Acetaldehyde Air Emissions Testing of EUAIRSTRIP

Airgas Carbonic
7031 Sibelhorn Highway
Blissfield, Michigan

Permit to Install 31-13
State Registration No. N8207

Prepared for:
Airgas, Inc.
Lawrenceville, Georgia

Bureau Veritas Project No. 11014-000206.00

January 6, 2015

Move Forward with Confidence

Bureau Veritas North America, Inc.
22345 Roethel Drive
Novi, Michigan 48375
248.344.2661
www.us.bureauveritas.com/hse

Executive Summary

Airgas, Inc. retained Bureau Veritas North America, Inc. to test air emissions from the EUAIRSTRIP source at their Airgas Carbonic facility in Blissfield, Michigan. The facility uses carbon dioxide (CO_2) from the adjoining Global Ethanol Riga facility to manufacture liquid and solid (dry ice) CO_2. The EUAIRSTRIP source uses a blower to aerate the facility's CO_2 scrubber wastewater. The applicable emission limit excerpted from the facility's Michigan Department of Environmental Quality (MDEQ) Permit to Install 31-13 is presented below:

Pollutant	Limit	Time Period / Operating Scenario	Equipment	Testing / Monitoring Method	Underlying Applicable Requirements
1. Acetaldehyde	0.745 tpy	12-month rolling time period as determined at the end of each calendar month	EUAIRSTRIP	SC VI.3	R 336.1225, R 336.1702(a)

Bureau Veritas measured acetaldehyde concentrations and mass emission rates at the outlet of the EUAIRSTRIP source. Three 60-minute test runs were performed following United States Environmental Protection Agency (USEPA) Methods 1A, 2C, 3, 4, and 320.

Detailed results are presented in Table 1 after the Tables Tab of this report. The following table summarizes the results of the testing conducted on November 19, 2014.

EUAIRSTRIP Acetaldehyde Emissions Results

Parameter	Units	Run 1	Run 2	Run 3	Average	Limit†
Acetaldehyde concentration	ppmv	156.1	124.0	145.6	**141.9**	**N/A**
Acetaldehyde mass emission rate	lb/hr	0.12	0.11	0.13	**0.12**	**N/A**
	ton/yr	0.541	0.466	0.571	0.526	**0.745**

ppmv part per million by volume
lb/hr pound per hour
ton/yr ton per year calculated based on continuous operation ((lb/hr) * (1 ton/2,000 lb) * (8,760 hr/yr))
† based on 12-month rolling time period as determined at the end of each calendar month

The results of the acetaldehyde emissions testing indicate that the EUAIRSTRIP source complies with the applicable limit of 0.745 tons per year.

1.0 Introduction

1.1 Summary of Test Program

Airgas, Inc. retained Bureau Veritas North America, Inc. to test air emissions from the EUAIRSTRIP source at their Airgas Carbonic facility in Blissfield, Michigan. The facility uses carbon dioxide (CO_2) from the adjoining Global Ethanol Riga facility to manufacture liquid and solid (dry ice) CO_2. The EUAIRSTRIP source uses a blower to aerate the facility's CO_2 scrubber wastewater prior to discharge to the municipal wastewater conveyance system. The applicable emission limit excerpted from the facility's Michigan Department of Environmental Quality (MDEQ) Permit to Install 31-13 is presented below:

Pollutant	Limit	Time Period / Operating Scenario	Equipment	Testing / Monitoring Method	Underlying Applicable Requirements
1. Acetaldehyde	0.745 tpy	12-month rolling time period as determined at the end of each calendar month	EUAIRSTRIP	SC VI.3	R 336.1225, R 336.1702(a)

Bureau Veritas measured acetaldehyde at the outlet of the EUAIRSTRIP source.

Three 60-minute test runs were performed following United States Environmental Protection Agency (USEPA) Methods 1A, 2C, 3, 4, and 320.

1.2 Key Personnel

The key personnel involved in this test program are listed in Table 1-1 on the following page. Mr. Dillon King, Consultant with Bureau Veritas led the emission testing. Mr. Daniel Schwartz, the Airgas Carbonic facility's Plant Manager provided process coordination and recorded operating parameters. Mr. Mark Dziadosz, and Ms. Diane Kavanaugh-Vetort, with Michigan Department of Environmental Quality witnessed the testing.

Table 1-1
Key Personnel

Airgas	Bureau Veritas
Daniel Schwartz Plant Manager **Airgas Carbonic – Riga Facility** 7031 Sibelhorn Highway Blissfield, Michigan 49228 Telephone: 517.682.1122 Facsimile: 866.422.7492 daniel.schwartz@airgas.com Stephen Petz EHS Manager **Airgas Dry Ice \ Carbonic** 2530 Sever Road, Suite 300 Lawrenceville, Georgia 30043 Telephone: 678.985.7320 Facsimile: 678.985.7321 stephen.petz@airgas.com	Dillon King, QSTI Consultant **Bureau Veritas North America, Inc.** 22345 Roethel Drive Novi, Michigan 48375 Telephone: 248.344.3002 Facsimile: 248.344.2656 dillon.king@us.bureauveritas.com
MDEQ	
Mark Dziadosz Environmental Quality Analyst Air Quality Division - Southeast Michigan District Office 27700 Donald Court Warren, Michigan 48092 Telephone: 586.753.3745 Facsimile: 586.753.3731 Email: dziadoszm@michigan.gov	Diane Kavanaugh-Vetort Environmental Quality Analyst Air Quality Division – Jackson District Office 301 East Louis Glick Highway Jackson, Michigan 49201 Telephone: 517.780.7864 Facsimile: 517.780.7855 kavanaughd@michigan.gov

2.0 Source and Sampling Locations

2.1 Process Description

Airgas Carbonic is a CO_2 liquefaction plant manufacturing liquid and solid (dry ice) carbon dioxide. A portion of the gaseous carbon dioxide generated from the fermentation process is pumped from the CO_2 scrubber exhaust at the adjoining Global Ethanol Riga facility to the Airgas Carbonic facility.

At the Airgas Carbonic facility, the CO_2 (95 to 97%), enters inlet coolers that lower the air temperature and remove some water. The gas passes through a blower where it is heated prior to entering two sets of heat exchangers. The heat exchangers cool the gas before a second cooler removes the remaining moisture.

The gas is then compressed in two stages, cooled, and dried within heat recovery aftercoolers. After the gas exits the aftercoolers, it enters the bottom of a reverse flow packed bed water scrubber that removes impurities to purify the gas stream. The gas exits the top of the scrubber and is then chilled and dried before entering carbon vessels that remove sulfur compound impurities.

As water is added to the scrubber, which is designed to maintain a fixed water level, excess water is released into the air-stripping tank (EUAIRSTRIP). A fan rated at 175 cubic feet per minute (CFM), blows air through the scrubber wastewater to remove CO_2 and acetaldehyde before the air is exhausted to atmosphere and the wastewater discharged to the municipal wastewater treatment system.

2.2 Process Operating Parameters

The process was operated under maximum routine operating conditions during testing. Table 2-1 on the following page summarizes the CO_2 flow rate,sc rubber water flow rate, and scrubber different pressure recorded during the test program. Refer to Appendix E for process data recorded by Airgas personnel during testing.

Table 2-1
Summary of Production Data

Parameter	Unit	Run 1	Run 2	Run 3	Average
CO_2 flow rate	ton/hr	15.33	15.50	14.68	15.17
Scrubber water flow rate	gal/min	25.92	26.05	26.00	25.99
Scrubber differential pressure	psid	1.58	1.57	1.56	1.57

ton/hr ton per hour
gal/min gallon per minute
psid pounds per square inch, differential

2.3 Control Equipment

The exhaust from EUAIRSTRIP is discharged to atmosphere without pollution control.

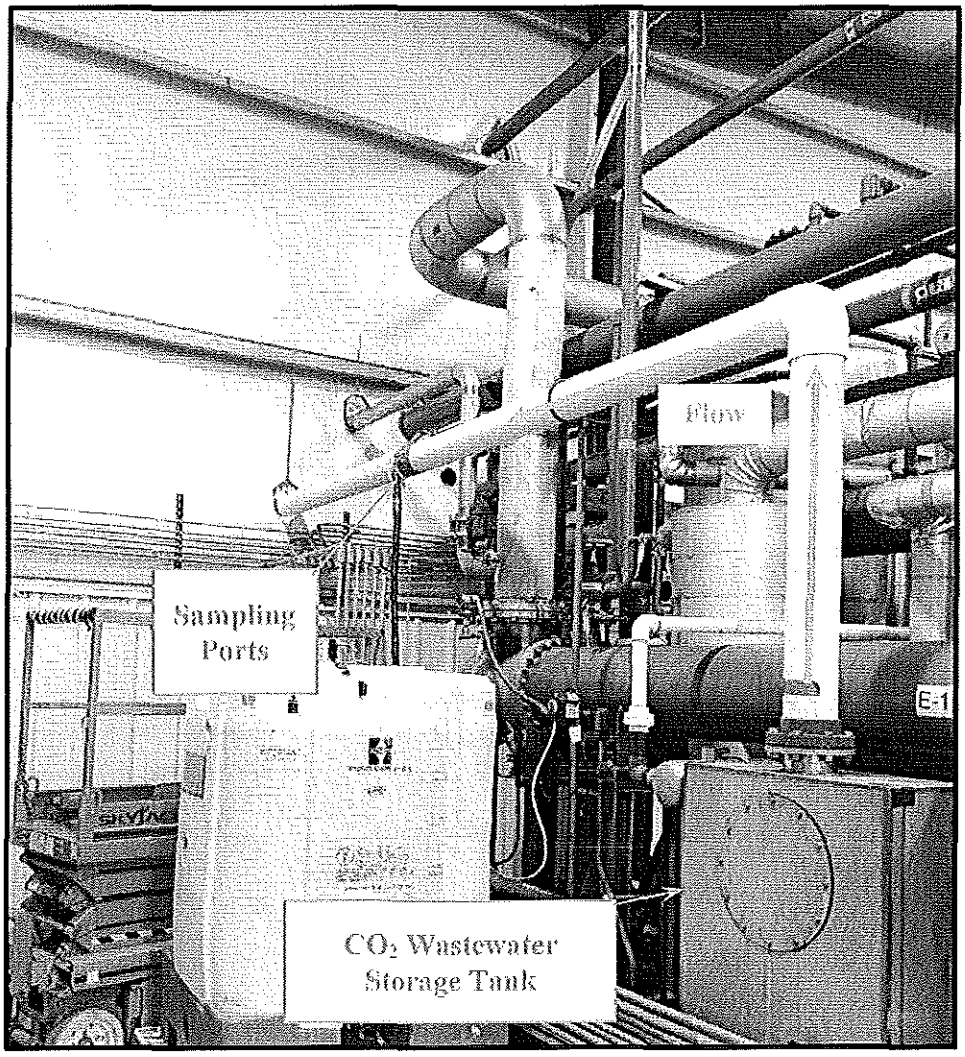
2.4 Flue Gas Sampling Locations

Two 3-inch-internal-diameter sampling ports, orientated at 90° to one another, are located in a section of the 6-inch-internal-diamter exhaust duct accessed via a man-lift. The sampling ports extend 0.25 inches outward from the stack interior wall. The ports are located at the following locations relative to the nearest flow disturbances:

- Approximately 11 feet downstream (22 duct diameters) of a 90° bend in the duct.
- Approximately 5.5 feet upstream (11 duct diameters) of another 90° bend in the duct on the exterior of the building.

The figure on the following page provides a photograph of the sampling ports at the sampling location for EUAIRSTRIP. Appendix Figure 1 presents the EUAIRSTRIP sampling ports and traverse point locations.

Figure 1-1. EUAIRSTRIP Sampling Location



2.5 Process Sampling Locations

Process sampling was not required during this test program. A process sample is a sample that is analyzed for operational parameters, such as calorific value of a fuel (e.g., natural gas, coal), organic compound content (e.g., paint coatings), or composition (e.g., polymers).

3.0 Summary and Discussion of Results

3.1 Objective

The purpose of the testing was to satisfy requirements and evaluate compliance with Permit to Install 31-13 issued April 30, 2013. Bureau Veritas measured acetaldehyde concentrations and mass emission rates at the outlet of the EUAIRSTRIP source. The applicable emission limit excerpted from the facility's Michigan Department of Environmental Quality (MDEQ) Permit to Install 31-13 is presented below:

Pollutant	Limit	Time Period / Operating Scenario	Equipment	Testing / Monitoring Method	Underlying Applicable Requirements
1. Acetaldehyde	0.745 tpy	12-month rolling time period as determined at the end of each calendar month	EUAIRSTRIP	SC VI.3	R 336.1225, R 336.1702(a)

3.2 Test Matrix

Three 60-minute test runs were performed following United States Environmental Protection Agency (USEPA) Methods 1A, 2C, 3, 4, and 320. Table 3-1 presents the sampling and analytical matrix.

Table 3-1
Test Matrix

Sampling Location	Runs	Sample/Type of Pollutant	USEPA Sampling Method	Analytical Method	Run Time (min)
EUAIRSTRIP	4	Gas flowrate (pre- and post-test)	1A, 2C, 3†, and 4†	Differential pressure, chemical absorption	≥5
	3	Acetaldehyde	320	Fourier transform infrared spectroscopy	60

† Method 320 was used to measure moisture content and carbon dioxide of the flue gas in lieu of Methods 3 and 4

3.3 Field Test Changes and Issues

No field test changes or issues were encountered during the test program. Communication between Airgas Carbonic, MDEQ, and Bureau Veritas allowed the testing to be completed as proposed in the October 20, 2014, Intent to Test Plan.

3.4 Summary of Results

Table 3-2 below summarizes the results of the testing conducted on November 19, 2014. Detailed results are presented in Table 1 after the Tables Tab of this report. Graphs of the acetaldehyde and CO_2 concentrations are presented after the Graphs Tab of this report. Sample calculations are presented in Appendix B.

Table 3-2
EUAIRSTRIP Acetaldehyde Emissions Results

Parameter	Units	Run 1	Run 2	Run 3	Average	Limit[†]
Acetaldehyde concentration	ppmv	156.1	124.0	145.6	**141.9**	**N/A**
Acetaldehyde mass emission rate	lb/hr	0.12	0.11	0.13	**0.12**	**N/A**
	ton/yr	0.541	0.466	0.571	0.526	**0.745**

ppmv part per million by volume
lb/hr pound per hour
ton/yr ton per year calculated based on continuous operation ((lb/hr) * (1 ton/2,000 lb) * (8,760 hr/yr))
[†] based on 12-month rolling time period as determined at the end of each calendar month

The results of the acetaldehyde emissions testing indicate that the EUAIRSTRIP source complies with the applicable limit of 0.745 tons per year.

4.0 Sampling and Analytical Procedures

Bureau Veritas measured emissions following the guidelines and procedures specified in 40 CFR 60, Appendix A, "Standards of Performance for New Stationary Sources," 40 CFR 63 and State of Michigan Part 10 Rules, "Intermittent Testing and Sampling." The sampling and analytical methods used are presented in Table 4-1.

Table 4-1
Emission Test Methods

Method	Parameter	Analysis
EPA 1A and 2C	Gas stream volumetric flowrate	Field measurement, standard Pitot tube
EPA 3 and 4[†]	Molecular weight; moisture content	Fyrite® chemical absorption
EPA 320	Acetaldehyde, CO_2, and moisture content	Extractive Fourier transform infrared spectroscopy (FTIR)

[†] Method 320 was used to measure moisture content and carbon dioxide of the flue gas in lieu of Methods 3 and 4

4.1 Emission Test Methods

The table below outlines the test methods for the test parameters, including ancillary measurements required by the USEPA methods (i.e., traverse point selection, velocity, molecular weight, and moisture content).

Table 4-2
Emission Test Parameters

Parameter	Source	USEPA Reference	
	Outlet of EUAIRSTRIP	Method	Title
Sampling ports and traverse points	•	1A	Sample and Velocity Traverses for Stationary Sources with Small Stacks or Ducts
Velocity and flowrate	•	2C	Determination of Gas Velocity and Volumetric Flow Rate in Small Stacks or Ducts (Standard Pitot Tube)
Molecular weight	•	3	Gas Analysis for the Determination of Dry Molecular Weight
Acetaldehyde, CO_2, and moisture content	•	320	Measurement of Vapor Phase Organic and Inorganic Emissions by Extractive Fourier Transform Infrared (FTIR) Spectroscopy

4.1.1 Volumetric Flowrate (USEPA Methods 1A and 2C)

Method 1A, "Sample and Velocity Traverses for Stationary Sources With Small Stacks or Ducts," from the Code of Federal Regulations, Title 40, Part 60 (40 CFR 60), Appendix A, was used to evaluate the sampling location, the number of traverse points for sampling, and the measurement of velocity profiles. Details of the sampling location and number of velocity traverse points are presented in Table 4-3.

Table 4-3
Sampling Location and Number of Traverse Points

Source	Sampling Location	Duct Diameter (inches)	Distance from Ports to Upstream Flow Disturbance (diameters)	Distance from Ports to Downstream Flow Disturbance (diameters)	Number of Ports Used	Traverse Points per Port	Total Traverse Points	Cyclonic Flow Null Angle (°)
EUAIRSTRIP	Outlet	6	11	22	2	4	8	12.5

Figure 2-1 is a photograph depicting the sampling location at the outlet of EUAIRSTRIP. Appendix Figure 1 presents the EUAIRSTRIP outlet sampling ports and traverse point locations. Method 2C, "Determination of Stack Gas Velocity and Volumetric Flow Rate in Small Stacks or Ducts (Standard Pitot Tube)," was used to measure flue gas velocity and calculate volumetric flowrate. A standard Pitot tubes and thermocouple assembly, calibrated in accordance with Method 2C, Section 10.0, was used during testing. Because the dimensions of the Pitot tube met the requirements outlined in Method 2, Section 10.1, and were within the specified limits, the baseline Pitot tube coefficient of 0.99 (dimensionless) was assigned. Refer to Appendix A for the Pitot tube inspection sheets.

Cyclonic Flow Check. Cyclonic flow is defined as a flow condition with an average null angle greater than 20°. The direction of flow can be determined by aligning an S-type Pitot tube to obtain zero (null) velocity head reading—the direction would be parallel to the Pitot tube face openings or perpendicular to the null position. By measuring the angle of the Pitot tube face openings in relation to the stack walls when a null angle is obtained, the direction of flow is measured. If the absolute average of the flow direction angles is greater than 20 degrees, the flue gas is considered cyclonic at that sampling location and an alternative location should be found.

The average of the measured traverse point flue gas velocity null angles was:

- 12.5° from the direction of flow for the EUAIRSTRIP outlet

The measurements indicate the absence of cyclonic flow at the sampling location. Field data sheets are included in Appendix C. Computer-generated field data sheets are included in Appendix D.

4.1.2 Molecular Weight (USEPA Method 3)

Molecular weight at the EUAIRSTRIP sampling location was measured using Method 3, "Gas Analysis for the Determination of Dry Molecular Weight." Flue gas was extracted from the stack through a probe positioned near the centroid of the duct and directed into a Fyrite® gas analyzer. The concentrations of oxygen (O_2) were measured by chemical absorption to within ±0.5%. The average O_2 results of the grab samples were used to calculate molecular weight.

4.1.3 Moisture Content (USEPA Method 4)

At the outlet sampling location, the moisture content of the flue gas was measured by infrared absorbance using USEPA Method 320.

4.1.4 Acetaldehyde, CO_2, and Moisture Content (USEPA Method 320)

Acetaldehyde, CO_2, and moisture content were measured in accordance with USEPA Method 320, "Measurements of Vapor Phase Organic and Inorganic Emissions by Extractive Fourier Transform Infrared (FTIR) Spectroscopy." Gaseous samples were withdrawn from the duct through a heated probe, filter, and transfer line connected to a MKS Instruments MultiGas 2030 FTIR spectrometer. Molecules in the sample absorb infrared radiation from the FTIR infrared beam in a characteristic and reproducible pattern. The frequency dependent infrared spectra is used to determine the compound concentration in the sample mixture. Acetaldehyde, CO_2, and moisture content were measured based on their infrared absorbance compared to reference spectra. Figure 2 in the Appendix depicts the USEPA Method 320 sampling train.

The probe, filter, transfer line, and FTIR multi-pass gas cell was maintained at 191° C (375° F) during testing. The FTIR analyzer scans the sample approximately once per second. A data point consists of the co-addition of 64 scans, with a data point generated every minute.

FTIR quality assurance procedures followed USEPA Method 320 and included: zero, calibration transfer standard (CTS), matrix gas, and analyte spike procedures. The results of the QA/QC activities were compared to the acceptance criteria of ±5% for the zero, CTS, matrix gas direct and system response procedures. The analyte spike recovery criterion is ±30% of the theoretical recovery value.

4.2 Procedures for Obtaining Process Data

Process data was recorded by Airgas Carbonic personnel during testing. Refer to Section 2.1 and 2.2 for discussions of process and control device data and Appendix E for the operating parameters recorded during testing.

5.0 QA/QC Activities

5.1 Pretest QA/QC Activities

Before testing, the sampling equipment was cleaned, inspected, and calibrated according to procedures outlined in the applicable USEPA sampling method and USEPA's "Quality Assurance Handbook for Air Pollution Measurement Systems, Volume and Principles" and, Volume III, "Stationary Source Specific Methods." Refer to Appendix A for inspection and calibration sheets.

5.2 QA/QC Audits

The results of select sampling and equipment QA/QC audits and the acceptable USEPA tolerance are presented in the following sections.

5.2.1 Instrument Analyzer QA/QC Audits

The FTIR analyzer met the QA/QC requirements of USEPA Method 320. Table 5-1 summarizes the FTIR QA/QC Procedures.

Table 5-1
FTIR QA/QC Procedures

QA/QC Specification	Purpose	Calibration Gas Analyte	Delivery	Frequency	Acceptance Criteria	Result
M320: zero	Verify the FTIR is free of contaminants; zero the FTIR	Nitrogen	Direct to FTIR	Pre-test	<MDL or noise	Pass
M320: Calibration transfer standard (CTS) direct	Verify FTIR stability, confirm optical path length	Ethylene	Direct to FTIR	Pre-test	±5% cert. value	Pass
M320: Matrix gas direct	Confirm FTIR calibration	Acetaldehyde, methanol, SF6	Direct to FTIR	Pre-test	±5% cert. value	Pass
M320: CTS response	Verify system stability and recovery	Ethylene	Sampling System	Pre- and post- test	±5% of direct measurement	Pass
M320: Zero response	Verify system is free of contaminants, system bias	Nitrogen	Sampling System	Pre- and post-test	bias correct data	Pass
M320: Matrix gas response	Verify system stability, recovery, and response time	Acetaldehyde, methanol, SF6	Sampling System	Pre-test	±5% Cert. value	Pass
M320: Analyte spike	Verify ability of FTIR system to delivery and quantify analytes of interest	Acetaldehyde, methanol, SF6	Sampling System	Pre-test	±30% theoretical recovery	Pass

Refer to Appendix A for the calibration documents and Appendix F for the FTIR calibration data.

5.3 QA/QC Problems

QA/QC problems were not encountered during this test program.

Limitations

The information and opinions rendered in this report are exclusively for use by Airgas, Inc. Bureau Veritas North America, Inc. will not distribute or publish this report without Airgas, Inc.'s consent except as required by law or court order. The information and opinions are given in response to a limited assignment and should be implemented only in light of that assignment. Bureau Veritas North America, Inc. accepts responsibility for the competent performance of its duties in executing the assignment and preparing reports in accordance with the normal standards of the profession, but disclaims any responsibility for consequential damages.

This report prepared by:

Dillon A. King, QSTI
Consultant
Health, Safety, and Environmental Services

This report reviewed by:

Thomas R. Schmelter, QSTI
Senior Project Manager
Health, Safety, and Environmental Services

Derek R. Wong, Ph.D., P.E.
Director and Vice President
Health, Safety, and Environmental Services

Table

Table 1

EUAIRSTRIP Acetaldehyde Emissions Results

Airgas Carbonic

Blissfield, Michigan

Sampling Date: November 19, 2014

Bureau Veritas Project No. 11014-000206.00

Parameter	Run 1		Run 2		Run 3		Average
Date	November 19, 2014						
Sampling Time	12:00 to 13:00		13:07 to 14:07		14:13 to 15:13		
Sample Duration (minutes)	60		60		60		60
	Time	Flowrate	Time	Flowrate	Time	Flowrate	
Pre-test Outlet Gas Stream Volumetric Flowrate (scfm)	11:50	110	13:05	121	14:08	129	
Post-test Outlet Gas Stream Volumetric Flowrate (scfm)	13:05	121	14:08	129	15:20	132	
Average Outlet Gas Stream Volumetric Flowrate (scfm)	115		125		130		123
Acetaldehyde molecular weight (gram/mole)	44.053		44.053		44.053		44.053
Average Outlet Acetaldehyde Concentration (ppmv)	156.1		124.0		145.6		141.9
Acetaldehyde Mass Emission Rate (lb/hr)	**0.12**		**0.11**		**0.13**		**0.12**
Acetaldehyde Mass Emission Rate (ton/yr)[1]	**0.541**		**0.466**		**0.571**		**0.526**

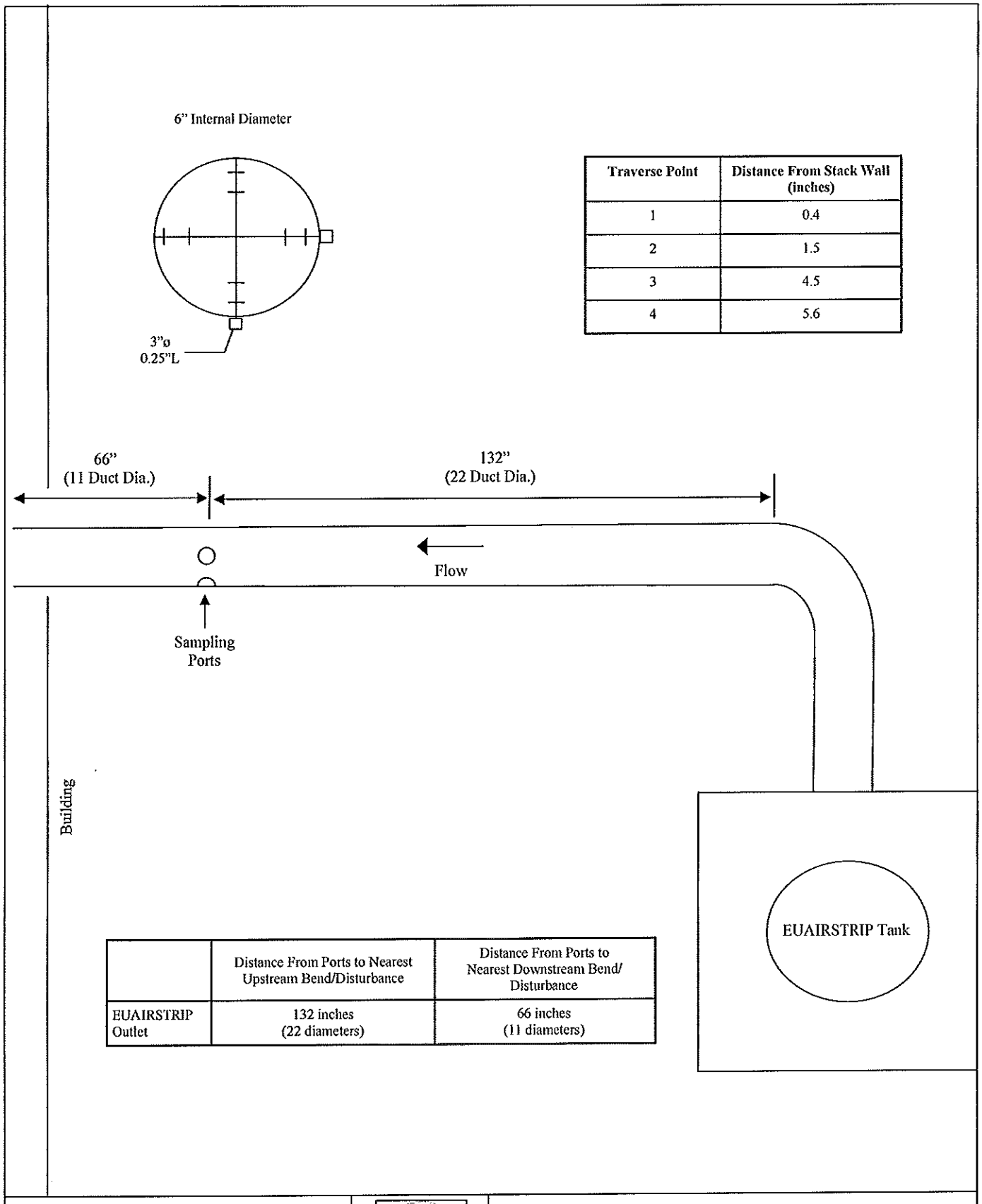
scfm standard cubic feet per minute

ppmv parts per million volume

lb/hour pounds per hour

[1] ton per year calculated based on continuous operation ((lb/hr) * (1 ton/2,000 lb) * (8,760 hr/yr))

Figure



Traverse Point	Distance From Stack Wall (inches)
1	0.4
2	1.5
3	4.5
4	5.6

	Distance From Ports to Nearest Upstream Bend/Disturbance	Distance From Ports to Nearest Downstream Bend/ Disturbance
EUAIRSTRIP Outlet	132 inches (22 diameters)	66 inches (11 diameters)

Figure 1
EUAIRSTRIP Outlet Sampling Ports and Traverse Points

Airgas Carbonic
Blissfield, MI

Project No. 11014-000206.00

Last Revision:
December 17, 2014

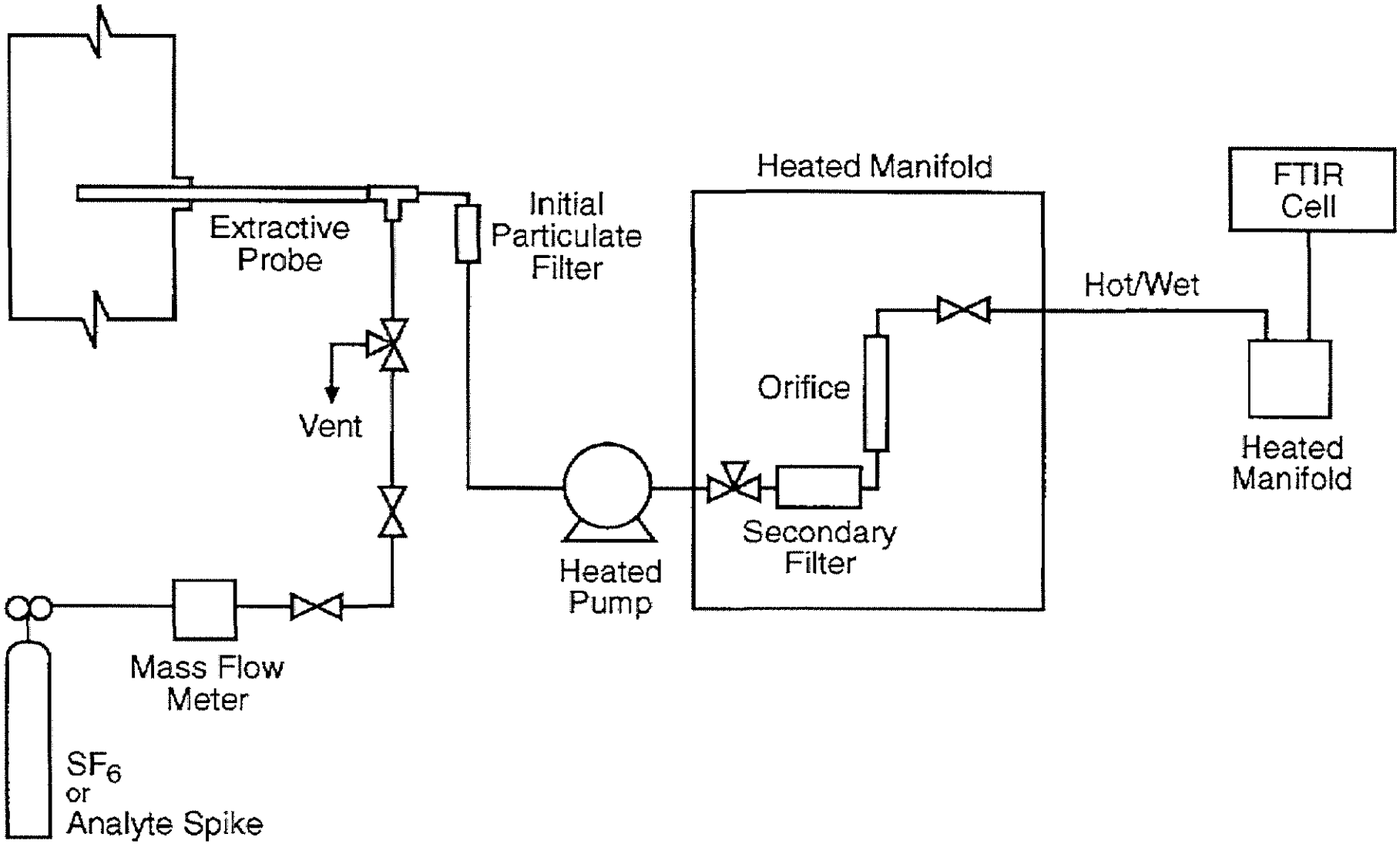


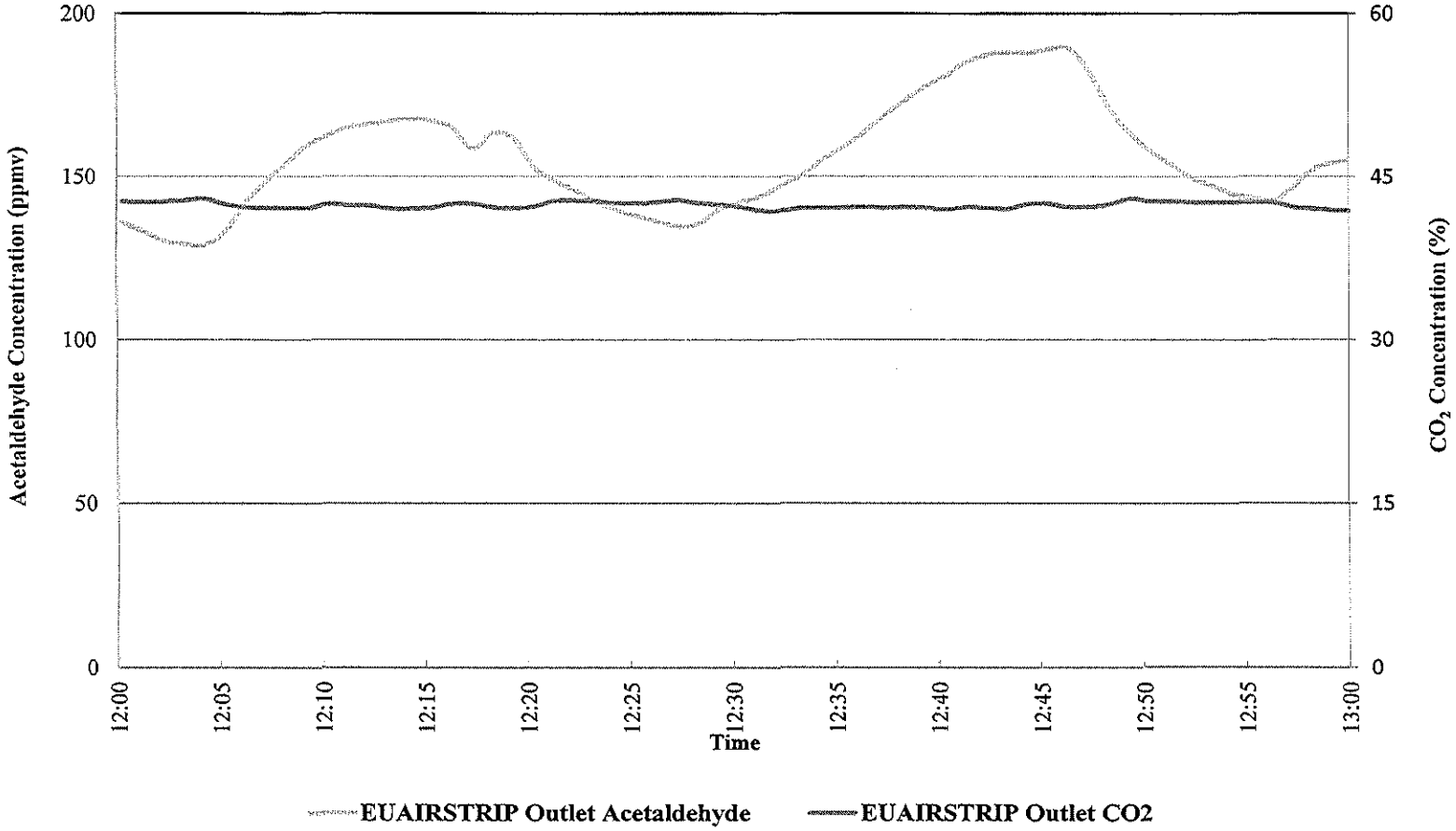
Figure 2
USEPA Method 320 Sampling Train

Airgas Carbonic
Blissfield, MI

Project No. 11014-000206.00 | Last Revision: December 18, 2014

Graph

EUAIRSTRIP Acetaldehyde and CO_2 Concentrations - Run 1
Airgas Carbonic
Blissfield, Michigan
Bureau Veritas Project No. 11014-000203.00
Sampling Date: November 19, 2014



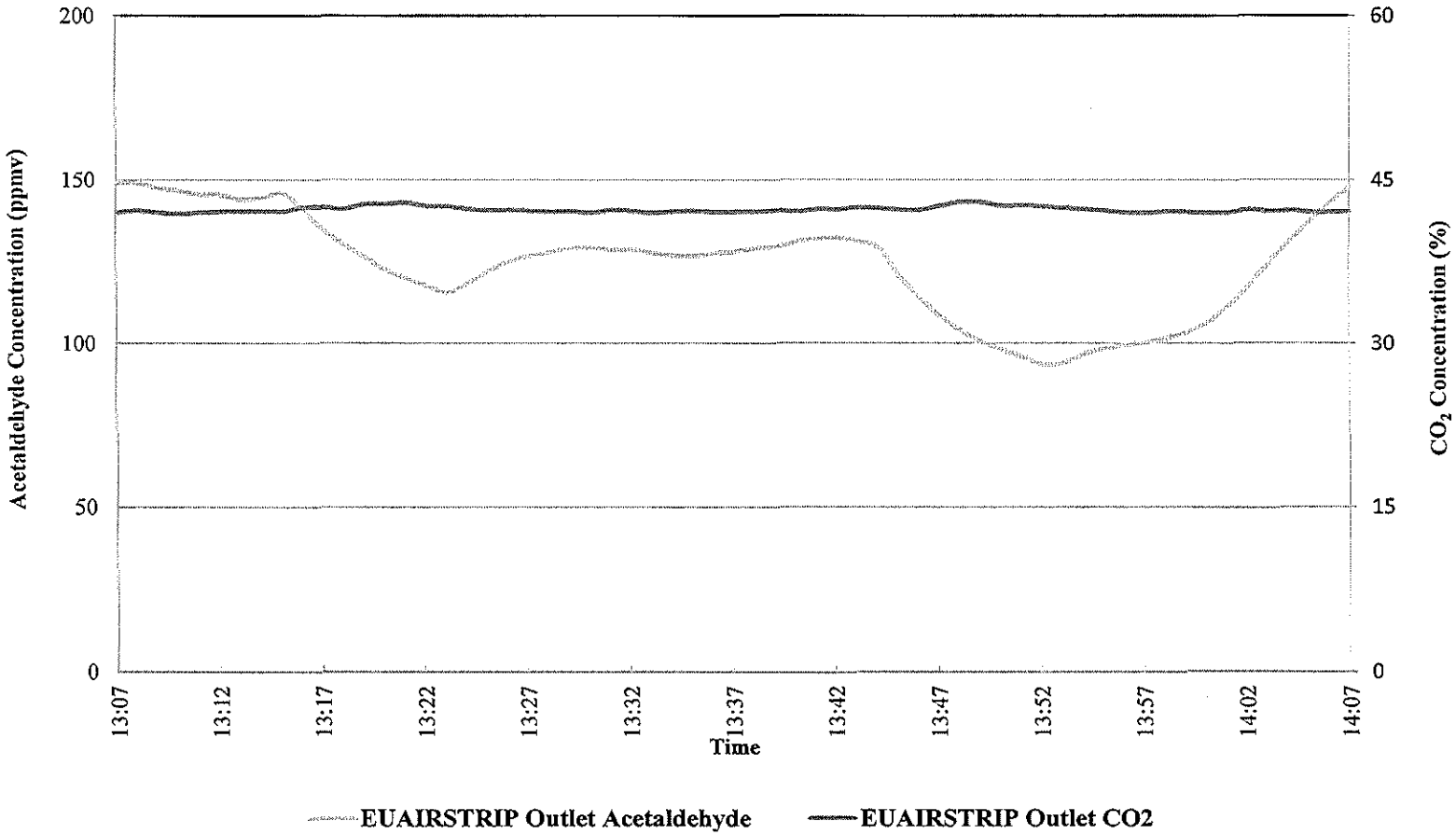
EUAIRSTRIP Acetaldehyde and CO_2 Concentrations - Run 2

Airgas Carbonic

Blissfield, Michigan

Bureau Veritas Project No. 11014-000203.00

Sampling Date: November 19, 2014



EUAIRSTRIP Acetaldehyde and CO_2 Concentrations - Run 3

Airgas Carbonic

Blissfield, Michigan

Bureau Veritas Project No. 11014-000203.00

Sampling Date: November 19, 2014