



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

Mr. Grant E. Dunham
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University of North Dakota
15 North 23rd Street, Stop 9018
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MAY 30 2018

OFFICE OF
AIR QUALITY PLANNING
AND STANDARDS

Dear Mr. Dunham:

This letter is our response to your submittal dated August 29, 2017, to Robin Segall of my staff, requesting approval on behalf of the Electric Power Research Institute, as well as coal-fired utilities subject to the Mercury and Air Toxics Standards (MATS), for use of a new test method in lieu of Method 26 or 26A (40 CFR 60, Appendix A) for (1) demonstration of compliance with hydrogen chloride (HCl) emission limits and (2) certification and ongoing quality assurance of HCl continuous emissions monitoring systems (CEMS). The EPA's Office of Air Quality Planning and Standards, as the delegated authority, must make the determination on any major alternatives to test methods and compliance testing procedures required under 40 CFR parts 59, 60, 61, 63, and 65.

You explain that the MATS rule (40 CFR part 63, Subpart UUUUU, National Emission Standards for Hazardous Air Pollutants: Coal- and Oil-fired Electric Utility Steam Generating Units) has led to a significant increase in Method 26 or 26A testing to collect data to demonstrate regulatory compliance with the HCl emissions limit on a quarterly basis or, if an electric generating unit (EGU) demonstrates compliance using an HCl CEMS, yearly relative accuracy testing. Because of the relatively high expense, number of personnel hours related to testing, and elaborate setup and recovery involved with Method 26 and 26A, you and your colleagues sought a simpler, cheaper method for measuring HCl emissions from coal combustion sources.

The alternative method proposed in your submittal relies on a sorbent trap technology approach similar to that of Method 30B for vapor phase mercury (40 CFR part 60, Appendix A). You provided a detailed method protocol with your request as a potential 'Other Test Method' to be posted on the EPA Emission Measurement Center website at www.epa.gov/emc. You assert that this method is simpler to perform, less expensive, and more robust in that it avoids sample contamination and does not require the use or transport of harmful chemicals. You also assert that your candidate method has the potential for improved sensitivity and equal or better accuracy when compared with Methods 26 and 26A. In particular, you have requested approval of this alternative method for application to coal-fired utility boilers with low moisture coal combustion flue gases at temperatures above 100 degrees C based on the data and information you have provided, which are described below.

In your August submittal and earlier correspondence, you provided Method 301 (40 CFR part 63, Appendix A, 2011 version) field validation test data for your candidate method from tests conducted at five coal-fired utility boilers using the nine-run, paired-train sampling approach

with Method 26A conducted non-isokinetically as the reference or ‘validated’ method.¹ Successful Method 301 test programs were conducted at three of the five electric utility boilers (Plants 1, 2 and 4) and the bias and precision results of those test programs are summarized in the table below.

Facility	Fuel/Boiler Configuration/ HCl Emission Level	Emission Controls	Method 301 Results
Plant 1	Lignite coal Overfire air 0.23 ppm at 3% O ₂	Low-NO _x burners Electrostatic precipitator Wet limestone scrubber	-3.5% Relative bias -Precision not significantly different than Method 26A
Plant 2	Lignite coal Overfire air 1.36 ppm at 3% O ₂	Electrostatic precipitator	-9.6% Relative bias -Precision not significantly different than Method 26A
Plant 4	Bituminous coal Circulating fluidized bed (CFB) 44.3 ppm at 3% O ₂	Selective non-catalytic reduction Fabric filter Limestone feed to CFB	-3.9% Relative bias -Precision not significantly different than Method 26A

The data from Plants 3 and 5 did not meet Method 301 requirements. The data collected at Plant 3, a small unit with a flooded-disc wet scrubber and flue gas containing entrained water droplets, yielded data that could not be used to determine the precision and bias of the candidate method. At Plant 5, only three paired-train runs were completed, which did not allow conduct of the Method 301 statistical calculations to determine bias and precision.

Additionally, you provided the results of several laboratory evaluations of the candidate method including ruggedness testing, spike recovery tests, and an evaluation of precision between spiked and unspiked traps. The ruggedness testing used a system capable of generating simulated coal combustion flue gas containing baseline levels of O₂, CO₂, NO, NO₂, N₂, and moisture where SO₂ and HCl could be varied and Cl₂, Br₂, HBr, and NH₃ could be introduced. The candidate method with one spiked and one unspiked trap and a quality-assured Fourier transform infrared spectroscopy (FTIR) were used to sample the simulated flue gas during each of ten experimental conditions. Quality-assured FTIR was chosen as the reference measurement for these experiments for its ability to deliver near real-time results and to avoid some of the potential biases of Method 26 and 26A. Results were analyzed to assess the effects of Cl₂, Br₂, HBr, SO₂, and NH₃ on HCl capture and HCl spike recovery for the candidate method.

In two experiments with 500 ppmv of SO₂ and low HCl present (levels of 0.5 and 1.0 ppmv), the average candidate method values were within 10 percent of the average FTIR values and the candidate method precision was also acceptable by Method 301 standards. In three experiments,

¹ “Request for Approval of OTM-XX as an Alternative to EPA Method 26,” Final Report, Energy & Environmental Research Center, University of North Dakota, August 2017.

2.0 ppmv Cl_2 was introduced to the simulated coal combustion flue gas first in the presence of SO_2 , then in the presence of HBr and HCl, and finally with HCl alone. The results for each of the three experiments showed a positive bias in the candidate sorbent trap method measurement of HCl with Cl_2 being measured as HCl. In addition, as indicated by the real-time FTIR measurements, the presence of HBr or SO_2 resulted in some conversion of the Cl_2 to HCl in the gas manifold prior to the gas entering the sorbent traps. In experiments where HBr was present without Cl_2 , the HBr did not appear to bias HCl measurement by the candidate method. One experiment examined HCl measurement in the presence of both Cl_2 and NH_3 . The FTIR measurements for this experiment indicated no loss (reaction) of NH_3 in the gas manifold system while a small amount of the Cl_2 introduced converted to HCl in the manifold. The candidate method again measured the majority of the Cl_2 as HCl.

You submitted spike recovery studies conducted by your collaborators, The Ohio Lumex Company, as well as EERC. For the candidate method, spiking is used both to confirm the analytical procedure and to assess the matrix effects on the field samples. A total of 27 samples were spiked at HCl levels ranging from 30 to 1200 μg . For all but one sample, the spikes were recovered within 10 percent of the spiked amount. For four spiked traps taken to the field and sampled, the spike recoveries were also within 10 percent. A third experiment evaluated the precision between paired spiked (100 μg HCl) and unspiked sorbent traps. Six of eight data sets of two to four pairs of traps yielded results that showed no statistical difference between the pairs. The remaining two data sets showed a 2.9 and 5.0 percent difference.

Also included in your submittal was a Method 301 detection limit study performed on the HCl sorbent trap analysis by your collaborators, The Ohio Lumex Company. This analytical study yielded a limit of detection (LOD) of 6.7 μg mass of HCl on a sorbent trap or 0.074 ppmv HCl assuming a nominal sampling rate of 1.0 L/min and sample run time of 1 hour, which is approximately the same as the estimated LOD for Method 26A using a 1-hour sampling time.

Finally, you noted that two other organizations had conducted comparisons of the candidate method with (1) Method 26 (40 CFR part 60, Appendix A) and/or (2) FTIR measurements. The first organization conducted comparison testing of the alternative method and Method 26 on units at two facilities, both burning Powder River Basin coal and controlled with dry sorbent injection and Br_2 addition, one with an electrostatic precipitator and the other with a fabric filter. These comparisons were made at HCl concentrations less than a quarter of the MATS emission limit and showed an average relative difference between the two methods of 8.2 and 7.6 percent, respectively.

We have reviewed your submittal in detail and thoroughly considered the performance of the candidate test method, which is posted as 'Other Test Method 40' or OTM-40 on EPA's Air Emission Measurement Center website at <https://www.epa.gov/emc/emc-other-test-methods>. With this letter, we are approving OTM-40 for application to affected sources under 40 CFR part 63, Subpart UUUUU according to the stated provisos listed later in this letter based on the following considerations:

- In view of the results of the ruggedness testing you submitted, we have concerns with the potential for high bias in the HCl measurement when Cl_2 is present in the gas matrix; however, we contemplated approval of your candidate method in consideration of several

studies^{2 3 4} which have yielded data suggesting that Cl₂ formed during coal combustion is relatively unstable, minimized in the presence of SO₂, and the resulting levels of Cl₂ in the gases emitted are low in comparison to the levels of HCl.

- The Method 301 test program data provided demonstrated that OTM-40 has acceptable bias and precision when compared to Method 26A when sampling low moisture emissions with no entrained water droplets from utility boilers combusting coal.
- The Method 301 level of detection (LOD) determination for OTM-40 demonstrated an LOD of 0.074 which is comparable to that of Method 26A and adequate for demonstrating compliance under Subpart UUUUU.
- An HCl test method following the sorbent trap approach of Method 30B would be a beneficial option considering cost; simplified sampling, sample storage, and sample shipping procedures; and the advantage of site-specific method performance obtained for each test program using NIST-traceable standards.

We are approving your proposed alternative test method, OTM-40, with the following required provisos:

- This alternative test method approval is applicable only to coal-fired electric utility steam generating units subject to 40 CFR part 63, Subpart UUUUU, with low moisture combustion flue gases at temperatures above 100 degrees C (212 degrees F) with no entrained water droplets. The alternative method may be used for both quarterly compliance testing and relative accuracy testing of HCl CEMS under Subpart UUUUU.
- You must notify the responsible agency before use of this alternative and OTM-40, and notification should include a copy of this letter.
- You must include a copy of this letter with each test report presenting results of testing using OTM-40. As noted on OTM-40, you must also submit of the test report for your first two applications of this alternative method for compliance and/or relative accuracy testing to Robin Segall of my staff.
- Once an affected source chooses to use this alternative method, it must continue to be used until the owner/operator receives approval from the responsible agency to use another method (see §63.7(f)(5)).

² Xie, Y. et al. The Effect of Sulfur Dioxide on the Formation of Molecular Chlorine during Co-combustion of Fuels. *Energy and Fuels* **2000**, 14, p. 597-602.

³ Zhao, Y. et al. Effects of Sulfur Dioxide and Nitric Oxide on Mercury Oxidation and Reduction under Homogeneous Conditions. *J. Air & Waste Manage. Assoc.* **2006**, 56, p. 628-635.

⁴ Lighty, J.S. et al. *Fundamentals of Mercury Oxidation in Flue Gas*. **2008**, DOE Grant Number DE-FG26-03NT41797.

- Use of this alternative denotes acceptance of possible high biases caused by the presence of Cl₂.

Because we have approved this alternative method for application to a subgroup of sources under 40 CFR part 63, UUUUU, we will post this letter as ALT-129 on the EPA website at <https://www.epa.gov/emc/broadly-applicable-approved-alternative-test-methods> for use by other interested parties.

If you have any questions regarding this approval or need further assistance, please contact Robin Segall of my staff at (919) 541-0893 or segall.rob@epa.gov.

Sincerely,



Steffan M. Johnson, Group Leader
Measurement Technology Group

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