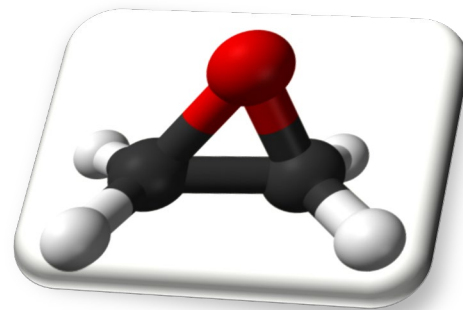




Ethylene Oxide Measurements

Method TO-15/TO-15A Overview, Challenges, Resources and Next Steps



OAQPS/AQAD/AAMG
Ambient Air Monitoring Group

4/15/2021

Outline

What we will cover:

- TO-15/TO-15A Overview;
 - Method analytical considerations, resources, and challenges of TO-15/TO-15A;
 - Sampling challenges with sampling media and sampling devices;
 - Next steps.
- This presentation is intended to inform and communicate challenges and progress associated with the TO-15/TO-15A method using canisters as sampling media and GC/MS as the analytical instrument for Ethylene Oxide (EtO) measurements.

TO-15/TO-15A Overview

- EPA Compendium Methods, TO-15 (1999) and TO-15A (2019), are widely adopted and effective methods for VOC analysis of air samples and have been used by National Air Toxics Trends Stations (NATTS) laboratories and contract laboratories alike for over 20 years.
<https://www.epa.gov/amtic/compendium-methods-determination-toxic-organic-compounds-ambient-air>
- The methods include a target list for 97 VOCs typically with concentrations range from approximately 0.010 to 10 ppbv levels in ambient air.
- Applications for this method include assessment of health impacts from inhalation exposure to VOCs from source emissions and long-term monitoring at sites of various representative scale.

EtO Method Analytical Considerations

Pervious webinar addressed and focused on analytical challenges in August 2019.

<https://www.epa.gov/sites/production/files/2021-03/documents/eto-method-for-natts-labs-2019.pdf>

- Standard Stability
- Method Sensitivity
- Specificity (Co-elution)

Previous EtO Communications and Resources

Standard Stability

- ✓ Technical note distributed for NATTS network's primary and secondary source EtO standards procurement (August 2019).
https://www.epa.gov/sites/production/files/2021-04/documents/eto_stability_memo_082219.pdf
- ✓ Office of Research and Development (ORD) presentation on EtO standard stability study on standards by various vendors and concentrations at NATTS Proficiency Test (PT) quarterly webinar in June 2020.



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711
OFFICE OF AIR QUALITY PLANNING AND STANDARDS

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Technical Note:

Secondary Calibration Source Use for Ethylene Oxide Analysis in the National Air Toxics Trends Stations Network

Ethylene oxide (EtO) is a volatile organic compound (VOC) that was recently updated in the Integrated Risk Information System (IRIS). EtO has not been a standard analyte in the suite of VOCs that are measured as part of the ongoing National Air Toxics Trends Sites (NATTS) program. However, based on the revised IRIS value as well as the results from local ambient monitoring studies conducted in CO, IL, and MI, an EPA priority now includes the addition of EtO to the NATTS Tier I compound list for analysis using TO-15.

EtO Method Analytical Challenges

Method Sensitivity

- EtO 100-in-1-million cancer risk level is 0.011 ppbv necessitating a need for Method Detection Limit (MDL) of at least this level;
- Analytical MDL is not low enough by TO-15/TO-15A to evaluate 100 in 1 million risk(Reported ranges of the analytical MDL are 0.02-0.09 ppbv);
- The overall method MDL will be higher than the analytical MDL ranges noted above when sampling media and sample handling are taken into consideration.

EtO Method Analytical Challenges, continued

Specificity (Co-elution)

- Retention time shift by commonly used GC/MS non-polar column (e.g., DB-1);
 - ✓ Peak tailing effect when polar analyte analyzed by a non-polar column.
- Potential interference by analytes using non-polar or slightly polar columns (e.g., DB-1 and DB-624).
 - ✓ Acetaldehyde
 - ✓ Methanol
 - ✓ Trans-2-butene
 - ✓ 2, 2-Dimethyl propane
 - ✓ Ethyl nitrite

EtO Sampling Issues - Canisters

EPA published an explainer document summarizing agency's work on background EtO including addressing the “canister effect” on EtO measurements (September 2020).

<https://www.epa.gov/hazardous-air-pollutants-ethylene-oxide/epas-work-understand-background-levels-ethylene-oxide>

Is EPA confident in its ethylene oxide monitoring results? (continued)

- As EPA and our state and local partners become more experienced in monitoring ethylene oxide at low levels, we have learned more about things that might affect monitoring results. Recently, EPA has been examining whether aspects of the canisters used to collect air samples may cause some results to be biased – meaning that the results are either higher or lower than the true amount of ethylene oxide in the air. The issues include the materials used to line the inside of the canisters and how the canisters are cleaned before they are put into service.

Canisters
sampling air
for ethylene



EtO Sampling Issues- Canisters

EtO canister effect

- Continued formation and growth of EtO in a subset of canisters over time with humid air;
- Increased overall MDL and reduced method sensitivity;
- Potential factors for certain canisters to exhibit elevated EtO readings include:
 - ✓ Canister inner surface lining characteristics;
 - ✓ Canister age and usage history;
 - ✓ Individual canister characteristics(e.g., active spots on inner lined surface);
 - ✓ Canister cleaning procedures.

Canister Effect Impact on EtO Ambient Measurement Data

Bias

- Ambient measurement results are most likely higher than the true amount of EtO in the air, especially at low levels.
- Bias due to elevated and unaccounted-for canister effect by certain canisters.

Precision

- When ambient measurements are closer to the MDL or below the MDL, this results in a decrease in the accuracy (decrease in precision and increase in bias).
- Analytical precision, as indicated by laboratory replicates, (multiple analyses of the same canister) has been within acceptable limits. This demonstrates repeatability of the analytical method.
- Overall method precision calculated by collocated/duplicate samples is impacted by various degrees of EtO canister effect by individual canisters of different characteristics and history.

Steps to Mitigate and Resolve Canister Issues

The chemical mechanism of EtO formation and growth in a subset of canisters remains unclear.

- OAQPS is working collaboratively with ORD, the national contract lab, and canister manufacturers to better understand and mitigate the issues.
- Updated requirements in TO-15A should help mitigate canister issues
 - ✓ Canister qualification/certification using humidified zero air versus nitrogen;
 - ✓ More stringent canister cleanliness acceptance limits;
 - ✓ TO-15A better tailored to identify and remove problematic canisters from EtO sampling.

More details in TO-15A webinar from June 2020.

https://www.epa.gov/sites/production/files/2020-06/documents/to-15a_webinar_slidedeck.pdf

EtO Sampling Cautions When Using Stand-Alone Timers

Released a new technical memorandum that addresses common challenges in VOC sampling.

Use of Stand-Alone Timers for Volatile Organic Compound (VOC) Sample Collection in Canisters (February 2021).

https://www.epa.gov/sites/production/files/2021-04/documents/use_of_stand-alone_timer_timer_guidance_for_voc_sampling.pdf

- Identifies cautions and issues related to sub-ambient sampling and timer use.
- Suggests best practices for sub-ambient sampling and timer use.

MEMORANDUM

SUBJECT: Use of Stand-Alone Timers for Volatile Organic Compound (VOC) Sample Collection in Canisters

FROM: Greg Noah, QA Team Lead
Air Quality Assessment Division, Ambient Air Monitoring Group

TO: EPA Regional Air Monitoring Contacts

EPA has received reports of issues with the use of stand-alone timers used for VOC sub-ambient sample collection. The issues involve potential leaks in the timer and/or sample flow controller that allow the sample canisters to drop to ambient pressure (0"Hg) during sampling and results in the invalidation of the sample. The invalidation requirement is consistent with direction in the National Air Toxics Trends Station Technical Assistance Document, Revision 3, Section 4.2.3.2.2 located here:

https://www3.epa.gov/ttn/amtic/files/ambient/airtox/NATTS%20TAD%20Revision%203_FINAL%20October%202016.pdf

Next Steps

- EPA continues to study EtO stability in calibration cylinders and work with gas standard vendors to ensure and improve EtO standard quality.
- Development of an addendum or supplement section to TO-15A to address and provide guidance on EtO specific analytical and sampling issues.
- Further laboratory and field evaluation of real-time EtO optical analyzers as well as an active sorbent based method for near source and ambient EtO monitoring.

Questions?

Q&As-1

Q: Do you have a timetable for the addendum or supplement for TO-15A for EtO?

A: We don't have a definitive timeline for the addendum or supplement section to TO-15A on EtO analysis at this point. While a lot of lab work has been delayed due to COVID-19 in 2020, this is a priority project once the ORD laboratory staff are able to be back working full time.

Q: Has there been any look at using HDPE canisters (if available) vs. stainless steel canisters for collecting samples?

A: Currently, stainless steel canisters are the canisters used by most laboratories, and these are the available canisters manufactured and on the market. Thus, we are focusing on evaluating the performance of currently available types of stainless steel canisters on the market and in use.

Q&As-2

Q: There was talk of glass bottles for sample collection.

A: It is important that any sample vessel be properly evaluated prior to use. We will reach out to our colleagues in ORD to see if this will be included in their evaluations.

Q: Can you provide more information on sorbent work?

A: The active sorbent method is still a bench scale analysis; we are looking for the sensitivity we need. We are currently working on evaluating it. There may be more to share in the next few months.

Q&As-3

Q: Can you provide a list of the labs that were used in this review?

A: Information derived and data showed in this presentation were mostly from EPA's national contract lab (ERG), the ORD lab and the various state NATTS labs.

Q: Can you confirm what you said that canister effects should decrease over time?

A: The EtO canister effect is believed to decrease over time to a certain extent when the canisters go through multiple and repeated cleaning cycles.

Q&As-4

Q: If you develop a standard method for EtO using optical technique, are we considering including TO-15 compounds so that one instrument could be used for all air toxics analysis?

A: The goal would be to develop performance-based procedures which could be applied to optical techniques for ambient level air toxics measurements and could be applied to many different compounds.

While it would be ideal to have a singular instrument for all air toxics compounds, the current optical approaches are selective and can be used for only a few specific compound(s).

Q&As-5

Q: Is an SOP available for EtO via TO-15A? We haven't seen one.

A: There is no SOP currently available on EtO analysis by TO-15A, but details on EtO analysis guidance and specifics will be provided once the addendum on EtO to TO-15A is developed.

Q: Being a reactive gas, what about HCL sorbent for ethylene chlorohydrin as a surrogate?

A: We are relying on brominated carbon traps for our sorbent work. We are building up from personnel exposure monitoring methods developed by OSHA and their previous evaluations demonstrated that this was the preferred derivatization approach (2- bromoethanol).

Q&As-6

Q: What is the best method in determining what interference we are seeing in our canisters when looking at EtO? Any more info on newly discovered interferences since the last presentation?

A: When following the peak identification and quantification criteria described in the NATTS TAD or TO-15A (Section 4.2.8.5.3 and Section 16.2), if the lab analyst suspects an interference, a non-target library search could be used to help identify the potentially interfering compound. And if possible, a reference standard should be acquired to confirm.

Q: Is there any data to show the same sample measured on the different columns (DB1 vs. DB624) is comparable?

A: There are participating NATTS labs with either the DB-1 or DB-624 type of columns in use, and according to the EtO Proficiency Test (PT) results reported, samples analyzed by either column were comparable and consistent.