



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
RESEARCH TRIANGLE PARK, NC 27711

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FEB 05 2018

OFFICE OF  
AIR QUALITY PLANNING  
AND STANDARDS

Mr. Tony Slapikas  
Product Manager for Mass Spectrometry  
AMETEK, Energy & Process Division  
150 Freeport Road  
Pittsburgh, PA 15238

Dear Mr. DeCarlo and Mr. Slapikas,

I am writing in response to your letter dated August 18, 2017, requesting approval for use of process mass spectrometers as part of an alternative to testing procedures utilizing calorimeters or gas chromatographs to measure Net Heating Value ( $NHV_{VG}$ ) in flare vent gas as required under 40 CFR Part 63, Subpart CC – National Emission Standards for Hazardous Air Pollutants from Petroleum Refineries. The owner or operator of facilities subject to Subpart CC must measure flare vent gas composition to determine  $NHV_{VG}$  in units of British Thermal Units per standard cubic foot (BTU/SCF). This BTU/SCF determination may be performed using a calorimeter capable of continuously measuring, calculating, and recording  $NHV_{VG}$  at standard conditions (40 CFR 63.670 (j)(3)) or equipment that determines the concentration of individual components in the flare vent gas (40 CFR 63.670 (j)(1)), such as a gas chromatograph, and, if desired, may directly measure the hydrogen concentration in the flare vent gas following the methods provided in 40 CFR 63.670 (j)(4). All monitoring equipment must meet the applicable minimum accuracy, calibration and quality control requirements specified in Table 13 and §63.671 of Subpart CC.

In your letter, you propose to use a process mass spectrometer analyzer and the following measurement approach as an alternative to measure  $NHV_{VG}$ :

- 1) The owner or operator of the affected facility will perform a pre-survey to determine the list and concentration of components that are present in flare vent gas feed. This pre-survey will be used in part to:
  - a) Determine an appropriate analysis method for the site-specific refinery flare vent gas;
  - b) Create a list of vent gas components to be included in calibration gas cylinders to be used to evaluate the quality of the measurement procedure used to determine  $NHV_{VG}$ ;
  - c) Define calibration standards to be prepared by a vendor at a certified accuracy of 2 percent and traceable to NIST; and
  - d) Perform an initial calibration to identify mass fragment overlap and response factors for the target compounds.

- 2) The process mass spectrometer will be calibrated using calibration gas standards consisting of a mix of the compounds identified in the site specific flare gas pre-survey.
- 3) During flare gas analysis, compounds that are not identified during the pre-survey and that have mass fragments identical to the compounds found during the pre-survey will be included in the calculation of  $NHV_{VG}$ .
- 4) Calibration error (CE) for each component in the calibration blend will be calculated using the following equation:

$$CE = \frac{C_m - C_a}{C_a} \times 100$$

Where :

$C_m$  = Average instrument response, (ppm)

$C_a$  = Cylinder gas value or tag value, (ppm)

- 5) The average instrument CE for each calibration compound at any calibration concentration must not differ by more than 10 percent from the cylinder gas value or tag value.
- 6) For each set of triplicate injections at each calibration concentration for each calibration compound, any one introduction shall not deviate more than 5 percent from the average concentration measured at that level.

Your supporting information included Method 301 calculations that showed acceptable bias and precision when you measured a mixture of gases from a vendor certified gas cylinder. Your request also includes reference to facilities needing to monitor flare gas composition continuously to effectively maintain flare efficiency while compensating for changes in the flare gas composition.

With this letter, we are approving your request to substitute continuous process mass spectrometry for continuous gas chromatography as allowed in 40 CFR 63.670 and 63.671 predicated on both your proposed use of these process mass spectrometers as described above and the additional provisos listed below:

- 1) You must meet the requirements in 40 CFR 63.671 (e)(1) and (2) including Table 13 requirements for Net Heating Value by Gas Chromatograph.
- 2) You may use the alternative sampling line temperature allowed in 40 CFR 63, Subpart CC, Table 13, under Net Heating Value by Gas Chromatograph.
- 3) You must meet applicable Performance Specification 9 (40 CFR part 60, appendix B) requirements for initial continuous monitoring system acceptance including, but not limited to:
  - Performing a multi-point calibration check at three concentrations following the procedure in Section 10.1; and
  - Performing periodic process mass spectrometer calibrations as directed for gas chromatographs in 40 CFR 63, Subpart CC, Table 13.
- 4) You may augment the minimum list of calibration gas components found in 40 CFR 63.671(e) with compounds found during the pre-survey as needed to develop a site-specific analysis method.

- 5) For unknown gas components that have similar analytical mass fragments to calibration compounds, you may report the unknowns as an increase in the overlapped calibration gas compound.
- 6) For unknown compounds that do not produce mass fragments that overlap calibration compounds, you may use the response factor for the nearest molecular weight hydrocarbon in the calibration mix to quantify the unknown component's NHV<sub>VG</sub>. This requirement parallels the requirements in 40 CFR Part 63.671 (e)(3) for gas chromatographs.
- 7) You may use the response factor for n-pentane to quantify any unknown components detected with a higher molecular weight than n-pentane.
- 8) You must meet all other applicable generic requirements of §§63.670 and 63.671 for measurement of NHV<sub>VG</sub> (i.e., measurement requirements not specifically targeted to gas chromatographs).
- 9) A copy of this approval letter must be included in the report for each testing program where these alternative testing procedures are applied.

Since this alternative test method approval under 40 CFR 63.7 (f) is appropriate for use at all facilities subject to 40 CFR 63, Subpart CC, we will announce on EPA's Web site (<https://www.epa.gov/emc/broadly-applicable-approved-alternative-test-methods>) that the alternative method is broadly applicable to determination of NHV<sub>VG</sub> under this subpart.

If you have any questions regarding this approval or need further assistance, please contact Ray Merrill at (919) 541-5225 or [merrill.raymond@epa.gov](mailto:merrill.raymond@epa.gov), or Robin Segall at (919) 541-0893 or [segall.robin@epa.gov](mailto:segall.robin@epa.gov).

Sincerely,



Steffan M. Johnson, Group Leader  
Measurement Technology Group

cc.

Gerri Garwood, EPA/OAQPS/SPPD  
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