"Regulatory and Analyzer Update for USEPA's New Formaldehyde Emissions Limit for Combustion Turbines"

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Executive Summary

Spectrum's technical team has demonstrated a <27 ppbvd Formaldehyde detection limit (DL) on its extractive FTIR equipped using a 5-meter cell pathlength. This formaldehyde detection is well below USEPA's 91 ppbvd emission threshold for Combustion Turbines now subject to regulation under NESHAP Subpart YYYY. A future field study using a 10-meter cell pathlength and a new detector configuration is anticipated to provide detection limit results on the order of 5 ppbvd or less. Of important note is that all the data, and presented DLs, were collected in a synthetically-generated turbine exhaust gas matrix.

Regulatory Update

Additional background information may be obtained from the USEPA website[1].

On April 12, 2019, the Environmental Protection Agency (EPA) proposed amendments to the National Emission Standards for Hazardous Air Pollutants (NESHAP, HAP) for Stationary Combustion Turbines to address the results of the residual risk and technology review (RTR) the EPA is required to conduct every eight years in accordance with the Clean Air Act (CAA).

Previous rulemaking chronology includes:

04/12/2019 - Proposed Rule
08/18/2004 – Final Rule; stay
04/07/2004 – Proposed Rule & Proposed Rule
03/05/2004 – Final Rule
01/14/2003 – Proposed Rule

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[1] https://www.federalregister.gov/documents/2019/04/12/2019-07024/national-emission-standards-for-hazardous-air-pollutants-stationary-combustion-turbines-residual

In its proposal, EPA stated they find that the risks from this source category due to emissions of air toxics remain acceptable and that the existing NESHAP provides an ample margin of safety to protect public health. The EPA identified no new cost-effective controls under the technology review that would achieve further emissions reductions from the source category. The EPA is also proposing to amend provisions addressing periods of startup, shutdown, and malfunction (SSM) and to require electronic reporting. In addition, EPA is proposing to remove the stay of the effectiveness of the standards for new lean premix and diffusion flame gas-fired turbines that was previously promulgated in 2004.[2]

The source category for Stationary Combustion Turbines is all equipment including, but not limited to, the turbine, the fuel, air, lubrication and exhaust gas systems, control systems (except emissions control equipment), and any ancillary components and subcomponents comprising any simple-cycle stationary combustion turbine, any regenerative/recuperative-cycle stationary combustion turbine, or the combustion turbine portion of any stationary combined-cycle steam/electric generating system. Stationary means that the combustion turbine is not self-propelled or intended to be propelled while performing its function.

Stationary combustion turbines have been divided into the following eight subcategories:

(1) Emergency stationary combustion turbines,
(2) stationary combustion turbines which burn landfill or digester gas equivalent to 10 percent or more of the gross heat input on an annual basis or where gasified municipal solid waste is used to generate 10 percent or more of the gross heat input to the stationary combustion turbine on an annual basis,
(3) stationary combustion turbines of less than 1 megawatt rated peak power output,
(4) stationary lean premix combustion turbines when firing gas and when firing oil at sites where all turbines fire oil no more than an aggregate total of 1,000 hours annually (also referred to herein as "lean premix gas-fired turbines"),
(5) stationary lean premix combustion turbines when firing oil at sites where all turbines fire oil more than an aggregate total of 1,000 hours annually (also referred to herein as "lean premix oil-fired turbines"),
(6) stationary diffusion flame combustion turbines when firing gas and when firing oil at sites where all turbines fire oil no more than an aggregate total of 1,000 hours annually (also referred to herein as "diffusion flame gas-fired turbines"),
(7) stationary diffusion flame combustion turbines when firing oil at sites where all turbines fire oil more than an aggregate total of 1,000 hours annually (also referred to herein as "diffusion flame oil-fired turbines"), and
(8) stationary combustion turbines operated on the North Slope of Alaska (defined as the area north of the Arctic Circle (latitude 66.5° North)).

The sources of emissions are the exhaust gases from combustion of gaseous and liquid fuels in a stationary combustion turbine. The organic HAPs that are present in the exhaust gases from stationary combustion turbines include formaldehyde, toluene, benzene, and acetaldehyde.

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[2] Proposed Rule 84 FR 15046 Page 15046-15077 (32 pages) at 40 CFR 63 under USEPA Docket Numbers: EPA-HQ-OAR-2017-0688 and FRL-9991-97-OAR

The NESHAP requires new or reconstructed stationary combustion turbines in the lean premix gas-fired, lean premix oil-fired, diffusion flame gas-fired, and diffusion flame oil-fired subcategories to meet a formaldehyde limit of 91 parts per billion by volume on a dry basis (ppbvd) at 15-percent oxygen (O2). Compliance with the formaldehyde emission limit is demonstrated through initial and annual performance testing and continuous monitoring of operating parameters.

As further background, Richard McRanie of RMB Consulting & Research, Inc. summarized that the original proposed rule as given by EPA in January 2003 provided an affected unit with two options whereby one can comply with the proposed rule.

> "It can install an oxidation catalyst and demonstrate a 95% reduction in CO emissions using continuous emissions monitoring (CEM) for CO before and after the catalyst. The second method is that the source can comply with a formaldehyde limit of 43 ppb @ 15% excess O2. EPA assumes that a diffusion flame CT will have to use the oxidation catalyst to achieve the 43 ppb limit and that the lean burn machine will not have to use a catalyst. They arrived at this conclusion by reviewing test data from a number of formaldehyde tests."[3]

However, the proposed 43 ppbvd emission limit was very strongly contested by industry at the time.

Just prior to the original proposed rule issuance for public comment, in August 2002, the Gas Turbine Association submitted a petition to delist two subcategories of stationary combustion turbines under CAA section 112(c)(9)(B). The subcategories were lean premix firing natural gas with limited oil backup and a low-risk subcategory where facilities would make site-specific demonstrations regarding risk levels. Additional information supporting the petition was provided in February 2003. On April 7, 2004, the EPA proposed to delist lean premix gas-fired turbines as well as three additional subcategories that were determined to meet the criteria for delisting in CAA section 112(c)(9)(B): Diffusion flame gas-fired, emergency, and turbines located on the North Slope of Alaska. At the same time, the EPA proposed to stay the effectiveness of the NESHAP for new lean premix gas-fired and diffusion flame gas-fired turbines to "avoid wasteful and unwarranted expenditures on installation of emission controls which will not be required if the subcategories are delisted." The standards for new oil-fired turbines were not stayed and have been in effect.

The NESHAP Subpart YYYY rule went final in March 2004, and immediately a proposed amendment was published by EPA in April 2004 to stay two of the subcategories related to CT burning gaseous fuels.

On August 18, 2004, the EPA finalized the stay of the effectiveness of the NESHAP for new lean premix gas-fired and diffusion flame gas-fired turbines, pending the outcome of the proposed delisting. The EPA stated that it would lift the stay if the subcategories were not ultimately delisted, and turbines constructed after January 14, 2003, would then be subject to the final standards. Those turbines would be given the same time to demonstrate compliance as they would have if there had been no stay.

In 2007, the Court held in NRDC v. EPA, 489 F.3d 1364 (D.C. Cir. 2007) that the EPA had no authority to delist subcategories under CAA section 112(c)(9)(B). According to the court decision, only entire source categories can be delisted under CAA section 112(c)(9)(B). Now, 12 years later, and based on the

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[3] Paper presented entitled "Proposed Combustion Turbine (CT) and Industrial Boiler (IB) MACT Rules – The Potential Impact on the Utility Industry" by McRaine and Berry of RMB Consulting & Research Inc. at the EPRI CEM Users Group Meeting, May 14-16, 2003, San Diego, CA.

proposed results of the residual risk analysis just concluded in 2019, the EPA states in April's proposed rule-making that it does not at this time have information to support a conclusion that the entire Stationary Combustion Turbines source category currently meets the criteria for delisting in CAA section 112(c)(9)(B).

Consequently, the EPA has now, in April 2019, proposed to remove the stay of the standards for new lean premix and diffusion flame gas-fired turbines. Turbines that are subject to the stay would be required to comply with all applicable regulatory requirements of 40 CFR part 63, subpart YYYY, (including the 91 ppbvd Formaldehyde emission limitation) immediately upon a final action to remove the stay. Required initial performance tests must be conducted within 180 calendar days after the effective date of a final action to remove the stay.

The EPA has identified 719 turbines at 242 facilities that are subject to the Stationary Combustion Turbine NESHAP. EPA is projecting 39 new stationary combustion turbines at 26 facilities will become subject over the next 3 years. The 39 turbines include 36 natural gas-fired units, 1 oil-fired unit, and 2 landfill gas or digester gas-fired units.

As these facilities are now considering emissions testing, one must consider the historical background to the means of testing assessed in the original rule-making process, namely EPA Test Method 320 of 40 CFR part 63, appendix A; or the use of ASTM D6348-12e1.

The initial and annual stack testing requirements have been prepared in Table 3 of the Rule to include:

Table 3 to Subpart YYYY of Part 63—Requirements for Performance Tests and Initial Compliance Demonstrations

As stated in § 63.6120, you must comply with the following requirements for performance tests and initial compliance demonstrations.

You must . . .	**Using . . .**	**According to the following requirements . . .**
a. demonstrate formaldehyde emissions meet the emission limitations specified in Table 1 by a performance test initially and on an annual basis *and*	Test Method 320 of 40 CFR part 63, appendix A; ASTM D6348-12e1 [1]provided that the test plan preparation and implementation provisions of Annexes A1 through A8 are followed and the %R as determined in Annex A5 is equal or greater than 70% and less than or equal to 130%; [2] or other methods approved by the Administrator	formaldehyde concentration must be corrected to 15 percent O_2, dry basis. Results of this test consist of the average of the three 1 hour runs. Test must be conducted within 10 percent of 100 percent load.
b. select the sampling port location and the number of traverse points *and*	Method 1 or 1A of 40 CFR part 60, appendix A	if using an air pollution control device, the sampling site must be located at the outlet of the air pollution control device.
c. determine the O_2concentration at the sampling port location *and*	Method 3A or 3B of 40 CFR part 60, appendix A; ANSI/ASME PTC 19-10-1981[1] (Part 10) manual portion only; ASTM D6522-11[1] if the turbine is fueled by natural gas	measurements to determine O_2concentration must be made at the same time as the performance test.
d. determine the moisture content at the sampling port location for the purposes of correcting the formaldehyde concentration to a dry basis	Method 4 of 40 CFR part 60, appendix A or Test Method 320 of 40 CFR part 63, appendix A, or ASTM D6348-12e1 [1]	measurements to determine moisture content must be made at the same time as the performance test.

[1] Incorporated by reference, see § 63.14.

[2] The %R value for each compound must be reported in the test report, and all field measurements must be corrected with the calculated %R value for that compound using the following equation:

Reported Results = ((Measured Concentration in Stack)/(%R)) × 100.

Regarding the origin of the proposed 43 ppbvd in January 2003, and then the final 91 ppbvd emission limitation then set in the rule in September 2003, a curious set of circumstances transpired. During the prior rulemaking period, in 2002, the Avogadro Group, LLC (Avogadro) and URS-Radian Corporation (URS) were contracted by the Electric Power Research Institute (EPRI) to perform a series of emission tests on a combined-cycle gas turbine with lean pre-mix low-NOX combustors. The introduction to EPRI's final report[4] provided publicly in 2004 states:

> "The unit tested included a Siemens-Westinghouse 501F combustion turbine with lean pre-mix low-NOX combustors, a heat recovery steam generator (HRSG), and selective catalytic reduction (SCR) and oxidation catalysts. Tests were conducted at the gas turbine exhaust (i.e. upstream from any catalysts) and at the HRSG stack. The testing program was performed to meet several objectives, the most important of which were:
>
> • To characterize formaldehyde and VOC emissions during operation at base load and lower load conditions, and during transients between loads.
> • To provide data for use in regulatory and permitting applications for gas turbines.
>
> In September 2003, EPA promulgated a final rule for formaldehyde emissions from new/reconstructed combustion turbines, requiring the combustion turbine to reduce the concentration of formaldehyde in the exhaust to 91 parts per billion by volume dry basis (ppbvd) or less, at 15 percent oxygen. This rule is available from EPA's web site, http://www.epa.gov/ttn/atw//turbine/turbinepg.html
>
> URS provided monitoring of concentrations of formaldehyde, VOC and other gases using a Fourier Transform Infrared (FTIR) spectroscopy in accordance to pertinent sections of EPA Test Method 320 "Measurement of Vapor Phase Organic and Inorganic Emissions by Extractive Fourier Transform Infrared (FTIR) Spectroscopy."
>
> Avogadro provided the "conventional" reference method sampling and analysis for measurement
> of formaldehyde and VOC, as well as continuous monitoring of NOX, CO, Total Hydrocarbon, O2 and CO2 concentrations.
>
> The tests were conducted on October 9 through 14, 2002."

In regards to the many requests to stay the formaldehyde emission limits for certain subcategories of combustion turbines, it was noted by EPA and others that the origination of the 43 ppbvd emission limit at 15% oxygen for Formaldehyde in the original proposed rule, was derived by an unusual means. EPA has stated that:

> "To determine the MACT floor for new stationary lean premix gas-fired turbines, we reviewed the emissions data we had available at proposal and additional test reports received during the comment period. In order to set the MACT floor for new sources in this

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[4] EPRI Technical Report entitled "Formaldehyde and VOC Emissions from a Siemens-Westinghouse 501F Combustion Turbine with Lean Pre-Mix Combustors and SCR and CO Catalysts", Report No. 1005408, January 2004.

> subcategory, we chose the best performing turbine. Emissions of each HAP are relatively homogeneous within the subcategory of stationary lean premix gas-fired turbines and any variation in HAP emissions cannot be readily controlled except by add-on control. The best performing turbine is equipped with an oxidation catalyst.
>
> The formaldehyde concentration from the best performing turbine was measured at the outlet of the control device using CARB 430. Concerns were raised during the public comment period that CARB 430 formaldehyde results can be biased low as compared to formaldehyde results obtained by FTIR. For a comprehensive discussion of test methods and the development of the correlation between CARB 430 and FTIR formaldehyde levels, please refer to the memorandum entitled “Review of Test Methods and Data used to Quantify Formaldehyde Concentrations from Combustion Turbines” in the docket. A bias factor of 1.7 was, therefore, applied to the formaldehyde concentration of the best performing turbine. The best performing turbine was tested twice under the same conditions about 2 years apart where one test measured 19 ppbvd and the other test measured 91 ppbvd formaldehyde (numbers have been bias corrected). We determined that since both of these tests were performed under similar conditions but at different times, this represented the variability of the best performing unit and used the higher value as the MACT floor. The MACT floor for organic HAP for new stationary lean premix gas-fired turbines is, therefore, an emission limit of 91 ppbvd formaldehyde at 15 percent oxygen.
>
> We recognize that our selection of an emission limit of 91 ppbvd formaldehyde is based on quite limited data. We think that each new combustion turbine in this subcategory should be able to achieve compliance with this limit if an oxidation catalyst is properly installed and operated. If actual emission data demonstrate that we are incorrect, and that sources which properly install and operate an oxidation catalyst cannot consistently achieve compliance, we will revise the standard accordingly.
>
> No beyond-the-floor regulatory alternatives were identified for new lean premix gas-fired turbines. We are not aware of any add-on control devices which can reduce organic HAP emissions to levels lower than those resulting from the application of oxidation catalyst systems. We, therefore, determined that MACT for organic HAP emissions from new stationary lean premix gas-fired turbines is the same as the MACT floor, i.e., an emission limit of 91 ppbvd formaldehyde at 15 percent oxygen.[5] “

In support of EPA’s conclusion above, earlier on June 30, 2003, Mr. Bradley Nelson of Alpha-Gamma Technologies, Inc., the EPA contractor at the time, provided a letter[6] to Mr. Roy Sims of EPA regarding a “Review of Test Methods and Data used to Quantify Formaldehyde Concentrations from Combustion Turbines”. Wherein Mr. Nelson summarized the CARB Method 430 and EPA Method 320 test results by stating:

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[5] EPA-452/R-03-014, August 2003, “Economic Impact Analysis of the Final Stationary Combustion Turbines NESHAP”, pp 3-19 to 3-19.

[6] Letter now available only in the USEPA docket.

> “A number of studies have been done on the accuracy of CARB 430 by organizations and interest groups. The conclusions from these studies indicate that CARB 430 understates the formaldehyde concentration in the exhaust gas. The reasons for the negative bias include errors in field sample collection, errors in laboratory analysis, the interference of NO, and the reaction of NO with the DNPH. The most prevalent problem with the CARB 430 method is NO, interference. The NO, in the exhaust gas stream reacts with the DNPH, and after the consumption of the DNPH, reacts with the formaldehyde-DNPH hydrazone. This interference can cause the formaldehyde analytical results to be less than actually present in the exhaust gas. Because of this interference, EPA Method 320 has been recommended for use in measuring formaldehyde concentrations in the turbine exhaust gas. The EPA Method 320 uses Fourier Transform Infrared Spectroscopy (FTIR) to analyze the infrared spectra of the exhaust gas stream to determine its composition; FTIR can accurately measure formaldehyde concentrations as low as 9 parts per billion (ppb). From the test report data received, where both CARB 430 and EPA Method 320 were both performed, only 1 out of 29 test runs reported the CARB 430 formaldehyde concentration greater than the EPA Method 320 formaldehyde concentration. A summary of the CARB 430 and EPA Method 320 data is presented in Table 4. Using the data from Table 2, a number of regression techniques, including linear, log, and exponential, were used to calculate a relationship between CARB 430 and EPA Method 320 formaldehyde concentrations. The linear regression was found to have the best fit and was used to develop a correction factor for CARB 430 results. The results of the linear regression gave a slope of 1.667 with a correlation coefficient of 0.764 and a R Square value (coefficient of determination) of 0.561. The correlation coefficient shows that there is a statistically significant and repeatable relationship (i.e. the relationship between the variables is sufficiently close and it could not have reasonably happened by chance) between the CARB 430 and EPA Method 320 data sets. Therefore, it is our recommendation to compensate the CARB 430 formaldehyde results (corrected to 15 percent oxygen) by multiplying by 1.667 to get the corresponding EPA Method 320 formaldehyde concentrations.”

In this manner, CARB Method 430 was also removed from the rule as a possible performance and annual test method, and the only means of compliance determination for Formaldehyde became EPA Test Method 320 of 40 CFR part 63, appendix A; and ASTM D6348-12e1 as stated above and referenced in Table 3 of NESHAP Subpart YYYY.

On August 18, 2004, the EPA finalized the stay of the effectiveness of the NESHAP for new lean premix gas-fired and diffusion flame gas-fired turbines – meaning these units have thus far not been required to test their emissions for Formaldehyde. These units are now searching for testing firms to assess their emissions status. Current source tester equipment is predominantly offered with a 5-meter pathlength cell and a standard HgCdTe (MCT) detector. The industry is concerned that these analyzers may not achieve the necessary detection limits required by the rule. Further, and of additional interest, this is of critical importance because “zeros” reported as the average concentration values in each of three, one-hour test runs, are reported at ½ the method detection limit (MDL) for compliance demonstration purposes.

Current Analyzer Update

Spectrum was retained by the Electric Power Research Institute of Palo Alto, California in 2019 to assess current capabilities and achievable detection limits of formaldehyde (H2CO) measurements using extractive Fourier Transform Infrared (FTIR) spectroscopy. The investigation of minimum detection limits (MDL) for various FTIR configurations focused on several key objectives and was performed in the laboratory only, without field validation. An additional future project for field validation of the new approaches at a potential combustion turbine is under consideration.

All laboratory measurements were made in a simulated turbine exhaust with a mixture of 100 ppm CO, 5% CO2, 0.5 ppm NO2, 10 ppm CH4 and 15% O2 all at 5% analytical accuracy. A custom gas blend containing these gases was procured and used in each test as the "combustion" blend.

Heated water injection was used to add water vapor to the sample at 8% to 12% levels

A precision (2% analytical accuracy) mix was used for H2CO injection which consisted of: 10.1 ppm of SF6 and 5.3 ppm of H2CO. The SF6 is a strong infrared absorber that is easily detected, it was used as a tracer to accurately track the injected levels of H2CO.

A depiction and photograph of Spectrum's sample preparation and test apparatus are presented in Figures 1 and 2.

FTIR systems from two common manufacturers (denoted as A and B) were used to perform the laboratory measurements. Two units of type A (units A1 and A2) were employed:

- Both A1 and A2 had maximum spectral resolutions of 0.125 cm-1 and were used at 0.5 cm-1 for all testing
- These units operated with custom operation and analysis software developed by the manufacturer

The A unit had path-adjustable absorption cells:

  - Unit A1 had a cell with an adjustable path-length from 1 meter to 10 meters and it was used for both the 5 meter and 10 meter measurements
  - Unit A2 had a long-path cell adjustable from 4 meters to 32 meters, it was used for the 29.23 meter measurements
  - Both Units A1 and A2 have the capability to be equipped with an alternative detector

Unit B had:

- A fixed 0.5 cm-1 spectral resolution and a non-variable, fixed 5.11 meter path-length cell
- The device comes with manufacturer's software for both FTIR control and data analysis.
- Unit B does not have an option for using any detector other than an MCT.

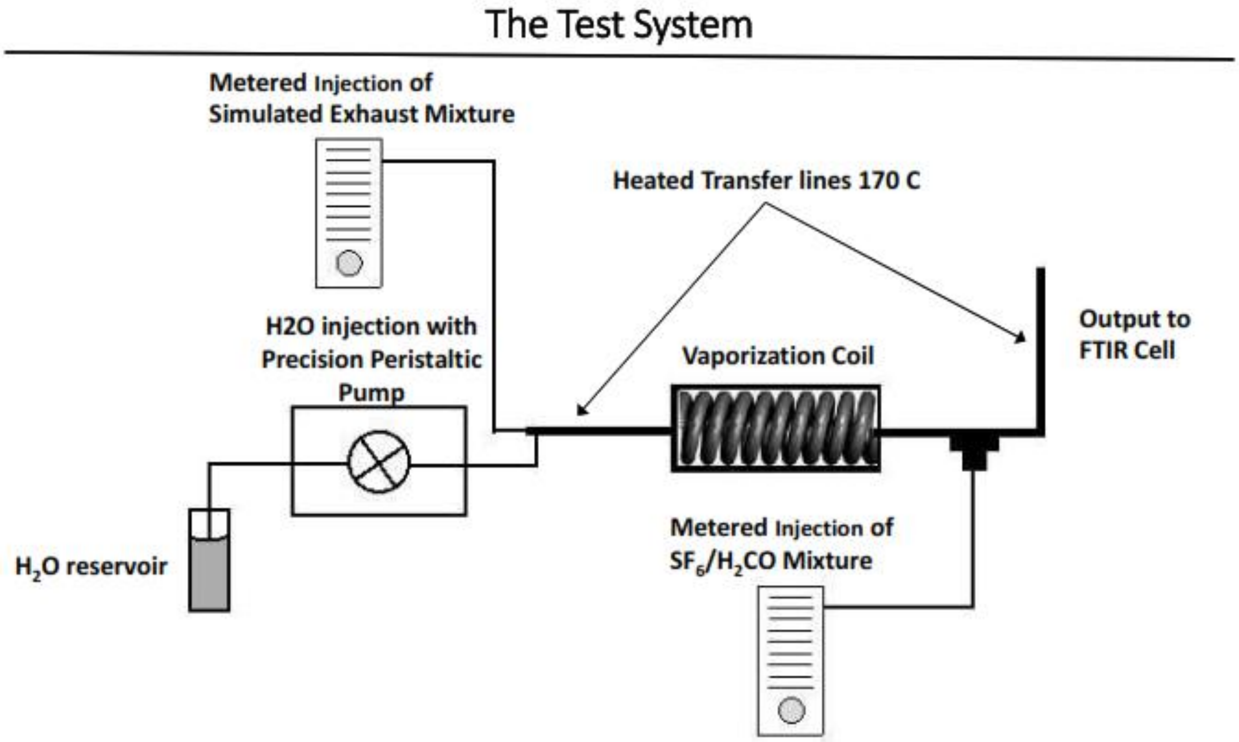


Figure 1. Diagram of the Sample Preparation Setup and Test Apparatus

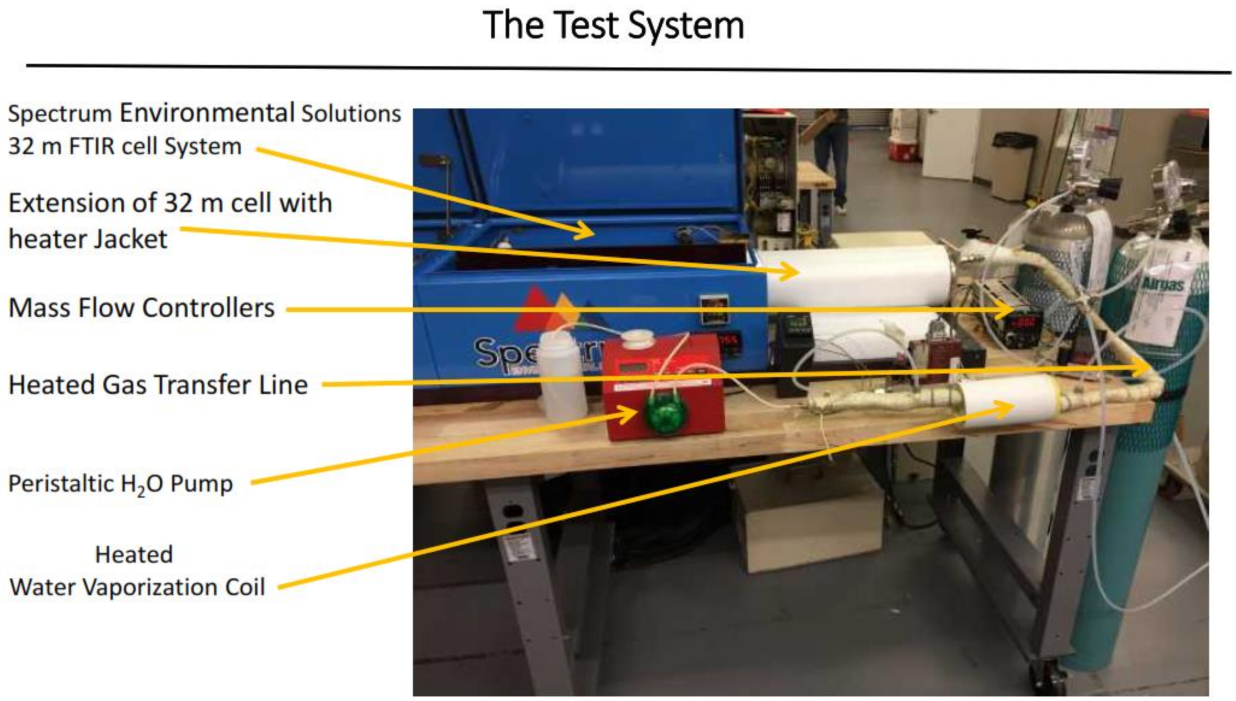


Figure 2. Photo of the Sample Preparation Setup and Test Apparatus

A typical measurement sequence consists of:

- Purge the complete system with pure N_2 until all atmospheric species are deleted.
- Collect a five-minute N_2 background spectrum
- Using a mass flow controller, set the N_2 flow to typical test flow conditions for the exhaust mixture and start water injection with the peristaltic pump.
- Once the water level has stabilized at the level desired collect a five-minute N_2/H_2O interference spectrum (“wet background”)
- Replace the N_2 flow with the exhaust gas mixture (the combustion blend gas standard) keeping flow rate constant
- Using a second mass flow controller, the SF_6/H_2CO flow is set to the formaldehyde concentration desired for the test.
- A minimum of 12, 2-minute averaged spectra of the mixture is then collected.
- The series of tests are then run varying the SF_6/H_2CO flow to produce H_2CO concentrations of: 150 ppb, 100 ppb, 50 ppb, and at the lowest detectable level. The results are presented below in Figures 3 and 4.

Collecting a “water interference” spectrum before testing is common practice for some FTIR operators *but it is not universal*, many operators simply use library reference spectra to treat the water interference. However, it is very difficult to exactly match the spectrum of water vapor in an arbitrary source using library spectra, the resulting miss-match has a significant influence on data accuracy as in the IR spectrum, water is the primary constituent overlapping (or interfering) with formaldehyde. Significant improvements in quantitation are obtained by measuring a water interference spectrum with the actual instrument used in the field, near the time of testing as this provides a “best fit” for the water interference.

Differences With FTIR A Using library and Measured H_2O Interference Spectra

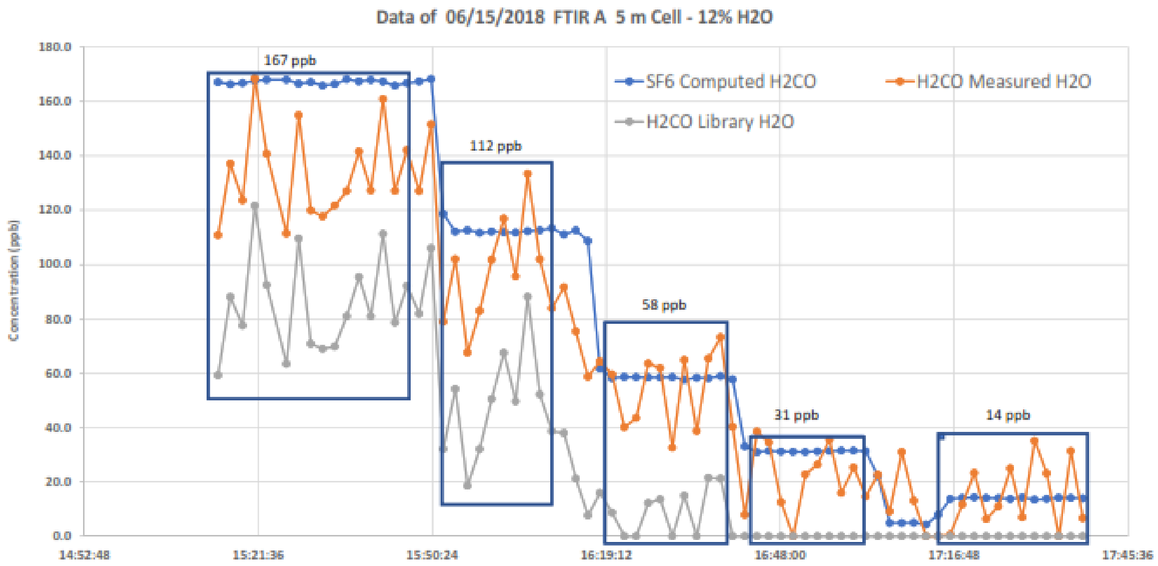


Figure 3. Differences using FTIR A using library and Measured H2O Interference

Example of Long-path (29.23 m) Formaldehyde Data FTIR A

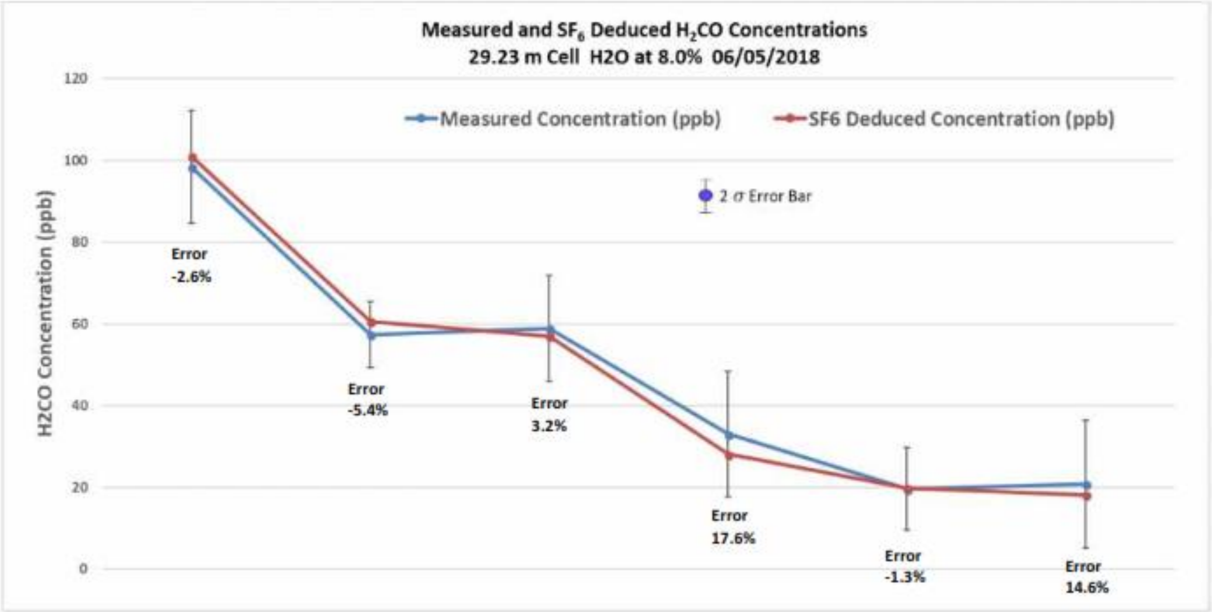
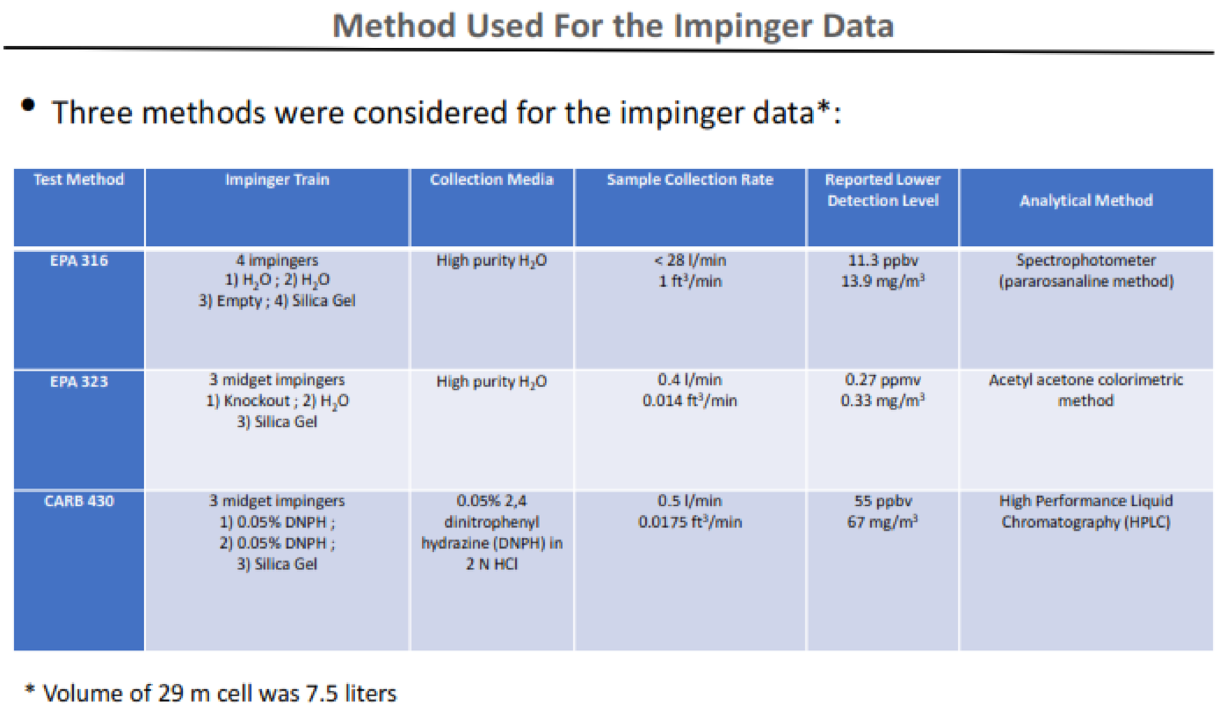


Figure 4. Long-Path data using FTIR A

EPRI wished to consider the other wet formaldehyde methods as well as summarized in Figures 5 and 6. Spectrum re-evaluated conceptually these EPA Methods:

323 – “Measurement of Formaldehyde from Natural Gas-Fired Stationary Sources”
This approach is restricted on how much volume one can sample (<0.4LPM). One needs to sample long periods to get low DLs. Precisely 1,603 min or 26+ hours would be required to properly obtain 0.2µg/mL - spectrophotometer DL as listed in method for a 10ppb formaldehyde sample. Industry of course would prefer to limit post-test rinse to no more than 10-15mL.

EPA Method 316 – Sample and Analysis for Formaldehyde Emissions in Mineral Wool and Wool Fiberglass Industries. This is another impinger method where EPA claims that 11.3ppbv formaldehyde DL over 1-hour sample period. It requires approximately 30 ft^3 of sample be collected (~35x max volume allowed by M323). Fortunately, this method uses larger tubing and impingers thus allowing for a much larger flow through the system than 323. Current lab DLs are 0.015µg/mL.



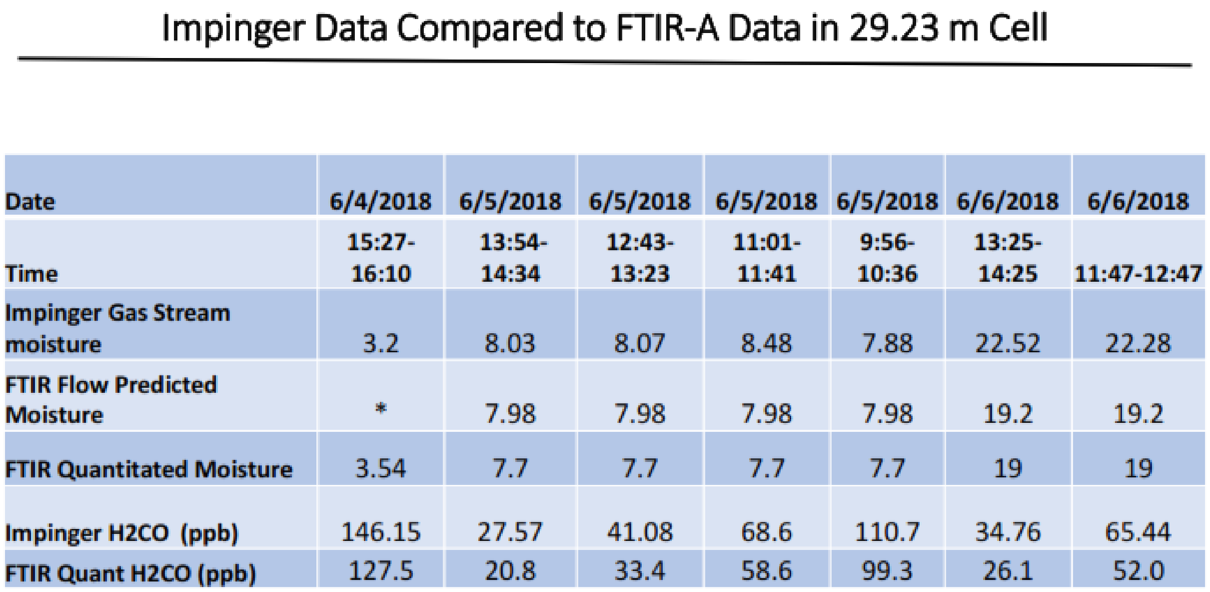
Method Used For the Impinger Data

- Three methods were considered for the impinger data*:

Test Method	Impinger Train	Collection Media	Sample Collection Rate	Reported Lower Detection Level	Analytical Method
EPA 316	4 impingers 1) H_2O ; 2) H_2O 3) Empty ; 4) Silica Gel	High purity H_2O	< 28 l/min 1 ft^3/min	11.3 ppbv 13.9 mg/m^3	Spectrophotometer (pararosanaline method)
EPA 323	3 midget impingers 1) Knockout ; 2) H_2O 3) Silica Gel	High purity H_2O	0.4 l/min 0.014 ft^3/min	0.27 ppmv 0.33 mg/m^3	Acetyl acetone colorimetric method
CARB 430	3 midget impingers 1) 0.05% DNPH ; 2) 0.05% DNPH ; 3) Silica Gel	0.05% 2,4 dinitrophenyl hydrazine (DNPH) in 2 N HCl	0.5 l/min 0.0175 ft^3/min	55 ppbv 67 mg/m^3	High Performance Liquid Chromatography (HPLC)

* Volume of 29 m cell was 7.5 liters

Figure 5. Impinger Data using Wet Chemistry Techniques



Impinger Data Compared to FTIR-A Data in 29.23 m Cell

Date	6/4/2018	6/5/2018	6/5/2018	6/5/2018	6/5/2018	6/6/2018	6/6/2018
Time	15:27-16:10	13:54-14:34	12:43-13:23	11:01-11:41	9:56-10:36	13:25-14:25	11:47-12:47
Impinger Gas Stream moisture	3.2	8.03	8.07	8.48	7.88	22.52	22.28
FTIR Flow Predicted Moisture	*	7.98	7.98	7.98	7.98	19.2	19.2
FTIR Quantitated Moisture	3.54	7.7	7.7	7.7	7.7	19	19
Impinger H2CO (ppb)	146.15	27.57	41.08	68.6	110.7	34.76	65.44
FTIR Quant H2CO (ppb)	127.5	20.8	33.4	58.6	99.3	26.1	52.0

Figure 6. Comparison of FTIR-A data to very limited Method 316 impinger data

Impinger Data from Method 316 Compared to FTIR-A Data in a 29.23 m Cell

The impinger and FTIR data agreed well, but the impinger method was consistently 4 to 5 ppb higher throughout our test runs. The analytical laboratory indicated that EPA Method 316 is a simple colorimetric analysis and prone to subjectivity by the operator (even the field blank and the reagent blank indicated some presence of formaldehyde). It can be biased by any compound having absorption in the 570 nm region. The problematic compounds could be sulfites or cyanide, although none of these were expected in the synthetic gas stream prepared for this study.

Detection Limits using procedures of ASTM 6348

The ASTM 6348 measurement method has three procedures for computing the minimum detection limit of an FTIR system, these procedures are:

- ASTM #1 Detection limit computed from the instrumental noise level
- ASTM #2 Detection limit computed as 3-times the standard deviation of measured gas concentrations of a blank sample
- ASTM #3 Detection limit computed from the spectral residual reported by the CLS analysis routine.

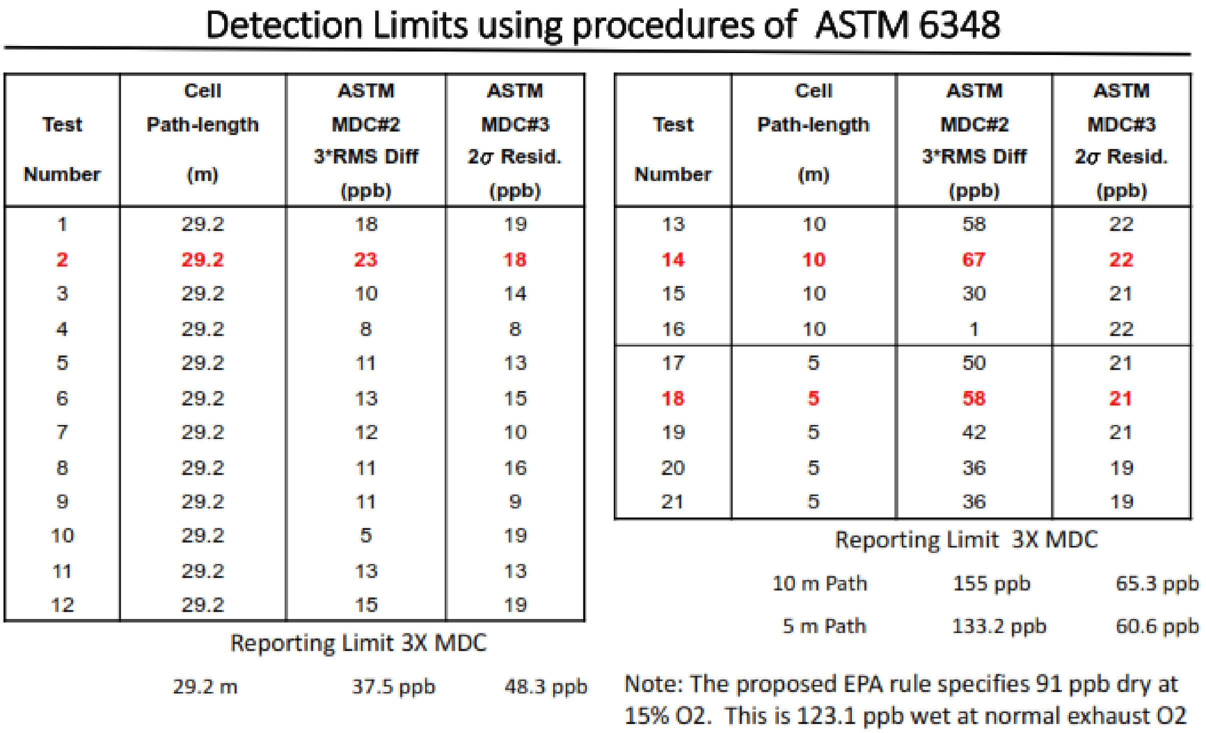
Because ASTM #1 provides a detection limit that is so low that ND does not consider matrix interference effects, it is rarely achievable in practice of limited practical use, and was not be computed here. ASTM #2 and #3 are both computed as they best represent achievable field detection limits. Figure 7 presents the MDCs for this testing.

ASTM #2 computes:

$$\text{MDC\#2} = 3 * \sqrt{\frac{1}{n} \sum_{i=1}^{n} (C_i - C_{ave})2}$$

ASTM #3 computes:

$$\text{MDC\#3} = \frac{RMS_{resid}}{RMS_{REF}} * \frac{C_{ref} * L_{ref}}{L_{cell}}$$



Detection Limits using procedures of ASTM 6348

Test Number	Cell Path-length (m)	ASTM MDC#2 3*RMS Diff (ppb)	ASTM MDC#3 2σ Resid. (ppb)
1	29.2	18	19
2	**29.2**	**23**	**18**
3	29.2	10	14
4	29.2	8	8
5	29.2	11	13
6	29.2	13	15
7	29.2	12	10
8	29.2	11	16
9	29.2	11	9
10	29.2	5	19
11	29.2	13	13
12	29.2	15	19

Reporting Limit 3X MDC

29.2 m	37.5 ppb	48.3 ppb

Test Number	Cell Path-length (m)	ASTM MDC#2 3*RMS Diff (ppb)	ASTM MDC#3 2σ Resid. (ppb)
13	10	58	22
14	**10**	**67**	**22**
15	10	30	21
16	10	1	22
17	5	50	21
18	**5**	**58**	**21**
19	5	42	21
20	5	36	19
21	5	36	19

Reporting Limit 3X MDC

10 m Path	155 ppb	65.3 ppb
5 m Path	133.2 ppb	60.6 ppb

Note: The proposed EPA rule specifies 91 ppb dry at 15% O2. This is 123.1 ppb wet at normal exhaust O2

Figure 7. Detection Limit Comparison using ASTM 6348

In theory, longer optical path-lengths produce detection to lower concentration levels and smaller data scatter, provided S/N was adequate for detection.

Except for the long path (29 m) data, the detection limits given by the ASTM MDC calculations, would indicate that neither the 5 m cell or the 10 m cell could meet the EPA regulation.

In these tests, all measurements were made with a standard HgCdTe (MCT) infrared detector with a 12**µ** cutoff. This is a liquid nitrogen cooled detector with a D* (sensitivity) of $1.5X10^{10}$.

As a recommendation to EPRI,

- A program has been initiated by EPRI looking at the improvement of formaldehyde detection with an FTIR outfitted with an alternative IR detector
- This program is being executed by Spectrum Environmental Solutions as was the program discussed here
- The A2 equipment is identical to that used for this study so results should be directly comparable
- The Concentrations to be studied are 80 ppb, 50 ppb, 25 ppb, and 12 ppb or at the lowest concentration possible, all tests will be done at 10% moisture and against the same simulated turbine exhaust gas-mixture as the present test.

Conclusion

Recent Spectrum laboratory results using only the standard MCT detector have yielded the conclusion that a 5 m cell could NOT provide low enough detection to meet the EPA reporting limit (data concentration >= 3X standard deviation of data collection). However, all of FTIR manufacturer B systems are 5 m cell systems and further, Manufacturer B does not have the option for using an alternative detector.

Spectrum provided a 10 and 29 m cell, and data indicates no difficulty meeting a reporting limit below the regulatory threshold, even below ~15 ppbvd concentrations.

Recent data resulting from the alternative detector on FTIR A devices pushed the standard deviation low enough that Spectrum could detect and report data < 27 ppb (at <3*S.D.) in a small 5 m cell. With this short cell, Spectrum demonstrated detection of formaldehyde concentrations of 12 ppbvd with a SD of 4 ppb. This early data set was taken at 3-minute time averages. Future studies will be increased to 5-minute averaging that should take the 0.004 SD to sqrt(3/5)*0.004 = 0.003 ppb.

Future field validations may be performed with EPRI to demonstrate even lower detection limits using Spectrum's standard 10 m cell and its new detector arrangement. Spectrum anticipates these future results to demonstrate a DL less than 5 ppbvd, and these results will be shared shortly.

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