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METHOD 205 - VERIFICATION OF GAS DILUTION SYSTEMS FOR FIELD INSTRUMENT CALIBRATIONS

1. Introduction

1.1 Applicability. A gas dilution system can provide known values of calibration gases through controlled dilution of high-level calibration gases with an appropriate dilution gas. The instrumental test methods in 40 CFR part 60 - e.g., Methods 3A, 6C, 7E, 10, 15, 16, 20, 25A and 25B—require on-site, multi-point calibration using gases of known concentrations. A gas dilution system that produces known low-level calibration gases from high-level calibration gases, with a degree of confidence similar to that for Protocol¹ gases, may be used for compliance tests in lieu of multiple calibration gases when the gas dilution system is demonstrated to meet the requirements of this method. The Administrator may also use a gas dilution system in order to produce a wide range of Cylinder Gas Audit concentrations when conducting performance specifications according to appendix F, 40 CFR part 60. As long as the acceptance criteria of this method are met, this method is applicable to gas dilution systems using any type of dilution technology, not solely the ones mentioned in this method.

1.2 Principle. The gas dilution system shall be evaluated on one analyzer once during each field test. A precalibrated analyzer is chosen, at the discretion of the source owner or operator, to demonstrate that the gas dilution system produces predictable gas concentrations spanning a range of concentrations. After meeting the requirements of this method, the remaining analyzers may be calibrated with the dilution system in accordance to the requirements of the applicable method for the duration of the field test. In Methods 15 and 16, 40 CFR part 60, appendix A, reactive compounds may be lost in the gas dilution system. Also, in Methods 25A and 25B, 40 CFR part 60, appendix A, calibration with target compounds other than propane is allowed. In these cases, a laboratory evaluation is required once per year in order to assure the Administrator that the system will dilute these reactive gases without significant loss.

Note: The laboratory evaluation is required only if the source owner or operator plans to utilize the dilution system to prepare gases mentioned above as being reactive.

2. Specifications

2.1 Gas Dilution System. The gas dilution system shall produce calibration gases whose measured values are within ± 2 percent of the predicted values. The predicted values are calculated based on the certified concentration of the supply gas (Protocol gases, when available, are recommended for their accuracy) and the gas flow rates (or dilution ratios) through the gas dilution system.

2.1.1 The gas dilution system shall be recalibrated once per calendar year using NIST-traceable primary flow standards with an uncertainty ≤ 0.25 percent. A label shall be affixed at all times to the gas dilution system listing the date of the most recent calibration, the due date for the next calibration, and the person or manufacturer who carried out the calibration. Follow the manufacturer's instructions for the operation and use of the gas dilution system. A copy of the manufacturer's instructions for the operation of the instrument, as well as the most recent recalibration documentation shall be made available for the Administrator's inspection upon request.

2.1.2 Some manufacturers of mass flow controllers recommend that flow rates below 10 percent of flow controller capacity be avoided; check for this recommendation and follow the manufacturer's instructions. One study has indicated that silicone oil from a positive displacement pump produces an interference in SO₂ analyzers utilizing ultraviolet fluorescence; follow laboratory procedures similar to those outlined in Section 3.1 in order to demonstrate the significance of any resulting effect on instrument performance.

2.2 High-Level Supply Gas. An EPA Protocol calibration gas is recommended, due to its accuracy, as the high-level supply gas.

2.3 Mid-Level Supply Gas. An EPA Protocol gas shall be used as an independent check of the dilution system. The concentration of the mid-level supply gas shall be within 10 percent of one of the dilution levels tested in Section 3.2.

3. *Performance Tests*

3.1 Laboratory Evaluation (Optional). If the gas dilution system is to be used to formulate calibration gases with reactive compounds (Test Methods 15, 16, and 25A/25B (only if using a calibration gas other than propane during the field test) in 40 CFR part 60, appendix A), a laboratory certification must be conducted once per calendar year for each reactive compound to be diluted. In the laboratory, carry out the procedures in Section 3.2 on the analyzer required in each respective test method to be laboratory certified (15, 16, or 25A and 25B for compounds other than propane). For each compound in which the gas dilution system meets the requirements in Section 3.2, the source must provide the laboratory certification data for the field test and in the test report.

3.2 Field Evaluation (Required). The gas dilution system shall be evaluated at the test site with an analyzer or monitor chosen by the source owner or operator. It is recommended that the source owner or operator choose a precalibrated instrument with a high level of precision and accuracy for the purposes of this test. This method is not meant to replace the calibration requirements of test methods. In addition to the requirements in this method, all the calibration requirements of the applicable test method must also be met.

3.2.1 Prepare the gas dilution system according to the manufacturer's instructions. Using the high-level supply gas, prepare, at a minimum, two dilutions within the range of each dilution device utilized in the dilution system (unless, as in critical orifice systems, each dilution device is used to make only one dilution; in that case, prepare one dilution for each dilution device).

Dilution device in this method refers to each mass flow controller, critical orifice, capillary tube, positive displacement pump, or any other device which is used to achieve gas dilution.

3.2.2 Calculate the predicted concentration for each of the dilutions based on the flow rates through the gas dilution system (or the dilution ratios) and the certified concentration of the high-level supply gas.

3.2.3 Introduce each of the dilutions from Section 3.2.1 into the analyzer or monitor one at a time and determine the instrument response for each of the dilutions.

3.2.4 Repeat the procedure in Section 3.2.3 two times, i.e., until three injections are made at each dilution level. Calculate the average instrument response for each triplicate injection at each dilution level. No single injection shall differ by more than ± 2 percent from the average instrument response for that dilution.

3.2.5 For each level of dilution, calculate the difference between the average concentration output recorded by the analyzer and the predicted concentration calculated in Section 3.2.2. The average concentration output from the analyzer shall be within ± 2 percent of the predicted value.

3.2.6 Introduce the mid-level supply gas directly into the analyzer, bypassing the gas dilution system. Repeat the procedure twice more, for a total of three mid-level supply gas injections. Calculate the average analyzer output concentration for the mid-level supply gas. The difference between the certified concentration of the mid-level supply gas and the average instrument response shall be within ± 2 percent.

3.3 If the gas dilution system meets the criteria listed in Section 3.2, the gas dilution system may be used throughout that field test. If the gas dilution system fails any of the criteria listed in Section 3.2, and the tester corrects the problem with the gas dilution system, the procedure in Section 3.2 must be repeated in its entirety and all the criteria in Section 3.2 must be met in order for the gas dilution system to be utilized in the test.

4. References

1. "EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards," EPA-600/R93/224, Revised September 1993.

Method 207—Pre-survey Procedure for Corn Wet-milling Facility Emission Sources

1.0 Scope and Application

1.1 *Analyte.* Total gaseous organic compounds.

1.2 *Applicability.* This pre-survey method is intended for use at corn wet-milling (CWM) facilities to satisfy the requirements of Method 18, Section 16 (Pre-survey). This procedure establishes the analytes for subsequent Method 18 testing to determine the total mass emissions

of VOCs from sources at CWM facilities. The specific objectives of the pre-survey procedure are:

- 1.2.1 Identify the physical characteristics of the VOC contained in the effluent.
 - 1.2.2 Determine the appropriate Method 18 sampling approach to ensure efficient collection of all VOC present in the effluent.
 - 1.2.3 Develop a specific list of target compounds to be quantified during the subsequent total VOC test program.
 - 1.2.4 Qualify the list of target compounds as being a true representation of the total VOC.
- 1.3 *Range.* The lower and upper ranges of this procedure are determined by the sensitivity of the flame ionization detector (FID) instruments used. Typically, gas detection limits for the VOCs will be on the order of 1–5 ppmv, with the upper limit on the order of 100,000 ppmv.

2.0 *Summary of Method*

Note: Method 6, Method 18, and Method 25A as cited in this method refer to the methods in 40 CFR Part 60, Appendix A.

This procedure calls for using an FIA in conjunction with various configurations of impingers, and other absorbents, or adsorbents to determine the best EPA Method 18 sampling train configuration for the assessment and capture of VOCs. VOC compounds present in the exhaust gas from processes located at CWM facilities fall into five general categories: Alcohols, aldehydes, acetate esters, ketones, and carboxylic acids, and typically contain fewer than six carbon atoms. This pre-survey protocol characterizes and identifies the VOC species present. Since it is qualitative in nature, quantitative performance criteria do not apply.

3.0 *Definitions*

- 3.1 Calibration drift means the difference in the measurement system response to a mid-level calibration gas before and after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.
- 3.2 Calibration error means the difference between the gas concentration indicated by the measurement system and the known concentration of the calibration gas.
- 3.3 Calibration gas means a known concentration of a gas in an appropriate diluent gas.
- 3.4 Measurement system means the equipment required for the determination of the gas concentration. The system consists of the following major subsystems:

3.4.1 Sample interface means that portion of a system used for one or more of the following: Sample acquisition, sample transportation, sample conditioning, or protection of the analyzer(s) from the effects of the stack effluent.

3.4.2 Organic analyzer means that portion of the measurement system that senses the gas to be measured and generates an output proportional to its concentration.

3.5 Response time means the time interval from a step change in pollutant concentration at the inlet to the emission measurement system to the time at which 95 percent of the corresponding final value is reached as displayed on the recorder.

3.6 Span Value means the upper limit of a gas concentration measurement range that is specified for affected source categories in the applicable part of the regulations. The span value is established in the applicable regulation and is usually 1.5 to 2.5 times the applicable emission limit. If no span value is provided, use a span value equivalent to 1.5 to 2.5 times the expected concentration. For convenience, the span value should correspond to 100 percent of the recorder scale.

3.7 Zero drift means the difference in the measurement system response to a zero level calibration gas before or after a stated period of operation during which no unscheduled maintenance, repair, or adjustment took place.

4.0 *Interferences [Reserved]*

5.0 *Safety [Reserved]*

6.0 *Equipment and Supplies*

6.1 *Organic Concentration Analyzer.* A flame ionization analyzer (FIA) with heated detector block and sample handling system, meeting the requirements of USEPA Method 25A.

6.2 *Heated Sampling System.* A sampling system consisting of a stainless steel probe with particulate filter, Teflon[®] sample line, and sampling pump capable of moving 1.0 l/min through the sample probe and line. The entire system from probe tip to FIA analyzer must have the capability to maintain all sample-wetted parts at a temperature >120°C. A schematic of the heated sampling system and impinger train is shown in Figure 1 of this method.

6.3 *Impinger Train.* EPA Method 6 type, comprised of three midjet impingers with appropriate connections to the sampling system and FIA system. The impinger train may be chilled in an ice bath or maintained at a set temperature in a water bath as indicated by the operator's knowledge of the source and the compounds likely to be present. Additional impingers or larger impingers may be used for high moisture sources.

6.4 *Adsorbent tubes.*

6.4.1 Silica gel, SKC Type 226–22 or equivalent, with appropriate end connectors and holders.

6.4.2 Activated carbon, SKC Type 226–84 or equivalent, with appropriate end connectors and holders.

6.5 *Tedlar bag*. 24 liter, w/ Roberts valve, for GC/MS analysis of “breakthrough” VOC fraction as needed.

7.0 *Reagents and Standards*

7.1 Organic-free water, HPLC, or pharmaceutical grade.

7.2 *Calibration Gases*. The calibration gases for the gas analyzer shall be propane in air or propane in nitrogen. If organic compounds other than propane are used, the appropriate corrections for response factor must be available and applied to the results. Calibration gases shall be prepared in accordance with the procedure listed in Citation 2 of section 16. Additionally, the manufacturer of the cylinder must provide a recommended shelf life for each calibration gas cylinder over which the concentration does not change more than ± 2 percent from the certified value. For calibration gas values not generally available (i.e., organics between 1 and 10 percent by volume), alternative methods for preparing calibration gas mixtures, such as dilution systems (Test Method 205, 40 CFR Part 51, Appendix M), may be used with prior approval of the Administrator.

7.3 *Fuel*. A 40 percent H₂/60 percent N₂ or He gas mixture is recommended to avoid an oxygen synergism effect that reportedly occurs when oxygen concentration varies significantly from a mean value.

7.4 *Zero Gas*. High purity air with less than 0.1 parts per million by volume (ppmv) of organic material (propane or carbon equivalent) or less than 0.1 percent of the span value, whichever is greater.

7.5 *Low-level Calibration Gas*. An organic calibration gas with a concentration equivalent to 25 to 35 percent of the applicable span value.

7.6 *Mid-level Calibration Gas*. An organic calibration gas with a concentration equivalent to 45 to 55 percent of the applicable span value.

7.7 *High-level Calibration Gas*. An organic calibration gas with a concentration equivalent to 80 to 90 percent of the applicable span value.

8.0 *Sample Collection, Preservation and Storage*

8.1 *Configuration*. The configuration of the pre-survey sampling system is provided in Figure 1. This figure shows the primary components of the sampling system needed to conduct a VOC survey. A dual-channel analyzer is beneficial, but not necessary. Only a single channel is indicated in the figure.

8.2 *Sampling*. The pre-survey system should be set up and calibrated with the targeted sampling flow rate that will be used during Method 18 VOC sampling. The targeted flow rate for capture of most expected VOC species is 400 cc/min. Since most FIA analyzers do not specifically allow for adjusting the total sample flow rate (only the back pressure), it may be necessary to insert a flow control valve at the sample inlet to the FIA. The total sample flow can be measured at the FIA bypass, since only a small fraction of the sample flow is diverted to analysis portion of the instrument.

The sampling system configuration shown in Figure 1 is operated using the process flow diagram provided in Figure 2. As noted in the process flowchart, the initial sampling media consists of the three midget impingers. The attenuation of the VOC sample stream is evaluated to determine if 95 percent or greater attenuation (capture) of the VOCs present has been achieved. The flow diagram specifies successive adjustments to the sampling media that are utilized to increase VOC capture.

A one-hour test of the final sampling configuration is performed using fresh media to ensure that significant breakthrough does not occur. Additional sampling media (more water, silica or carbon tubes) may be added to ensure that breakthrough is not occurring for the full duration of a test run.

If 95 percent or greater attenuation has not been achieved after inserting all indicated media, the most likely scenario is that methane is present. This is easily checked by collecting a sample of this final bypass sample stream and analyzing for methane. There are other VOC compounds which could also penetrate the media. Their identification by gas chromatography followed by mass spectrometry would be required if the breakthrough cannot be accounted for by the presence of methane.

9.0 *Quality Control*

9.1 *Blanks*. A minimum of one method blank shall be prepared and analyzed for each sample medium employed during a pre-survey testing field deployment to assess the effect of media contamination. Method blanks are prepared by assembling and charging the sample train with reagents, then recovering and preserving the blanks in the same manner as the test samples. Method blanks and test samples are stored, transported and analyzed in identical fashion as the test samples.

9.2 *Synthetic Sample (optional)*. A synthetic sample may be used to assess the performance of the VOC characterization apparatus with respect to specific compounds. The synthetic sample is prepared by injecting appropriate volume(s) of the compounds of interest into a Tedlar bag containing a known volume of zero air or nitrogen. The contents of the bag are allowed to equilibrate, and the bag is connected to the sampling system. The sampling system, VOC characterization apparatus and FIA are operated normally to determine the performance of the system with respect to the VOC compounds present in the synthetic sample.

10.0 *Calibration and Standardization*

10.1 *Calibration.* The FIA equipment is able to be calibrated for almost any range of total organic concentrations. For high concentrations of organics (>1.0 percent by volume as propane), modifications to most commonly available analyzers are necessary. One accepted method of equipment modification is to decrease the size of the sample to the analyzer through the use of a smaller diameter sample capillary. Direct and continuous measurement of organic concentration is a necessary consideration when determining any modification design.

11.0 Procedure

11.1 *Analytical Procedure.* Upon completion of the pre-survey sampling, the sample fractions are to be analyzed by an appropriate chromatographic technique. (Ref: Method 18) The resulting chromatograms must be reviewed to ensure that the ratio of known peak area to total peak area is 95% or greater. It should be noted that if formaldehyde is a suspected analyte, it must be quantitated separately using a different analytical technique.

12.0 Data Analysis and Calculations

Chromatogram peaks will be ranked from greatest area to least area using peak integrator output. The area of all peaks will then be totaled, and the proportion of each peak area to the total area will be calculated. Beginning with the highest ranked area, each peak will be identified and the area added to previous areas until the cumulative area comprises at least 95% of the total area. The VOC compounds generating those identified peaks will comprise the compound list to be used in Method 18 testing of the subject source.

13.0 Method Performance [Reserved]

14.0 Pollution Prevention [Reserved]

15.0 Waste Management [Reserved]

16.0 References

16.1 CFR 40 Part 60, Appendix A, Method 18, Measurement of Gaseous Organic Compound Emissions by Gas Chromatography.

16.2 CFR 40 Part 60, Appendix A, Method 25A, Determination of Total Gaseous Organic Concentration Using a Flame Ionization Analyzer.

16.2 CFR 40 Part 60, Appendix A, Method 6, Determination of Sulfur Dioxide Emissions from Stationary Sources.

16.3 National Council for Air and Stream Improvement (NCASI), Method CI/WP-98.01 "Chilled Impinger Method for Use at Wood Products Mills to Measure Formaldehyde, Methanol, and Phenol.

17. Tables, Diagrams, Flowcharts, and Validation Data

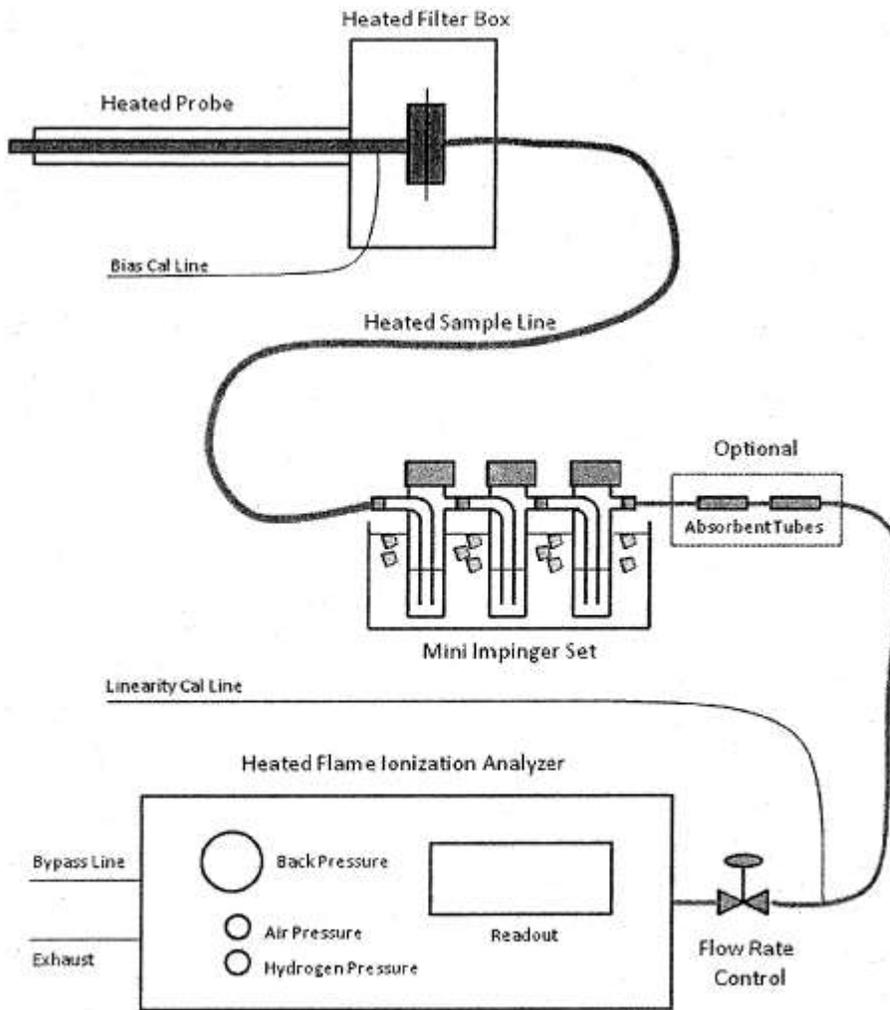


Figure 1. Pre-Survey Sampling System

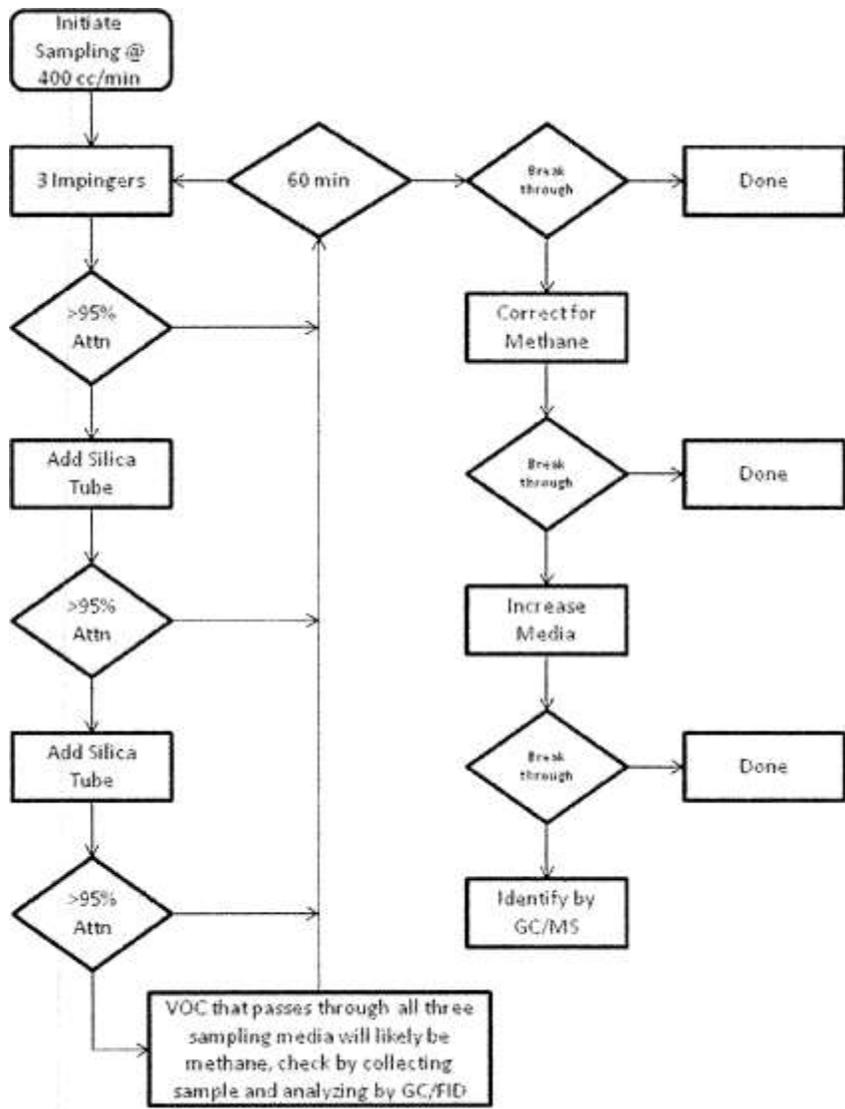


Figure 2. Method 207 Flowchart