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TO-15 Quality Assurance

Requirements and Best Practices

TO-15 Quality Assurance

- TO-15 was promulgated in January 1999
- Instrumentation may vary, but basic QA tenets apply
 - Bias
 - Precision
 - Calibration Frequency
 - Cleanliness

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Overview

- Canister cleanliness
- Stock standard certification
- Standard dilution
- Method detection limits
- Instrumentation
- QC samples
- Critical criteria
- All of these should be addressed in the SOP(s)

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- Canister cleanliness
 - TO15 prescribes < 0.2 ppbv for each target compound
 - In reality, ambient concentrations are much lower than this
 - Recommended to certify new canisters

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- Canister cleaning certification blanks
 - Should be taken from each cleaning batch
 - A “batch” should be defined in the SOP
 - Recommend a “batch” be defined as “all canisters connected to a common manifold during the cleaning process”
 - Best practice is to take the canister with the highest concentration (single compound or total of all target compounds) for blank certification

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- Canister health
 - Negative bias
 - Positive bias
- As practical, test canisters annually

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- Stock Standard Certification
 - Primary and Secondary source standards
 - Only a few places to source certified standards
 - Higher concentrations (> 500 ppb)
 - Generally need to be recertified annually

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- Working Standard Preparation
 - Static dilution
 - Syringes
 - Pressure gauges
 - Dynamic dilution
 - Mass flow controllers
 - Calibrate minimally annually using a calibrated flow standard
 - Dilution gas cleanliness
 - Humidification – 50-100 μL deionized water
 - Let sit minimally overnight to allow displacement of molecules from the canister surface

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- Method Detection Limits
 - 40CFR Part 136 Appendix B
 - Minimum of 7 spiked samples
 - Must be in canister matrix
 - Not simply analyzing 7 replicates of a standard or 1 canister
 - Spike at 1 to 5 times to estimated MDL
 - Too high – too precise – artificially low MDL
 - Too low – may not meet 3:1 S:N
 - Set recovery acceptance criteria (i.e. 20-150%)
 - Test the determined MDL by analyzing spikes at the MDL

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- It is critical to get the MDL process correct
- Data reported to AQS are evaluated at the MDL
- An artificially low MDL means that data users are giving more importance to concentrations that are not meaningful
- For more information, refer to the Wisconsin DNR document from 1996:
Analytical Detection Limit Guidance & Laboratory Guide for Determining Method Detection Limits

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- Instrumentation – GC/MS
- Tuning – BFB criteria in TO-15 Table 3 – every 24 hours
- Instrument cleanliness – zero check using no sampled gas, only preconcentrator bake out and injection
- Initial calibration at minimum of five levels (typically 0.5 to 5 ppbv)
 - From separate canisters or one canister using different volumes
 - RSD < 30% for RRf (no provision for quadratic)
 - Must be done following instrument maintenance changing characteristics (ion source cleaning, column replacement, etc)

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- QC Samples
 - Second source calibration verification – mid-range in curve
 - Internal standards – minimum of three compounds
 - 1,4-Difluorobenzene
 - Chlorobenzene-d5
 - Bromochloromethane
 - Laboratory Control Sample
 - Check of standard dilution gas in Method Blank
 - Continuing Calibration Verification (CCV)

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- Leak checking
 - Verify canister pressure when received from field and just before analysis
 - Perform leak check once connected to autosampler
 - Set criteria for decision points for:
 - Rejection (i.e. vacuum < 28” Hg)
 - Invalidation (i.e. change of > 0.5 psia)
 - Corrective action

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- Critical QC criteria
 - Internal Standards must be within 40% of the average of the initial calibration (change in sensitivity may mean that MDLs can not be met)
 - Relative retention time (RRT) must be within 0.06 min for target compounds
 - Blank criteria
 - TO-15 states < 0.2 ppbv for each target compound
 - Recommend < MDL for each target compound
 - Continuing calibration verification within 30% of nominal

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- QUESTIONS?