EPA Method 624.1

A Summary of the Changes in the Newly Promulgated GC/MS Method for Volatile Organics in Wastewater

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"The best laid schemes o' Mice an' Men, Gang aft agley "

Robert Burns, *To a Mouse*, 1786

Method 624 – The Original

- Purge-and-trap sample introduction
- *Packed column* GC
- MS detector
- 31 volatiles listed as target analytes, all of which are listed in Table IC of 40 CFR 136 and are part of the "priority pollutant list"
- Developed in the early 1970s
- Proposed in 1979 and promulgated in 1984

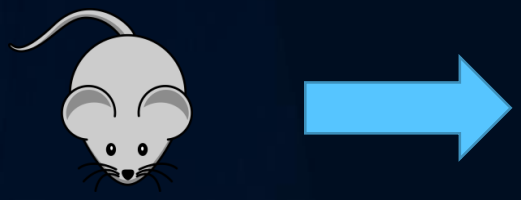
Changes Over Time

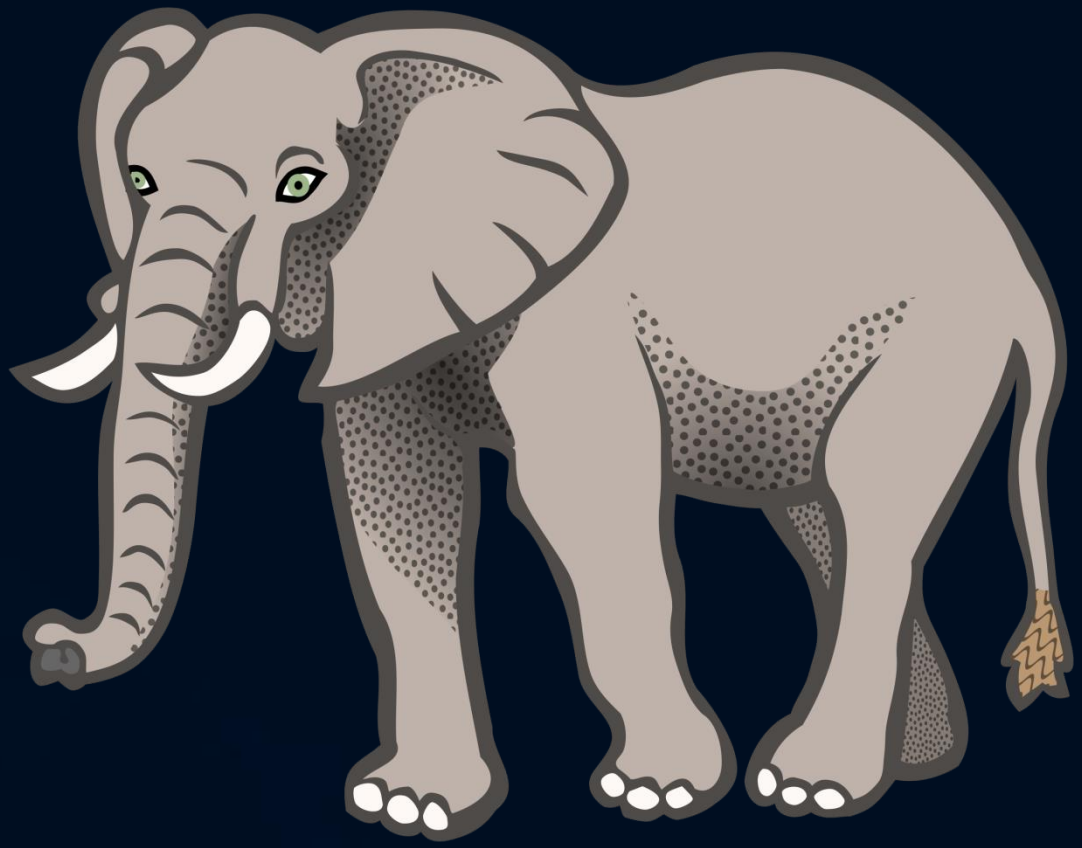
- The Office of Water issued various clarifications about Method 624 over the years that allowed:
  - New trap materials and configurations
  - Use of capillary columns
  - Several industry-specific modifications to add analytes
- All of these have been formalized in the revised method

Method 624.1

- Revisions requested by various stakeholders
- One goal was to "harmonize" volatiles methods across EPA Programs
- Process began June 2012 and continued for two years
- Multiple rounds of internal and external reviews

Methods by Committee





- ✓Gray?
- ✓4 legs?
- ✓Long tail?
- ✓Big ears?

But everything else is wrong!

Focus on "Analytes of Interest"

- Analytes of interest are those required to be determined by a regulatory/control authority, in a permit, or for a client
- Quality control (QC) tests must be performed, and QC acceptance criteria must be met, for the analytes of interest
- If analytes of interest are not specified to the laboratory by the regulatory/control authority, by a permit, or by a client, the analytes in Table 1 of 624.1 must be determined
- All of the analytes from the original version are in Table 1

Other Analytes

- Added Table 2 of "Additional Analytes"
- Over 100 volatiles from other methods and EPA programs (e.g., RCRA, SDWA, CLP)
- Many are alcohols and ketones that may not purge as well as the original analytes, or require heated purge
- Six of the entries are for the xylene isomers, individually (3) and as all 3 possible pairs of coeluters

Explicit Flexibility

- Cites 40 CFR 136.6 for examples of allowed changes. For Method 624, those *already* include:
  - Changes in chromatographic columns or temperature programs
  - Changes in calibration range and calibration model
  - Use of relative standard error (RSE) instead of RSD
  - Use of selected ion monitoring (SIM)
  - Changes in purge volumes, purge times, purge gas, purge-gas flow rates, purge temperature, trap sorbent, desorb time, and use of water management techniques

Other Flexibility

- Added new text to Section 8.1.2 that describes (at length) what a laboratory can and cannot modify in the method and what documentation they must generate to demonstrate that any allowed modifications are effective
- This discussion is common to all newer 1600-Series methods and the latest ATP protocols
- Table 5 contains a long list of alternative surrogates and internal standards

QC Requirements

- Largely the same QC operations as in the original method, with a few name changes
- Most substantive change was going from one matrix spike to a matrix spike/matrix spike duplicate pair to allow for estimation of both precision and bias
- Moved responsibility for identifying samples to be spiked from lab to the discharger
- QC limit for calibration linearity metric of RSD was lowered to 20% (from 35%)
- Explicit allowance for using other BFB tuning criteria

QC acceptance criteria

- All of the original target analytes (Table 1) have QC acceptance criteria for LCS, DOC, and MS/MSD
- For all other analytes (Table 2), lab has the option to establish in-house QC acceptance criteria for the LCS and for the MS/MSD, for each analyte and surrogate, as:
  - Mean recovery ± 3 standard deviations, and
  - Mean RPD + 3 standard deviations
- Criteria must be based on analysis of a minimum of 20 samples; interim criteria of 60 – 140% recovery and 30% RPD must be used until 20 results are obtained.

Other Changes

- Require reporting of results for the blank and sample separately.
- Allow reporting a blank-subtracted result *only* if required by a regulatory/control authority or in a permit.
- Provide procedures for dilution of a sample when a pollutant concentration exceeds the calibration range
- Provide suggestions for analysis of complex samples
- Allow reporting of problems with results when QC tests are failed repeatedly
- Require reporting to the Minimum Level of Quantitation (ML)

Method Detection Limits

- Method 624.1 was proposed as part of the same Methods Update Rule that included the revised MDL procedure
- Therefore, EPA opted to retain the original MDLs from the 1984 version of the method for now
- However, given the overall improvements in instrumentation, EPA anticipates that laboratories will be able to achieve better sensitivity and better performance than in the past.

MUR Comments on 624.1

- 412 comments received from at least 35 organizations or individuals representing:
  - Commercial laboratories
  - POTWs
  - Regulated industries
  - Utility laboratories
  - State regulatory agencies
  - Federal agencies
  - Consultants
  - Private individuals
- 195 pages of comments and EPA's responses are summarized in the docket for the final rule

MUR Comments (continued)

- Many supportive comments, but nobody was completely happy with the revised method
- Concerns included:
  - Simple typos,
  - Removal of the ancient figures,
  - Use of other carrier gases,
  - Storage conditions for standards,
  - New MS/MSD requirements,
  - QC acceptance criteria
  - Remaining differences with other EPA methods or NELAC standards

Changes in Response to Comments

- Standards storage harmonized across methods where practical
- MS scan conditions clarified
- SIM conditions suggested
- Reporting requirements clarified (samples to the ML, and blanks to the MDL)

Final Promulgation?

Method 624.1 has been hermetically sealed in a mayonnaise jar on Funk and Wagnall's front porch since January 2017.