200 pptv or 3xMDL, whichever is lower*
- Known standard challenge
  - ~100 to 500 pptv
  - Initially 24 hours after filling
  - At a later timepoint - typical holding time (i.e., 30 days)
  - Results within ±30% of theoretical at initial and later timepoints

Canister Qualification – Case Study

- Previous case study
  - NATTS PT canisters
  - Brand new from manufacturer
  - 1 canister (of 14) failed criteria
    - Acrolein (recovery > 160%)
    - 1,3-butadiene (recovery < 20%)



Canister Hygiene

- Eliminating sampling of particulate matter (PM) - Required
  - PM in canisters is extremely difficult to remove
    - Not removed by typical pressurization/evacuation
  - Employ sintered stainless steel filters
  - Replace PM filters frequently
    - High PM areas
    - Heavy pollen
- Canister valve opening is to be capped with brass plug
  - Prevents introduction of PM
  - Brass caps will deform before valve threads
  - Stainless caps require care to avoid deforming threads
- Replace leaking valves
  - Perform canister qualification

Sampling Inlet Probe

Inlet probes are project-specific

- Method includes details to avoid sampling bias
- Ambient air monitoring
  - Probe within breathing height
  - 2 to 6 m above ground level
  - Collocated probes within 12 inches vertically
- Probe material constructed of inert materials:
  - Chromatographic grade stainless steel
  - Borosilicate glass
  - Quartz glass
  - Minimize Viton®, PTFE, PFA
  - Do not use:
    - FEP Teflon®
    - Tygon®
    - Rubber
    - Copper
    - Brass
    - Aluminum

Potential Sampling Interferences

- Leaks in flow path (may introduce shelter air)
- Particulate matter (PM)
  - Employ sintered stainless steel particulate filters (e.g., 2-µm)
  - Buildup of PM or biological growth can behave as sorbents
    - Algae, insect nests, spider webs
- Contamination from solvents
  - Stored in shelters (paints, adhesives, aerosol cans, etc.)
  - Nearby sources
  - Environmental laboratory (e.g., organic extraction use of dichloromethane)
- Sample carryover
  - Purge collection lines prior to starting sample collection

Methods of Sample Collection

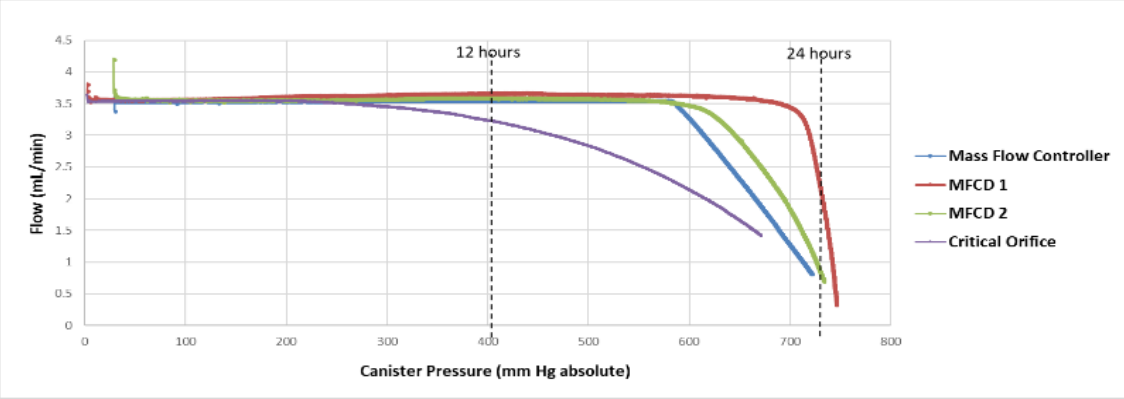
- Routine monitoring – fixed monitoring sites (e.g., NATTS)
- Special investigations – temporary monitoring (complaints, site evaluation)
  - Subambient sample
  - Pressurized sample collection
  - Grab sample collection

Methods of Sample Collection (continued)

- Subambient sample collection
  - Ending pressure should be 1.5 to 3 psi below ambient pressure to ensure a constant sampling rate over the 24-hour period
    - Usually employs canister vacuum to drive flow
    - Use of sampling pumps not typical for subambient collection
    - Dependent on flow controller to ensure constant flow rate over collection period
- Pressurized sample collection
  - Strongly recommends sample collection pressure of ≤3 psig to limit condensation inside canister
  - Employs a pump to pressurize canister
- Canisters at ambient pressure should be considered suspect
  - Indicate a leak occurred
  - Exception for grab samples (not common for routine monitoring)

Sampling - Flow Control

- Mass flow controller (MFC) – typical for routine monitoring
  - Subambient and pressurized sampling
- Mechanical flow controlling device (MFCD) – not typical for routine monitoring
- Critical orifice – not adjustable and not typical for routine monitoring



Sampling – Flow Rate Verification

- Flow rate depends on final desired collection pressure/vacuum and canister volume
- Flow control should be constant over the collection period
- Verify flow rate with calibrated flow standard
  - Ensure constant over desired collection duration

https://drycal.mesalabs.com/wp-content/uploads/sites/5/2013/11/Defender-Series-Home-300x294.png

Sampling Unit Bias Qualification

- Prior to initial deployment and annually thereafter
  - Following maintenance and calibration
    - Replace sintered stainless steel particulate filter
    - Calibrate/verify flow controller (absolute accuracy not critical)
    - Calibrate pressure gauge (if equipped)
- Collect samples of challenge gases
  - Upstream (reference sample)
  - Through the sampling unit (challenge sample)
- Zero Challenge
- Known Standard Challenge

Sampling Unit Bias Qualification (continued)

- Humidify challenge gas (~40 to 50% RH)
- Zero challenge
  - HCF zero air (N_2 not permitted)
    - *NATTS TAD permitted N_2*
  - All target VOCs < 20 pptv greater than reference sample
    - *NATTS TAD required < 200 pptv or 3xMDL, whichever is lower*
- Known standard challenge
  - HCF zero air as diluent
  - 100 to 500 pptv for each target VOC
  - All target VOCs within ±15% of the reference sample

BREAK

QUESTIONS AND OPEN DISCUSSION

???

Standard Gases

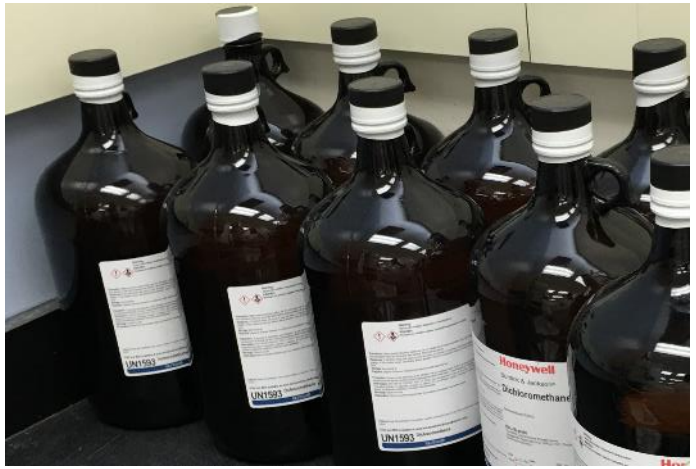
- High pressure cylinders
- Certificate of analysis (COA) with traceability information
  - Primary standard – for calibration
  - Second source standard – for independent verification
- Recommend ~100 ppbv to 1 ppmv
  - Custom blend
  - Readily stocked 65-component mix
- Recertification may extend expiration
  - Not typical for small lecture bottle standards

Standards Preparation

- Dynamic Dilution
  - Mass flow controller for diluent and each standard gas
  - Requires passivation time and constant gas flow
  - MFCs must be calibrated at the flow rates employed
    - Flows can be verified against a certified flow meter
- Static Dilution
  - Static dilution instrument (manifold)
  - Addition of gases by partial pressures (canister)
  - Pressure measurement sensitivity limits dilution factor capability
    - Serial dilution may be necessary to achieve desired concentrations
  - Vacuum gauges/pressure transducers must be calibrated

Common Analysis Interferences

- Laboratory solvent vapors
- Carryover from high concentration standards or samples
- Impurities in humidification water
- Contaminants in internal standard gases
  - Dichloromethane and carbon disulfide are common
- Co-eluting interferences
  - Silanols from breakdown of silicon ceramic linings
  - Siloxanes from column stationary phase
  - Compounds with shared MS ion responses



Instrument Qualification

- Performed when instruments placed into service
- Zero air challenge
  - Analysis of HCF zero air humidified to ~40 to 50% RH
  - All target VOCs < 20 pptv
  - Should not show other significant non-target VOCs or baseline artifacts
- Known standard challenge
  - Replicate injections of a 100 to 500 pptv standard humidified to ~40 to 50% RH
  - Sufficient and consistent area response with repeated analysis
  - Missing or low response peaks should prompt troubleshooting

http://www.nutechins.com/public/upload/image/20200414/15868462708587.jpg

Autosampler Qualification

- Performed following instrument qualification and calibration, canister qualification
  - All ports employed for analysis must be evaluated
  - Repeat after replacing port connections and lines and after servicing switching valve
- Zero air challenge
  - Analysis of HCF zero air humidified to ~ 40 to 50% RH
  - All target VOCs < 20 pptv
  - Analysis of high concentration samples to verify absence of carryover
- Known standard challenge
  - Analysis of 100 to 500 pptv standard humidified to ~40 to 50% RH
  - All target VOCs within ±15% of theoretical concentration

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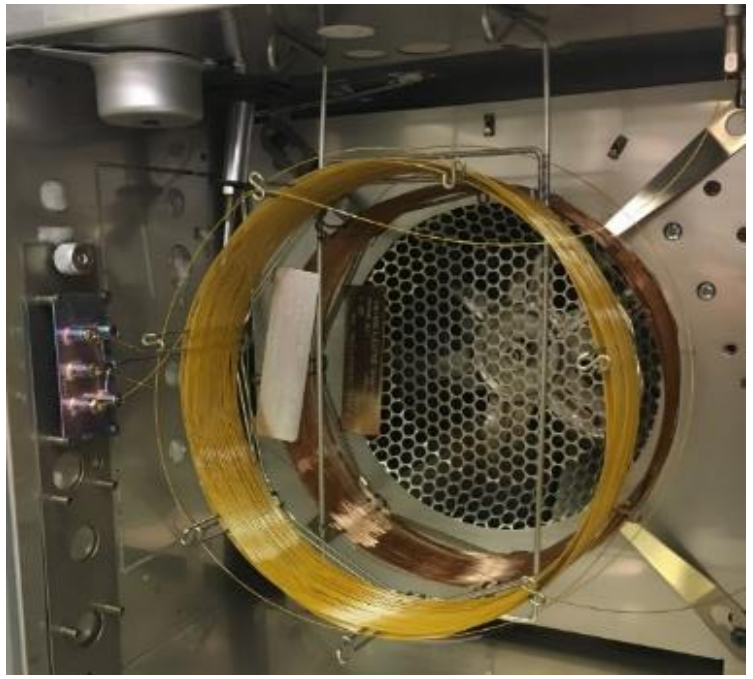
Analysis - Preconcentration

- Manage (remove) water
- Allow bulk gases (O_2, N_2, CO_2, and Ar) to pass through
- Multi-trap cryogenic
  - Employs empty or glass bead traps
  - Subsequent traps employ sorbent to retain VOCs
  - Heated desorption from sorbent to focusing trap and injection to GC
- Series of capillary columns
  - Trap VOCs and allow water and bulk gases through
  - Backflush VOCs for focusing and injection to GC

Analysis – GC Separation Columns

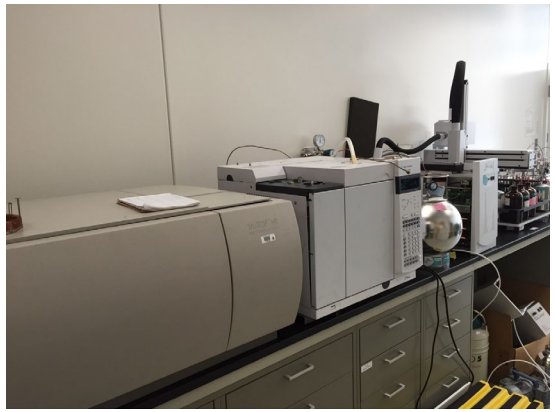
- Non-polar Stationary Phase - dimethylpolysiloxane
  - E.g., HP-1, BP-1,
- Low Polarity Stationary Phase – cyanopropylphenyl polydimethylsiloxane
  - E.g., DB-624
- Typical Specifications:
  - length 60-m
  - 1-um film (stationary phase) thickness
  - Internal diameter 0.25 to 0.32 mm



Analysis – Mass Spectrometer Detection

Mass Spectrometer (MS) Detection – typical configurations

- Linear quadrupole MS
  - Electron Ionization (EI) mode at ionization energy of 70 eV
  - Scan range 35 to 270 amu unless other range needed
  - m/z 28, 32, and 44 may see interferences due to N_2, O_2, and CO_2 respectively
  - Scan rate sufficient to provide 12 or more scans/peak (10 scans/peak is minimum)
  - Operate in SCAN mode, select ion monitoring (SIM) mode, or simultaneous SIM/SCAN
  - Bromofluorobenzene (BFB) tuning is no longer required
- Ion trap MS
  - Electron Ionization (EI) mode at ionization energy of 70 eV
  - Scan range 35 to 270 amu unless other range needed
  - Scan rate of 0.4 to at most 1 second/scan (faster scan rates provide better resolution)
  - Operate in selected ion storage (SIS) mode
- Time-of-Flight (TOF) MS
  - Electron Ionization (EI) mode at ionization energy of 70 eV
  - Ion source temperature 260°C
  - Spectral acquisition rate of 2 to 4 Hz or higher



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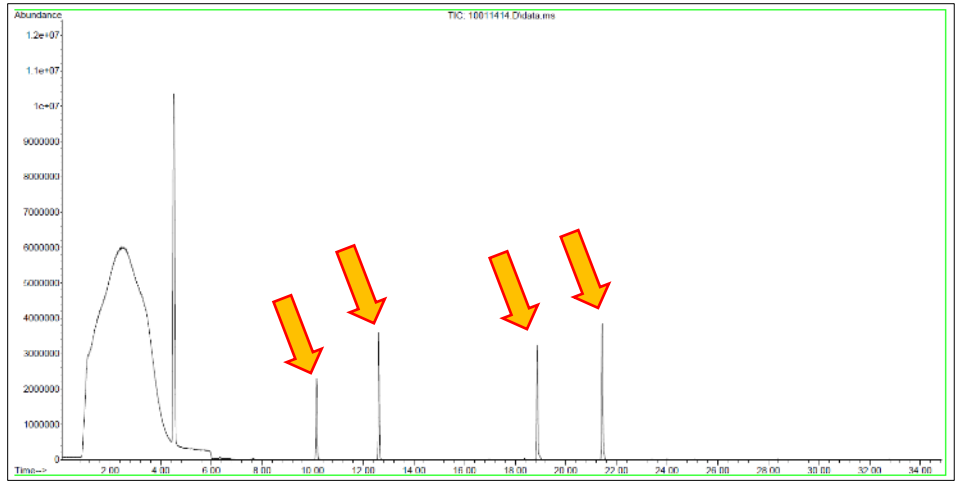
Analysis – Internal Standards



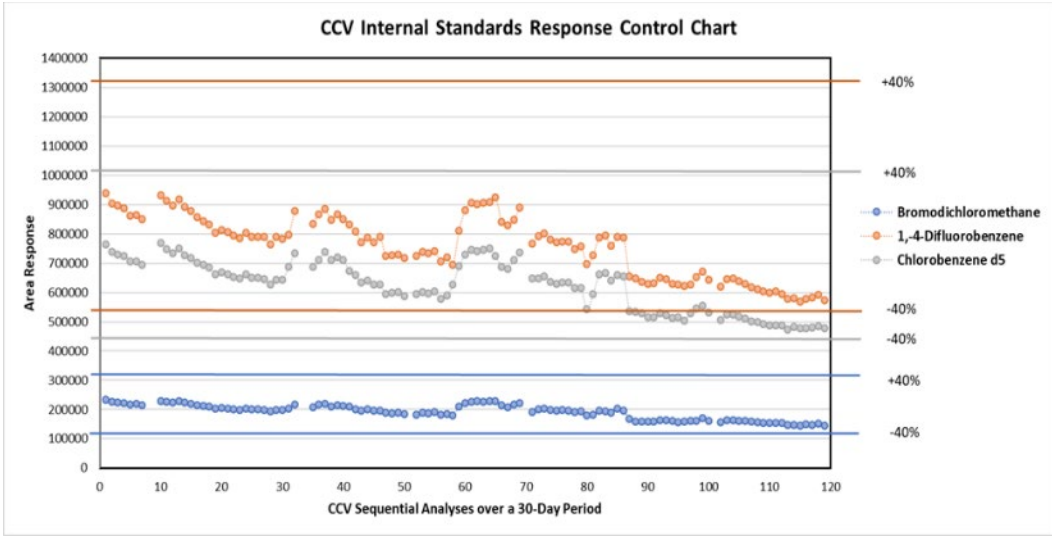
Selection

- IS are deuterated or VOCs not expected in sample
- Minimally one IS compound required
- Three recommended to cover retention time range
  - Typical include: bromochloromethane, 1,4-difluorobenzene, and d_5-chlorobenzene
  - Others: 1,2-dichloroethane-d_4, hexane-d_{14}, toluene-d_8, and 1,2-dichlorobenzene-d_4
- Qualify IS gas by analyzing increasing volumes and examining for concomitant proportional increases in area response of potential contaminants
  - Carbon disulfide
  - Dichloromethane

Analysis – Internal Standards

Use

- Select amount of IS to approximate target VOCs response in lower half of calibration curve
  - On scale
  - Not to exceed response of high calibration standard
- Inject the same amount of IS with every blank, standard, and sample injection
- Establish IS performance during initial calibration
  - Retention time (RT) window
  - Average area response
- With each injection:
  - Each IS must elute within ±2 seconds of the average RT from the ICAL
  - Each IS compound area response must be within ±40% of the average response from ICAL (preferably not exceed ±30%)



Analysis - Calibration

Initial Calibration (ICAL) – Concentration Levels

- Minimum of 5 concentration levels
  - Minimum of 8 levels if employing quadratic model
- Recommended range 20 to 5000 pptv (lower than NATTS TAD)
  - Half or more of levels in lower half of curve range
- Recommend triplicate measurement of each level
- Recommend zero concentration calibration point
  - May be useful for compounds with background
  - Not applicable for average relative response factor (RRF)

Analysis – Calibration (continued)

GC/MS Calibration - Conventions

- Individual Standards Method
  - Each concentration level is prepared in a canister
    - E.g., 20, 50, 100, 250, 1000, 2000, and 5000 pptv
  - Same volume injected for each standard level (typical analysis volume for standards and samples is 250 mL)
  - Consistent amount of water introduced
  - Must separately demonstrate preconcentrator can handle different amounts of water
- Effective Dilution Method
  - Inject differing volumes from two or more standard canisters
    - Errors in standard preparation will not be apparent with one canister
  - Prepare canisters at 250 pptv and 5000 pptv
  - Example: Typical sample analysis volume is 250 mL
    - Inject 20, 50, 100, and 250 mL from the 250 pptv canister
    - Inject 50, 100, and 250 mL from the 5000 pptv canister
  - Varies amount of water introduced to the preconcentrator

Analysis – Calibration (continued)

GC/MS Calibration – Regression Modeling

- *Additional options than that included in NATTS TAD*
  - Relative Response Factor (RRF)
  - Linear model (intercept and slope)
  - Quadratic model (intercept, slope, and quadratic term)
  - Considerations
    - Backcalculated concentration of each standard must be within ± 30% of the theoretical concentration
    - Only exclude standard levels when technically justified
      - Preparation error
      - Faulty injection
      - Obvious chromatography problem

Analysis – Calibration (continued)

Instrument Calibration – Regression Modeling

- Relative Response Factor (RRF)
  - Average RRF of all concentration levels employed for quantitation
  - Relative standard deviation (RSD) of RRF must be ≤ 30% for each target VOC
  - Assumes calibration curve passes through origin
  - May not represent compounds with background or non-linear behavior

Method Path : D:\msdchem\2\METHODS\
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Title :
Last Update : Wed Apr 12 07:36:22 2017
Response Via : Initial Calibration

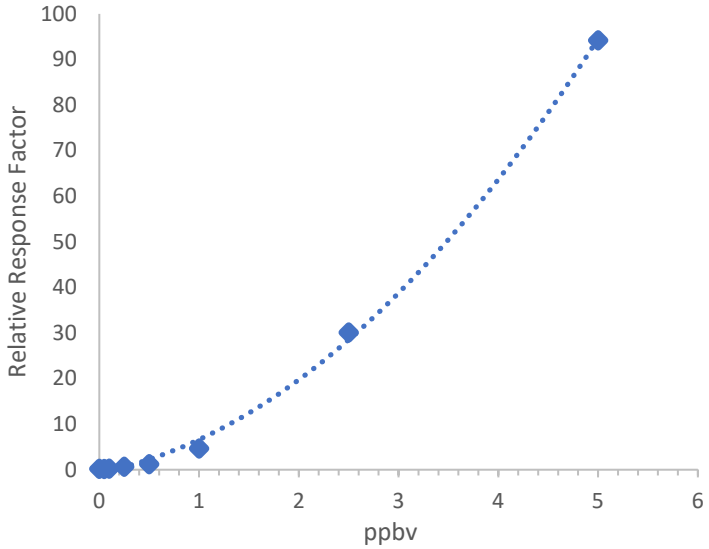
Calibration Files
2 =04111704.D 3 =04111705.D 4 =04111706.D 5 =04111707.D 6 =04111708.D

	Compound	2	3	4	5	6	Avg	%RSD
1)	Bromochloromethane	ISTD						
2)	propylene	0.315	0.317	0.345	0.383	0.399	0.352	10.81
3)	Freon-12	2.236	2.131	2.023	1.884	1.747	2.004	9.68
4)	methyl chloride	0.623	0.566	0.527	0.521	0.516	0.550	8.15
5)	Freon-114	2.703	2.492	2.362	2.303	2.313	2.434	6.89
6)	vinyl chloride	0.975	0.886	0.821	0.810	0.807	0.860	8.39
7)	methanol	0.185	0.167	0.151	0.144	0.138	0.157	12.14
8)	1,3-butadiene	0.540	0.536	0.526	0.519	0.520	0.528	1.79
9)	methyl bromide	1.156	1.061	0.993	0.948	0.955	1.022	8.49
10)	ethyl chloride	0.494	0.447	0.427	0.432	0.424	0.445	6.45
11)	ethanol	0.232	0.224	0.202	0.188	0.179	0.205	11.06
12)	vinyl bromide	1.230	1.103	1.030	1.022	1.025	1.082	8.27
13)	acrolein	0.295	0.289	0.262	0.281	0.282	0.282	4.36
14)	acetone	1.101	0.952	0.886	0.869	0.873	0.936	10.46
15)	Freon-11	2.169	2.002	1.859	1.848	1.834	1.942	7.39
16)	isopropyl alcohol	0.716	0.703	0.720	0.718	0.708	0.713	0.99
17)	isoprene	0.561	0.621	0.707	0.792	0.811	0.698	15.40
18)	1,1-dichloroet...	0.869	0.795	0.839	0.904	0.922	0.866	5.87
19)	methylene chlo...	1.116	0.860	0.723	0.690	0.674	0.812	22.72
20)	Freon-113	1.528	1.407	1.364	1.381	1.409	1.418	4.55
21)	carbon disulfide	2.361	2.100	2.064	2.120	2.136	2.156	5.44
22)	trans-1,2-dich...	0.667	0.613	0.651	0.701	0.740	0.675	7.16
23)	1,1-dichloroet...	1.193	1.129	1.093	1.115	1.141	1.134	3.33
24)	methyl tert-bu...	1.227	1.277	1.426	1.581	1.628	1.428	12.46
25)	vinyl acetate	1.185	1.206	1.259	1.388	1.399	1.287	7.82
26)	2-butanone	0.934	1.012	1.029	1.102	1.117	1.039	7.12
27)	cis-1,2-dichlo...	0.648	0.644	0.688	0.771	0.794	0.709	9.79
28)	ethyl acetate	0.118	0.144	0.170	0.186	0.160	0.156	16.49
29)	hexane	0.844	0.834	0.867	0.912	0.912	0.874	4.22
30)	chloroform	1.729	1.619	1.544	1.545	1.542	1.596	5.10
31)	tetrahydrofuran	0.402	0.460	0.520	0.588	0.616	0.517	17.12
32)	1,2-dichloroet...	0.861	0.823	0.789	0.773	0.797	0.808	4.25
33)	1,4-difluorobenzene	ISTD						
34)	1,1,1-trichlor...	0.431	0.418	0.402	0.408	0.420	0.416	2.68
35)	benzene	0.489	0.499	0.540	0.582	0.592	0.540	8.64
36)	carbon tetrach...	0.494	0.456	0.441	0.461	0.473	0.465	4.26
37)	cyclohexane	0.220	0.225	0.242	0.259	0.264	0.242	7.99
38)	1,2-dichloropr...	0.198	0.191	0.188	0.196	0.203	0.195	3.01
39)	bromodichlorom...	0.467	0.451	0.447	0.457	0.465	0.457	1.89
40)	trichloroethene	0.270	0.280	0.301	0.322	0.328	0.300	8.52
41)	1,4-dioxane	0.089	0.108	0.120	0.117	0.124	0.112	12.51
42)	methyl methacr...	0.153	0.165	0.182	0.198	0.202	0.180	11.62
43)	heptane	0.182	0.176	0.198	0.208	0.211	0.195	7.92
44)	cis-1,3-dichlo...	0.248	0.254	0.303	0.332	0.346	0.296	15.00
45)	methyl isobuty...	0.122	0.129	0.144	0.157	0.159	0.142	11.76
46)	trans-1,3-dich...	0.226	0.235	0.278	0.307	0.322	0.274	15.57
47)	1,1,2-trichlor...	0.236	0.211	0.210	0.220	0.221	0.220	4.83

Analysis – Calibration (continued)

GC/MS Calibration – Regression Modeling

- Linear model
  - Unweighted
  - Weighted (e.g., 1/concentration, 1/concentration^2)
- Quadratic model
  - May better represent calibrations covering a large dynamic range for analytes with a non-linear response
  - Caution recommended
    - Non-linear behavior may be due to standards preparation error
    - Background contamination
    - Weighting schema for linear modeling applies



Analysis – Compound Identification

- All four criteria must be met for positive identification
  - Retention time (RT) [A]
  - Qualifier ion abundance ratios [B]
  - Signal-to-noise ratio (S:N) [C]
  - Target and qualifier ion peaks must be co-maximized [D]

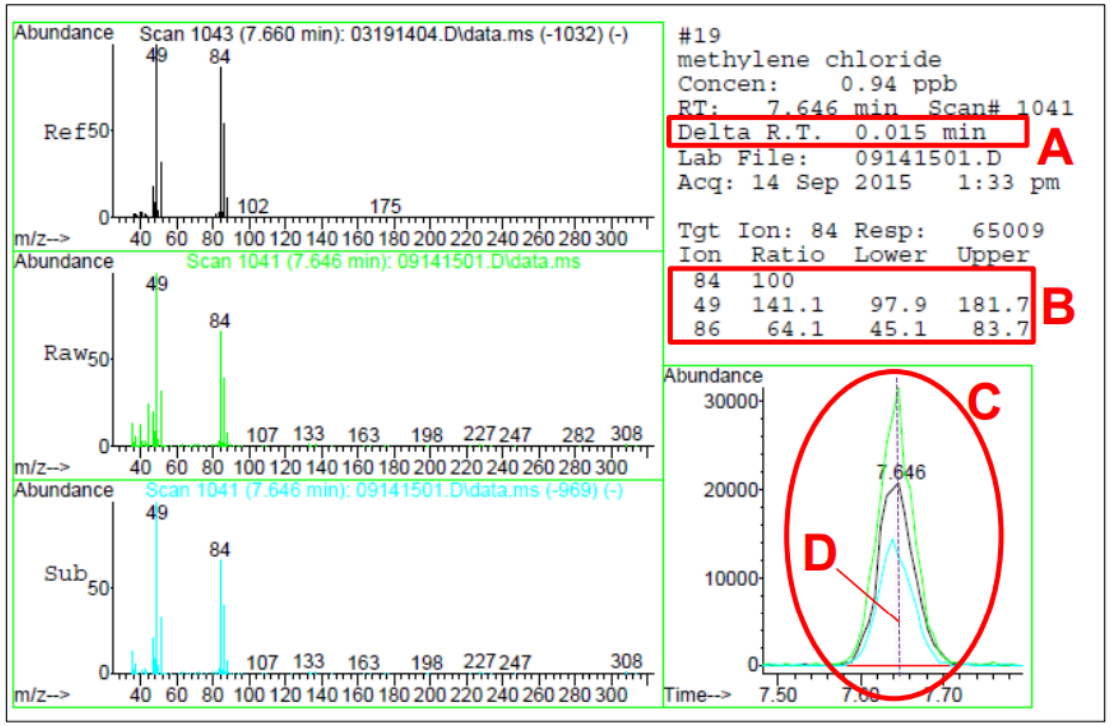


Figure 16-1: Qualitative identification of GC-MS target analytes.

Analysis – Compound Identification (continued)

- Retention time (RT) [A]
  - Within ±2 seconds (±0.033 min) of the average RT from the ICAL
    - NATTS TAD specified ±0.06 relative retention time (RRT) units
  - Update with each new ICAL
  - Chromatography data system (CDS) can flag when RTs outside this window

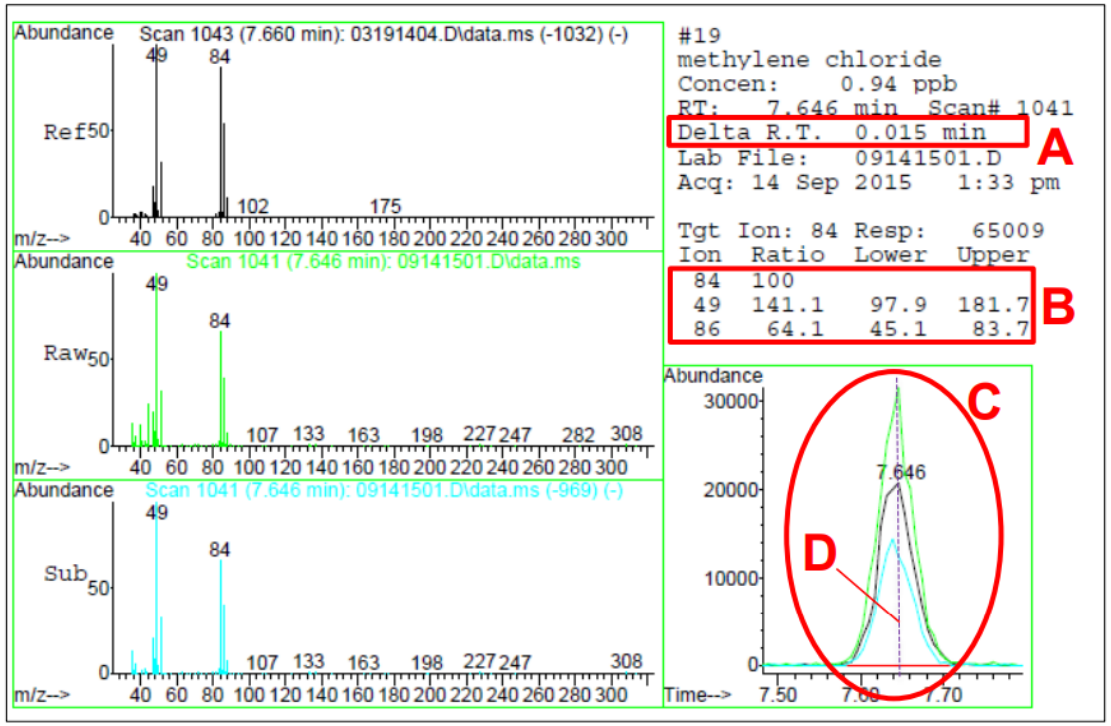


Figure 16-1: Qualitative identification of GC-MS target analytes.

Analysis – Compound Identification (continued)

- Qualifier ion abundance ratios [B]
  - Minimally one qualifier ion must be within ±30% of the average **relative** abundance ratio established from the ICAL
    - NATTS TAD did not specify relative abundance
    - Assigning as absolute abundance will result in overly narrow or wide acceptance windows (false positive or false negative)
  - Update ratios with each new ICAL
  - CDS can be programmed to flag compounds when this criterion is exceeded

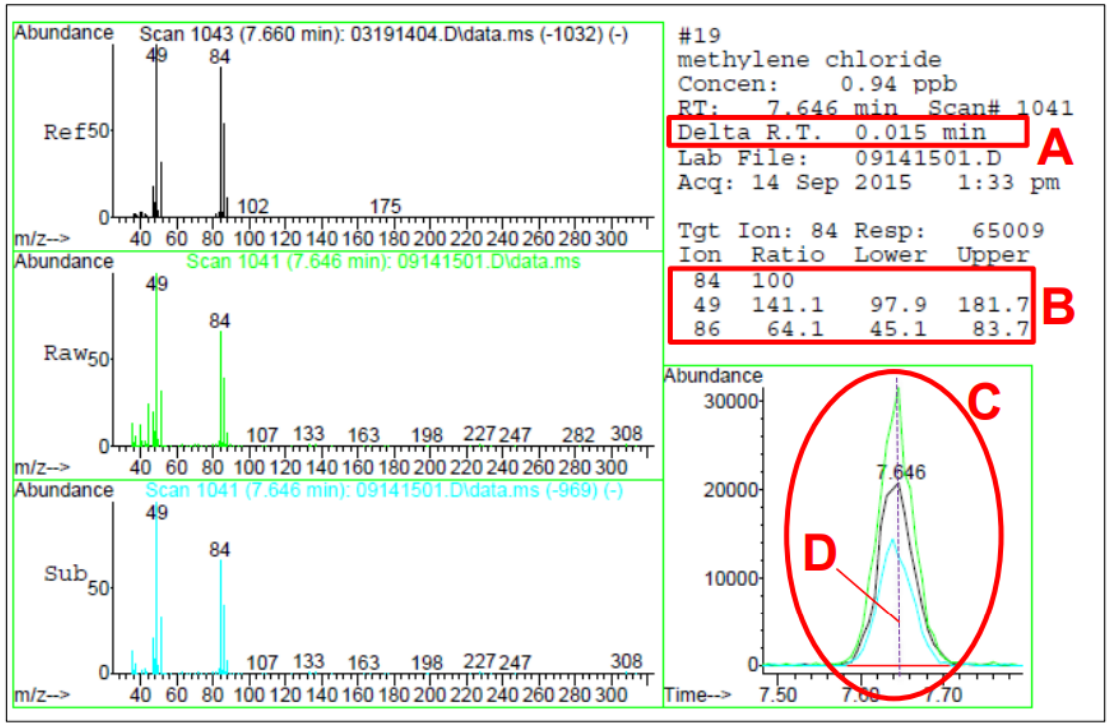
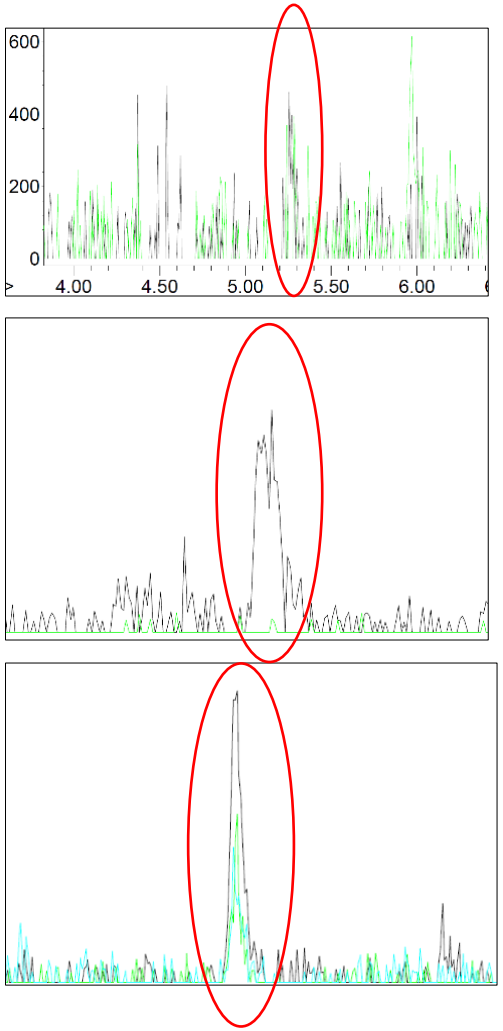


Figure 16-1: Qualitative identification of GC-MS target analytes.

Analysis – Compound Identification (continued)

- Signal-to-noise ratio [C]
  - S:N should be > 3:1, preferably > 5:1
  - Simplest to measure noise height and peak height
  - May also use area ratios
  - CDS may include S:N calculators



Analysis – Compound Identification (continued)

- Target and qualifier (Q1 and/or Q2) ion peaks must be co-maximized [D]
  - Peak apexes preferably within one scan
  - Experienced analyst interpretation should weigh heavily

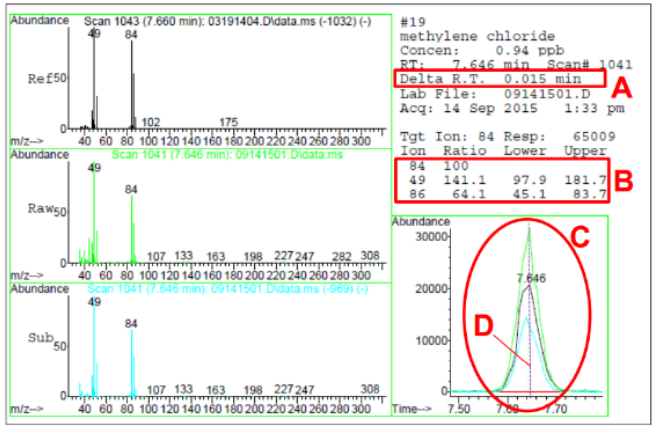
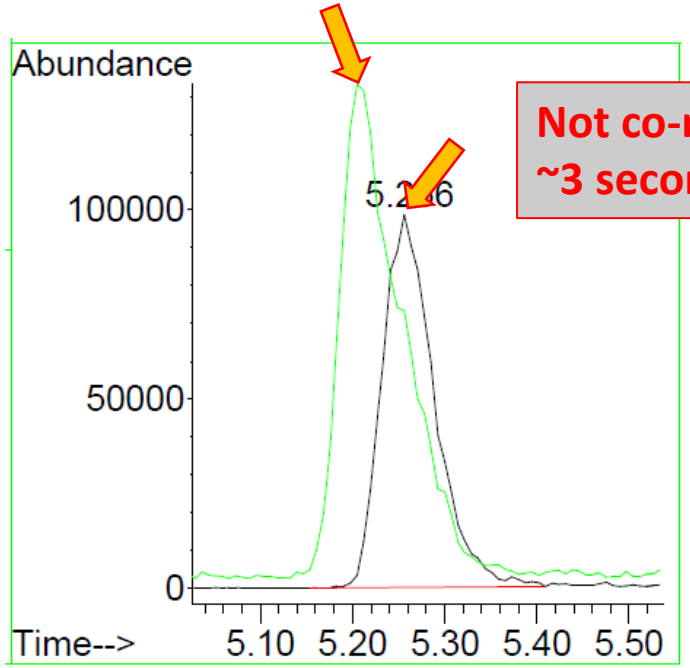
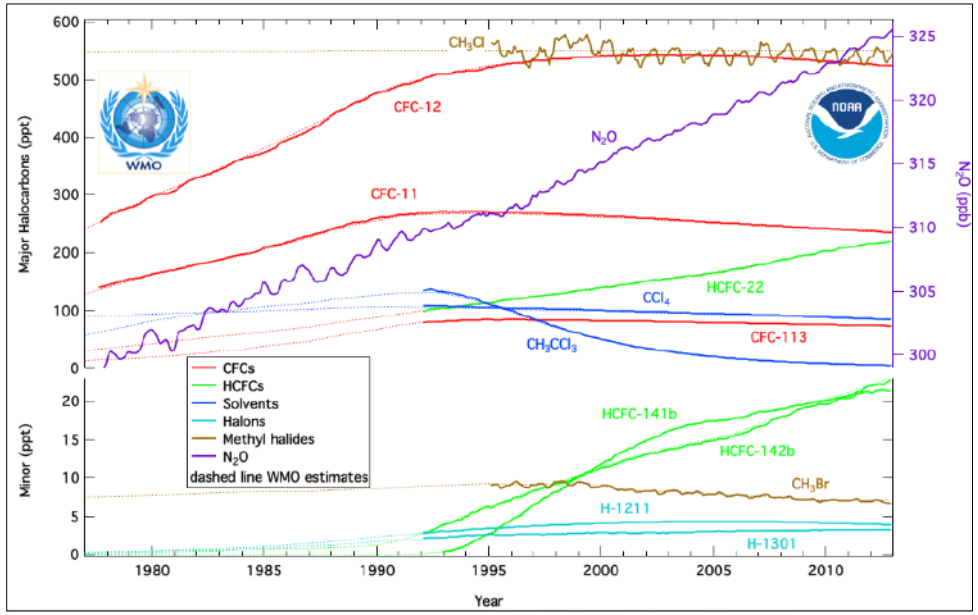


Figure 16-1: Qualitative identification of GC-MS target analytes.



Analysis – Ambient Air Check

- Chlorofluorocarbons are ubiquitous
  - Should be detected in every ambient sample
  - Trichlorofluoromethane (Freon 11)
  - Dichlorodifluoromethane (Freon 12)
  - Carbon tetrachloride
  - 1,2-dichloro-1,1,2,2-tetrafluoroethane (Freon 114)
- Qualitative check on ambient air collection and analysis
  - Should not alone be rationale for data invalidation
- https://www.esrl.noaa.gov/gmd/hats/



https://www.esrl.noaa.gov/gmd/hats/about/cfcs.png

Analysis – Method Detection Limits

Method Detection Limits (MDLs)

- Performed per MDL Method Update Rule (MUR) in 40 CFR Part 136 Appendix B
- Determined initially and annually thereafter
- MDL MUR prescribes determination of MDLs
  - Spiked samples (MDL_{sp})
  - Method blank samples (MDL_b)

https://www.ecfr.gov/cgi-bin/text-idx?SID=b577759fcc62d77f535f33b795864a9f&mc=true&node=ap40.25.136_17.b&rgn=div9

Analysis – Method Detection Limits (continued)

Preparation of method blanks and spikes

- Minimum of 7 each in separate canisters
- Prepared on three separate dates (preferably non-consecutive)
- Must include all aspects of the method (e.g. humidity)
- Each VOC is considered uniquely

Analysis – Method Detection Limits (continued)

Preparation of MDL Spikes (MDL_{sp})

- Must be in HCF zero air
- Spike concentration <u>for each VOC</u>:
  - Equivalent to S:N of 3:1 to 5:1
  - At which qualitative identification criteria are lost
  - Estimate of 3-fold standard deviation of area response of minimally 3 method blanks
  - From previous acceptable MDLs

Preparation of Method Blanks (MDL_b)

- Routine method blanks (HCF zero air or UHP N_2)

Analysis – Method Detection Limits (continued)

Calculating MDL_{sp}

- Calculate standard deviation for each target VOC (s_{sp})
- Multiply the standard deviation by the appropriate Student's *t*-value (*t*)
  - Student's *t*-value for the single-tailed 99th percentile *t*-statistic and a standard deviation estimate with *n*-1 degrees of freedom

$$MDL_{sp} = t_{(n-1,1-\alpha=0.99)} \cdot s_{sp}$$

- MDL_{sp} must be between 10 and 100% of the spiked concentration
- If outside these criteria, adjust spiking level and repeat MDL_{sp}
  - *Relative abundance and S:N criteria may be waived for MDL spike samples*

Analysis – Method Detection Limits (continued)

Calculating MDL_b

- If MB concentrations are ND, the MDL_b does not apply
- If some, but not all, MBs have numerical results (are not ND), MDL_b = highest of MB concentrations
  - Exception if $n > 100$, then 99th percentile value
- If all concentrations are numerical
  - Calculate average ($\bar{x}_b$) for each target VOC in the method blanks
    - If $\bar{x}_b < 0$, let $\bar{x}_b = 0$
  - Calculate standard deviation (s_b) for each target VOC in the method blanks
  - Multiply the blank standard deviation (s_b) by the appropriate Student's t-value (t) and add this to the average blank value ($\bar{x}_b$)

$$MDL_b = (t_{(n-1,1-\alpha=0.99)} \cdot s_b) + \bar{x}b$$

Analysis – Method Detection Limits (continued)

Determining the Reported MDL

- Compare MDL_b and MDL_{sp}
- Whichever is larger is the reported MDL for that VOC
- If MDL_{sp} is higher, optionally confirm MDL
  - Prepare one or more spikes at 1- to 5-fold the MDL_{sp}
  - Analyze and evaluate recovery
    - Suggested recovery criteria are 40 to 160%
    - If outside these criteria, examine determined MDL for reasonableness
    - Typical MDLs should be in the low single-digit or tens of pptv

QUESTIONS AND OPEN DISCUSSION

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Thank you

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Work Assignment 5-04 Amendment 4
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