



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
RESEARCH TRIANGLE PARK, NC 27711

MAY 07 2013

OFFICE OF  
AIR QUALITY PLANNING  
AND STANDARDS

Mr. Bryan D. Tyler  
Enthalpy Analytical, Inc.  
800-1 Capitola Dr.  
Durham, NC 27713

Dear Mr. Tyler:

This letter is in response to your request of November 21, 2012, and subsequent communications in January and March of 2013, for approval of alternative sampling and analysis procedures for flare gas fuel heat content (BTU value) measurement under 40 CFR 60.18(f)(3). The requested alternatives would apply to Method 18 (40 CFR Part 60, Appendix A), which is required to be used to measure the organic content in order to determine the BTU content of the flare gas. In your request, you also requested broad applicability for these alternatives to measure BTU content of flare gas fuels.

In summary, you requested alternatives to the requirements in Method 18 in four areas:

- 1) Sampling flare gas fuel streams using electro-polished stainless canisters.
- 2) Applying heating values to unknown hydrocarbons based on retention times of the unknown chromatographic peaks relative to the hydrocarbons used to calibrate your analysis method.
- 3) Relaxation of the spike recovery requirement in Method 18 for fuel gas BTU analysis.
- 4) Relaxation of the requirement for triplicate analysis of samples to quantify compounds for BTU determination.

Regarding your first alternative request, you requested the use of an electro-polished 3L stainless steel container for sample collection to meet the requirements of 40 CFR 60.18(f)(3). Your rationale includes reference to EPA Method 18, which allows canisters only for pre-survey purposes. When used for compliance testing, Method 18 requires sample collection in Tedlar bags, direct interface, or adsorbent sampling. You propose the alternative use of stainless steel containers since flare gas is being used as a fuel, is collected prior to being combusted, and is composed of hydrogen, carbon monoxide, and various hydrocarbons rather than combustion "emissions". The requirements in 40 CFR 60.18(f)(3) for flare fuel gas sample collection and analysis are intended to demonstrate that the BTU/SCF of the flare gas are above a minimum requirement as opposed to demonstrating that volatile organic emission level is below a regulated emission limit. Thus, if some portion or component of the organic sample were to be lost to the walls of the canister, the result would negatively impact the BTU/SCF demonstration.

You also provided data demonstrating that hydrocarbon fuel samples typically consist of hydrocarbon components containing 6 or less carbons. You assert that these hydrocarbons are stable VOC, and are not subject to the same stainless steel canister wall effects as combustion samples, considering the volatility, relative inertness, and the absence of water vapor and acid gases in these flare fuel gas samples. To support this contention, you supplied data comparing the results of samples collected simultaneously in Tedlar bags and stainless steel canisters. These data were provided to EPA to show that electro-polished stainless steel container results compare well with Tedlar bag sample results for fuel gas hydrocarbon analysis.

In addition, your request includes reference to shipping safety issues, and you provided a short description of the prime safety reasons for use of electro-polished canisters including:

- The Federal Aviation Administration (FAA) requirement that flammable gases be shipped in hard sided containers for commercial air shipments, and
- Department of Transportation (DOT) requirement that flammable gas, which you contend most all flare samples are, be shipped in a hard sided container for commercial ground shipments.

You noted that electro-polished stainless steel containers would meet both the FAA and DOT safety requirements for sample transportation.

Regarding your second request for alternative sample analysis, you requested an approach for quantifying the BTU content that includes assigning quantitative values to unknown compounds detected during analysis of flare gas fuel samples. You requested unknown hydrocarbon compounds eluting near one of the C2 through C6 n-alkanes be reported based on the calibration response for the nearest alkane. You provided background, rationale, and justification for this request based on the following information:

- Your calibration consists of using each of the C1 through C6 n-alkanes (methane through hexane).
- Your capability to extend calibration to n-dodecane (C12) using NIST- traceable calibration standards.
- Your field sample data demonstrate that other branched, unsaturated or cyclic hydrocarbons that are not in the calibration mixture can contribute significantly to the heat content of the fuel.
- One cannot calibrate for unknown hydrocarbons before sample analysis.

Regarding your third alternative request, you requested relief from the Method 18 spike and recovery procedure for the 40 CFR 60.18 flare gas heat content measurement requirements. You assert that Method 18 spike and recovery quality control requirements to assess the stability of the analyte and the appropriateness of the collection technique are not practical for unknown compounds. Since C1 through C6 calibration compounds are both stable and sufficiently volatile, and that canisters are received under pressure and at such high concentrations, you contend that spike recovery of the calibration compounds is not practical.

Regarding the fourth alternative request, you requested reducing the requirement for triplicate injections in Method 18 to duplicate injections with +/-5% reproducibility to be consistent with ASTM Method D 1946-90.

We have reviewed your requests as well as the requirements of 40 CFR 60.18 and approve/disapprove your four proposed testing alternatives as explained:

- 1) Regarding sampling with stainless steel electro-polished canisters, we agree that for safety reasons, the use of stainless steel electro-polished canisters, SUMMA passivated canisters, or silica lined stainless steel canisters or cylinders is an acceptable alternative for hydrocarbon flare fuel gas sample collection. Your results demonstrated an average difference in hydrocarbon concentration between Tedlar bags and stainless steel cylinders of approximately 13%. This alternative is approved provided that the fuel gas is under pressure and is primarily composed of combustible hydrocarbons, which are inert to reaction with ambient temperature stainless steel.
- 2) Section 60.18(f)(3) requires that the net heating value of the gas being combusted in a flare shall be calculated using the sum of the individual compound contributions to BTU content. We agree that it may be impractical to identify and quantify all unknown compounds in the potentially complex mixtures of hydrocarbons present in flare fuel gas. For purposes of hydrocarbon fuel BTU analysis, the fundamental heating value is a function of the number of carbon atoms. Gas chromatographic retention times for both known and unknown compounds under the conditions of this analysis is a function of vapor pressure. Therefore, you may use the response factor for the nearest normal hydrocarbon (i.e., n-alkane) in your calibration mixture to quantify unknown components detected in your BTU analysis. This approval is predicated on the requirement that you calibrate for this analysis using standard(s) containing normal hydrocarbons C1 through C7 that meet Method 18 calibration standard requirements. Unknown compounds that elute after n-heptane must either be identified and quantified using an identical compound standard, or you must extend your calibration range to include the additional normal hydrocarbons necessary to perform the unknown hydrocarbon quantitation procedure described elsewhere in this alternative test method approval.

- 3) We agree that, in lieu of the spike recovery requirement in Method 18, you may report calibration results that demonstrate linear response of each calibration compound up to the highest concentration that you measure in each flare fuel gas sample.
- 4) We do not approve relaxation of the requirement to perform triplicate analysis of BTU samples. ASTM D1946-90 is not included in the rule requirements as an alternative method for analysis of hydrocarbons to determine BTU. While duplicate analysis simplifies the analysis procedure, we believe triplicate analysis of a canister sample is necessary to evaluate the consistency of the compound recovery from the canister as the pressure changes, and thus should be a continued practice for this rule.

To use the approved alternative sampling and analysis approaches for flare fuel gas heat content measurement:

- You must demonstrate that each batch of stainless steel canisters cleaned for fuel gas BTU determination has a Flame Ionization Detector response less than 1 percent or less than 3 BTU/SCF, whichever is less, of the value of the samples subsequently collected and analyzed from a certified batch of clean canisters.
- You must follow the requirements of Method 18 for sample collection substituting electro polished stainless steel canisters or SUMMA passivated canisters, or silica-lined stainless steel canisters/cylinders for the Tedlar bag required in the method.
- You must calibrate your gas chromatograph with C1 through C7 normal hydrocarbons certified by the gas vendor to meet Method 18 requirements.
- You must follow the calibration and quality control procedures found in Sections 8.2.1.5, 10.0, and 13.0(a) of Method 18.

This approval does not include or approve using stainless steel canisters for collection or analysis of combustion samples. Steel canisters are not appropriate for direct sampling of combustion gas samples potentially containing acid gases and moisture. Stainless steel canisters are also not approved for sampling and analysis of oxygenated fuels containing percent levels of ethanol or other oxygenated additives. Stainless steel canisters are not appropriate for sampling and analysis of reduced sulfur compounds in flare gas. However, for safety reasons, we agree that reduced sulfur compounds may be sampled with silica-lined stainless steel canisters or cylinders under 40 CFR 60.18 for the purpose of BTU determination when the reduced sulfur species are a significant component of the flare gas heat content.

We will announce on EPA's website (at <http://www.epa.gov/ttn/emc/approalt.html>) that our approval of this alternative is broadly applicable to testing the heat content of flare fuel gas under 40 CFR 60.18.

If you need further assistance, please contact Ray Merrill of my staff at (919) 541-5225, or [merrill.raymond@epa.gov](mailto:merrill.raymond@epa.gov).

Sincerely,



Conniesue B. Oldham, Ph.D., Group Leader  
Measurement Technology Group

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