TECHNICAL MEMORANDUM

DATE: September 28, 2015

SUBJECT: Proposal to remove EPA Methods 18, 320, and ASTM D6348-03 as acceptable methods for measuring total VOC under 40 CFR 60, Subpart JJJJ

FROM: Steffan Johnson – OAQPS AQAD Measurement Technology Group Leader

TO: Docket # EPA-HQ-OAR-2014-0292-0001

Background

On September 8, 2015 the Measurement Technology Group of the EPA published proposed revisions to Test Methods, Performance Specifications, and Testing Regulations for Air Emission Sources (80 FR 54146). In this rulemaking, we propose to remove EPA Methods 18, 320, and ASTM D6348-03 as acceptable methods for measuring total Volatile Organic Compounds (VOC) under 40 CFR 60, Subpart JJJJ. It has come to our attention that we have not supplied sufficient information supporting our rationale for making this change in the rule package and docket. The intent of this memo is to provide the rationale for this proposed action.

For clarification we would also point out that the September 8, 2015 proposal did not remove an option to use Method 320, ASTM 6348, and EPA Method 18 for methane and ethane determination, however this is not clearly stated in the preamble of the Revisions to Test Methods, Performance Specifications, and Testing Regulations for Air Emission Sources; Proposed Rule (80 FR 54146).

The EPA recognizes that the measurement technologies used in these methods are appropriate for the purpose of measuring specific organic compounds, and will continue to specify their use for compliance measurement for this purpose. While these measurement techniques excel in speciated VOC measurements, Methods 18, 320 and ASTM D6348-03 are not robust total VOC measurement methods as currently required by Subpart JJJJ, where the measurement result is the basis for determination of compliance with a total VOC emissions limit.

EPA Methods 18, 320, and ASTM D6348-03 were included in ”Standards of Performance for Stationary Spark Ignition Internal Combustion Engines” 40 CFR 60, Subpart JJJJ in 2008 (73 FR 3568) as alternative methods to Method 25A, based on recommendations by two commenters (EPA-HQ-OAR-2005-0030-0150 - American Petroleum Institute and EPA-HQ-OAR-2005-0030-0157 - Interstate Natural Gas Association of America) during the comment period of the proposed rule dated June 12, 2006 (71 FR 33804). Both commenters specifically requested use of EPA Method 320 for measurement of nitrogen oxides and carbon monoxide. Both commenters also requested the need for a method to determine non-methane hydrocarbons and proposed use of Method 18 and pointed out that a “validated” FTIR method could also be acceptable.

Discussion

The proposed removal of EPA Method 320 and ASTM D6348-03 (both of which rely on Fourier Transform infrared (FTIR) technology) is due to the lack of a consistent, demonstrable, and validated approach to measuring total VOC emissions, primarily due to the lack of a discrete list of compounds identified as those constituting the total VOC for the emissions sources affected by this rule. Since promulgation of the revisions to Subpart JJJJ in 2008, EPA's Office of Air Quality Planning and Standards, Measurement Technology and Measurement Policy Groups have been unable to provide adequate technical assistance to regulatory agencies who must make compliance determinations for Subpart JJJJ sources with data collected using these methods. The complexity of attempting to accurately quantify a total VOC value using FTIR technology should not be underestimated.

A primary point of concern is that neither EPA Method 320 nor ASTM D6348-03:

(1) Include procedures and quality assurance /quality control processes for conducting a summed measurement of large numbers of VOC analytes or,

(2) Describe how this sum equates to total VOC in the sampled gas streams.

The list of potential VOC species which must be addressed by a total VOC method is extensive. EPA defines VOC in §60.2 as "…any organic compound which participates in atmospheric photochemical reactions; or which is measured by a reference method, an equivalent method, an alternative method, or which is determined by procedures specified under any subpart".

In addition, the applicability, accuracy, and precision of FTIR measurements are influenced by a number of interrelated factors, which may be divided into two classes: Sample-independent and sample-dependent factors, and these factors must be considered for each analyte measured with this approach.

Examples of sample independent factors are system configuration and performance (e.g., detector sensitivity and infrared source output), quality and applicability of reference absorption spectra, and type of mathematical analyses of the spectra. These factors define the fundamental limitations of FTIR measurements for a given system configuration. These limitations may be estimated from evaluations of the system before samples are available. For example, the detection limit for the absorbing compound under a given set of conditions may be estimated from the system noise level and the strength of a particular absorption band. Examples of sample-dependent factors are spectral interferents (e.g., water vapor and CO_2, both present in quantity from engine emissions) or the overlap of spectral features of different compounds and contamination deposits on reflective surfaces or transmitting windows. To maximize the effectiveness of the mathematical techniques used in spectral analysis, identification of interferents (a standard initial step) and analysis of samples (including the effect of other analytical errors) are necessary. As stated above, such measurement interferences and effects must be understood for each analyte measured, thus exacerbating the difficulty of measurement where a large number of individual compounds are present (or may be present) in the emissions stream.

EPA Method 320 incorporates method specific data validation processes by which data collected is quality controlled and assured; likewise, ASTM D6348-03 includes a number of Annexes that perform a similar function. Appropriate use of these QA/QC procedures requires a full understanding of the individual compounds being measured along with the gas matrix containing the compounds, such that the QA/QC challenges presented to the sampling and analytical systems are appropriate to qualify the

most difficult to measure compounds. With an extensive list of compounds to be measured, such QA/QC procedures to validate these data are both expensive and time consuming.

Another concern that complicates measurement of total VOC using these FTIR methods is the variability of the matrix of pollutant species that make up total VOC emissions from engine exhaust. The EPA does not have sufficient information in hand to know when Methods 320 or ASTM D6348-03 have actually measured and correctly quantified each constituent VOC in the exhaust stream, unless each compound has been validated through the QA/QC procedures outlined in Section 13.0 of Method 320 or Annex 5 of ASTM D6348-03. We also recognize that the potential VOC compounds emitted from an internal combustion engine vary depending on several factors including but not limited to fuel type (engines combusting No. 2 diesel will have a different VOC emission profile than engines combusting landfill gas, bio gas, ag-grade diesel, or one combusting field gas at an upstream oil and gas facility). Other factors influencing variable emissions include (but are not limited to) engine maintenance, age, make-up air temperature, and humidity. Additionally, we are aware that many FTIR measurement approaches are not sensitive enough to individually quantify all compounds present, and may not quantify benzene, toluene, ethylbenzene, and xylenes (BTEX) due to water interference, a common concern with FTIR measurement. Furthermore, we have apprehensions with the ability of FTIR device software to correctly identify and quantify the potential target compounds in the engine exhaust such as speciation of C3+ alkane mixtures to properly account for number of carbons for proper conversion to a propane basis.

It is our understanding that following promulgation of the revisions to Subpart JJJJ in 2008, some compliance test protocols have been submitted where emissions test firms base compliance testing on an approach to measure total VOC by quantifying a specific list of VOC compounds they believed to best match the effluent of Subpart JJJJ engines. This may be a credible way to perform <u>speciated</u> VOC sampling for those targeted compounds, however we have not seen any evidence to support that such a targeted list represents the total VOC from these sources, much less during different operations or when burning different fuels. As such, this VOC list has been determined by the tester or an instrument vendor, and not the regulatory authority.

These target compound lists are very important, as they may not meet the definition of "total volatile organic compounds" as stated in Subpart JJJJ, and the associated measurement would then not demonstrate compliance. For these reasons, we are proposing to remove Method 320 and ASTM D6348-03 as total VOC compliance methods from Subpart JJJJ until there is an establishment of a comprehensive, standardized measurement protocol that can be used to accurately identify and quantify a value representative of total VOC from the wide variety of these engine and fuel emissions profiles.

We believe that establishment of a comprehensive standardized protocol for FTIR measurement of total VOC under Subpart JJJJ is dependent on developing an understanding of some very complex concerns. First, a sufficient catalog of speciated VOC emissions data from a wide variety of engine exhausts must be developed to determine if a discrete list of VOC compounds could be derived for each process configuration (engine and controls) and fuel type. This information could then be used to design a total VOC measurement approach which accurately quantifies each compound in a specified list of VOC list representative of the total VOCs from a given process and control configuration. Additionally, we would need to evaluate the suite of VOC emissions from such lists to determine applicable target analytes for spiking and recovery studies, and from there would be also be the need to develop a list of standard response factors with which to equate the speciated VOC to a propane basis for a final compliance determination. While this represents a substantial amount of work, it is not insurmountable, although

we are lacking the raw data with which to begin such analysis, making a timeline to resolution lengthier than we would like.

Unlike the FTIR methods discussed above, EPA Method 18 does include guidance for total VOC measurement which involves a process known as "screening" whereby the source is pre-surveyed prior to conducting the emissions test for all possible VOC compounds according to Section 16.1 of Method 18. Compounds that are detected in a measureable quantity during this intensive screening process are then targeted in the subsequent compliance test. We find this procedure impractical for use in subpart JJJJ as the wide scope of sampling protocols involved, and subsequent calibration and QA/QC requirements (use of calibration standards for and spiking of each VOC to be quantified) required to conduct Method 18 would be exceedingly costly, rendering the requirement to conduct such a pre-survey at each source as cost prohibitive. Indeed, to date, no data has been presented to EPA showing speciated VOC sampling according to Method 18 as accurate or viable, though it may be achievable through a good deal of effort and expense. Like with the FTIR, we believe a comprehensive measurement protocol could be developed for GC measurement based upon a sufficient catalog of Method 18 screening data from a wide variety of engine exhausts (engine, controls and fuel type) to develop a target list of VOC compounds.

With the proposed removal of EPA Methods 18 and 320, as well as ASTM D6348-03 for use in measuring total VOC under Subpart JJJJ, owners and operators must use EPA Method 25A as the methodology to perform VOC measurements. Method 25A measures the aggregate of total VOC that respond to the FIA detector as measurement of total VOC as defined by §60.2. Using EPA Method 25A to determine compliance with the emission limit incorporates the reduced response of the aldehydes and other oxygenated organics considered when the emission limits were set and therefore remains consistent with the procedures used to establish the emission limit.

Closing

The EPA recognizes the utility of both GC and FTIR technologies and has routinely required their use in air emissions standards; however, we are concerned that current implementation of these test methods under Subpart JJJJ does not provide for proper and consistent quality assurance for compliance demonstration with total VOC measurement as required by the subpart. Because of these concerns and implementation issues, we are proposing to remove the use of Method 18, Method 320, and ASTM D6348-03 for total VOC compliance determination under 40 CFR 60 Subpart JJJJ.

We are interested in identifying a standardized approach that would provide consistent and repeatable measurement of total VOC using these techniques, and whereby we could again allow the use of these test methods to demonstrate compliance for total VOC emissions limit(s) under Subpart JJJJ. How quickly the EPA can proceed on this path will depend on our access to data necessary in order to develop the protocol laid out above.