

OTM-11: USEPA Method 18 Pre-Survey Procedure for Corn Wet-Milling Facility Emission Sources

1.0 Scope and Application

- 1.1 Analytes. Volatile Organic Compounds (VOCs) present in the exhaust air from production processes located at corn wet milling (CWM) facilities. The target VOC analytes fall into five (5) general categories: alcohols, aldehydes, acetate esters, ketones, and carboxylic acids, and typically contain fewer than 6 carbon atoms.
- 1.2 Applicability. This protocol is intended for use at CWM facilities to satisfy the requirements of USEPA Method 18, Section 16 (Pre-survey). This procedure establishes the analytes for subsequent USEPA Method 18 testing to determine the total mass emissions of VOCs from sources at CWM facilities. The specific objectives of the pre-survey are to:
 - 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; and
 - 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 ppm, with the upper limit on the order of 100,000 ppm.

2.0 Summary of Procedure

This procedure calls for using a FID 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.

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 [To be determined]*

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.
- 6.3 Impinger Train. USEPA Method 6 type, comprised of three (3) midget 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. a.) Silica gel, SKC Type 226-22 or equivalent, with appropriate end connectors and holders; and b.) 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.
- 6.6 FIA fuel, zero and calibration gases. Hydrogen or hydrogen/helium fuel, ultra-zero synthetic air, and propane in air mixtures, meeting the requirements of Section 7 of USEPA Method 25A.
- 6.7 Organic-free water, HPLC or pharmaceutical grade.

7.0 Reagents and Standards

- 7.1 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; then 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.

- 7.2 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.
- 7.3 Zero Gas. High purity air with less than 0.1 part 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.
- 7.4 Low-level Calibration Gas. An organic calibration gas with a concentration equivalent to 25 to 35 percent of the applicable span value.
- 7.5 Mid-level Calibration Gas. An organic calibration gas with a concentration equivalent to 45 to 55 percent of the applicable span value.
- 7.6 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, Storage and Transport*

The configuration of the pre-survey sampling system is provided in Diagram 1. This Diagram 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 Diagram.

The pre-survey system should be set up and calibrated with the targeted sampling flow rate that will be used during EPA Method 18 VOC sampling. The targeted flow rate for capture of most expected VOC species is 400 cc/min. Since most FID 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 FID. The total sample flow can be measured at the FID bypass, since only a small fraction of the sample flow is diverted to analysis portion of the instrument.

The sampling system configuration shown in Diagram 1 is operated using the process flow diagram provided in Flowchart 1. 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% 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 CSC tubes) may be added to ensure that breakthrough is not occurring for the full duration of a test run.

If 95% 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 GC/MS would be required if the breakthrough can not be accounted for by the presence of methane.

9.0 *Quality Control*

9.1 Blanks

9.1.1 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)

9.2.1 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 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 *Analytical Procedure*

Upon completion of the pre-survey sampling, the sample fractions are to be analyzed by an appropriate chromatographic technique. (Ref: USEPA 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 *Calculations and Data Analysis*

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*

13.1 This pre-survey protocol characterizes and identifies the VOC species present. Since it is qualitative in nature, quantitative performance criteria do not apply.

14.0 *Pollution Prevention [Reserved]*

15.0 *Waste Management [Reserved]*

16.0 *References*

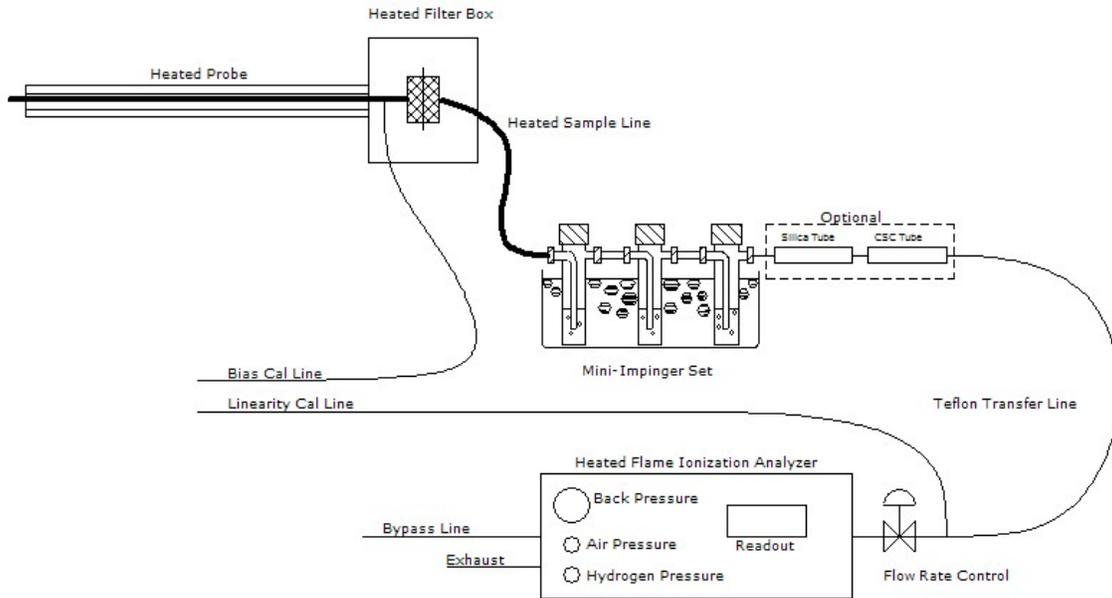
16.1 CFR 40 Part 60, Appendix A, Method 18 "MEASUREMENT OF GASEOUS ORGANIC COMPOUND EMISSIONS BY GAS CHROMATOGRAPHY"

16.2 CFR 40 Part 60, Appendix A, Method 25A "DETERMINATION OF TOTAL GASEOUS ORGANIC CONCENTRATION USING A FLAME IONIZATION ANALYZER"

16.3 National Council for Air and Stream Improvement (NCASI) METHOD CI/WP-98.01 "CHILLED IMPINGER METHOD FOR USE

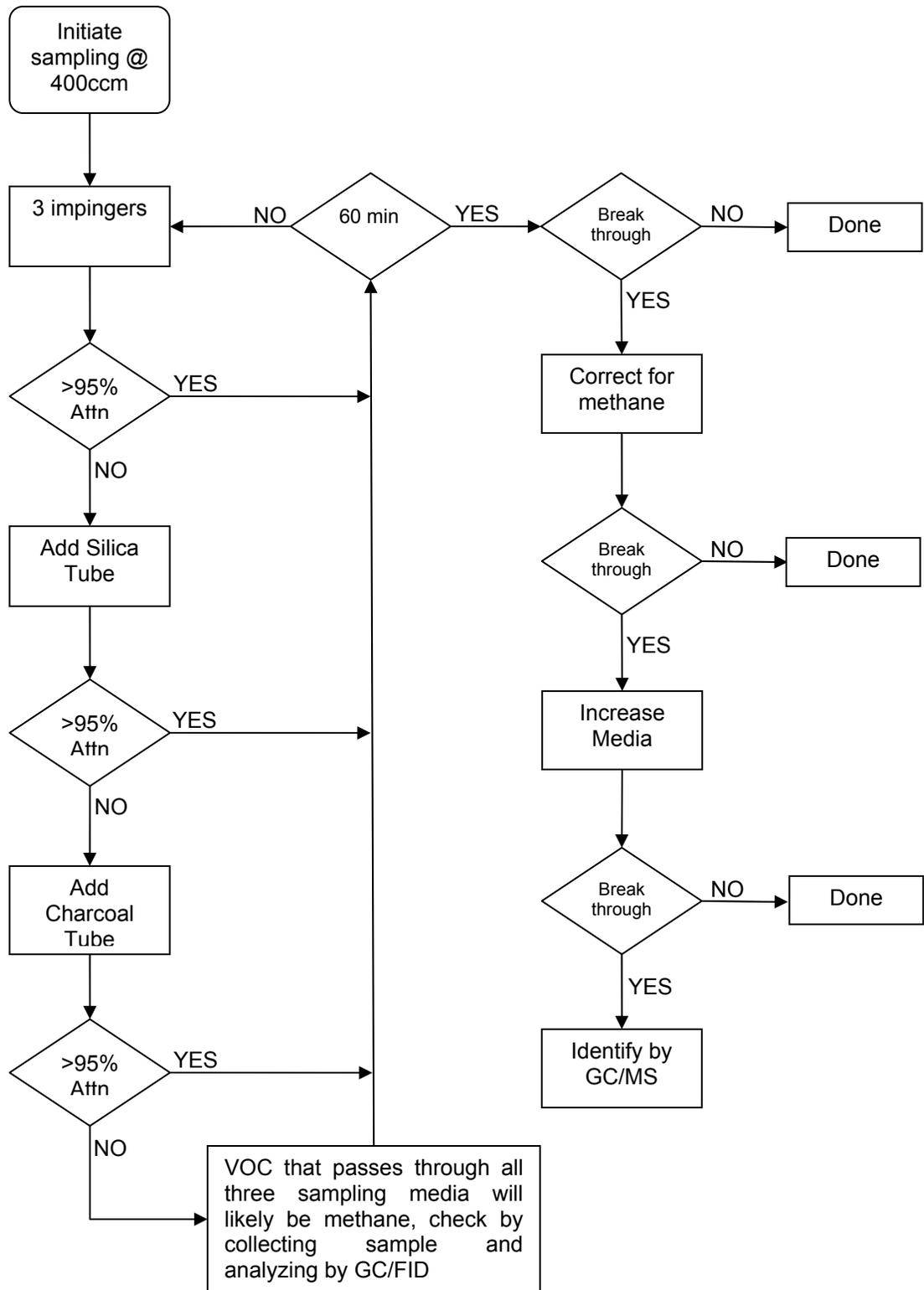
AT WOOD PRODUCTS MILLS TO MEASURE FORMALDEHYDE, METHANOL, AND PHENOL”

17.0 Tables, Diagrams, Flowcharts, and Validation Data



CRA Pre-Survey Sampling System

Diagram 1.



Flowchart 1.