UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

AUG 0 5 2019

Mr. Bryan Tyler
Enthalpy Analytical
800-1 Capitola Drive
Durham, North Carolina 27713

OFFICE OF
AIR QUALITY PLANNING
AND STANDARDS

Dear Mr. Tyler:

We are writing in response to your letter of May 3, 2018, requesting approval of alternative procedures for analysis of samples from Methods 6, 8, 15A[1], and 16A (40 CFR 60, Appendix A). You requested a broad alternative method approval to apply in all Federal rules that require measurement by these methods. The Office of Air Quality Planning and Standards, as the delegated authority, must make the determination on any major alternatives to test methods and associated procedures required under 40 CFR parts 59, 60, 61, 63, and 65.

In your letter, you request to follow the applicable analytical procedures and quality control procedures in SW-846 Method 9056A "Determination of Inorganic Anions by Ion Chromatography," using ion chromatography (IC), a type of high performance liquid chromatography, to analyze samples collected by Methods 6, 8, 15A, and/or 16A for sulfate ion (SO^{-2}_4) in lieu of the barium-thorin titration procedure specified in each of these EPA methods. While intended for waste analysis, SW-846 9056A is also applicable to aqueous matrices that are consistent with the impinger solutions used in EPA Methods 6, 8, 15A, and 16A.

You indicate in your request that there are elements of the titration procedure that make it difficult to generate reproducible results in the field sufficient for the intended regulatory purpose. To illustrate these challenges, you discuss how known interferences, which may be present in the sample (e.g., ammonia and/or some metals), can react with the thorin indicator making it difficult to determine the endpoint (color change) of the titration. Beyond the known interferences referenced in the methods, you also state that improper lighting, parallax effects, and sample matrix may also contribute to difficulty in determining the color change resulting in an inaccurate measurement. You are proposing the use of Method 9056A because you contend that it will not be subject to the common interferences of the barium-thorin titration procedure and that instrumental derived results reduce the measurement uncertainty of the measurement.

Based on our recognition that IC is an effective measurement in aqueous impinger matrices as demonstrated by our inclusion of this analysis into multiple sampling methods[2], the comparison data you provided, and that the requested alternative test method includes robust quality assurance and quality control procedures, we are approving SW-846 Method 9056A as an

[1] Method 15A was not included in the original alternative method request, but is included in this approval letter as Method 15A shares the same analytical procedures as Methods 6, 8, and 16A.
[2] Method 5F - Particulate Matter Fluid Catalytic Cracking Unit, CTM-13A – Determination of H_2SO_4 and SO_2 emissions from combination fuel boilers and recovery furnaces, and CTM-13B - Determination of H_2SO_4 and SO_2 emissions from combination boilers, recovery furnaces, and thermal oxidizers.

alternative to the analytical procedures (barium-thorin titration) found in Section 11 of EPA Methods 6, 8, 15A, and 16A so long as the following conditions are met:

1) *The analytical test reports must include all calibration data, run data, and quality assurance/quality control data. These data must at least include retention time, area counts, peak heights, and the associated chromatograms.*

2) *The analytical test reports must also include records of the preparation of the stock solutions, calibration standard preparation, chromatographic equipment (i.e., precolumn, analytical column, conductivity suppressor, conductivity detector), and chromatographic conditions.*

3) *Calibration curves must be generated from standards prepared in solutions that match the collection matrix used for sampling. Sample dilution as a means to matrix match samples with calibration curves is not appropriate. Dilution is appropriate when sample concentration is above the calibration curve and samples require dilution to be within the bounds of the calibration concentrations.*

4) *A sample matrix spike (not a blank spike) and a matrix spike duplicate must be performed for each performance test and for each method where IC is used as an alternative.*

5) *Before each analysis sequence and after every ten injections, analyze and report a midrange calibration standard as a continuing calibration verification as well a blank sample of the sampling matrix. If the instrument response has changed by more than 5%, you must recalibrate and reanalyze the affected samples.*

6) *Analyze one in every ten samples in duplicate. Take the duplicate sample through the entire sample preparation and analytical process.*

7) *Report your dilution corrected method detection limit determined following 40 CFR part 136, Appendix B, using spiked samples in a solution of the sampling matrix.*

8) *For calculating the concentrations of analytes:*

   a) *Sulfur dioxide (SO_2), use the following equation in lieu of Equation 6-2 in Method 6 and Equation 8-2 of Method 8.*

$$C_{SO2} = 0.375 \frac{0.653(MS_{SO4}V_S - MB_{SO4}V_B)}{Vm_{std}}$$

   b) *Sulfuric Acid Mist (H_2SO_4), use the following equation in lieu of Equation 8-1 of Method 8.*

$$C_{H2SO4} = 0.245 \frac{1.021(MS_{SO4}V_S - MB_{SO4}V_B)}{Vm_{std}}$$

   c) *Total Reduced Sulfur as SO_2, use the following equation in lieu of Equation 15A-3 of Method 15A.*

$$C_{TRS} = .375 \frac{0.653(MS_{SO4}V_S - MB_{SO4}V_B)}{Vm_{std} - Vmc_{std}}$$

d) Total Reduced Sulfur as SO_2, use the following equation in lieu of Equation 16A-2 of Method 16A.

$$C_{TRS} = 0.375 \frac{0.653(MS_{SO4}V_S - MB_{SO4}V_B)}{Vm_{std}}$$

Where:

0.245 = *Conversion constant, mg/m3 to ppmv H_2SO_4*
0.375 = *Conversion constant, mg/m^3 to ppmv SO_2*
0.653 = *Gravimetric factor, $SO_2/SO_4(2-)$*
1.021 = *Gravimetric factor, $H_2SO_4/SO_4(2-)$*
C_{SO2} = *Measured Concentration of SO_2, ppmv*
C_{H2SO4} = *Measured Concentration of H_2SO_4, ppmv*
C_{TRS} = *Measured Concentration of Total Reduced Sulfur as SO_2, ppmv*
MB_{SO4} = *Measured Concentration of $SO_4(2-)$ in blank by IC, mg/l*
MS_{SO4} = *Measured Concentration of $SO_4(2-)$ in sample by IC, mg/l*
V_B = *Volume of blank sample, liters*
Vmc_{std} = *Dry gas volume of the combustion air dry gas meter, dry standard cubic meters*
Vm_{std} = *Dry gas volume of the dry gas meter, dry standard cubic meters*
V_S = *Volume of sample collected, liters*

9) You must cite the use of this alternative in any site-specific test plan(s) and associated test report(s) (e.g., stack test reports and analytical laboratory reports).

It is reasonable that this alternative test method approval be broadly applicable to conducting measurements according to Methods 6, 8, 15A, and 16A of 40 CFR Part 60. For this reason, we will post this letter as ALT-133 on our website at https://www.epa.gov/emc/broadly-applicable-approved-alternative-test-methods for use by other interested parties. This alternative is valid until revisions are made to these methods to incorporate this alternative, and at such time, this alternative will be withdrawn.

If you should have any questions or require further information regarding this approval, please call Ned Shappley of my staff at 919-541-7903 or email him at *shappley.ned@epa.gov*.

Sincerely,

Steffan M. Johnson, Group Leader
Measurement Technology Group

cc: Lula Melton, EPA/OAQPS/AQAD
Ray Merrill, EPA/OAQPS/AQAD
Ned Shappley, EPA/OAQPS/AQAD
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