UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

OFFICE OF
AIR QUALITY PLANNING
AND STANDARDS

Solid Waste Working Group
c/o Matthew W. Morrison
Pillsbury Winthrop Shaw Pittman LLP
1200 Seventeenth Street NW
Washington, DC 20036-3006

10/06/2021

Dear Mr. Morrison:

I am writing in response to the letter from the National Waste & Recycling Association, the Solid Waste Association of North America, Waste Management, and Republic Services (collectively, the Solid Waste Working Group or SWWG) requesting approval of an alternative test method. The original request was submitted on May 28, 2021, and the final version was submitted on September 27, 2021. In that letter, the SWWG, on behalf of their member organizations, seek the use of an alternative test method in lieu of a requirement found in 40 CFR 63, Subpart AAAA - National Emission Standards for Hazardous Air Pollutants: Municipal Solid Waste Landfills Residual Risk and Technology Review (Subpart AAAA).

Subpart AAAA, §63.1961(a)(5) states that when a facility seeks to demonstrate compliance with the operational standard for temperature found in §63.1958(c)(1), the facility must initiate enhanced monitoring at each wellhead with a landfill gas temperature greater than 62.8 degrees Celsius (145 degrees Fahrenheit). That enhanced monitoring includes, among other things, measuring the carbon monoxide concentrations using Method 10 (40 CFR 60, Appendix A), as specified by §63.1961(a)(5)(vi). In lieu of Method 10, you propose the use of an alternative method where landfill gas samples are collected in passivated canisters or sampling bags from each wellhead subject to enhanced monitoring through existing monitoring ports and the samples are analyzed using an instrument that employs gas chromatography (GC) to separate CO from a sample and then catalytically reduce the CO to methane that is passed by a Flame Ionization Detector (FID) for quantification. A copy of your alternative method is included as an attachment to this letter. The original alternative method was developed by the SWWG, and the work group members conferred with EPA staff to develop the attached final version.

We have reviewed your original submittal and the attached final version of the method in detail and based on that review, we are approving your alternative test method request to allow the use of the test method included as an attachment to this letter in lieu of Method 10, as specified by §63.1961(a)(5)(vi) of Subpart AAAA. We believe this alternative method will be adequate for measurement of carbon monoxide from the wellheads and will not impact the stringency of Subpart AAAA. We also find it reasonable that this alternative test method approval be broadly applicable to facilities subject to Subpart AAAA including the requirements of §63.1961(a)(5)(vi), which specify the use of Method 10 and, for that reason, we will post this letter as ALT-144 on our website at http://www3.epa.gov/ttn/emc/approalt.html for use by facilities subject to those requirements.

This alternative test method approval is applicable to demonstrate compliance with the requirements of §63.1961(a)(5)(vi) of Subpart AAAA. This approval does not address the use of this alternative method for performance testing required under State Implementation Plans (SIP) or state/local/tribal regulations. Application of this alternative test method for such regulations is subject to the approval of the administrative authority for the applicable regulation(s).

If you should have any questions or require further information regarding this approval, please call Kim Garnett of my staff at 919-541-1158 or email her at *garnett.kim@epa.gov*.

Sincerely,

Johnson, Steffan

Digitally signed by Johnson, Steffan
Date: 2021.10.06 08:04:09 -04'00'

Steffan M Johnson

Steffan M. Johnson, Group Leader
Measurement Technology Group

attachment

cc: Amy Banister, Waste Management
Jason DeWees, EPA/OAQPS/SPPD
Robin Dunkins, EPA/OAQPS/SPPD
Kim Garnett, EPA/OAQPS/AQAD
Anne Germain, National Waste and Recycling Association
Michael Jensen, Waste Management
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DETERMINATION OF CARBON MONOXIDE CONCENTRATION INLANDFILL GAS WELLHEADS – GAS CHROMATOGRAPHIC MEASUREMENT (FID)

1.0 Scope and Application

1.1 Analytes. What does this method determine?

This method measures the concentration of carbon monoxide (CO) in landfill gas.

Analyte	CAS No.	Minimum Detection Limit
CO	630-08-0	100 ppmv

1.2 Applicability. When is this method required?

This method may be used to demonstrate the carbon monoxide concentration as specified in 40 C.F.R. § 63.1961(a)(5)(vi)(A) for each wellhead subject to enhanced monitoring as required by 40 C.F.R. § 63.1961(a)(5).

1.3 Data Quality Objectives.

The objective is to ensure reasonable accuracy of the data to effectuate the appropriate monitoring frequency following the requirements of 40 C.F.R. Part 63, Subpart AAAA.

2.0 Summary of Method

In this method, landfill gas samples are collected in passivated canisters or gas sampling bags from each wellhead subject to enhanced monitoring through existing monitoring ports and the samples are analyzed using an instrument that uses gas chromatography (GC) to separate CO from a sample and then catalytically reducing the CO to methane that is subsequently passedby a Flame Ionization Detector (FID) for quantification. The performance requirements of this method must be met to validate the data.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Resolution interferences that may occur can be eliminated or minimized by appropriate GC column and detector choice or by shifting the retention times through optimization of column flow, column temperature or temperature programming. Particular attention must be paid to the separation of CO from large methane peaks present in the landfill gas (LFG) matrix.

4.2 The analytical system is demonstrated to be essentially free from contaminants by periodically analyzing blanks that consist of hydrocarbon-free air or nitrogen daily or per QC batch as appropriate.

4.3 Sample cross-contamination that occurs when high-level and low-level samples or standards are analyzed alternately is best dealt with by thorough purging of the GC sample introduction system and sample loop prior to and between samples.

4.4 To assure consistent detector response, calibration gases are contained in dry air or nitrogen. Calibration gases in a landfill gas matrix are also acceptable.

4.5 The gas chromatograph run time must be sufficient to clear all eluting peaks from the column before proceeding to the next sample run to prevent sample carryover. This can be accomplished by a backflush configuration employing pre-columns or by use of temperature programming.

5.0 Safety

It is essential that all personnel conducting the monitoring described in this method follow established company and/or facility Health and Safety Plans (HASPs) while at a landfill and wear Personal Protection Equipment (PPE) as appropriate including items necessary to address potential hazards at a landfill and surface temperatures above 145 °F.

Landfill gas is combustible and could form an explosive mixture under the right conditions for example, accumulating in well vaults. Landfill gas is also considered a simple asphyxiant that coulddisplace ambient air under those same conditions and may contain trace compounds, includinghydrogen sulfide, that if inhaled could cause harm. In addition, this method requires workingon a landfill that could have moving equipment and vehicles in proximity to the wellheads.

Other precautions for conducting the sample collection described in this method include smoking prohibitions and other safety recommendations published in thegas analyzer user's manual and other similar resources. Occupational Safety and Health Administration (OSHA) regulations concerning cylinder and noxious gases may also apply.

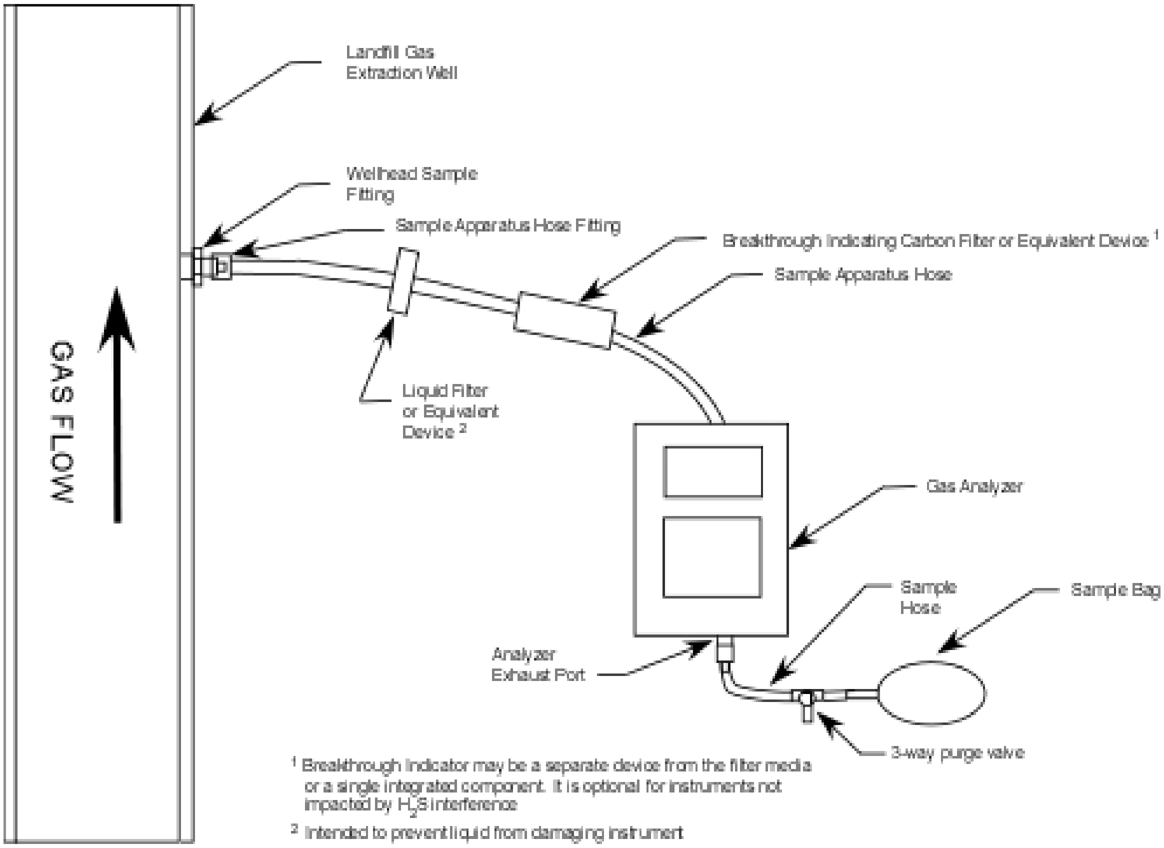
6.0 Equipment and Supplies

To perform the enhanced monitoring required by 40 C.F.R. Part 63, Subpart AAAA, using this method an integrated sampling approach as described in this section is acceptable.

6.1 *Integrated Sampling*

Collect the sample from the wellhead sampling port through a hose and fitting to a passivated canister or gas sampling bag (such as the multi-layer foil Cali-5-Bond Bag, Tedlar® Bag, or other similar type gas sample bags) and analyze that sample using an analyzer conforming to this method. The sampling system shown in Method 25C, Figure 25C-2is required for sample collection in canisters, except that a 3-way valve is inserted on the sample hose before the canister connection to allow for connection of a field analyzer pump for purging and leak checks. The sampling train shown in Figure 6.1-1 is required for sample collection in bags. Alternatively, the sampling train shown in Figure 10A-1 of Method 10A can be used for sample collection in bags.

Figure 6.1-1 Gas Bag Sampling System



The gas analyzer requires a pump suitable to overcome a vacuum in the gas well and an exhaust port capable of delivering a sample to a gas collection bag.

Use of equipment and supplies in the sampling system meeting the following specifications is acceptable:

6.1.1 *Sample Apparatus Hose Fitting*. The sample hose fitting must connect to the wellhead sample fitting firmly and without leaks. Gaskets, O-rings, or other such seals must be replaced if damaged prior to collecting the sample. Use of a 3-way valve to allow for purging and leak checks of the sample hose is recommended.

6.1.2 *Sample Apparatus Hose*. The sample hose from the wellhead to the sample canister or bag must be made of silicone, PVC or other similar material that does not absorb or otherwise alter the sample gas.

6.1.3 Integrated sampling may rely on any of the following:

a) vacuum in a passivated canister,

b) use of a gas pump from a landfill gas field analyzer,

c) use of an alternative leak-free diaphragm type pump, or

d) an equivalent mechanism to overcome vacuum within the landfill gas wellhead to transport gas to the sample canister or sample bag.

6.2 *Gas Chromatograph.* GC conforming to EPA Method 25, section 6.3 when calibrated for CO and operated in accordance with EPA Method 25, section 11.0:

6.2.1 *Separation Column.* Appropriate column(s) to resolve CO from other gas components that may be present in the sample.

6.2.2 Sample Loop. Teflon, stainless-steel tubing, or other inert polymeric materials tubing with a volume of at least 0.5 mL. Larger volumes are acceptable up to 5 mL for low concentration analytes.

6.2.3 *Reduction catalyst*. A tube of sufficient length and diameter packed with a nickel powder mounted in a furnace that can attain a minimum of 400 °C.

6.2.3.1 Conduct an initial efficiency check following the procedures in EPA Method10B, section 10.2 and EPA Method 10B, sections 7.2.2 – 7.2.3.

6.2.4 *Flame Ionization Detector.* Capable of measuring a minimum of 10 ppm to greater than 10,000 ppm.

6.2.4.1 The detector shall have a linear response over the operatingrange of the instrument with a linear calibration model least squares regression of >0.99.

6.2.5 *Recorder.* Digital or analog method of integrating peaks.

6.2.6 *Carrier Gas Tubing.* Diameter and length determined by connection requirements of cylinder regulators and the GC.

6.2.7 *Regulators.* To control gas cylinder pressures consistent with the GC manufacturers specifications.

6.2.8 *Carrier Gas Adsorption Tubes.* Applicable traps to remove any oxygen, water vapor or trace hydrocarbons from the carrier gas.

7.0 Reagents and Standards

*7.1 Calibration and Linearity Gases. A*t least three concentrations of CO in nitrogen shall be used for calibration. These levels must include a low, mid, and high-level concentration that will allow for the determination of CO contractions ranging from a minimum of 100 ppmv to at least 1,000 ppmv. These calibration gases can be blended at the lab from Standard Gas cylinders containing CO in nitrogen certified to an analytical accuracy of +/-2% or can be from a third party supplier providing a gas mixture containing CO at a known concentration produced and certified to have an analytical uncertainty of +/- 2% verified by direct comparison to calibration standards traceable to National Institute of Standards and Technology (N.I.S.T.) weights and/or N.I.S.T. Gas Mixture reference materials. If the calibration gases are blended, then the procedure for blending and the results must be documented. This documentation must be made available upon request.

7.2 *Carrier Gas.* Helium Ultra High Purity (99.999%), consistent with GC manufacturer recommendations.

7.3 *Combustion Gas*. Either air (less than 0.1 ppm total hydrocarbon content) or O_2 (purity 99.99 percent or greater), as required by the detector.

7.4 *Fuel Gas.* Hydrogen, at least 99.999 percent pure.

8.0 Sample Collection, Preservation and Storage

8.1 Sampling Site and Sampling Points.

Sampling must occur at landfill gas wellhead sampling ports installed into the well casingor wellhead such that gas can be freely extracted when a sample hose is attached. The fitting must allow for the secure connection of the sampling hose. Assemble and inspect hoses and fittings of the sampling system replacing gaskets, O-rings, or similar seals, as necessary. Samples may be collected in a passivated canister following the procedures in Section 8.2 or in a sample bag (*Cali-5-Bond Bag, Tedlar® Bag or other similar sampling bag)* using the procedures in Section 8.3..

8.1.1 Sampling Apparatus Leak Check. How do I prepare my sampling system?

a) Assemble and inspect hoses and fittings of the sampling system replacing gaskets, O-rings, or similar seals, as necessary. Replace filters or other similar devices in-line between the extraction well and sample bag or canister if called for by the manufacturer's recommendations or if conditions otherwise indicate that they should be replaced.
b) Apply a calibration gas that contains no oxygen to the sampling apparatus.
c) For canister sampling, connect sample analyzer to 3-way valve exhaust port installed on sample hose before the canister connection in accordance with Section 6.1. Close the valve on the calibration gas while the sample analyzer pump is activated.
d) Verify that the pump in the meter fails on a low flow alarm (or over pressure) before any oxygen is detected in the sample stream.
e) A value greater than 0.5% O_2, as measured by a calibrated oxygen sensor/monitor, indicates a leak. Check all fittings and replace, as necessary. Repeat procedure.

8.2 Collecting a Sample in a Canister.

8.2.1 Laboratory Pre-sampling Canister Preparation

a) Sample canisters must be evacuated, leaked-checked, and pre-charged with helium at the laboratory.

  - Note that laboratories clean canisters using a combination of dilution, heat, and high vacuum prior to shipping to sites for sampling for purposes of volatile organic compounds (VOC) analysis, certifying each cleaning batch as clean at VOC target concentrationsbelow 0.2 ppbv. Canisters that have been prepared for VOC analysis are acceptable for the purpose of sampling and analyzing for CO. Alternately, canisters can be shown to be free of carbon monoxide contamination at ½ the reporting limit.

b) The canister is prepared for sampling by evacuating the contents to a vacuum of approximately 29.9 inches of Mercury (in Hg). Helium is used to pre-charge the canisters to allow for return shipping of a landfill gas sample. The laboratory must use a chain of custody to establish the canister conditions prior to shipping and upon receipt back from the facility after sampling, recording the canister pressure after the addition of helium.

8.2.2 Connect the sample apparatus hose to the wellhead or well casing sample port fitting.

8.2.3 Purge the collection hose for at least 30 seconds before collecting the sample. This can be accomplished by using the landfill gas field meter typically used for sampling or an equivalent pump apparatus.

8.2.4 Prior to sample collection, confirm that the canister has not leaked during transport from the laboratory. Connect the vacuum gauge and flow controller to the canister. Ensure that all fittings are tight, and that the cap on the flow controller is secure. Open the canister valve and observe the pressure on the vacuum gauge; close the canistervalve. The canister is acceptable if there is no greater than 50.8 mm Hg (2 inches Hg) vacuum difference compared to the vacuum noted on the Chain of Custody. Continue to observe the vacuum gauge (with the valve closed) to assess if there is a leak of the sample train gauge and flow controller. They are acceptable if a change in vacuum of less than 1 inch of Hg is noted over 5 minutes. While conducting this check, ensure that the canister is in an area with constant ambient temperature.

8.2.5 To begin sampling in a canister, open the sample canister valve. Using a flow control valve, typically provided by the laboratory, set the flow through the sample train to a rate not less than 100 cc/minute, and not greater than 500 cc/minute. Adjust the flow rate as necessary to maintain a constant rate (±10 percent) throughout the duration of the sampling period. Record the sample canister vacuum and flowmeter setting at the beginning and end of the sampling. End the sampling when a constantflow rate can no longer be maintained because of reduced sample canister vacuum.

8.2.6 After sampling is completed, close the flow control valve, and record the final canistervacuum; then record the wellhead gas temperature and barometric pressure. Closethe sample canister valve and disconnect the sample canister from the sample system. Note that the wellhead gas temperature can be measured either before or after collecting the sample in a manner consistent with normal wellhead monitoring procedures.

8.3 Collecting a Sample in a Bag (multi-layer foil Cali-5-Bond Bag, Tedlar® Bag or other similar sample bag).

8.3.1 Confirm that the bag is not damaged by inspecting it before use.

8.3.3 Connect the sample apparatus hose to the wellhead or well casing sample port fitting, a field analyzer with pump, a 3-way valve, and sample bag as shown in Figure 6.1-1 or alternatively the equipment shown in Method 10, Figure 10-1.

b) Make sure that the pump provides the vacuum necessary to extract a sample from the well.
c) When using a field analyzer, it must have an exhaust port with a fitting to allow the connection of a sample bag.

8.3.4 With 3-way valve open to atmosphere, turn on pump or field analyzer.

8.3.4 Completely purge the collection hose before collecting the sample.

a) Close 3-way valve
b) If sample bag has been used for previous samples, purge bag a minimum of 3 times before collecting the current sample. Fill bag completely, disconnect bag from sample hose, release gas in bag, and repeat. Make sure bag is fully evacuated before sampling.

8.3.5 To begin sampling in a bag, close the 3-way valve, open the bag sample valve and fill slowly until it is approximately half full. This will prevent accidental over-inflation if the bag is exposed to a change in ambient pressure.

8.3.6 After sampling is completed, close the bag sample valve; then record the wellhead gas temperature and barometric pressure. Disconnect the sample bag from the sampling system. Note that the wellhead gas temperature can be measured either before or after collecting the sample in a manner consistent with normal wellhead monitoring procedures.

9.0 Quality Control

What quality control measures must I take?

The following table is a summary of the quality assurance and quality control measures and the associated frequency and acceptance criteria. The QC data, along with the sample data, must be documented.

QA/QC specification	Acceptance criteria	Checking frequency
Reference Standard	Analytical Uncertainty of +/-2%, verified by direct comparison to calibration standards traceable to National Institute of Standards and Technology (N.I.S.T.) weights and/or N.I.S.T. Gas Mixture reference materials	Every Cylinder of Standard Gas
Precision	Within 25% (Relative Percent Difference (RPD) for detections > 5 X's the Reporting Limit (RL)	Daily
Catalyst Reduction Efficiency	Within ≤ 5.0% of certified value	Weekly
Linearity Check	The percent relative standard deviation (%RSD) of the response factors must be <15%. Alternatively, a linear calibration model least squares regression must be >0.99.	Initial instrument setup prior to running samples, when major maintenance is performed, instrument response changes as indicated by the failure of the CCV, or at least annually
Continuing Calibration Verification (CCV)	85-115% recovery when compared to the initial calibration curve	Daily prior to sample analysis and after every 20 samples
Method Blank	Less than the Limit of Quantitation (100 ppmv)	After the calibration check and prior to the field samples

10.0 Calibration and Standardization

10.1 *Preparation of GC.* Before putting the GC analyzer into routine operation, optimize the operational conditions according to the manufacturer's specifications to provide good resolution and minimum analysis time and conduct the calibration procedures in this section.

At a minimum this must include establishing the appropriate carrier gas flow. Adjusting the column and detector temperatures to the recommended levels. Allow sufficient time for temperature stabilization. This may typically require 1 hour for each change in temperature.

10.2 *Precision:* Duplicate samples will be analyzed at a rate of 1 per batch minimum. Precision, within 25% (Relative Percent Difference (RPD) for detections > 5 X's the Reporting Limit (RL), is expressed in terms of the relative percent difference (RPD) between two sample measurements (A and B), and is computed as follows:

$$\%RPD = (A\text{-}B \times 100)/ ([A+B]/2) \qquad \text{Eq. 1}$$

10.3 *Initial Catalyst ReductionEfficiency:* With the reduction catalyst bypassed, make triplicate injections of the high-level CO standard. Repeat this procedure with catalyst operative. The reduction catalyst operation is acceptable if the responses under both conditions agree within 5 percent of their average.

10.4 *Initial Calibration Linearity Check*: Analyze a minimum of 3 concentration levels (low, mid, and high) spanning the desired concentration range with the lowest calibration standard prepared at or below the limit of quantitation (100 ppmv).

For each instrument calibration, record instrument method parameters and documentation of results. This includes method acquisition parameters, chromatograms, peak areas, retention times and calculated results. They can be kept in paper or electronic format.

Linearity is evaluated using an average response factor or a linear regression calibration model. For the average response factor model, a response factor is calculated for each concentration level based on the ratio of peak area and concentration. The percent relative standard deviation (%RSD) for the average of the response factors must be <15%. Alternatively, a linear calibration model using a least squares regression can be applied plotting standard concentrations against peak areas. The R-squared value must be >0.99.

The initial calibration linearity check must be conducted prior to running samples, and must be conducted when major maintenance is performed, instrument response changes as indicated by the daily calibration check recoveries, or at least annually.

10.5 *Daily Continuing Calibration Verification.* A mid-level calibration check is analyzed prior to analyzing a batch of samples and at the end of the batch[1], or 20 field samples, whichever comes first. The recovery of the calibration verification checks must be

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[1] A batch is a collection of no more than 20 samples, from a single site, collected during an enhanced monitoring sampling event.

85-115% when compared to the initial calibration curve.

If the recovery criterion is not met for the initial check, corrective action must include repeating the initial calibration as described in 10.4 prior to analysis of samples. If the ending check fails, the samples bracketed by the failing check must be reanalyzed unless recovery is high and sample concentrations are below the detection limit.

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10.5.1 Calibration verification is performed at the mid-point standard. Calculate the percent difference (%D) of the continuing calibration RF from the average RF_a from the initial calibration curve using the following equation:

$$\%D = [(RF - RFa)*100/RF_a] \qquad \text{Eq. 2}$$

where:

RF_a = The mean response factor from the initial calibration curve.
RF = The response factor from the continuing calibration standard.

10.5.2 The percent difference (%D) must be less than 15%. If this criterion is exceeded, a new calibration curve must be established.

11.0 Analytical Procedures

11.1 Sample Analysis. Adequately purge the sample loop with sample according to the GC manufacturer's instructions. This includes a proper purge of any sampling introduction device and tubing connecting the sample container and the GC beforeeach injection. Analyze each sample and calculate the average sample area (A). Determine the bag or canister CO concentration according to section 12.2.

11.2 *Negative Pressure Samples.* If analyzing vacuum samples, record the sample pressure and pressurize the sample cylinder to approximately 1,060 mm Hg (567 in. H2O) absolute pressure with helium. Record the final pressure.

12.0 Calculations and Data Analysis

Follow the procedures for calculations and data analysis listed in this section.

12.1 *Nomenclature.*

The terms used in the equations are defined as follows:

A = Instrument response of CO in the sample,
C = Concentration (ppmv) CO in the sample,
R = Mean calibration response factor for CO, area/ppmv.
P_{ti} = Canister pressure after charging with helium, mm Hg absolute
P_t = Canister pressure after sampling but prior to pressurization, mm Hg absolute
P_{tf} = Final canister pressure after pressurization, mm Hg absolute
m = Slope of the regression line of concentration vs. instrument response
b = y- intercept of the regression line of concentration vs. instrument response

12.2 CO Concentration in the canister or bag.

$$C = A / R * (P_{tf}) / (P_t - P_{ti}) \qquad \text{Eq. 3}$$

The pressure terms in Eq. 3 apply to CO concentrations in samples collected in canisters only.

You may use the following alternative equation when using a linear regression factor from the initial calibration curve as described in Section 10.4.

$$C = ((A-b)/m) * (P_{tf}) / (P_t - P_{ti}) \qquad \text{Eq. 4}$$

13.0 Method Performance [Reserved]

14.0 Pollution Prevention

The venting of gases from analytical instruments used in the method does not result in any quantifiable release of ambient air pollutants. Emissions are minimized by limiting purge and sample time.

15.0 Waste Management

The method does not produce significant waste. Disposable instrument parts such as filters or carbon can be landfilled in accordance with facility protocols. These components are replaced infrequently in accordance with manufacturer requirements.

16.0 References

1. *DETERMINATION OF CARBON MONOXIDE EMISSIONS FROM STATIONARY SOURCES, Method 10B, 40 Code of Federal Regulations, Part 60, Standards of*

Performance for New Stationary Sources, Appendix A-7.

2. *DETERMINATION OF GASEOUS NONMETHANE ORGANIC EMISSIONS AS CARBON, Method 25, 40 Code of Federal Regulations, Part 60, Standards of Performance for New Stationary Sources, Appendix A-7.*

17.0 Tables, Diagrams, Flowcharts and Validation Data [Reserved]

------ End of Method ----