MONTROSE
AIR QUALITY SERVICES

Corteva Agriscience
Harbor Beach, MI

TTUs 850, 855, 860, 865, & 870
Formaldehyde and Methanol Relative Accuracy Test Audit

December 12th – 15th, 2023
PROJ-023583

By

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Scope

Montrose Air Quality Services (MAQS, Mt. Pleasant, MI) was contracted to perform Relative Accuracy Audit (RAA) of the formaldehyde and methanol Continuous Emissions Monitoring System (CEMS) for the TTU 850, TTU 855, TTU 860, TTU 865, and TTU 870 at Corteva Agriscience, Harbor Beach, MI. Testing was performed December 12th, 13th, 14th, and 15th, 2023 to determine concentrations of gaseous formaldehyde (CH_2O) and methanol (MeOH) content from the outlet of each unit.

Extractive Fourier transform infrared (FTIR) spectrometry following USEPA Method 320 was the Reference Method performed to quantify the concentration levels of the target analytes from the outlet of the unit. Shane Douglas (MAQS) performed data collection. Andrew Leffel (MAQS) performed FTIR data validation and report generation. Phillip Kauppi (MAQS) reviewed the test data and report. A summary of testing below in Table 1.

Table 1 – Test Summary Table

Test Parameters	TTU850	TTU855	TTU860	TTU865	TTU870
PROCESS DATA*					
Fire Box Temperature (°F)	676.1	686.3	674.7	675.2	1550.1
Catalyst Inlet Temperature (°F)	676.1	686.3	674.7	675.2	NA
Catalyst Outlet Temperature (°F)	672.9	675.2	666.0	669.3	NA
Catalyst Temperature Differential (°F)	-3.2	-11.1	-8.7	-5.9	NA
Natural Gas Flow (scf/hr)	5893.0	2609.9	3482.2	4686.6	2686.8
Combustion Air Rate (scfm/hr)	61633.8	29589.6	35728.6	45554.7	50813.1
Process Vent Rate (lb/hr)	26803.6	22714.8	13765.4	21073.3	20336.5
Performance Load (%)	100%	100%	100%	100%	100%
EMISSIONS DATA					
CH2O(ppmv)	1.63	1.31	3.65	2.74	0.72
RATA (%)	1.80	1.96	2.48	1.50	1.08
MeOH (ppmv)	0.22	1.86	0.27	4.77	7.13
RATA (%)	0.23	2.05	1.13	2.53	2.20

*All process data were provided directly by Corteva Agriscience and is considered confidential. Reach out to Corteva directly with any production related questions.

Procedures

FTIR Instrumental Configuration

Reference method (FTIR) data were collected using an MKS MultiGas 2030 FTIR spectrometer. See Table 2 below for sampling system details.

The FTIR was equipped with a temperature-controlled, 5.11-meter multipass gas cell maintained at 191°C. Gas flows and sampling system pressures were monitored using a rotameter and pressure transducer. All data were collected at 0.5 cm^{-1} resolution. Each spectrum was derived from the coaddition of 64 scans, with a new data point generated approximately every sixty seconds.

Table 2 – FTIR Sampling System Parameters

Source	MKS Serial #	Sampling Line	Probe Assembly	Particulate Filter Media	Operating Temperatures
TTU 850, TTU 855, TTU 860, TTU 865 TTU 870	01864828	100' 3/8" dia., heated Teflon	Heated 3', 3/8" dia. SS	0.01µ heated borosilicate glass fiber	191°C

FTIR QA/QC Methodology

QA/QC procedures followed the procedures of US EPA Method 320. See Tables 3 and 4 below for QA/QC procedure details and list of calibration gas standards. All calibration gases were introduced to the analyzer and the sampling system using an instrument grade stainless steel rotometer. All QA/QC procedures were within the acceptance criteria allowance of the applicable EPA methodology. See the FTIR QA/QC Data Appendix for tabulated results.

Table 3 – FTIR QA/QC Procedures

QAQC Specification	Purpose	Calibration Gas	Delivery	Frequency	Acceptance Criteria	Result
M320: Zero	Verify that the FTIR is free of contaminants & zero the FTIR	Nitrogen (zero)	Direct to FTIR	pretest	< MDL or Noise	**Pass**
M320: Calibration Transfer Standard (CTS) Direct	Verify FTIR stability, confirm optical path length	Ethylene	Direct to FTIR	Pretest TTU 870 TTU 865	+/- 5% cert. value	**Pass**
M320: Calibration Transfer Standard (CTS) Direct	Verify FTIR stability, confirm optical path length	Methane	Direct to FTIR	Pretest TTU 850 TTU 855 TTU 860	+/- 5% cert. value	**Pass**
M320: Analyte Direct	Verify FTIR calibration	CH_2O, SF6	Direct to FTIR	pretest	+/- 5% cert. value	**Pass**
M320: CTS Response	Verify system stability, recovery, response time	Ethylene, Methane	Sampling System	pre/post run	+/- 5% of Direct Measurement	**Pass**
M320: Zero Response	Verify system is free of contaminants, system bias	Nitrogen (zero)	Sampling System	pre/post test	Bias correct data	**Pass**
M320: Analyte Spike	Verify system ability to deliver and quantify analyte of interest in the presence of other effluent gases	CH_2O	Dynamic Addition to Sampling System, 1:10 effluent	Pretest, daily	+/- 30% theoretical recovery	**Pass**

Table 4 – Calibration Gas Standards

Components	Concentration (ppm)	Vendor	Cylinder #	Standard Type
Ethylene	99.98	Airgas	CC18207	Primary +/- 1.0%
Methane	50.01	Airgas	CC172052	+/- 0.7% NIST
Formaldehyde /SF6	32.63 / 5.139	Airgas	CC734790	Certified Standard-Spec +/- 5.0%
Nitrogen	99.95%	Airgas	CC64137	UHP Grade

FTIR QA/QC Calculations

Method 320: Analyte Spiking

Formaldehyde spiking was performed at each source to verify the ability of the sampling system to quantitatively deliver a sample containing CH_2O from the base of the probe to the FTIR. Analyte spiking assures the ability of the FTIR to deliver and quantify CH_2O in the presence of effluent gas. In addition, analyte spiking serves as an effective leak check of the sampling system.

As part of the spiking procedure, samples from each unit were measured to determine native CH_2O concentrations to be used in the spike recovery calculations. The system equilibration time was measured as the amount of time from the last native effluent gas point to the first analyte spike gas response. The analyte spiking gases contained a low concentration of sulfur hexafluoride (SF_6). The determined SF_6 concentration in the spiked sample was used to calculate the dilution factor of the spike and thus used to calculate the concentration of the spiked CH_2O. The spike target dilution ratio was 1:10 or less.

The following equation illustrates the percent recovery calculation.

$$DF = \frac{SF6(spk)}{SF6(dir)} \qquad \text{(Sec. 9.2.3 (3) USEPA Method 320)}$$

$$CS = DF * Spike(dir) + Unspike(1 - DF) \qquad \text{(Sec. 9.2.3 (4) USEPA Method 320)}$$

DF = Dilution factor of the spike gas
$SF_{6(dir)}$ = SF_6 concentration measured directly in undiluted spike gas
$SF_{6(spk)}$ = Diluted SF_6 concentration measured in a spiked sample
$Spike_{dir}$ = Concentration of the analyte in the spike standard measure by the FTIR directly
CS = Expected concentration of the spiked samples
Unspike = Native concentration of analytes in unspiked samples

FTIR Post Collection Data Validation

As part of the data validation procedure, reference spectra are manually fit to that of the sample spectra and a concentration is determined. The reference spectra are scaled to match the peak amplitude of the sample, thus providing a scale factor. The scale factor multiplied by the reference spectra concentration is used to determine the concentration value for the sample spectra. Sample pressure and temperature corrections are then applied to compute the final sample concentration. The manually calculated results are then compared with the software-generated results. The data is then validated if the two concentrations are within ± 20% agreement. If there is a difference greater than ± 20% the spectra are reviewed for possible spectral interferences or any other probable causes leading to misquantified data.

Reference Method Detection Limit

The detection limit of each analyte was calculated following Annex A2 of ASTM D6348-12 procedure using spectra that contained similar amounts of moisture.

Table 5 - FTIR Detection Limits

Analyte	Detection Limit (ppmwv)
Formaldehyde	0.5
Methanol	0.2

Results and Discussion

Twelve, thirty-one-minute RATA test runs were performed on TTU 850 and ten, thirty-one-minute RATA test runs were performed on TTU 855, TTU 860, TTU 865, and TTU 870. All reference method (RM) samples were analyzed for gaseous formaldehyde and methanol on a wet volume basis. CH_2O spiking was performed on all units to confirm the RM measurement system's ability to deliver and quantify CH_2O. See the FTIR QA/QC Data Appendix for results.

Test Runs 2 and 3 were omitted from the TTU 850 RATA results due to the CEMS data not being collected during this time. Test Run 8 was omitted from the TTU 855 RATA results due to zero gas still flowing through the sampling system during official run times resulting in an incomplete data set for the run.

See FTIR Test Run Data Appendix for all RM (FTIR) concentration data, included all omitted test runs. The sample and data collection followed the procedures of USEPA Method 320 and MAQS SOP 207. See The RATA Calculations in the Appendix for all TTU RATA calculations.

Relative Accuracy Audit Determination

The relative accuracy of the Corteva FTIR CEMS analyzer was determined following the procedures of USEPA Performance Specification 2. The calculations used to determine results are presented in detail below and were obtained from Performance Specification 2 Section 12.

Arithmetic Mean

$$\bar{d} = \frac{1}{n}\sum_{i=1}^{n} d_i \qquad \text{Eq. 2-3}$$

Where:

n = Number of data points.

$\sum_{i=1}^{n} d_i$ = Algebraic summation of the individual differences d_i.

Standard Deviation

$$S_d = \left[\frac{\sum_{i=1}^{n} d_i^2 - \frac{\left[\sum_{i=1}^{n} d_i\right]^2}{n}}{n-1} \right]^{\frac{1}{2}} \qquad Eq.\ 2\text{-}4$$

Confidence Coefficient

$$CC = t_{0.975}\frac{S_d}{\sqrt{n}} \qquad Eq.\ 2\text{-}5$$

Where:

$t_{0.975}$ = t-value

Relative Accuracy

$$RA = \frac{\left[\left|\bar{d}\right| + \left|CC\right|\right]}{\overline{RM}} \times 100 \qquad Eq.\ 2\text{-}6$$

Where:

$|\bar{d}|$ = Absolute value of the mean differences (from Equation 2-3).

|CC| = Absolute value of the confidence coefficient (from Equation 2-3).

RM = Average RM value. In cases where the average emissions for the test are less than 50 percent of the applicable standard, substitute the emission standard value in the denominator of Eq. 2-6 in place of RM. In all other cases, use RM. The applicable standard of 20 ppm was used in all RATA calculations.

Corteva Agriscience provided all CEMS concentration data on a wet ppmv basis. All RATA calculations were made using RM and CEMS concentrations on a wet ppmv basis.

The following Appendices include:

- RM Run Data Summary
- RATA Calculations
- FTIR Test Run Data
- FTIR QA/QC Data
- Gas Certificates
- Corteva Agriscience CEMS and Process Data

Date: January 24, 2024

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APPENDIX

RM Run Data Summary