April 30, 2024

Via electronic submission (http://www.regulations.gov)
Attn: EPA–HQ–OAR–2022–0491
United States Environmental Protection Agency
EPA Docket Center
WJC West Building, Room 3334
1301 Constitution Avenue NW
Washington, DC 20004

**Re: EPA-HQ-OAR-2022-0491; EPA Method 320—Measurement of Vapor Phase Organic and Inorganic Emissions by Extractive Fourier Transform Infrared (FTIR) Spectroscopy, 89 Fed. Reg. 15,101 (Mar. 1, 2024)**

Dear Sir or Madam:

GPA Midstream Association ("GPA Midstream") appreciates this opportunity to submit comments on the U.S. Environmental Protection Agency's ("EPA") proposed rulemaking, Measurement of Vapor Phase Organic and Inorganic Emissions by Extractive Fourier Transform Infrared (FTIR) Spectroscopy, 89 Fed. Reg. 15,101 (Mar. 1, 2024).

GPA Midstream has served the U.S. energy industry since 1921 and represents over 50 domestic corporate members that directly employ 55,000 employees that are engaged in the gathering, transportation, processing, treating, storage and marketing of natural gas, natural gas liquids (NGLs), crude oil and refined products, commonly referred to as "midstream activities." The work of our members indirectly creates or impacts an additional 400,000 jobs across the U.S. economy. In 2022, GPA Midstream members operated over 250,000 miles of gas pipelines, gathered over 85 Bcf/d of natural gas, and operated over 375 natural gas processing facilities that delivered pipeline quality gas into markets across a majority of the U.S. interstate and intrastate pipeline systems.

GPA Midstream regularly comments on EPA rulemakings important to our members. Here, we write to support the following comments on this proposal: Comments submitted by Randy Bartley, Re: Revision to USEPA Method 320 (Apr. 28, 2024); Comments submitted by Martin L. Spartz, Ph.D., Re: Revision to USEPA Method 320 (Apr. 22, 2024). Copies of Mr. Bartley's and Dr. Spartz's comments are attached.

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GPA Midstream appreciates the opportunity to submit these comments and is standing by to answer any questions you may have.

Respectfully submitted,

Matt Hite
Senior Vice President, Government Affairs
GPA Midstream Association

Attachments

# Attachment 1

Date: April 28, 2024

To: USEPA

From: Randy Bartley

Re: Revision to USEPA Method 320

**ENVIRONMENTAL PROTECTION AGENCY**
**40 CFR Part 63**
**[EPA–HQ–OAR–2022–0491; FRL–9992–01–OAR]**
**RIN 2060–AV81**
**EPA Method 320—Measurement of Vapor Phase Organic and Inorganic Emissions by Extractive Fourier**
**Transform Infrared (FTIR) Spectroscopy**
**AGENCY:** Environmental Protection Agency (EPA).

IV. Summary of Proposed Revisions to Method 320

*"In this action, the EPA proposes technical revisions that update the validation and quality assurance (QA) spiking procedures of Method 320 to provide a more performance-based approach."*

COMMENT: Having performed or reviewed thousands of compliance tests over the last 15 years utilizing and FTIR analyzer and conforming to the data quality objectives in ASTM d6348, the analyte spiking procedures, which are similar to those in RM 320 only show the ability of the sampling system to be able to transport the compound or target analyte(s) of interest. For the Stationary RICE source category, this is already accomplished by doing a system calibration where calibration gas is introduced to the system and response times are recording as well as system bias determinations. These procedures are required for other EPA test methods such as RM 3a, 7e, 10, 25a for the measurement of O2, NOx, CO, and THC or VOC concentrations. However, none of these other methods are required to conduct any further analysis of the sampling system's ability to transport the target analytes. Why must it be included in RM 320 or any FTIR sampling method such as ASTM d6348? I believe that this requirement should be removed, certainly in the case of testing according to NSPS 40 CFR 60 Subpart JJJJ or NESHAP 40 CFR 63 Subpart ZZZZ for Stationary RICE. Stationary RICE is the largest source category in the USA and there are tens of thousands of data sets that show there are no issues in transporting the compounds or target analytes of interest in the testing matrix for these sources.

SUGGESTION: Remove this requirement for all source categories impacted by this revision as identified in Table 1 of the revision except for those categories required to sample for HCl (i.e. cement manufacturing and lime manufacturing plants). Otherwise, make this a requirement for all EPA analytical sampling test methods to keep the methods uniform in data quality objectives.

IV. G. Section 7.0 (Reagents and Standards)

*The EPA proposes to remove sections 8.3.1 and 8.3.2, which provide the options to verify detector linearity by varying the power incident on the detector by modifying the aperture setting or by using neutral density filters to attenuate the infrared beam in current, respectively.*

COMMENT: I agree with this change since most FTIRs cannot perform this requirement as described in the previous version of the method.

*8.1.3.3 Reference spectra incorporated in the program must either bracket the observed sample matrix concentration or use a direct injection to verify the calibration curve.*

COMMENT: This is another example of the method requiring an FTIR analyzer to do something not required with other analytical technologies and should not be a part of the method. Bracketing is this manner is in contrast to how FTIR gas analysis algorithms are designed to work.

SUGGESTION: Remove this bracketing requirement and align the language with other analytical EPA Reference Methods that allow a zero gas for low end calibrations.

*8.7 Sampling. See section 11.5 of this method. While sampling, monitor the signal transmittance. If the transmittance (relative to background) changes by 5% or more in any analytical spectral region, obtain a new background spectrum.*

COMMENT: There seems to be confusion with running a background and running a zero-system bias as in EPA RM 7e, where drift assessments can be performed. There are requirements where analyzers must be recalibrated on a 3-point linearity curve, by introducing calibration gases of known concentrations directly to the analyzer, but a background check is not the same and should not be reacquired during a compliance test.

*8.6 Pre-Test Calibrations.*

COMMENTS: In Paragraph IV of the Revision Publication, it states, "The proposed revisions would more closely align Method 320 with the EPA's approach to emissions measurement, which emphasizes specifying performance-based criteria in test methods." However, in Section 8.6, only a CTS calibration is required. What about direct and system calibrations for target analytes?

SUGGESTION: If the intent is to align RM 320 with other EPA RMs, then utilize the same language and data quality objectives to simplify the requirements and continuity.

*9.1.2 Post-Test QA.*
*9.1.2.1 Inspect the sample spectra immediately after the run to verify the gas matrix composition was close to the expected matrix composition.*
*9.1.2.2 Verify that the sampling and instrumental parameters were appropriate for the actual stack conditions. For example, if the moisture of the sampled gas was much higher than anticipated, a shorter pathlength cell or more dilute sample may be needed.*

COMMENTS: In Paragraph IV of the Revision Publication, it states, “The proposed revisions would more closely align Method 320 with the EPA’s approach to emissions measurement, which emphasizes specifying performance-based criteria in test methods.” However, this section addresses Post-Test QA without any well-defined Pre-Test QA.

SUGGESTION: If the intent is to align RM 320 with other EPA RMs, then utilize the same language and data quality objectives to simplify the requirements and continuity.

*9.3.1.2 It is recommended that spiking be performed after each run to ensure continued compliance with the required spike recovery criteria. If spiking is not performed after each run and the post-test spike fails, all data for that test are invalid. However, if spiking is performed after each run, data bracketed on each end by a successful spike are valid test data.*

COMMENTS: Why is so much proof of system performance required? No other EPA analytical test method requires this. What does doing this procedure in 3 replicates prove? A replicate is defined as the following measurement sequence: native gas concentration, SA-elevated gas concentration, native gas concentration. Requiring six to eight replicated spikes is excessive.

SUGGESTION: If the desire is to see this added level of system performance confirmed, require one Pre-test replicate for an analyte spike recovery. To confirm both the system and analytical performance in a Post-run and Post-test capacity, require a CTS system calibration.

*9.3.3 Determine the response time (RT) of the system. First, inject zero air into the system. For standard addition RT determination, next measure the native stack concentration of the species to be spiked. The concentration has stabilized when variability appears constant for five minutes.*

COMMENTS: How does this show response time? No other method defines a response time measurement in this manner. What is described here is not an evaluation of response time. It might be an evaluation of how long it takes to conduct a spike recovery, but that does not equate to a system response time. This procedure just does not make sense.

SUGGESTION: Remove this language and use a standard response time procedure as shown in EPA RM 7e.

*9.3.4.4.1 Dual FTIR and Extractive Systems Approach. This field approach is performed using two independent FTIRs and sample extraction systems that use tubing of the same length and diameter and that pull the sample at approximately the same flow rate. One FTIR characterizes the fluctuations of the target analyte(s) over time and the second FTIR performs the spike recoveries. Note that testers can use either a single probe attached to both systems or separate probes for each system with the probe tips co-located (within 6 inches) in the sample duct. In either case, it is mandatory for the spike to occur prior to the PM filter. Perform the spiking procedure as follows.*

COMMENTS: I cannot think of another more fiscally inefficient manner than what is suggested here to address what is already an overly cumbersome and unnecessary requirement that no

other technology is asked to make. My firm cannot afford to add a secondary FTIR to our mobile laboratory for this purpose.

SUGGESTION: Run a longer spike recovery to allow for variability. We currently and commonly do this on rich burn Stationary RICE. Make an allowance for a spike utilizing a higher flow rate. The current requirement is no greater than 10%, so perhaps expand this to 20-30% of the sample flow.

*11.1 Leak Check. Verify that there are no significant vacuum-side leaks using one of the leak tests described in this section. Perform the vacuum-side leak check after each installation at the sampling or measurement location. Leak check must be performed prior to the start of the field test, and after any relocation or maintenance to the sample transport system. A leak may be detected either by measuring a small amount of flow when there should be zero flow, or by measuring the vacuum decay rate. To test for leaks using loss of vacuum you must know the vacuum-side volume of your sampling system to within ±10% of its true volume.*

*11.1.1 Low-Flow Leak Test. Test a sampling system for leaks using low-flow measurements as follows:*

*11.1.1.1 Seal the probe end of the system by capping or plugging the end of the sample probe.*

*11.1.1.2 Start sampling pumps and operate them until the pressure stabilizes.*

*11.1.1.3 Observe/measure the flow through the vacuum-side of the sampling system. A flow of less than 0.5% of the system's normal in-use flow rate is acceptable.*

*Note: For bypass systems, where the sample flow rate through the vacuum side of the sample system is greater than the FTIR cell flow rate, the higher flow rate (bypass plus analyzer/FTIR flow rate) is used as the in-use flow rate when calculating acceptability of the leak level.*

*11.1.2 Vacuum-Decay Leak Test. Perform a vacuum-decay leak test as follows:*

*11.1.2.1 Seal the probe end of the system as close to the probe opening as possible by capping or plugging the end of the sample probe.*

*11.1.2.2 Operate all vacuum pumps. Draw a vacuum on the sampling system and let the pressure on the system stabilize.*

*11.1.2.3 Turn off the sample pumps and seal the system under a vacuum of 250 mmHg greater than the source static pressure. Record the absolute pressure and the system absolute temperature every 30 seconds for 5 minutes. The leak rate must be equal to or less than 2.5 mmHg per minute.*

COMMENTS: No method performance requirements should ever be written in a manner that would create system contamination in any part of the system. I do NOT care to have to clean my gas cell and essentially start all calibrations over because of an erroneous method requirement.

Furthermore, would not a system calibration at zero and high for any target analyte confirm that the sample is being transported in an acceptable and leak free manner?

SUGGESTION: Use other RM criteria for system calibration checks for continuity and alignment.

*11.5.1 Stratification Check. A stratification check must be performed, per the steps in this section, to justify sampling at a single location during testing.*

*11.5.1.1 Use a probe of appropriate length to measure the analyte of interest at each of 12 traverse points (MNi, where i = 1 to 12) located according to section 11.3 of Method 1 in appendix A–1 to 40 CFR part 60 for a circular stack or nine points at the centroids of similarly shaped, equal area divisions of the cross section of a rectangular stack.*

*11.5.1.2 Calculate the mean measured concentration for all sampling points (MNavg).*

*11.5.1.3 Calculate the percent stratification (St) of each traverse point using the following equation:*

*11.5.1.4 The gas stream is considered to be unstratified and you may perform testing at a single point that most closely matches the mean if the concentration at each traverse point differs from the mean concentration for all traverse points by no more than 5.0% of the mean concentration.*

*11.5.1.5 If the criteria for single point sampling is not met, but the concentration at each traverse point differs from the mean concentration by no more than 10% of the mean, the gas stream is considered minimally stratified, and you may sample using the "3-point short line."*

*11.5.1.6 If the concentration at any traverse point differs from the mean by more than 10%, the gas stream is considered stratified, and you must sample using the stratification check procedure specified in section 11.5.1.1 of this method.*

COMMENTS: Why not allow alternative methods of stratification checks as seen in EPA RM 7e Section 8.1.2 (below)?

*8.1.2 Determination of Stratification. Perform a stratification test at each test site to determine the appropriate number of sample traverse points. If testing for multiple pollutants or diluents at the same site, a stratification test using only one pollutant or diluent satisfies this requirement. A stratification test is not required for small stacks that are less than 4 inches in diameter. To test for stratification, use a probe of appropriate length to measure the NOX (or pollutant of interest) concentration at 12 traverse points located according to Table 1-1 or Table 1-2 of Method 1. Alternatively, you may measure at three points on a line passing through the centroidal area. Space the three points at 16.7, 50.0, and 83.3 percent of the measurement line. Sample for a minimum of twice the system response time (see section 8.2.6) at each traverse point. Calculate the individual point and mean NOX concentrations. If the concentration at each traverse point differs from the mean concentration for all traverse points by no more than: ±5.0 percent of the mean concentration; or ±0.5 ppm (whichever is less restrictive), the gas stream is considered unstratified, and you may collect samples from a single point that most closely matches the mean. If the 5.0 percent or 0.5 ppm criterion is not met, but the concentration at each traverse point differs from the mean concentration for all traverse points by not more than: ±10.0 percent of the mean concentration; or ±1.0 ppm (whichever is less restrictive), the gas stream is considered to be minimally stratified and you may take samples from three points. Space the three points at 16.7, 50.0, and 83.3 percent of the measurement line. Alternatively, if a 12-point stratification test was performed and the emissions were shown to be minimally stratified (all points within ± 10.0 percent of their mean or within ±1.0 ppm), and if the stack diameter (or equivalent diameter, for a rectangular stack or duct) is greater than 2.4 meters (7.8 ft), then you may use 3-point sampling and*

*locate the three points along the measurement line exhibiting the highest average concentration during the stratification test at 0.4, 1.2 and 2.0 meters from the stack or duct wall. If the gas stream is found to be stratified because the 10.0 percent or 1.0 ppm criterion for a 3-point test is not met, locate 12 traverse points for the test in accordance with Table 1-1 or Table 1-2 of Method 1.*

Does language found in NSPS 40 CFR 60 Subpart JJJJ and/or NESHAP 40 CFR 63 Subpart ZZZZ supersede this stratification check requirement?

SUGGESTION: Use other promulgated RM criteria for stratification checks for continuity and alignment.

*I. National Technology Transfer and Advancement Act (NTTAA)*

This action involves technical standards. While the EPA identified ASTM D6348 as being potentially applicable, the Agency does not propose to use it. Currently, ASTM International (formerly the American Society for Testing and Materials) is revising ASTM D6348 (Standard Test Method for Determination of Gaseous Compounds by Extractive Direct Interface FTIR Spectroscopy), which specifies sampling and analytical procedures that are similar to EPA Method 320. Because the revised ASTM D6348 may be an equivalent method, the EPA will reconsider it when the revised ASTM D6348 becomes available.

COMMENTS: This move by NTTAA will have an extraordinary impact on the Stationary RICE source category since the ASTM D6348 method is commonly used instead of RM 320. One of the primary reasons is because ASTM D6348 has less restrictive analyte spike recovery procedures than RM 320, allowing more efficient field-testing events. This is critical in Stationary RICE testing due to the volume of sources and market pricing pressure to test two engines per day. However, although the ASTM D6348 method allows for more field efficiency, it also has a critical requirement that is the best way to confirm and validate that the FTIR analysis conducted in the field is comprised of good data that can be found in Annex A8 POST-TEST QUALITY ASSURANCE/QUALITY CONTROL PROCEDURES.

*A8.1 Post-test QA/QC is aimed at spot checking the large data sets that can result from FTIR systems and confirming that the concentrations returned by the automated analytical algorithms are valid, within the stated test data quality objectives, and not influenced by interference. This is done through manual quantitation of select spectra.*

There is no such requirement discussed in any of the RM 320 revisions. Why not? Every FTIR manufacturer has software that can perform this manual spectral analysis. The fact that this is required in ASTM D6348, makes it the more comprehensive QAQC method and should therefore not be disallowed. Tens of thousands of compliance test have been conducted utilizing this method. On what basis is EPA proposing to no longer use it?

SUGGESTION: Add manual validation to QAQC procedures to RM 320, while reducing spike recovery requirements, OR continue to recognize ASTM D6348 as an equivalent method. If nothing else, consider recognizing ASTM D6348 as an equivalent method for the Stationary RICE source category.

ONE FINAL COMMENT: Concerning the Stationary RICE source category, several EPA regions and several states have been adequately resourced to evaluate the strength of testing firms and their conformity with FTIR analysis. However, states with higher volumes of Stationary RICE have not had the same level of regulatory oversight. This has put a tremendous strain on reputable testing firms that make every effort to adhere to the data quality objectives found in both FTIR methods and other methods that are a part of Stationary RICE testing programs (i.e. RM 1, 2, 3a, 7e, 10, 19, and 25a). If these revisions are approved, please ensure that all EPA regions and states have the resources to observe, regulate, enforce, and protect all stakeholders, especially those required to make the capital investments needed to equip, train, and execute according to method conformance.

# Attachment 2

Date: April 22, 2024

To: USEPA

From: Martin L. Spartz, Ph.D.

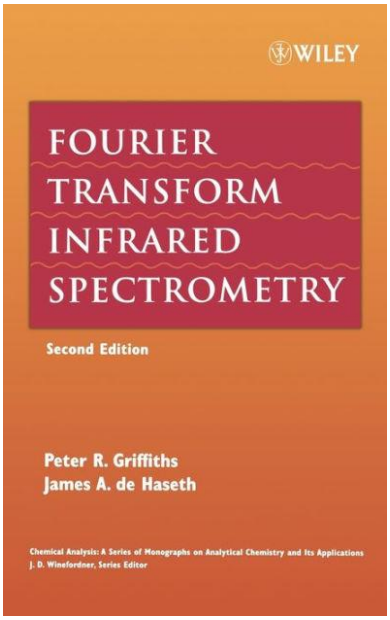
Re: Revision to USEPA Method 320

Comments:

I will again suggest that the name of the method be corrected to use proper terminology. We correct terms and definitions when they are mis-defined, why should we not correct other items discussed in the method when they are mis-identified?

*Method 320 describes the procedures for the measurement of vapor phase organic and inorganic emissions by Fourier Transform Infrared (FTIR) spectroscopy.*

The term Fourier Transform Infrared (FTIR) spectroscopy is an incorrect use of the term "spectroscopy". It is infrared spectroscopy, which is the fundamental concept of infrared absorption, but it is FTIR spectrometry since we are discussing the instrumental technology. The book by Griffiths and de Haseth, shown below, is considered to be the "bible" on the topic. No where will you see the term FTIR spectroscopy because it is incorrect. Just because the original authors of the method did not understand the distinction between spectroscopy and spectrometry, doesn't mean that we should continue to use an improper term.



This initial statement is very troubling:

*In this action, the EPA proposes technical revisions that update the validation and quality assurance (QA) spiking procedures of Method 320 to provide a more performance-based approach.*

I believe there to be a fundamental misunderstanding of the purpose of analyte spiking. First, spiking only tells the user something about the sampling system, nothing about the underlying analytical technique. I have sat in too many meetings discussing FTIR analysis where others try to explain that spiking tells the user about the infrared method. This is an uneducated statement. The only thing that spiking does and should be required to provide is whether the analyte can make it from the source to the analytical instrumentation for measurement. Any other information that others think that it provides can be demonstrated to be false by simple testing (for instance bias checking, it provides no definitive information on this issue). Additionally, if spiking only provides transport information, then any spiking suggestion here should be required of all EPA methods, not just those using FTIR spectrometry. To do otherwise is to handicap a technology due to its acronym (FTIR), instead of other methods like Method 25A or Method 3 or 7E, etc. So, if we are going to add significantly more sampling QA/QC to this method that has nothing to do with the analytical method, the same should be done for all EPA methods.

The main application where spiking is considered most important is for the determination of HCl from Cement and Lime facilities, a small source category and for one that has its own method, USEPA Method 321. In this case, spiking clearly demonstrates the transport of the HCl to the analyzer, not the ability of the FTIR to measure HCl. Most other FTIR applications have no need for spiking since the gases are freely transported to the FTIR (think NO, CO, $CO_2$, Hydrocarbons, etc). To require FTIR to perform spike checks when other technologies performing the same analysis do not, is not fair or appropriate.

Interestingly, (and contradictory to my previous statement) if spiking were required of Method 25A in certain applications, one would observe that the reading of the FID analyzers are incorrect due to the matrix (e.g., natural gas fired Lean Burn RICE). In this case, it is not a transport issue but an error in the actual analytical analysis. Unfortunately, in this case the transport issue and analytical issue cannot be separated since there is no underlying data to review to demonstrate that it is in fact an analytical issue, not a sampling issue. An analyzer like an FTIR could easily differentiate these two issues. The FTIR would get the correct hydrocarbon reading while the FID would give the incorrect low reading, demonstrating that it is not a sampling issue at all.

If the user is incorporating a poor FTIR method, this should be observed and corrected by performing a correct bias analysis, which spiking does not provide. **It is the interference specie that is causing the potential bias not the analyte of interest.**

**Section 3 Terms**

Interestingly, the revised method is removing terms that are important while leaving in terms that are not important or outright inappropriate. Example:

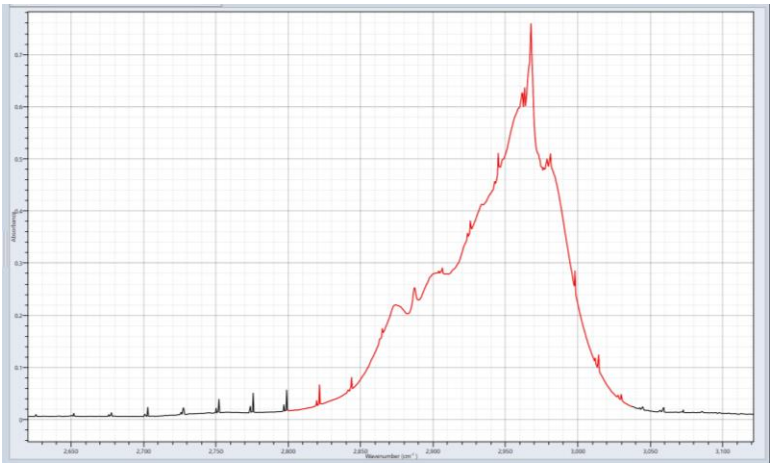
*(Background Deviation)* Background deviation *means a deviation from 100% transmittance in any region of the 100% line.*

Two issues with this term.

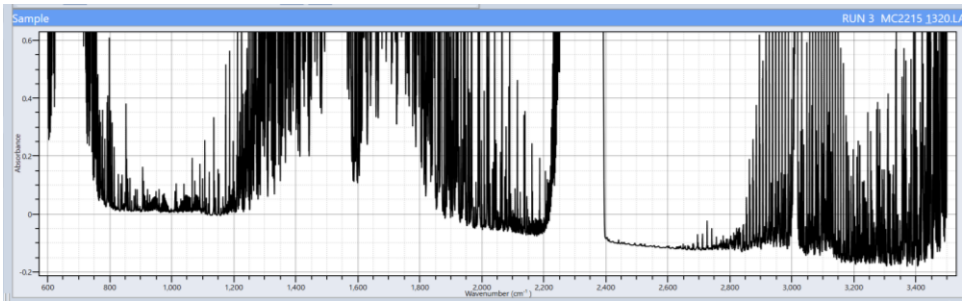
1. Most FTIR gas analyzers do not even calculate a 100% T line since no one does quantitative analysis in % T, but rather in absorbance. So, any value or requirement here is not possibly determined by many users of FTIRs. If regulators ask for it, the user cannot provide this information. Nor is it important, see 2 below.

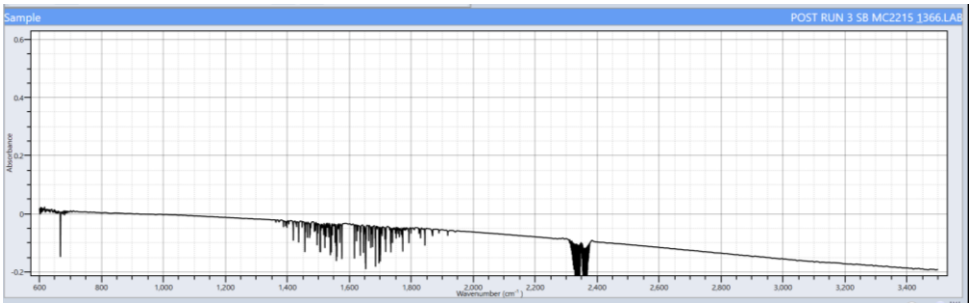
2. The drift of the FTIR baseline for most applications is irrelevant. All FTIR software packages are able to baseline correct the spectral absorbance data. If they cannot, they should not be utilized. It should be obvious in any Residual Spectrum calculated if the baseline has not been appropriately accounted for. To prove that a baseline requirement is poor science you must understand how FTIR gas analysis data are created. When gases in the infrared spectrum are measured (if done properly) the resultant spectra of all the gases present are a linear combination of all the individual gases within the mixture. (If this weren't true, no FTIR gas analysis software could analyze a resultant combustion spectrum to determine its underlying components.) Which means, each gas adds a certain level of absorption to the "sample spectrum" and each is added to the others.

   See example spectrum below. In this spectrum, there are three compounds all over lapping with the others: propane, butane and HCl. For those trained in IR gas analysis, the doublets of the HCl spectrum are obvious. If the baseline must stay within say 5%, this is clearly a violation of that statement. Far worse though is that the propane and/or the butane are sitting on top of the other. In this case, there is a baseline shift that is approximately half of the large peak, or 0.3 abs (which is 50% of the light absorbed). So, if we assume the baseline is the butane going up to 0.3 abs, then the propane is sitting on top of a huge baseline shift. So, the propane measurement cannot be made if we stipulate a baseline criterion to the method. In this case, both are 100 ppm, levels that are exceeded all the time. Both are easily measured by the software. This demonstrates that no overriding baseline criterion should be placed on IR data.



Additionally, any baseline shift that is caused by particulate on the mirrors or FTIR instability should not be removed by re-zeroing the analyzer once a measurement is started. **This is the worst mistake a source tester could make.** Instead, they should complete the test and then run $N_2$ at the end to get a spectrum of the particulate matter or baseline shift. Then they would add that to their method since particulate spectra and baseline shifts due to FTIR performance are linear at any loading level since they are broad absorbances or shifts. This "new calibration" will provide an exact correction for the particulate or baseline instability as it is increasing throughout the measurement. The baseline shift in the data below would easily be fixed (all throughout the run) by adding the single $N_2$ spectrum at the end of the measurement back into the method.




Baseline drift is important to watch and make sure it is being handled properly in the analysis but there is not an appropriate level for all applications and as such should not be part of this method. The better thing to do is to re-perform an MDL test if much of the light is actually lost due to particulate. Again, that could be performed by collecting a series of $N_2$ spectra.

**Minor Point regarding CTS definition**

*Calibration transfer standard (CTS) means a certified gas calibration standard used to verify instrument stability.*

I am not sure the word stability is the most appropriate word, since the FTIR stability does not affect the CTS reading. I think a better word would be "accuracy" or a synonym to that word.

**Term Absorbance**

*The negative logarithm of transmission represented by the relationship $A = -\log(I/I_0)$, where I is the transmitted intensity of light, and $I_0$ is the incident intensity of light upon a molecule.*

There are at least two issues with this definition.

1. It is $\log_{10}$ or log base 10. There are different logarithms, we should be specific here.
2. The definition is not correct, and any definition could be problematic for those measurements where a background is not actually acquired.
    a. "I" is the intensity of light remaining and measured by the detector that is transmitted through the sample at each frequency or wavelength.
    b. "$I_0$" which is sometimes called the background spectrum is "normally" the light intensity measured by the detector at each frequency or wavelength when the sample is not present. In most cases, this is collected when $N_2$ or another infrared transparent gas is passing through the gas cell.
    c. But again, many methods now allow for "AutoRef" type methods where the $I_0$ is calculated by a truncated or shortened interferogram (noting that the term truncation has been removed from the term list!!)

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**Term Absorptivity**

If we are going to put this term in the method, we should again be clear what it is.

*The amount of infrared radiation absorbed by each molecule.*

Again, this is a poor definition. A more definitive definition would be something like: "amount of light absorbed by a molecule at each wavelength or frequency at a certain concentration and pathlength".

**Term Analyte Spiking**

*The process of quantitatively adding calibration standards to source effluent. Analyte spiking is used to evaluate the ability of the sample transport and FTIR measurement systems to quantify the target analyte(s).*

As mentioned above, I fundamentally disagree with this definition since it can be shown by simple testing not to be correct. Analyte spiking is used to evaluate the sampling systems ability to transport each analyte to the measurement system (only). It does not matter that it is FTIR, a filter-based analyzer, a FID, a GC or a chemiluminescence analyzer.

If the FTIR analysis is incorrect (due to, say, bias), a spike will not tell the user that they have a poor method, only a proper bias measurement will provide that information. I will provide a very simple example. If you have a source that is reporting an analyte at 10 ppm (that is all bias) and you spike in 10% of a calibration gas certified at 10 ppm, the resultant value (since both the sample reading and the standard are the same) should be 10 ppm. So, if the user gets a reported spike of 10 ppm, they might incorrectly assume the instrument and method are working properly. The problem with this example is that the 10 ppm analyzer result was all bias due to say water. So, the user just confirmed they have a good method when the actual value for the analyte was zero (this happens all the time with water interference that is not being properly handled). This simple explanation demonstrates that a spike cannot identify a bias issue. Depending on the setup you might observe some level of bias, but you cannot determine the actual bias. **Again, the bias is coming from the interference not the analyte.**

We need to stop convolving QA/QC steps. Each QA procedure should tell us one thing about the data quality, not multiple things.

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**Term Apodization**

Apodization *means a mathematical transformation used to adjust the instrument line shape for measured peaks. There are various types of apodization functions; the most common are boxcar, triangular, Happ-Genzel, and Beer-Norton functions.*

This is an incorrect definition as well. Yes, an apodization function affects the line shape of the calculated spectrum but that is not its purpose.

Apodization is a mathematical function applied to the phase corrected interferogram to remove artifacts such as “feet” or additional features created by the Fourier transform due to the finite nature of the interferogram. Since the apodization function generally de-emphasizes the terminal end of the interferogram the resultant calculated spectrum has a reduced resolution or broader line shape.

**Term Background Deviation**

*Background deviation* means a deviation from 100% transmittance in any region of the 100% line.

Remove this term or use it in the proper context. We should only be talking about absorbance here, since no analysis is performed in %T, nor can many FTIR gas analyzers provide that information.

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**Term Background Spectrum**

*Background spectrum* means a spectrum taken in the absence of absorbing species or sample gas matrix, typically conducted using nitrogen or zero air.

Background spectrum is a single beam spectrum normally collected in the absence of any infrared absorbing species or sample gas matrix. It is typically collected while nitrogen or zero gas is flowing through the gas cell. Background spectra can also be obtained by other methods such as truncation of the raw sample interferogram sometimes known as “AutoRef”.

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**Term Calibration transfer standard**

*Calibration transfer standard (CTS)* means a certified gas calibration standard used to verify instrument stability.

The word stability is not appropriate since there are many types of instability in FTIR gas analyzers that are unrelated to quantitative measurement. A better word would be “accuracy”.

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**Term Interferogram**

Interferogram *means a pattern that contains the effects of the wave interference that are produced from an interferometer.*

Since you talk about Retardation later (should be Optical Retardation) this should be used to define an interferogram.

Interferogram is created by collecting the detector response as a function of optical retardation. The larger the optical retardation, the higher the resolution.

Term Interferometer

Interferometer *means a device used to produce interference spectra, by dividing a beam of radiant energy into two or more paths. One path strikes a fixed mirror, and the second path strikes a moving mirror generating an optical path difference that varies over time between them. The recombined beams produce constructive and destructive interference as a function of changing pathlength. The Michelson interferometer, used in FTIR instruments, performs this function.*

First, an interferometer does not produce "spectra". Second, most FTIRs have 2 optical paths, I am not sure I know of any that have more than 2, Third, many FTIRs have 2 moving mirrors unlike a Michelson. So, this definition is a bit inappropriate.

Interferometer is device that allows incident light to be split into two approximately equal halves by a beam splitter. These two beams then travel separate paths and are then recombined at the beam splitter to create an interference pattern as a function of optical retardation. Interferometers can have one fixed mirror and one moving mirror or two moving mirrors to produce the required optical retardation.

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**Term Resolution**

*Resolution* means the minimum separation that two spectral features must have to distinguish one feature from the another.

Although that is one definition to this term, I am not sure it is the proper definition for this Method. Generally, when discussed in FTIR gas analysis, "resolution" is the instrument resolution that the data are being collected. So, we are collecting 0.5 $cm^{-1}$ resolution data. To have this spectral resolution, you must have a point spacing that is half of this resolution, or 0.25 $cm^{-1}$ point spacing. The spectral resolution has nothing to do with resolving two features, only how close the resolving points are.

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**Term Retardation**

*Retardation* means the optical path difference between two beams in an interferometer.

First, to be correct the term is Optical Retardation not Retardation. Optical Retardation is the difference in distance that two beams travel through an interferometer in centimeters.

Centimeters is important since the Fourier transform inverts the unit from cm to $cm^{-1}$. That is where the term "wavenumber" comes from.

This is also why we don't use sec and hertz ($sec^{-1}$), since time is not constant through an interferometer because the mirror speed is not constant, but distance is a constant.

**Term Single Beam Spectrum**

*Single beam spectrum* means the Fourier transformed interferogram representing detector response versus wavenumber.

Since we are discussing FTIR, that might be okay but here is a term that is over constrained.

Single beam spectrum is the detector response as a function of frequency or wavelength.

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**Term Transmittance**

*Transmittance* means the amount of infrared radiation that is not absorbed by the sample. Percent transmittance is represented by the following equation: $\%T = (I/I_0) \times 100$.

Remove this term. It has no bearing on the data collected or how they are analyzed. Many FTIR gas analyzers, as mentioned above, have no setting that allows them to provide this form of the spectral data.

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## G. Section 7.0 (Reagents and Standards)

*In this action, the EPA proposes to rename current section 7.1 from "Analyte(s) and Tracer Gas" to "Analyte(s) and Tracer Standard Gases" and to require the use of EPA protocol gases (with expanded uncertainty ≤2%) be used for criteria pollutants.* ***The EPA proposes to specify that other pollutants (non-criteria) be dual certified and that target analytes be within 25% of the emission source level or applicable compliance limit.***

More a question and observation about this requirement. I understand the purpose of this but what if the emission limit is not a single compound? What if the emission limit is total VOC? How does one select a concentration for a target analyte? What if the wrong target analyte is chosen? And if the source is varying, that variability could easily exceed the 25% requirement.

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*The EPA also proposes to remove the suggestion regarding the use of sulfur hexafluoride ($SF_6$) tracer gas. The EPA is specifically soliciting comment on the approach of using expanded uncertainty for criteria pollutants as well as not being prescriptive on the tracer that is used.*

I will not comment on expanded uncertainty, but I do agree that any tracer gas could in theory be usable and to spell out $SF_6$ is probably not appropriate. I also believe it is important to allow the tracer to be the source gas in some cases as well. If $CO_2$ is very stable from the source, when a spike is added, the reduction in the $CO_2$ can provide the required flow ratio information.

*The EPA is soliciting comments regarding CTS gases and providing standardization there to ensure coverage over a wide wavelength range by using one of the listed gases.*

In theory many gases could be a CTS. I also agree that $CO_2$ and $CH_4$ could be ideal since they have features throughout the mid-iR. They are easy gas standards to obtain at very high quality.

If there is one area that source testers still make mistakes is that the CTS calibration cannot be spanned. If it is, it removes the whole purpose of performing a CTS measurement in the first place. So, if other gases are utilized that are part of the emission test, it is possible they might span the calibration to get a closer result for gases like $CO_2$ and $CH_4$. This should invalidate the test. Any gas used for CTS cannot be spanned, whether or not it is a gas reported as part of the emission results.

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*The EPA proposes to remove sections 8.3.1 and 8.3.2, which provide the options to verify detector linearity by varying the power incident on the detector by modifying the aperture setting or by using neutral density filters to attenuate the infrared beam in current, respectively.*

I agree a 100% with this change. Most FTIRs cannot make the measurement as described in the previous version of the method.

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*In section 8.5 (Background Spectra), the EPA proposes to remove the requirement to evacuate the gas cell and fill the cell with dry nitrogen to ambient pressure.*

I agree with this removal as well. Most gas cells are very small today and can be purged with $N_2$ very quickly.

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*1.2 Applicability. This method applies to the analysis of vapor phase compounds that absorb energy in the mid-infrared spectral region, from about 400 to 4000 $cm^{-1}$ (25 to 2.5 µm). The method is used to determine compound-specific concentrations in a multi-component gas sample extracted from a stack or ducted source.*

A minor point, but no one does source testing down to 400 $cm^{-1}$ since it is completely obliterated by water and $CO_2$. In many cases the FTIRs optics and detectors do not allow for measurement below 600 $cm^{-1}$. But many people measure above 4000 $cm^{-1}$ when they are performing HF measurements and, in some cases, very high CO measurements.

I would suggest that the range be listed as 500 – 5000 $cm^{-1}$ (20 to 2 µm), since it better covers the actual range one might use for a compliance test.

Consistency.

*6.1.3 Gas Absorption Cell.*

We identify a term and then we don't use it. See the Sections listed below and all the different terms for the same thing.

*6.2.1 Sampling Probe. Glass, stainless steel, polytetrafluoroethane (PTFE), or other appropriate material to transport analytes to the **IR gas cell.***

*8.1.1.3 Heat sample transport lines to maintain sample temperature at least 10 °F (5 °C) above the dew point for all sample constituents. Sample transport lines and system components must be heated sufficiently through their entire length to transport target compounds to the **IR sample cell.***

If we are going to have terms, we should use them throughout so there is no question whether we are talking about the same thing. So, is it an IR gas cell or Gas Absorption Cell or IR sample cell??

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*8.1.2 Select Spectroscopic Setup. Select a spectroscopic configuration for the application. Approximate the absorption pathlength, sample pressure, absolute sample temperature, and signal integration period necessary for the analysis. **Specify the nominal minimum instrumental linewidth (MIL) of the system.***

Again, many questions, then a comment. Where is this MIL term defined??? How does one decide on this??

Are we talking about selecting the resolution to perform the compliance test? Are we talking about testing the line shape of the instrument?

If a "Peak Analysis" must be done (MKS term) we should define it and how we expect it to be performed. This is and has always been the problem with this method. We define terms at the top that are never used in the Method. Then we get to the Method and we create new terms that are important but never defined.

Also, any definition of "MIL" is probably wrong anyway. It is more important that the achievable resolution of the instrument be constant. So, if we are running 0.5 $cm^{-1}$ resolution, the instrument is operating somewhere between 0.48 and 0.52 $cm^{-1}$. But again, I have no idea what "MIL" is.

**Major Concern**

*8.1.3.3 Reference spectra incorporated in the program must either bracket the observed sample matrix concentration or use a direct injection to verify the calibration curve.*

**No FTIR should be calibrated to bracket the sample matrix or the analyte on the low end of the calibration range.** To require this is to not understand how FTIR and FTIR gas analysis algorithms work. Also, other analyzers are not required to bracket the low end of the calibration range. They are only required to run a zero gas.

FTIR calibration curves are generally multi-point curves with sometimes 10 to 20 or more calibration points, far more than any other method. In the case of organics and VOCs the calibration curves tend to be linear since they are linear according to "Beer's law". So, one point can define the entire curve.

For those compounds that are not, like CO, HCl, NO, etc. (light gases), calibration curves that go low enough to have a linear section demonstrate the calibration curve is linear from that point to zero.

The reason the calibration should not be bracketed is that many advanced algorithms use the calibration point closet to the sample point. So, as the concentration goes down, it uses the lowest point on the calibration curve. (These are dynamic algorithms.) If one were to use a calibration point within the noise of the spectrum, the MDL will increase by a factor of about 3 for many compounds. So, by requiring for this bracket the EPA has just raised the MDL of the system by a factor of 3 because they don't understand how the algorithm works. We want to use low-level calibration points and multiply by a small number (something much less than 1) because that reduces the noise of the calibration spectrum being utilized, thus allowing for lower MDLs.

Older systems and some current systems still only use the highest point on the calibration curve and then use the calibration curve to determine the concentration. These older methods produce much higher errors since the interference spectra (water) never match the sample spectra. Remember, water is a non-linear curve so that means the low-level concentration and high-level concentration spectra are not multiples of each other. This is the definition of non-linear.

So, if you are going to require FTIRs to bracket the low-end calibration range, the technology will go backwards since all FTIR manufacturers will put the points on the curve but never use them by telling the software to use the highest point instead of using dynamic algorithms.

**Major Concern**

*8.1.3.4 Analysis regions selected for a target compound(s) must have an absorbance value of less than 1. You must select specific wavelengths in each region where the target analyte does not overlap with an interfering compound and use the selected wavelengths throughout the entire validation (section 9.4), QA spiking (section 11.4), and testing campaign.*

I hope I am reading this section incorrectly but unfortunately if I am, a regulator will read it the same way I am reading it now.

*You must select specific wavelengths in each region where the target analyte does not overlap with an interfering compound…*

Is the EPA now saying the quant region must have points with no interfering species? If that is what is being required, then almost all FTIR measurements will no longer be valid for any testing procedure. Certainly, regulators will look at it this way, unless you can prove there is no overlap you cannot use FTIR. They already don't allow FTIR for applications where it is the best solution and much better than the other allowed methods. FTIRs by design are able to differentiate many overlapping compounds. That is their advantage over other technologies. This isn't chromatography where every peak has to be completely separate from the next to be able to identify it.

If this is not what the EPA meant, then this statement must be removed or edited to say what it is they want to see. Requiring no overlap is an obvious misunderstanding of what FTIR data look like.

Also, the first part of this statement is troubling as well, since many compounds have peaks greater than 1 absorbance. This happens all the time, in almost every sample. Think water, think $CO_2$, they have peaks greater than 1 abs in every measurement and are reasonably quantified on those peaks.

---

*8.5 Background Spectrum. Flow dry nitrogen through the gas cell and verify that no significant amounts of absorbing species are present. Collect a background spectrum, using a signal averaging period equal to or longer than that being used for averaging of source sample spectra. Assign a unique file name to the background spectrum.*

I actually appreciate that the EPA defines how to collect "a" background. And $N_2$ should always be run through the cell for every test to show that it is clear of analytes and interferences.

However, by doing so and not providing any other verbiage, this appears to be the only way one can collect a background. Having had to deal with regulators that take the document as gospel, there has to be more to this statement, or it will have debilitating consequences for source testers in specific applications. Example, Formaldehyde from gas fired turbines (YYYY) is one leading technology that does not collect a background this way.

**Possible Suggestion:** Alternative backgrounding methods are also allowed such as "AutoRef" where the sample spectrum is processed at 2 resolutions to generate both the background and sample spectra.

Multiple issues with this section

*8.6.1 Calibration Transfer Standard. Flow the CTS gas through the cell and verify that the measured concentration is stable to within the uncertainty of the gas standard. Record the spectrum. Additionally, measure the linewidth of appropriate CTS band(s) to verify instrument resolution. Alternatively, compare CTS spectra to a reference CTS spectrum, if available, measured at the nominal resolution.*

First, measuring CTS does not determine the instrument resolution, it shows the line shape of one band of the CTS gas, whatever gas that might be, for a specific absorption line. Second, many instrument manufacturers use water from ambient air to confirm that the instrument's resolution is within specification for that instrument at that resolution setting. Not the CTS. Third, there is no criterion here for one to meet. "Comparing CTS Spectra to a reference" is not quantitative and is barely qualitative. Again, what is the metric? In the early version of the method, the resolution had to be with 15% of the resolution setting. If we assume that means at 0.5 $cm^{-1}$ we can have a variance of 15% or +/- 0.075 $cm^{-1}$ resolution. This almost certainly guarantees data that are no good with significant biases. So, that allowance was far too great, but it least it was something we could point to as the spec.

Not sure how to deal with this issue without further discussion but the EPA has to understand that line shape for a specific molecule and instrument resolution are two very different metrics.

I don't disagree that one could look at a sample spectrum and a corresponding calibration spectrum and say okay things are good. I do that all the time. But it is not an achievable metric.

---

**Major Concern**

*8.7 Sampling. See section 11.5 of this method. While sampling, monitor the signal transmittance. If the transmittance (relative to background) changes by 5% or more in any analytical spectral region, obtain a new background spectrum.*

**As mentioned at the beginning of my comments, this is absolutely the worst thing a source tester could do in the middle of a compliance test.** Once a background is collected it should be used until which time $N_2$ spectra can be collected with that same background, so that any features in the "changing" background can be accounted for by the method.

Second, many FTIRs baseline stability will not meet the 5% requirement. Remember these instruments are infrared (heat) optical based and they are mounted in trailers where the temperatures can change widely. When that happens the baseline shifts and, in some cases, can shift significantly.

With the way this is written if the background (or sample for that matter, the source tester may not be able to differentiate the two) moves 5% then the regulator may invalidate the test run if a new background isn't acquired. Again, the sample itself can move the background that much.

Additionally, no one does quantitative analysis in %T so baseline drift in % is a poor choice of a metric. That is only a 0.022 abs shift in the baseline. The example I provide above is 10 times worse than that

and this is commonly observed in the field. And in that example, the results are reasonable and able to be validated regardless of the baseline drift.

We need to remove any requirement for % or abs baseline drift. If you want to make a statement that if large baseline drifts are observed, then do something, but 5% is a requirement most FTIR systems cannot meet, and results under these conditions have been validated as compliant time and time again.

---

*8.6 Pre-Test Calibrations.*

I got to the bottom of this section, there is no discussion about collecting calibration gases other than CTS. Is there no requirement to run calibration gases as direct and system checks any longer?

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*9.1.1.1 Prior to testing, verify that the sample integration time is sufficient to achieve the required signal-to-noise ratio.*

I understand the purpose of this requirement but there is no discussion on how to do it, and that it varies across the spectrum, etc.

Also, at the end of the day, it is not about SNR at all since that doesn't take into account very important factors like path length. What is important is, what is noise in the resultant quantified data (not SNR)? Take the final results and perform a standard deviation and calculate an estimated MDL.

---

*9.1.2 Post-Test QA.*

*9.1.2.1 Inspect the sample spectra immediately after the run to verify the gas matrix composition was close to the expected matrix composition.*

*9.1.2.2 Verify that the sampling and instrumental parameters were appropriate for the actual stack conditions. For example, if the moisture of the sampled gas was much higher than anticipated, a shorter pathlength cell or more dilute sample may be needed.*

Shouldn't we make sure things are fine up front?? Isn't it a bit late at this point to realize the system is not set up properly for the measurement? These are pre-test questions, not post-run.

Where is there any discussion of bias determination or assessment?

Where is there a detailed discussion or explanation on one of the most important Post Test QA procedures of performing a manual data validation? This can help identify many issues, like poor methods, bias issues, baseline correction issues, etc.

*9.1.2.3 Compare the pre- and post-test CTS spectra. The peak absorbance in the pre- and post-test CTS must be ±5% of the mean value.*

This is not how this should be performed. We should only use the quantified result, not the peak absorbance since baseline and pressures may not or are not accounted for in the peak height. Also, using the quantified result allows for more than one band to be used which better deals with small changes in gas temperature.

---

*9.2 Quality Control (QC). The analyte spike procedure in section 9.3 of this method and the validation procedure in section 9.4 of this method are used to evaluate the performance of the sampling system and to quantify sampling system effects, if any, on the measured concentrations. This method is self-validating provided that the results meet the performance requirement of the QA spike in section 11.4 of this method.*

This I agree with, since we are only discussing the performance of the sampling system or the ability of the molecule to make it to the instrument. But again, I raise my objection that FTIR is required to perform more QA/QC than other methods just because it can, and others can't or aren't required to.

---

**Major Concern**

*9.3.1.1 Pre and post-test spiking must consist of at least 3 replicates. A replicate is defined as the following measurement sequence: native gas concentration, SA-elevated gas concentration, native gas concentration. In addition to the pre-test spike instance, spiking must also be performed post-test.*

What other EPA method requires this level of spiking? Method 3, 4, 7E, 10 etc? Why must an FTIR do all these spikes when it has nothing to do with the FTIR. This is purely a test of the sampling system as was just mentioned in Section 9.2.

So, why does Method 320 require 6 spikes when others require none?

Method 320 is the only method used in the field that can tell if a calibration cylinder is incorrect, all other methods just calibrate to the poor cylinder.

**Major Concern continued**

*9.3.1.2 It is recommended that spiking be performed after each run to ensure continued compliance with the required spike recovery criteria. If spiking is not performed after each run and the post-test spike fails, all data for that test are invalid. However, if spiking is performed after each run, data bracketed on each end by a successful spike are valid test data.*

So, you are now requiring not 6 spikes but 8 spikes. Again, this should not be required unless all other EPA Methods require this same level of QA/QC since this is a sampling issue, not an FTIR issue.

*9.3.3 Determine the response time (RT) of the system. First, inject zero air into the system. For standard addition RT determination, next measure the native stack concentration of the species to be spiked. The concentration has stabilized when variability appears constant for five minutes.*

This does not tell anyone how to do a proper Response Time check and it convolves two QA/QC procedures which should never be done. If this is Response Time, tell the source tester and the regulator what you want to see. This current requirement has no information whatsoever.

---

*9.3.4 You must determine a dilution factor (DF) for each dynamic spike. Determine the DF via a tracer, and use the following equation for a source where the tracer is not native to the source emissions:*

$$DF = \frac{M_{spiked\ tracer}}{C_{tracer\ spiked}} \qquad \text{Equation 1}$$

Unfortunately, this equation is wrong and has always been wrong.

The Numerator should be the (spiked reported tracer value – native reported tracer value)

If there is significant amounts of $NH_3$ in a sample, there is always a bias on $SF_6$ if that is the tracer. That bias must be subtracted or an error in the Dilution Factor will be created. We see this all the time when rich burn RICE are being tested. There are 1,000s of these compliance tests a year.

$C_{tracer\ spiked}$ *= the tracer gas concentration injected with the spike gas.*

Unfortunately, the denominator is also incorrect and always has been.

It should be the direct reading of the tracer gas (undiluted). It is very common for the tracer gas not to report exactly what the tag value says and again if the tag value is utilized you will generate an error on your Dilution Factor.

$C_{native\ tracer}$ *= the undiluted tracer gas concentration in the cylinder.*

Again, this should be the direct reading of the cylinder with the native tracer.

Missing is an equation that allows the tracer to be the sample itself. We should be able to use the dilution of a stable gas to determine the DF. As an example, use the $CO_2$ from the sample as the tracer gas. See example equation below:

DF = ($CO_2$ sample reading - $CO_2$ from spiked sample) / $CO_2$ sample reading

*9.3.4.1 Standard Addition Response. The standard addition response (SAR) represents the difference between the measured native source concentration and the concentration measured upon introduction of the standard addition (source + SA) via dynamic spike. Calculate the SAR via the following equation:*

*Where:*

$MC_{spiked}$ *= the measured reference analyte concentration.*

$MC_{native}$ *= the measured concentration of the analyte in the native effluent.*

***Note:*** *Use consistent concentration units for each relevant variable in Equation 3.*

*9.3.4.2 Effective Spike Addition. The effective spike addition (ESA) is the expected increase in the measured concentration as a result of injecting a spike. For the section 11.4 QA spike, the ESA must be within 50% of the native stack concentration. Calculate the ESA with the following equation, for use when using a certified cylinder:*

$$ESA = DF * (C_{spike} - MC_{native}) \qquad \text{Equation 4}$$

*Where:*

$C_{spike}$ *= the certified reference analyte concentration.*

*When using a non-certified cylinder, replace the* $C_{spike}$ *term in Equation 4, with* $MC_{spiked}$*.*

***Note:*** *Use consistent concentration units for each relevant variable in Equation 4.*

*9.3.4.3 Spike Recovery. The degree to which the SAR and the ESA agree represents the spike recovery (SR), or the ability to measure the spiked analyte on top of the amount of that analyte native to the stack. Spike recovery is calculated according to the following equation:*

$$SR = \frac{SAR}{ESA} \qquad \text{Equation 5}$$

Equation 4 is incorrect.

If we are going to calculate Spike Recoveries this way (See below, I disagree with this procedure), Equation 4 should only be DF times $C_{spike}$. Otherwise, the equation goes to zero at certain values and the spike recovery goes to infinity. Take the case where the spike gas and the measured concentration are the same. Say 10 ppm, the term in the parentheses goes to zero and ESA goes to zero. Thus, SR goes to infinity.

I appreciate all the math (since the correct equation wasn't here before either), but why? Why not just calculate the Spike Recovery? Adding more equations tells us nothing and only has the regulators asking for more information that is not used anywhere.

We should only have equations that are needed, and the spike recovery can easily be written as a single equation. You also added new terms that are not defined above ("Effective Spike Addition" and others)

**A nitpicking point**

Also, it appears the term Standard Addition is being used quite liberally here. Normally a Standard Addition process is used to determine the concentration of the original sample (not the recovery of that material) and the analyte is added at multiple concentrations to determine the slope of the calibration line. We are not doing any of that here. Yes, we are adding a standard to the sample, but this is not the definition of a standard addition in the classical quantitative analysis application. See Harris, Quantitative Chemical Analysis probably any Edition 1 through 10.

In Harris & Lucy., Edition 10,

"In standard addition, known quantities of analyte are added to the unknown. From the increase in the signal, we deduce how much analyte was in the original sample."

Again, we are not spiking an unknown with multiple known quantities nor is this process telling us the concentration of an unknown sample. We are trying to demonstrate transport of the analyte to the analyzer only. And yet again, we added a Term way down the procedure that has no definition in the Term section. Why can't we keep it simple and just produce the Spike Recovery, which is also not a defined Term.

One other issue that is not discussed in the proposed document is what is an actual spike or native measurement? In the original document, it suggested switching between the two quickly, which frankly does not work for most sources where recoveries are actually in question. It would be far better to perform a spike where we have statistical information of the native (say 8 measurements) and then statistical information on the spike (again 8 measurements). This way, anyone trained in reviewing the data will be able to tell if the spike was indeed stable. There is no discussion in the method up to this point about how to perform a proper spike (I see it later in Section 9.3.4.4 but that section has worse issues). This is and has been the problem with Method 320 from its founding, that source testers don't know what to do to meet the requirements and regulators aren't sure what to ask for.

**Major Concern**

*9.3.4.4.1 Dual FTIR and Extractive Systems Approach. This field approach is performed using two independent FTIRs and sample extraction systems that use tubing of the same length and diameter and that pull the sample at approximately the same flow rate. One FTIR characterizes the fluctuations of the target analyte(s) over time and the second FTIR performs the spike recoveries. Note that testers can use either a single probe attached to both systems or separate probes for each system with the probe tips co-located (within 6 inches) in the sample duct. In either case, it is mandatory for the spike to occur prior to the PM filter. Perform the spiking procedure as follows.*

Frankly, adding this requirement does nothing but add complexity and costs that are not required nor feasible. Most source testers don't have an extra FTIR along with a full section sampling system laying around to perform this secondary test, so to suggest it causes more harm that help. By adding this section, the EPA is basically saying, and the Regulators are assuming, you must perform the spike recovery this way if you have a varying source. There must be an easier, less costly way to handle this issue with 1 FTIR. Some potential suggestions:

1. Run the spike for long enough to account for variability, then use the full test run as the Native.
2. Since the source is varying in the analyte, that means the analyte is most likely making it to the analyzer and changing quickly (which means it is not sticking). This means you generally don't have a recovery issue. Since that is normally the case, you should be able to spike at the level of variation of the analyte. So, allowing for spikes of up to say 20 or 30% of the sample flow should be allowed in this case. This is much easier and still demonstrates the Spike Recovery.

Strong Recommendation

**Section 9.3.4.4 and all the following sub-sections as written should be removed from the method or changed to allow a variance in how the Spike Recovery is performed.** Requiring a second analyzer should never be the solution as it just handicaps FTIR even further and in my opinion is a non-starter. Again, unless you are going to require every other analyzer that performs EPA compliance work to do the exact same thing, you should not require FTIRs to perform this type of test.

It is interesting in this sub section there is at least a discussion of how many samples to collect but there is no discussion about this in the main spike recovery section.

**Equation 6 is incorrect and different than Equation 3.** Just because you are using a separate analyzer does not remove the requirement of reducing the un-spiked sample by the dilution factor. In this case, the numerator in the Recovery Calc would go to zero if both the sample and spike had the same concentration. So, in the above equation the spike recovery goes to infinity and here it goes to zero for the same data. Clearly the equations are incorrect.

**Equation 7 is actually correct and it is different than Equation 4.**

We should have 1 equation that calculates Spike Recovery not multiple equations and certainly not multiple equations in multiple sections all that are incorrect.

*9.4 Method Validation Procedure.*

*This validation procedure, which is based on EPA Method 301 (40 CFR part 63, appendix A), must be used to validate this method for the analytes in a gas matrix. Analytes that have not been validated for a particular source type may not be measured using Method 320. Validation at one source may also apply to another type of source, if it can be shown that the exhaust gas characteristics are similar at both sources.*

Comment and Recommendation

This section has always bothered me since the Regulators do not know how to enforce this issue, there must be a better way to define this or there will remain significant confusion on when Method Validation is required.

Examples of issues with current language.

The term "method" is used. Are we talking about the specific analysis method that the source tester is running? Or is method defining Method 320? Or something else? One analysis method might work and another fail (spectral region selection), one resolution might work and another might fail (0.5 $cm^{-1}$ vs 2.0 $cm^{-1}$).

Does the source testing company have to validate all sources before they perform any by FTIR? Or once one source testing company have validated this source all can use that?

Additionally, the most concerning part, Method 320 was written as a self-validating method, that is why it has spike recoveries, system checks, direct calibrations, CTS calibrations, zero checks, so why is another validation required? I don't see the purpose of performing Method 301 if the method is self-validating? Seems very redundant and, worse, it suggests that Method 320 is not truly self-validating if another method must be performed first to prove that it is a valid method.

Enforcing manual spectral data validation would be a far better requirement than performing Method 301. It would force the source tester to demonstrate to the regulator that the compound can be visually validated at some level.

My recommendation would be to remove all of Section 9.4 since it is redundant to Method 320 and provides no additional value. Instead focus on proving that the data collected during the compliance test are in fact correct data and results using manual spectral validation.

*10.3 CTS Absorption Bands. Absorption bands used for CTS quantitation must be at least ten times the root mean square (RMS) value of the noise equivalent absorbance (NEA) of a wavelength range nearest to that absorption band. This value, $NEA_{RMS}^{CTS}$ can be determined as follows:*

Couple of comments here.

"CTS quantitation" is an incorrect term. It should always be "CTS quantification"

Second, we should remove any use the of the Term "NEA" as it adds no value to the method nor is it important in demonstrating detection limits. NEA is an anachronism from when many quantitative results were calculated by hand not by very powerful computers of today. All FTIR gas analyzers can quickly determine the concentration of any gas and the noise of its reading which couples detector noise, interference noise, spectral absorption cross-section, temperature, pressure, and pathlength. As such, NEA is and has been for a long time no longer required. And frankly it is a complete waste of time.

Also, by requiring the CTS to be only 10 times the RMS noise suggests that the CTS measurement will fail in certain circumstances since the CTS must be within 5% of the certified value. The simple math here would suggest that the CTS better be at least 20 times or more of the RMS or the CTS measurement is bound to fail due to the noise being too high.

---

*10.3.1 Determine the absolute noise equivalent absorption (NEA) for an analytical region by flowing nitrogen or zero air through the gas sample cell. The NEA is the peak-to-peak noise in a spectrum resulting from collection of two successive background spectra. Therefore, collect two background spectra in succession while the nitrogen or zero air is continuously flowing through the cell. Note that the same averaging time must be used for NEA determination as will be used for actual sample collection.*

*10.3.2 Calculate $NEA_{RMS}^{CTS}$ per the following equation:*

*Where:*

*$N_{CTS}$ = the number of absorbance points in the analysis region for the CTS.*

*$NEA_i^{CTS}$ = the individual absorbance values of the noise spectrum in the analysis region, i.*

Strong Recommendation

Remove or replace all of Section 10.3.1., if you want to prove the CTS has a strong enough feature to be used as a CTS for this analyzer setup. Use a straightforward standard deviation calculation of the recorded zero readings directly from the FTIR software. There is no need to calculate NEA to get that information.

Also, why not just measure the CTS gas?? If the CTS reading is within 5% of the certified level, what is the purpose of this zero assessment?

Again, a nitpicky point.

*10.4.1 The tester must report traceability and other pertinent information for each reference spectrum, for each compound, including: temperature, pressure, concentration, cylinder source and specifications, spectral regions of analysis used for quantitation (with specific wavelength ranges used), and calibration fit equations and correlations.*

Comment

The correct term is quantification, not quantitation. It should be changed throughout the document. There are other locations in the document where this term is used and should be changed to the correct term.

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*10.4.2 If commercially prepared, or other available reference libraries are used to quantify data, the FTIR spectral resolution and line position, cell pathlength, temperature and pressure, and apodization function must be known and reported. Resolution, line position, and apodization function used for collection of sample spectra must be the same as those of the reference spectra used for quantitation.*

Comment

It is stated that the "line position" must be known and reported. Reported how? Most infrared absorbing species have multiple "lines", many of which overlap other lines from the same molecule. It is not possible to state the line position and it would be better to say the quantification range for a molecule, for instance, from 980 – 1035 $cm^{-1}$.

---

*10.4.3 Reference spectra for each target compound must bracket the concentration of that compound in the sample stream.*

*10.4.3.1 In the case where traceable reference spectra provided by the FTIR manufacturer do not bracket the concentration of a particular compound, two options are available. A direct injection of the compound of interest (NIST traceable and certified to ±5%) into the FTIR at a concentration lower than that found in the sample stream and within three times the method detection level, may be performed to demonstrate the appropriateness of the calibration line at this level. To perform this check, while directly injecting the compound of interest into the FTIR, wait for the concentration of the compound to stabilize. Once stable, verify that the concentration as determined via the calibration curve is within 10% of the cylinder value or else do not proceed with testing.*

*10.4.3.2 Alternatively, calculated spectra, such as those from HITRAN or PNNL, may be used at the lower end of the bracketing range, within three times the method detection level, as well.*

Strong Recommendation

Just like in Section 8.1.3.3, I strongly disagree with the need to bracket on the low end of the calibration range. This suggests a lack of understanding how infrared spectra relate at different concentration levels.

Also, no other analytical method requires this, they only require a zero value. Which FTIRs collect as well.

Additionally, this is essentially redundant to the spike recovery for sources where the analyte is below detection. If the analyte level is high, we don't have an issue and if it is low we are performing a spike recovery to demonstrate. Which demonstrates that this section is redundant and not necessary.

Also, how do we deal with all hydrocarbons that are not in a certified cylinder. Most hydrocarbons due to the broad absorption patterns are, by definition, linear through their entire range, so testing linearity is not relevant.

---

*10.5 Absorption Cell Path Length Determination.*

*10.5.1 Flow the CTS through the FTIR cell. Once the absorbance of two consecutive spectra differ by less than or equal to the uncertainty of the cylinder standard, the CTS spectrum may be recorded. Note that the CTS gas must be one of the following gases: ethylene, methane, or carbon dioxide.*

*10.5.2 Record a set of the absorption spectra of the CTS, and record the temperature, pressure, and concentration of the CTS.*

*10.5.3 Record the instrument manufacturer's nominal absorption pathlength, nominal spectral resolution, and the CTS signal integration period.*

*10.5.4 Calculate the reference cell absorption pathlength, according to the following equation:*

$$L_r = L_f \left(T_r / T_f\right)\left(P_f / P_r\right)\left(C_f / C_r\right)\left\{A_r / A_f\right\} \qquad \text{Equation 9}$$

*Where:*

*Lr = reference cell absorption pathlength.*

*Lf = fundamental CTS absorption pathlength.*

*Tr = absolute temperature of reference CTS gas.*

*Tf = absolute temperature of fundamental CTS gas.*

*Pr = absolute pressure of reference CTS gas.*

*Pf = absolute pressure of fundamental CTS gas.*

*Cr = concentration of the reference CTS gas.*

*Cf = concentration of the fundamental CTS gas.*

*{Ar /Af } = ratio of the reference CTS absorbance to the fundamental CTS absorbance, determined by classical least squares, integrated absorbance area, spectral subtraction, or peak absorbance techniques.*

Strong Recommendations

Like above, this calculation of FTIR gas cell pathlength is anachronism from when concentrations of analytes were calculated by hand. Software today do all these calculations before reporting any values. As such, this should no longer be discussed or required. I have never instructed anyone to do this calculation. Instead just confirm that the FTIR CTS is within the 5% requirement, because if it isn't there is a problem with the FTIR set up and most likely not a gas cell pathlength issue.

To make this section valuable, it should be changed from a "pathlength" specific QA procedure to an "Instrument Calibration" procedure. Almost all FTIRs today use a fixed pathlength gas cell, so the pathlengths are not changing, so that is not what is being measured anyway with this CTS measurement.

The QA/QC we should be doing here is confirming that the CTS is within 5% of the certified value. This demonstrates that the FTIR is in calibration and can be utilized for other gases that may not have certified cylinders. Reasons for failure would be a poor pressure reading, detector linearity, resolution control, and frequency control, if the gas cell pathlength is adjustable (that the wrong pathlength is selected), if the gas cell has an alignment requirement (it is possible that some light will not make the required number of passes) so a convolved pathlength issue as well, or somewhat frequently a CTS gas with a bad certification (this happens more than you would expect).

My recommendation is to make this an "Instrument Calibration" section that just requires the CTS to be within 5% and if it fails this test, figure out why before starting. That has always been my recommendation to users of my equipment.

---

*10.6 Instrument Resolution.*

*10.6.1 Flow ambient air through the gas cell.*

*10.6.2 Verify the instrument resolution using a water absorbance peak near either 1,918 cm−1, 3,050 cm−1, or 3,920 cm−1.*

*10.6.3 The absorbance of the peak being used for the resolution determination should be approximately 0.25 absorbance units. Mix additional humified air or nitrogen with the ambient flow, to achieve this absorbance.*

*10.6.4 Record an absorbance spectrum and measure the FWHH of the chosen water peak. The measured FWHH of the water peak must be within 5% of the nominal instrument resolution to proceed with testing.*

Comments

I am a bit conflicted on this section since the Instrument Resolution is not necessarily the resolution used to perform infrared gas analysis. Take for instance when an FTIR can generate 0.5 $cm^{-1}$ resolution spectra but is being utilized at 2 or 4 $cm^{-1}$. Does the 0.5 $cm^{-1}$ even matter at that point? But the analyzer might not be configured to measure the apodized resolution at 2 or 4 $cm^{-1}$. Or a case when we are measuring say ethanol at 0.5 $cm^{-1}$, the band width of ethanol is so broad any small resolution issue would be immaterial.

Also, by stating 3 water lines, it suggests that these are the only lines that can be utilized when there are many lines that could be used depending on the water or say methane levels. It should allow for other gases and frequencies to be utilized. The sample itself should be usable if we are measuring formaldehyde only.

One thing that may not be fully understood is that FTIRs ability to hit "resolution" improves as the frequency that is being measured is reduced. So, measuring "resolution" at 3,920 vs 1,918 $cm^{-1}$ is not a fair comparison. The band at 1,918 could be at 0.5 +/- 0.02 $cm^{-1}$ but the band at 3,920 would be +/-0.04 $cm^{-1}$. Any frequency check would have the same discrepancy due to how FTIR spectra are collected.

If we are going to use the term FWHH, we should also use the Term FWHM, since it is a more correct term.

**Recommendations**

There needs to be more ways to calculate resolution and more gases that are allowed.

There needs to be outs when resolution is not important.

There needs to be allowances for FTIRs being used for a single gas measurement like ETO or formaldehyde when other regions may not be available. The analyte gas itself?

Varying the apodization function to help "improve" the affective resolution when necessary, due to scattering of light through an optical window that might have contamination on it.

---

*11.1 Leak Check. Verify that there are no significant vacuum-side leaks using one of the leak tests described in this section. Perform the vacuum-side leak check after each installation at the sampling or measurement location. Leak check must be performed prior to the start of the field test, and after any relocation or maintenance to the sample transport system. A leak may be detected either by measuring a small amount of flow when there should be zero flow, or by measuring the vacuum decay rate. To test for leaks using loss of vacuum you must know the vacuum-side volume of your sampling system to within ±10% of its true volume.*

*11.1.1 Low-Flow Leak Test. Test a sampling system for leaks using low-flow measurements as follows:*

*11.1.1.1 Seal the probe end of the system by capping or plugging the end of the sample probe.*

*11.1.1.2 Start sampling pumps and operate them until the pressure stabilizes.*

*11.1.1.3 Observe/measure the flow through the vacuum-side of the sampling system. A flow of less than 0.5% of the system's normal in-use flow rate is acceptable.*

*Note: For bypass systems, where the sample flow rate through the vacuum side of the sample system is greater than the FTIR cell flow rate, the higher flow rate (bypass plus analyzer/FTIR flow rate) is used as the in-use flow rate when calculating acceptability of the leak level.*

*11.1.2 Vacuum-Decay Leak Test. Perform a vacuum-decay leak test as follows:*

*11.1.2.1 Seal the probe end of the system as close to the probe opening as possible by capping or plugging the end of the sample probe.*

*11.1.2.2 Operate all vacuum pumps. Draw a vacuum on the sampling system and let the pressure on the system stabilize.*

*11.1.2.3 Turn off the sample pumps and seal the system under a vacuum of 250 mmHg greater than the source static pressure. Record the absolute pressure and the system absolute temperature every 30 seconds for 5 minutes. The leak rate must be equal to or less than 2.5 mmHg per minute.*

Comments

I have never been a fan of any of these procedures since they can cause particulate contamination to make into the FTIR gas cell and cause more harm than good. When the vacuum is released, a high flow rate is directed to the gas cell and particulate material in the lines anywhere can make it to the gas cell and cause the system to lose signal, possibly way more than the 5% baseline drift mentioned earlier in the document, which would then require the entire system to be taken apart, cleaned and reassembled. Just for this same problem to happen again on the next leak check.

If the system can run $N_2$ and CTS system checks and spike recoveries this should be good enough to demonstrate that there are no leaks through the measurement system. The $N_2$ demonstrates that no water and $CO_2$ are making into the system. The CTS demonstrates that 100% of the direct reading is possible, if there were a leak that would not be possible. Lastly, the only time I have ever found a leak that the two above didn't catch, I caught it with the spike recovery, because the spike recovery was greater than 100%. The leak was at the Swagelok nut from the calibration line (not tight) just a head of the particulate filter. Since the spike flowed out the leak area, the emission level increased and we got a high spike recovery.

Recommendation

My recommendation would be to write this section such that $N_2$, CTS and spike can provide the required leak test. Otherwise, we are risking particulate contamination of the gas cell every time the current procedure is performed. Not a good solution.

*11.2 Detector Linearity. Observe the single beam instrument response in the frequency region below the detector cutoff (usually <400 cm−1), where the detector response is known to be zero. Verify that the detector response is "flat" and equal to zero in this region, or at least 100 times less than the peak signal in the entire spectrum. If the response is not linear, decrease the aperture or attenuate the IR beam, and repeat the linearity check until the detector response is linear.*

Comment

I agree this is an important step, but one simple correction has been left out. "Relinearize" the detector using the Manufacturer's recommended procedure.

Also, I am not sure what 100x the peak signal in the entire spectrum means. A single beam spectrum has multiple different signals, some that are only a few times that of the detector cutoff (near detector cutoff). Or, are we saying the peak signal must be 100x greater than the detector cutoff value? If so, the language needs to be clarified.

---

*11.3 Gas Cell Pathlength. Verify the gas cell pathlength of your instrument by following the procedure found in section 10.6.4 of this method.*

Comment

Again, I disagree that this is what Section 10.6.4 does or what it should be utilized for. My recommendation would be to remove any discussion of calculating Gas Cell Pathlength since we are not performing this by measuring a gas.

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*11.4.1 QA Spike Option 1. Use a certified standard (±2% accuracy) for an analyte that has been validated at the source. One may either spike each analyte of interest or choose an appropriate surrogate. An appropriate surrogate must have a vapor pressure that is less than or equal to the analyte of interest and be less soluble in water. The wavelength at which the surrogate is to be quantified must be reported and be within 100 wavenumbers of a wavenumber that will be used to quantify the analyte of interest. Additionally, the pKa of a surrogate must be within 20% of the pKa of the analyte of interest. Surrogates are not allowed for the following analytes: formaldehyde, HCl, HF, NH3, and vinyl chloride. If the spike recovery, as calculated by Equation 5 of this method, is within 70–130% then proceed with the testing.*

## Major Concerns

There a multiple points that I strongly disagree with here.

1. We should never convolve pKa into this document as many compounds do not have pKa values or ones that are readily searchable. Also, this is a gas phase document, pKa is an acid dissociation constant for liquid solutions (WE DON'T HAVE LIQUIDS). For instance, good luck finding the pKa for formaldehyde that is listed in this section. Water solubility is fine but convolving solubility with acid dissociation or pKa should never happen. I strongly suggest that this whole line of discussion be removed.

2. FTIR is the only method that can confirm the concentration of a certified gas. If the gas must meet the 2% certified as measured by the FTIR, what is the purpose of the calibration gas???? No, other method requires the analyzer to tell the source tester that the gas is correct. They just calibrate to the tag value on the cylinder. This is not a fair requirement to make of the FTIR, just because it can do something no other analyzer can provide.

---

**Major Concerns**

*11.4.2 QA Spike Option 2. Use a non-certified cylinder for an analyte that has been validated at the source. As with Option 1, one may either spike each analyte of interest or choose an appropriate surrogate. If the spike recovery, as calculated by equation 5 of this method, is within 90–110%, then proceed with the testing.*

Just like above, we are requiring the FTIR to do things other analyzers are not required to do.

First, equation 5 is incorrect and must be corrected (should just be a Spike Recovery Calc).

Second, whether the spike gas is certified to one standard or another misses the point of the a Spike Recovery. What the proposed method is trying to do here is convolve two issues QA/QC issues that should not be convolved: Calibration and Spike Recovery. Again, no other technique is required to do either in most cases. The instrument doesn't have to tell the source tester that the cylinder is not correct and in many instances, they don't have to run a spike recovery at all.

**Strong Recommendation**

This section should be completely removed since it is convolving 2 QA/QC procedures and no other method is required to do this.

---

*11.5 Sampling. Sampling must be done using a continuous flow of source gas.*

*11.5.1 Stratification Check. A stratification check must be performed, per the steps in this section, to justify sampling at a single location during testing.*

*11.5.1.1 Use a probe of appropriate length to measure the analyte of interest at each of 12 traverse points ($MN_i$, where i = 1 to 12) located according to section 11.3 of Method 1 in appendix A–1 to 40 CFR part 60 for a circular stack or nine points at the centroids of similarly shaped, equal area divisions of the cross section of a rectangular stack.*

*11.5.1.2 Calculate the mean measured concentration for all sampling points ($MN_{avg}$).*

*11.5.1.3 Calculate the percent stratification ($S_t$) of each traverse point using the following equation:*

$$S_{ti} = \frac{MN_i - MN_{avg}}{MN_{avg}} * 100 \qquad \text{Equation 11}$$

*11.5.1.4 The gas stream is considered to be unstratified and you may perform testing at a single point that most closely matches the mean if the concentration at each traverse point differs from the mean concentration for all traverse points by no more than 5.0% of the mean concentration.*

*11.5.1.5 If the criteria for single point sampling is not met, but the concentration at each traverse point differs from the mean concentration by no more than 10% of the mean, the gas stream is considered minimally stratified, and you may sample using the "3-point short line."*

*11.5.1.6 If the concentration at any traverse point differs from the mean by more than 10%, the gas stream is considered stratified, and you must sample using the stratification check procedure specified in section 11.5.1.1 of this method.*

**Strong Objection**

Once again, I object that EPA Method 320 is being required do something similar methods like EPA Method 18 are not required to do. This new requirement makes it even less likely people will choose FTIR as the compliance method since the requirements are more onerous.

---

*11.5.2 Assign a unique filename to each spectrum and separately to each corresponding interferogram. Spectra and interferograms must be providable in ".spc" format upon request.*

**Comment**

I hate to comment on every subsection but what possibly is the explanation that the data must be presented in .spc format. Most FTIR manufacturers do not use .spc or have converters to provide this. The actual industry standard is JCamp and no one uses it.

Unless you have the exact method, all the calibration data and the software there is no way to reproduce the results from the source tester. So, supplying data in one specific format has no purpose.

**Recommendation**

This requirement be removed or changed to say that the raw spectral data must be provided if requested.

---

*11.5.3 Temperature. The temperature of the gas cell must be measured directly. The temperature measurement device must be calibrated to within ±0.1 °C every 12 months.*

**Comment**

Again, what a ridiculous requirement. If we are measuring gases at 191C or 375F, which is common, a 0.1 C error is a 0.02% error in the analytical reading. 0.1 K / 464 K x 100 = 0.02%. Even having to calibrate temperature devices is a ridiculous request since many are imbedded deep within the analyzers and cannot be removed in some cases without damage (which would require replacement).

The purpose of the CTS is to demonstrate that the instrument is in calibration. If the temperature were off by 4 C at 191C, that would be less than a 1% error in the quantified result for all compounds. I have never seen a thermocouple be off by 4 C if it works at all. It would have to be off by 23 C for 5 % error.

**Recommendation**

Remove this requirement completely, since it can't be performed on many FTIRs and the requirement is not valid. Confirm the temperature with the CTS measurement.

---

*11.5.4 Pressure. The gas cell pressure must be measured empirically. The measurement device must be calibrated to within ±1 mmHg every 12 months.*

**Comment**

Hate to pile on but another ridiculous requirement. A 1 mm Hg error would be 0.13% error in the quantified results. 1 mm Hg / 760 mm Hg (atm) x 100 = 0.13%. Since FTIRs work on an absolute scale, mm Hg is not an appropriate unit to report and calibrate the drift. All quantitative work is performed in atmospheres. A 5% error in atmospheres is +/- 0.05 atm or 38 mm Hg, is a 5% quantitative error.

At least in this case, the atmospheric pressure can be compared to a Hg manometer to demonstrate that the pressure is correct, but a 1 mm Hg requirement is way too stringent.

Again, if the pressure reading drifted by a sizeable amount, it is easily demonstrated by running the CTS.

**Recommendation**

Remove or edit this requirement to something appropriate like +/0.01 atm or +/- 7.6 mm Hg (Torr).

---

*11.5.5 Inspect the sample spectra immediately after the run to verify that the gas matrix composition was close to the expected (assumed) gas matrix. Additionally, look at the residual spectra for each sample spectrum to confirm interferences have been accounted for.*

**Comments**

I am not sure what one can do if the matrix is different, or there should be some discussion.
I agree that you should always look at the residual spectrum to determine interferences, but this would be a perfect place to describe how to properly do this.

---

*11.6 Post-Test CTS. At the end of each test, record another CTS spectrum. Compare the pre- and post-test CTS spectra. The peak absorbance in pre- and post-test CTS must be ±5% of the mean value.*

**Comments**

Again, I will reiterate that any discussion of peak height is inappropriate as it doesn't allow for changes in pressure and that more than one band is being measured. The only thing that should be compared is the resulting concentration from the software.

**Recommendation**

Change from peak absorbance to quantified result of the CTS.

*13.1 Detection Level (DL). The DL of this method is defined as the SAR value where the SAR is greater than three times the residual value of the corresponding standard addition elevated concentration (MCspiked). The DL for this method must be less than or equal to 20% of the applicable compliance limit for the compound being measured. If this is not the case, Method 320 cannot be used for such an application.*

**Concern**

The quantified results should be good enough to determine the detection limit. 3 x the STDev of any gas provides the approximate DL in all cases. The reported results take everything into account: spectral region, spectral absorption cross-section, detector noise, varying interferences, temperature and pressure.

If there is a bias, the residual data does not provide that information either. A bias can only be determined by performing a detailed analysis of the interference. Spike recovery does not provide this, since the spike is of the analyte not the interference.

**Strong Recommendation**

All detection limits should be calculated based on 3 x the STDev of the reported value either from $N_2$ or the sample stream if the analyte levels are below detection.

---

**Major Concern**

*13.2 Background Deviation. Deviations in absorption greater than ±5% in an analytical region are unacceptable, and Method 320 cannot be used under this condition.*

**Concerns**

As pointed out above, background drift is important that it be dealt with, but an absolute baseline drift spec is not appropriate. If the software cannot handle the baseline drift, it will be observed in the residual analysis or observed by a bias in the quantified result.

**Strong Recommendation**

Remove this requirement from the method. In its place monitor the baseline drift for particulate loading. If it becomes significant a new baseline or cleaning the gas cell may be appropriate.

---

Lastly, again there is no real discussion in the proposed Method 320 of bias checking or manual data validation, two of the most critical parts of performing FTIR gas analysis. Manual data validation is critical to finding method errors, unexpected spectral interferences and can assist in observing biases. A method without those steps clearly spelled out, is a method that is less valuable.