

## Frequently Asked Questions For Use of PS 9 in 40 CFR Part 63 Subpart CC

### Use of Performance Specification 9 for Gas Chromatographic Continuous Emission Monitoring Systems for Determination of Net Heating Value for Flares in 40 CFR part 63 subpart CC

1. Are there differences between the initial and ongoing quality control (QC) requirements in PS 9 and the procedure for using PS 9 in 40 CFR part 63 subpart CC for continuously determining Net Heating Value (NHV)?

Yes. 40 CFR part 63 subpart CC (hereafter referred to as Subpart CC) overrides some of the requirements of PS 9. In Table 13 – Calibration and Quality Control Requirements for CPMS, Subpart CC allows the following modifications:

- a. A single daily mid-level calibration check in lieu of PS 9 Section 8.3.7 triplicate analysis.
- b. Quarterly multi-point calibrations in lieu of PS 9 Section 10.1 monthly calibrations.
- c. Minimum sampling line temperature of 60°C in lieu of the PS 9 Section 6.2 minimum of 120°C.

2. What test gases are required for PS 9, as implemented for flares in Subpart CC?

There are two options for test gases when complying with subpart CC:

- a. Gases that contain the specific compounds listed in 40 CFR 63.671(e)(2)(i). The compounds may be contained in one or multiple cylinders.
- b. Gases containing hydrogen and C1 through C5 normal hydrocarbons. The compounds may be contained in one or multiple cylinders. (40 CFR 63.671(e)(2)(ii))

You must 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. Unknowns above the molecular weight of pentane will be determined using the response factor for n-pentane. Instrument specific response factors must be generated through initial and periodic calibrations.

3. Is it okay to add additional minor components to the hydrogen plus C1 through C5 blend?

If a facility wants to add a compound for compliance with other requirements (e.g., permit, consent decree) no approval is needed for this inclusion. However, this additional compound should not be used in Subpart CC NHV calculations. If you want to include the additional compound (or substitute for a required compound) in the Subpart CC NHV calculation, you currently need to make an alternative test method request following the requirements in guidance document [GD-22](#) on the Emission Measurement Center (EMC) website.

4. Must QC checks be performed against all the individual compounds in the test gas cylinders or can I perform QC checks against NHV instead?

Typically, PS 9 is used to continuously monitor low concentrations of gaseous target compounds, generally hazardous air pollutants. As such, QC is based on the ability to accurately measure the individual compounds in the relevant permit or rule. However, the requirements in Subpart CC for flares employ PS 9 to measure NHV, which has raised some unique issues. EPA

has attempted to address these issues in several alternative test methods, which have been issued with broad applicability for Subpart CC. One of these alternative test methods, [ALT-131](#), was written to allow the use of the total NHV for calibration checks and performance audits required in PS 9, in lieu of performing these checks against the individual compounds in the test gases. This includes the 7-day calibration error test.

5. What standards must test gases meet to comply with PS 9?

You must use test gases that meet the following requirements:

- a. For daily calibration check - a gas vendor certified standard that is within 2% of the value on the label. (PS 9 Section 7.1)
- b. For the quarterly performance audit - a certified EPA audit gas or EPA Protocol Gas if available; otherwise use a separate cylinder gas standard certified by the vendor to be within 2% of the tag or labeled value. (PS 9 Section 7.2)
- c. For quarterly multi-point calibration - gases at three concentrations (low-, mid-, and high-level) for each analyte, certified to be within 2% of the value on the label. (PS 9 Section 7.1)

6. Section 7.1 of PS 9 requires 3 levels of calibration gas:

- a. Low-level: 40-60 percent of measured concentration
- b. Mid-level: 90-110 percent of measured concentration
- c. High-level: 140-160 percent of measured concentration

What is measured concentration?

The measured concentration for the individual analytes is based on the presurvey concentration determined under Section 6.1 of PS 9.

7. If concentrations for low-, mid-, and high-level calibration gases are specified in a permit or consent decree and differ from the requirements of PS 9, how can this be addressed?

You can make an alternative test method request following the requirements in guidance document [GD-22](#) on the EMC website.

8. How often must I perform QC and calibration assessments?

You must perform the following QC activities:

- a. You must perform an initial 7-day calibration error test. (PS 9 Section 8.3)
- b. A performance audit must be completed once during the initial 7-day test and then quarterly thereafter. (PS 9 Section 8.4)
- c. A multi-point calibration must be completed after the initial setup, after maintenance and/or repair, and at least quarterly. (PS 9 Section 10.1, as implemented by Appendix to Subpart CC of Part 63, Table 13)
- d. A daily calibration must be completed once every 24 hours. Perform a single daily mid-level calibration check. (PS 9 Section 10.2, as implemented by Appendix to Subpart CC of Part 63, Table 13)

9. Does the requirement in Section 10.2 of PS9 to conduct a multi-point calibration after a failed daily calibration apply to flares in Subpart CC?

Yes. This requirement was not excepted by Subpart CC, and as such, it still applies.

10. Are quarterly multi-point calibrations and performance audits (sometimes referred to as cylinder gas audits or CGAs) both required if they are essentially the same test?

Performance audits are comprised of a mid-level calibration gas injected three times through the sample transport system. Multi-point calibrations are comprised of low, mid, and high-level calibration gases injected in triplicate (PS 9 Section 10.2) directly to the instrument, unless the applicable permit or rule directs differently. As such, these tests are not the same, and both must be performed.

11. Can multi-point calibration standards be used to meet the requirement for performance audit checks?

While both tests are on the same frequency (quarterly) and may be performed using the same quality gases if EPA audit gases are not available, the intent of PS 9 is these are separate gas cylinders, where the performance audit cylinder comes from a more rigorous preparation procedure if possible and/or from a second source.

12. Section 13.3 of PS 9 states that the sample to be analyzed shall flow continuously through the sampling system. The calibration error test and multi-point calibration reference section 13.3. This could be interpreted to mean that items must have calibration gas injected at the probe as opposed to the inlet of the GC. Which QC samples must be introduced at or near the sampling probe tip?

Good measurement science dictates that initial and periodic calibration, including calibration checks, of the instrument can be performed at the injection loop of the gas chromatograph (GC), but that performance audits should be treated as samples and not as calibration gases.

Therefore, Section 13.3 of PS 9 is applicable, and the audits must be injected at the probe. We believe that this intent can be inferred from the definition of sampling system in Section 6.2 of PS-9, as the definition include a calibration valve prior to the sample lines:

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).

13. Where in PS 9 does it state that the performance audit is a single mid-level calibration check?

The requirement for performance audit gas is in Section 7.2 of PS 9. PS 9 requires the use of a single concentration within the calibration range. Note that the requirement is "A gas mixture...within the calibration range...", implying one gas.

14. When does the 5% precision and linearity check apply in PS 9?

Unless otherwise specified in a permit, the precision specification applies when the instrument is initially set-up and accepted, following significant changes to the system that require repeating the initial instrument evaluation, and any time triplicate injections are made. The precision specification applies at each concentration when multiple concentrations are injected. The linearity specification applies when the instrument is initially set-up and accepted, following significant changes to the system that require repeating the initial instrument evaluation, and any time multiple concentrations are injected. (PS 9, Section 13.2) Note that subpart CC allows the use of a single daily mid-level calibration check (rather than triplicate analysis), and as such, the requirements in Section 13.2 of PS 9 are not applicable to daily calibration checks for this rule.

15. For the 7-Day Calibration Error Test, must the multi-point calibration be performed each day, or does it need to be performed on just the first day?

The initial multi-point calibration should be performed on Day 0 and on each of the subsequent 7 days. The instrument set points are set on Day 0 and do not necessarily have to be reset on the subsequent 7 days prior to each 24-hour period (similar to other performance specifications, such as PS 2, in which the calibration can be reset immediately after error is determined and prior to the next 24-hour period). The specifications for calibration precision and linearity in Section 13.2 of PS 9 would also have to be met for all 8 days; the rationale for this is that although Section 13.3 is referenced in Sections 8.3 and 10.1, Section 13.2 specifies that “each triplicate injection” (i.e., any triplicate injection) must meet these specifications.

16. Does the 7-Day Calibration Error Test have to meet the 10% specification of Section 13.1 of PS 9?

Yes. Section 13.1 of PS 9 states, “The average CEMS calibration response must not differ by more than 10 percent of calibration gas value at each level after each 24-hour period of the initial test.” The 10% specification is also stated in Section 8.3, so this requirement clearly applies to the 7-Day Calibration Error Test.

17. 40 CFR 63.670(j)(1) and 40 CFR 63.655(i)(9) require facilities to record and maintain the individual component concentrations for a minimum of 2 years. When using the calibration gas option in 40 CFR 63.671(e)(ii), are the individual components used for calibration (H<sub>2</sub>, C<sub>1</sub>, n-C<sub>2</sub> through n-C<sub>5</sub>), sufficient for recordkeeping purposes, or should the facility group the peaks (given the same response factor) as an individual component concentration (i.e., six components would be recorded but the C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub> and C<sub>5</sub> groups would contain normal and olefin (unknown) concentrations)?

Because records are intended to demonstrate compliance with the rule, it is best to keep records that allow a reviewer to recreate the compliance demonstration. As such, we recommend that facilities group the peaks, given the same response factor, as an individual component concentration. This will allow a reviewer to be able to recalculate the NHV and compare it to the reported value.

18. When using the calibration gas option in 40 CFR 63.671(e)(ii), should we compare the group concentrations to the tag on the calibration cylinder or would the normal peak be sufficient (given the calibration bottle only contains normal components)?

The individual compound analysis results should be recorded to allow a reviewer to compare the concentrations of the bottle tag values to the calculated values from the analysis.

19. Is a GC considered a CPMS, and if so, does the definition of out-of-control in 40 CFR 63.671(c)(1) apply?

For the purposes of Subpart CC, the GC is considered a CPMS and the definition of out-of-control in 40 CFR 63.671(c)(1) does apply.

20. Does the analyzer remain out-of-control until a multi-point calibration is successfully performed?

The analyzer remains out-of-control until completion of corrective action and successful demonstration that the system is within limits (i.e., successful calibration).

21. May I use a mass spectrometer (MS) to measure NHV instead of a GC or calorimeter?

Yes. Please see alternative test method [ALT-119](#) for more information on this option.

## Appendix to FAQ for PS 9 use with 40 CFR 63 Subpart CC

### Relevant Performance Specification and Rule Sections

#### *PS 9 Section 6.2*

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).

#### *Rule Exception – Subpart CC Table 13*

Follow the procedure in Performance Specification 9 of 40 CFR part 60, appendix B, except that...the sampling line temperature must be maintained at a minimum temperature of 60°C (rather than 120°C).

#### *PS 9 Section 7.1*

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.

#### *PS 9 Section 7.2*

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.

**Note:** If a certified EPA audit gas or a traceability protocol gas is not available, you may use a gas manufacturer's standard accurate to 2%.

#### *PS 9 Section 8.3*

7-Day Calibration Error (CE) Test Period. At the beginning of each 24-hour period, set the initial instrument set points 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.

**Note:** This is only done at initial instrument installation and evaluation.

#### *PS 9 Section 8.4*

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 Section 10.1*

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.

**Note:** This part of PS 9 requires multi-point calibration across the range of calibrated concentrations. Because it requires injection of three calibration gases in triplicate, requirements in Section 13 for triplicate injections apply, *i.e.*, the linear regression requirement must be met for each calibration.

#### *Rule Exception – Subpart CC Table 13*

Follow the procedure in Performance Specification 9 of 40 CFR part 60, appendix B, except that...**the multi-point calibration can be conducted quarterly (rather than monthly)**.

#### *PS 9 Section 10.2*

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.

#### *Rule Exception – Subpart CC Table 13*

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)**...

#### *PS 9 Section 10.2*

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.

#### *Rule Exception – Subpart CC Table 13*

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)**...

**Note:** While this part of PS 9 requires triplicate injections, because Subpart CC allows a **single** daily mid-level calibration check rather than a triplicate, Section 13.2 requirements for precision do not apply.

#### *PS 9 Section 13.1*

Calibration Error (CE). The CEMS must allow the determination of CE at all three calibration levels. The average CEMS calibration response must not differ by more than 10 percent of calibration gas value at each level **after each 24-hour period of the initial test.**

#### *PS 9 Section 13.2*

Calibration Precision and Linearity. **For each triplicate injection** at each concentration level for each target analyte, any one injection shall not deviate more than 5 percent from the average concentration measured at that level. **The linear regression curve for each organic compound at all three levels shall have an  $r^2 \geq 0.995$  (using Equation 9-1).**

**Note:** This part of PS 9 only applies when there are triplicate injections.

#### *PS 9 Section 13.3*

Measurement Frequency. The sample to be analyzed shall flow continuously through the sampling system. The sampling system time constant shall be  $\leq 5$  minutes or the sampling frequency specified in the applicable regulation, whichever is less. Use Equation 9-3 to determine T. The analytical system shall be capable of measuring the effluent stream at the frequency specified in the appropriate regulation or permit.

#### *40 CFR 63.671(e)*

*Additional requirements for gas chromatographs.* For monitors used to determine compositional analysis for net heating value per §63.670(j)(1), the gas chromatograph must also meet the requirements of paragraphs (e)(1) through (3) of this section.

(1) The quality assurance requirements are in table 13 of this subpart.

(2) The calibration gases must meet one of the following options:

(i) 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.

(L) Acetylene (optional).

(M) Carbon monoxide (optional).

(N) Propadiene (optional).

(O) Hydrogen sulfide (optional).

(ii) 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.

(3) 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.