

Flare Gas Composition Analysis and QA/QC – Lessons Learned and Lessons Lost

HERMAN HOLM – SPECTRUM ENVIRONMENTAL SOLUTIONS, LLC
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Today's Discussion

- QA/QC requirements under MACT CC for Gas Chromatographs (GCs)
 - List of Compounds
 - Surrogate Compounds
- Performance Specification (PS) 9
 - MACT CC modifications
- Areas of Concern/Interest
- How broadly applicable AMP for mass spectrometry compares (Alt 119)

Calibration Option 1

The owner or operator must use a calibration gas or multiple gases that include all of compounds listed in paragraphs (e)(2)(i)(A) through (K) of this section that may be reasonably expected to exist in the flare gas stream and optionally include any of the compounds listed in paragraphs (e)(2)(i)(L) through (O) of this section. All of the calibration gases may be combined in one cylinder. If multiple calibration gases are necessary to cover all compounds, the owner or operator must calibrate the instrument on all of the gases.

(A) Hydrogen. (B) Methane. (C) Ethane. (D) Ethylene. (E) Propane. (F) Propylene. (G) n-Butane. (H) iso-Butane.

(I) Butene (general). It is not necessary to separately speciate butene isomers, but the net heating value of trans-butene must be used for co-eluting butene isomers.

(J) 1,3-Butadiene. It is not necessary to separately speciate butadiene isomers, but you must use the response factor and net heating value of 1,3-butadiene for co-eluting butadiene isomers.

(K) n-Pentane. Use the response factor for n-pentane to quantify all C5+ hydrocarbons.

Optional - (L) Acetylene. (M) Carbon monoxide. (N) Propadiene. (O) Hydrogen sulfide.

Calibration Option 2

The owner or operator must use a surrogate calibration gas consisting of hydrogen and C1 through C5 normal hydrocarbons. All of the calibration gases may be combined in one cylinder. If multiple calibration gases are necessary to cover all compounds, the owner or operator must calibrate the instrument on all of the gases.

If the owner or operator chooses to use a surrogate calibration gas under paragraph (e)(2)(ii) of this section, the owner or operator must comply with paragraphs (e)(3)(i) and (ii) of this section.

(i) Use the response factor for the nearest normal hydrocarbon (*i.e.*, n-alkane) in the calibration mixture to quantify unknown components detected in the analysis.

(ii) Use the response factor for n-pentane to quantify unknown components detected in the analysis that elute after n-pentane.

Performance Specification (PS) 9

40 CFR Part 60, Appendix B - SPECIFICATIONS AND TEST PROCEDURES FOR GAS CHROMATOGRAPHIC CONTINUOUS EMISSION MONITORING SYSTEMS IN STATIONARY SOURCES

Presurvey Sample Analysis and GC Selection.

Determine the pollutants to be monitored from the applicable regulation or permit and determine the approximate concentration of each pollutant (this information can be based on past compliance test results). Select an appropriate GC configuration to measure the organic compounds.

- The GC components should include a heated sample injection loop (or other sample introduction systems), separatory column, temperature-controlled oven, and detector. If the source chooses dual column and/or dual detector configurations, each column/detector is considered a separate instrument for the purpose of this performance specification and thus the procedures in this performance specification shall be carried out on each system...

Similar requirement for mass spec – but can augment the minimum list.

PS 9 - Sampling System.

The sampling system shall be heat traced and maintained at a minimum of 120 °C with no cold spots. All system components shall be heated, including the probe, calibration valve, sample lines, sampling loop (or sample introduction system), GC oven, and the detector block (when appropriate for the type of detector being utilized, e.g., flame ionization detector).

PS 9 - Calibration Gases.

Obtain three concentrations of calibration gases certified by the manufacturer to be accurate to within 2 percent of the value on the label.

- A gas dilution system may be used to prepare the calibration gases from a high concentration certified standard if the gas dilution system meets the requirements specified in Test Method 205, 40 CFR Part 51, Appendix M...The calibration gas concentration of each target analyte shall be as follows (measured concentration is based on the presurvey concentration determined in Section 6.1).
- NOTE: If the low level calibration gas concentration falls at or below the limit of detection for the instrument for any target pollutant, a calibration gas with a concentration at 4 to 5 times the limit of detection for the instrument may be substituted for the low-level calibration gas listed in Section 7.1.1.

Low-level. 40–60 percent of measured concentration.

Mid-level. 90–110 percent of measured concentration.

High-level. 140–160 percent of measured concentration, or select highest expected concentration.

PS 9 - Performance Audit Gas.

A certified EPA audit gas shall be used, when possible. A gas mixture containing all the target compounds within the calibration range and certified by EPA's Traceability Protocol for Assay and Certification of Gaseous Calibration Standards may be used when EPA performance audit materials are not available. The instrument relative error shall be ≤ 10 percent of the certified value of the audit gas.

PS 9 - 7-Day Calibration Error (CE) Test Period.

At the beginning of each 24-hour period, set the initial instrument setpoints by conducting a multi-point calibration for each compound. The multi-point calibration shall meet the requirements in Section 13.3. Throughout the 24-hour period, sample and analyze the stack gas at the sampling intervals prescribed in the regulation or permit. At the end of the 24 hour period, inject the three calibration gases for each compound in triplicate and determine the average instrument response. Determine the CE for each pollutant at each level using the equation in Section 9–2.

Each CE shall be **≤10 percent**. Repeat this procedure six more times for a total of 7 consecutive days.

Calibration Precision and Linearity – any one injection shall not deviate more than 5% from the average concentration.

PS 9 - Performance Audit Test Periods.

Conduct the performance audit once during the initial 7-day CE test and quarterly thereafter. Sample and analyze the EPA audit gas(es) (or the gas mixture prepared by EPA's traceability protocol if an EPA audit gas is not available) three times. Calculate the average instrument response. Report the audit results as part of the reporting requirements in the appropriate regulation or permit (if using a gas mixture, report the certified cylinder concentration of each pollutant).

PS 9 – Calibration and Standardization

Initial Multi-Point Calibration.

After initial startup of the GC, after routine maintenance or repair, or at least once per month, conduct a multi-point calibration of the GC for each target analyte. The multi-point calibration for each analyte shall meet the requirements in Section 13.3.

Daily Calibration.

Once every 24 hours, analyze the mid-level calibration standard for each analyte in triplicate. Calculate the average instrument response **for each analyte**. The average instrument response shall not vary more than 10 percent from the certified concentration value of the cylinder for each analyte. If the difference between the analyzer response and the cylinder concentration for any target compound is greater than 10 percent, immediately inspect the instrument making any necessary adjustments, and conduct an initial multi-point calibration as described in Section 10.1.

- Calibration Precision and Linearity – any one injection shall not deviate more than 5% from the average concentration.

PS 9 MACT CC Modifications

Follow the procedure in Performance Specification 9 of 40 CFR part 60, appendix B, except that

- a single daily mid-level calibration check can be used (rather than triplicate analysis),
- the multi-point calibration can be conducted quarterly (rather than monthly), and
- the sampling line temperature must be maintained at a minimum temperature of 60 °C (rather than 120 °C).

Comparison – PS 9 vs Table 13

Specification	PS 9	MACT CC
Daily Calibration Check for Each Analyte	Triplicate mid-level	Single mid-level
Multi-point Calibration	Monthly	Quarterly
Sampling Line Temperature	120 °C	60 °C

Areas of Concern/Interest

- Sample line minimum temperature below 100°C could have issues of condensation (plugging) for sample system or analyzer.
- The beginning of the out-of-control period is the hour a performance check (e.g., calibration drift) that indicates an exceedance of the performance requirements...is conducted.
- The end of the out-of-control period is the hour following the completion of corrective action and successful demonstration that the system is within the allowable limits.
- The owner or operator shall not use data recorded during periods the CPMS is out of control in data averages and calculations, used to report emissions or operating levels, as specified in paragraph (d)(3) of this section.

Areas of Concern/Interest

The Presurvey Sample Analysis in PS 9 allows for the use of past compliance test results.

- No mention of engineering evaluations
- No mention of how many samples are required or under what operating scenarios

The CPMS must be capable of measuring the appropriate parameter over the range of values expected for that measurement location.

- Is the parameter NHV or analyte concentration?
- The more analytes with potentially high concentrations will increase the number of cylinders needed for daily CE and time spent in “required monitoring system quality assurance or quality control activities.”

The data recording system associated with each CPMS must have a resolution that is equal to or better than the required system accuracy.

- Required accuracy is 10% of each analyte.

Questions?

Herman Holm

Director – Specialty Environmental Services

Spectrum Environmental Solutions, LLC

herman@spectrumenvsoln.com

678-727-2147

