

Data Quality Evaluation Guidelines for Ambient Air Acrolein Measurements

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Overview

In 2010, OAQPS completed a study that determined acrolein monitoring results could be affected by factors that include how canisters are cleaned in preparation for sample collection and the gas standards used to calibrate analytical equipment. Due to the resulting data quality concerns, EPA worked with the NACAA Monitoring Steering Committee to develop an AQS reporting framework for acrolein measurements that bins data as either “acrolein - *unverified*” or “acrolein - *verified*”. This document is intended to support state, local, and tribal air pollution control agencies who must decide whether to leave their data in the re-named “unverified” parameter code or move the data to a new “verified” parameter code, both of which are described below.

Background

Historically, the default method for measuring ambient air acrolein concentrations was by collection on a DNPH-coated silica gel cartridge followed by HPLC analysis (e.g., EPA Method TO-11A). However, the “Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air — Second Edition” (<http://www.epa.gov/ttn/amtic/files/ambient/airtox/toxcompd.pdf>) was amended in October 2000 to remove acrolein from the list of applicable target analytes due to significant data quality concerns.

In 2002, OAQPS released the first National Air Toxics Assessment based upon 1996 air toxics emissions; acrolein was the dominant non-cancer risk driver. Given the significant risk from acrolein, OAQPS began to investigate alternative means of measuring ambient air acrolein concentrations. Air samples collected in canisters and analyzed by GC/MS (i.e., EPA Method TO-15) emerged as the most feasible option. The National Contract Laboratory (Eastern Research Group) was tasked with evaluating this approach, the results from which supported the viability of ambient acrolein measurements via EPA Method TO-15. These results are documented in a report and are available at <http://www.epa.gov/ttn/amtic/files/ambient/airtox/finacrolein.pdf>.

As this approach was implemented over the course of several years, questions arose regarding the potential for growth of acrolein in canisters, a problem that could result in a high bias. In 2010, OAQPS worked with several state and local air quality agencies to conduct a study to determine whether monitoring results were affected by the process used to clean canisters in preparation for sample collection. The study showed that acrolein can be elevated even in canisters that are considered clean, resulting in ambient measurements that were biased high.

Additionally, the study demonstrated that the accuracy of acrolein gas standards used to calibrate analytical systems was quite variable between different laboratories, resulting in significant biases that worsened the uncertainties arising from the growth issue.

While there are continuing OAQPS/ORD efforts to improve acrolein monitoring methods for the future, there are several key factors that can be considered now to significantly improve the accuracy of acrolein sampling and analysis by EPA Method TO-15. EPA recommends that agencies monitoring ambient air acrolein concentrations (via TO-15 or comparable) consider adopting the practices described below.

Sampling and Analysis Guidelines

Canister Cleaning Practices

An important factor in preparing canisters for acrolein sampling is the addition of heat to the cleaning process (i.e., heat the canisters to a temperature on the order of 90°C). Following cleaning, initially and periodically (e.g., annually) test each canister for acrolein growth over a two to three week period. This is done by adding humidified air or nitrogen to each canister (to 5-10 psig) and testing each canister for cleanliness by GC/MS using an ambient air pre-concentrator. Test each canister immediately after cleaning and then once a week for two to three weeks to help determine whether acrolein is likely to “grow” in the canister. Plot the data from each test to assess whether or not (and if so, the degree to which) there is growth of acrolein over time. If there is evidence of acrolein growth in a particular canister, it may be prudent to repeat the cleaning and testing until negligible growth is evident. Some canisters may not pass the acrolein growth test even after repeated cleaning; such cans may not be suitable for measuring ambient air acrolein.

Calibration Standards

The other factor that can play a large role in the acrolein sampling results is the calibration gas standards that laboratories use to calibrate their GC/MS analytical systems. Performance tests for the National Air Toxics Trends Station (NATTS) Network over the past five years have yielded acrolein results that are quite variable. As part of the 2010 study, several laboratories analyzed samples containing known values of acrolein. The study results indicated that labs using higher concentration acrolein standards (*diluted to target range concentrations*) to calibrate their equipment provided more consistent analytical results. The higher concentration standards are more stable; however, it is important to have the TO-15 standard re-certified by the manufacturer at their suggested frequency or at least every year to ensure the best acrolein stability possible.

Timeliness

In the interest of sample stability and integrity, EPA recommends analyzing samples (particularly whole air samples) as soon as reasonably possible after collection.

Quality Assurance (QA) Guidelines

Acrolein data can also be assessed using the conventional Data Quality Indicators (DQIs) of precision and bias that allow for an understanding of data certainty.

Method precision is determined by calculating the coefficient of variation (CV) between collocated or duplicate sample analyses. Analytical precision is determined by calculating the CV between replicate (split sample) analyses. For the NATTS Network, a CV within 15% is considered acceptable.

Bias is the systematic or persistent distortion of a measurement process that causes the expected sample measurement value to trend either higher or lower from the sample’s true value. For the NATTS program, bias is determined by creating and distributing single blind proficiency test (PT) samples to all participating laboratories, the analysis results from which are compared with the

known concentration values. For the NATTS Network, a Relative Percent Difference (RPD) within 25% is considered acceptable.

Further information on the NATTS Network Quality Assurance Program is available at <http://www.epa.gov/ttn/amtic/airtoxqa.html>.

Summary of Reporting Guidelines: Acceptable Parameter and Method Codes

Because of the uncertain accuracy of acrolein measurements, OAQPS has changed the name of the existing acrolein parameter code in AQS (43505) to “Acrolein - Unverified” to indicate the current level of uncertainty that exists with the data already reported to AQS. Correspondingly, a new parameter code (43509) has been created in AQS for “Acrolein - Verified.” Whether or not all or a subset of existing data remain in the unverified parameter code, or are re-categorized as verified and moved / reported to this new parameter code, is a choice over which each owning agency has complete discretion. Until such time as agencies evaluate their acrolein monitoring procedures and the quality of reported data, we recommend that already-reported data remain in the unverified method code.

At the time during which this document was written, there were 29 method codes for acrolein in AQS. Data arising from methods which collect samples via canister and analyze those samples via GC/MS are acceptable for consideration as either unverified or verified acrolein data in AQS. These method codes are listed below in Table 1.

Method Code	Sample Collection Description	Sample Analysis Description
101	CANISTER SUBAMBIENT PRESSURE	MULTI DETECTOR GC
109	SS-CANISTER-SUBAMBIENT-PRESURE	GAS CHROMATOGRAPH MASS SELECTIV DET
110	SS-CANISTER-PRESSURIZED	GAS CHROMATOGRAPH MASS SPECTRO
113	SS-Canister Pressurized	Capillary GC ITD Mass Spectro
127	6L SUBAMBIENT SS-CANISTER	INCOS 50XL GC/MS
129	6L SUBAMBIENT SS-CANISTER	VARIAN SATURN-2 GC/MS
136	6L Pressurized Canister	Entech Precon w/ Agilent GC/MS/FID
145	6 L SS Canister Subamb press, passive coll	GC/Mass Spectro
147	6L PRESSURIZED CANISTER	ENTECH PRECON - SATURN II GC/FID
148	6L PRESSURIZED CANISTER	ENTECH PRECON - HP GC/FTIR/MS
149	6L SUBATM CANISTER	Entech Precon- GC/FID/MSD
150	SS 6L- PRESSURIZED CANISTER	CRYOGENIC PRECON: GC/MS
153	Pressurized Canister	GC with Multiple Detectors
171	6L Pressurized Canister	Precon Saturn GC/MS
172	6L Pressurized Canister	Precon HP GC/MS
175	Passivated Canister	Cryogenic Preconcentration GC/MS
176	6L SUBATM SS CANISTER	ENTECH PRECONCENTRATOR GC/MS
210	SS 6L Pressurized Canister	Cryogenic Precon GC/MS
211	SS Canister Subambient Pressure	Gas Chromatograph Mass Spectro

For more information on acrolein reporting procedures, please contact Mike Jones of OAQPS at jones.mike@epa.gov or 919-541-0528.