Alternative Test Method and Procedure Application – Field Determination of Carbon Monoxide Concentration in Landfill Gas Extraction Wells

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The following 5 sections provide the reasons for the request for an alternative procedure for landfill gas monitoring at extraction wells, the contacts at EPA, the technical liaison for industry, a detailed outline of the proposed method and a justification supporting it.

I. Deficiencies of Applying EPA Method 10 to the Field Testing of Raw Landfill Gas

EPA Method 10 is a field method principally developed for measuring carbon monoxide (CO) emissions from stationary source combustion units by means of extracting continuous samples from an exhaust stack.[1] Although the method is considered versatile by EPA because it is performance based, landfills and the extraction wells on which the measurement for CO is to occur, are not the same, either physically or in function, as combustion sources. They are so different that demonstrably, for the following reasons, EPA Method 10 is not suitable for field or laboratory testing of CO concentrations in raw landfill gas:

1) The gas composition of stationary source combustion emissions from continuous samples extracted from exhaust stacks is significantly different than the gas composition of raw landfill gas extracted from landfill wellheads, and these differences impact instrument adaptability. The volumetric percentage of carbon dioxide (CO_2) in a combustion stack, for example, is less than half the typical concentration of CO_2 present in raw landfill gas. These differences influence the instruments available to obtain analytical measurements.[2]

2) Trace compounds largely are oxidized in combustion stacks but not in landfill gas, altering the chemical makeup of the gas being measured and consequently the interferences the analyzer experiences.[3] Instruments designed for combustion sources may have different responses in raw landfill gas applications, and no instrument is universally adaptable without undergoing modification.

3) The presence of a vacuum on landfill wellheads significantly alters the sampling method compared with combustion stacks. Sampling of combustion stacks is performed by inserting a probe into the gas flow stream of the stack. This cannot be accomplished with

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[1] *See* "Method 10—Determination of Carbon Monoxide Emissions from Stationary Sources (Instrumental Analyzer Procedure)", 81 Fed. Reg. 59,800 (Aug. 30, 2016).

[2] Instruments using NDIR, FTIR, and GC technology rely on peak separation, which is fundamentally different for the gases present in combustion stacks compared with landfill wellheads. Higher concentrations result in larger CO_2 response peaks that can obscure those from CO; the difference can be orders of magnitude. While this problem can be overcome, it requires substantial testing and instrument adjustment (filters, carrier gas flow adjustment, etc).

[3] The altered chemical makeup is readily apparent regarding the impact of gas interference. Nitrogen dioxide is found in combustion gas but does not occur in raw landfill gas. Similarly, hydrogen can be found in landfills but is not common in combustion exhaust stacks. Instruments designed to address one interference are not necessarily able to accommodate another.

landfill wellheads. Each well operates with negative pressure that prohibits insertion of a probe and sample traversing, as required by the direct measurement specifications of EPA Method 10.

II. Names, Addresses, and E-Mails for Responsible EPA Regional Office Contacts

Name	Address	E-mail
Jason Dewees	Emission Measurement Center Mail Code E143–02 Office of Air Quality Planning and Standards U.S. Environmental Protection Agency Research Triangle Park, North Carolina 27711	Dewees.jason@epa.gov
Kim Garnett	Emission Measurement Center Mail Code: E143-02 Office of Air Quality Planning and Standards U.S. Environmental Protection Agency Research Triangle Park, NC 27711	Garnett.kim@Epa.gov
Andy Sheppard	Sector Policies and Programs Division Mail Code: E143-03 Office of Air Quality Planning and Standards U.S. Environmental Protection Agency Research Triangle Park, NC 27711	Sheppard.andrew@Epa.gov
Robin Dunkins	Sector Policies and Programs Division Mail Code: E143-03 Office of Air Quality Planning and Standards U.S. Environmental Protection Agency Research Triangle Park, NC 27711	Dunkins.robin@Epa.gov

III. Requestor Name, Address, Telephone Number, and E-Mail Address

Name	Address	Telephone Number	E-mail
Amy Banister	Waste Management 1021 Main St. Office 536 Houston, TX 77002	713-328-7340	abaniste@wm.com

IV. Alternative Test Method and Procedure

The following alternative test method and procedure, submitted for agency review and approval, follows the format guidelines developed by the Environmental Monitoring Management Council (GD-45).

FIELD DETERMINATION OF CARBON MONOXIDE CONCENTRATION IN LANDFILL GAS EXTRACTION WELLS

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.	Sensitivity
CO	630-08-0	<2% of Instrument Span

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) for each extraction well 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, and to establish the veracity of a measurement above 1,000 ppmv. To meet this objective, the use of certified standard gases and industry standard measurement system performance tests are required.

2.0 Summary of Method

In this method, a landfill gas sample is collected from each extraction well subject to enhanced monitoring through existing monitoring ports and analyzed using an instrument that continuously measures the concentration of CO. The performance requirements of this method must be met to validate the data.

3.0 Definitions

3.1 *Instrument Error* means the absolute difference between the certified concentration of a standard gas and the measured concentration of the same gas when it is introduced into the gas analyzer divided by the Instrument Span.

3.2 *Certified Standard Gas* means 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.

3.2.1 *Low-Level Gas* means a certified standard gas with a concentration that is at least 20 percent less than the 100 ppmv target threshold.

3.2.1.1 This gas may contain zero CO (less than 1 ppmv).

3.2.1.2 Ambient air may be used for this purpose if it is not near a known source of CO e.g. within 50 feet of a combustion device or operating vehicle.

3.2.2 *High-Level Gas* means a certified standard gas with a concentration that is at least 20 percent greater than the 1,000 ppmv target threshold.

3.3 *Instrument Span* means the upper limit of the gas analyzer's operation or function.

3.3.1 Set by the manufacturer based on the CO electrochemical cell sensor specification or limit or,

3.3.2 For other types of instruments, set in practice as 100% of the instrument analytical range

3.4 *Data Recorder* means a record of the concentration reported by the gas analyzer. The record can be stored digitally or in written format but must contain, at a minimum, the date and time of sampling, a unique well ID and the concentration. A corresponding calibration record should include the date and time of the most recent passing calibration validation test. The calibration record can be a separate data file or paper record.

3.5 *Drift* means the difference between instrument error checks at both a low-level (less than 100 ppmv) and high-level gas concentration (greater than 1,000 ppmv) conducted at the start of a monitoring event and at the end of the enhanced monitoring event for a facility (no less than weekly).

3.5.1 A Drift check is dependent on sampling conditions but no less than the minimum monitoring frequency established for sampling the extraction wells at a site following the requirements of 40 C.F.R. Part 63, Subpart AAAA.

3.5.2 A Drift check is necessary if the gas analyzer does not return to zero ±20 ppmv within 5 times the response time after landfill gas is removed from it.

3.5.3 A Drift check is necessary if any filters or other such devices on the sampling apparatus indicate that they require replacement or abnormal conditions (e.g. excessive liquids) occurred during sampling.

3.6 *Gas Analyzer* means the equipment that senses the CO in landfill gas and generates an output proportional to its concentration.

3.7 *Response Time* means the time it takes the gas analyzer to respond to a change in gas concentration after it is introduced to the instrument.

3.8 *Sampling Apparatus* means the wellhead connection fitting, sample hoses, filters, or any similar device between the gas analyzer and the landfill gas wellhead.

4.0 Interferences

Portable landfill gas analyzers that use CO electrochemical cells can experience cross interference with hydrogen (H_2) and hydrogen sulfide (H_2S), both of which can be present in raw landfill gas. These types of analyzers should be equipped with a H_2 compensated CO sensor that measures and reduces H_2 interference to less than 2.5% of the standard gas concentration applied by design and/or mathematically up to a minimum of 10,000 ppmv H_2 concentration in landfill gas. Alternatively, the instrument can address interference of H_2 on the CO sensor by other appropriate means provided that the interference response is no greater than 2.5% of the standard gas concentration.

In addition, electrochemical type analyzers should be equipped with physical filtration (internal and/or external) and/or an internal carbon filter to remove H_2S. The removal of H_2S less than 1,000 ppmv by these filters will not significantly alter the concentration of any other measured compound because the volume removed is less than the accuracy limits of the instrument.

Trace amounts of ammonia (NH3) may be present in landfill gas; however, it does not affect the electrochemical CO cell at the levels typically observed in landfill gas. Finally, the concentrations of methane (CH_4), carbon dioxide (CO_2), oxygen (O_2), and nitrogen (N_2) typically found in landfill gas do not affect the CO cell to any significant amount.

Electrochemical type analyzers may also be equipped with an H_2 sensor that acts as an indicator of H_2 concentration intensity providing an alarm or other similar notification that concentrations have exceeded or are approaching the design limits of the instrument compensation.

To minimize the potential for damage of the sensors, liquid should be prevented from entering the analyzer by a water trap or similar filter. These devices do not remove CO_2. Therefore, no compensation is required.

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 e.g. accumulating in well vaults. Landfill gas is also considered a simple asphyxiant that could displace ambient air under those same conditions and may contain trace compounds that if inhaled could cause harm. In addition, this method requires working on a landfill that could have moving equipment and vehicles in proximity to the extraction wells.

Among other precautions include no smoking, and other safety recommendations published in the gas 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, a continuous field sampling approach as described in this section is acceptable. Sites may choose to use another method, as accepted by EPA, on any given well subject to the enhanced monitoring requirement during any single monitoring event and may opt to switch the method used for those wells in subsequent events.

6.1 *Field Sampling*

Use of any equipment and supplies in the sampling system (Figure 1) meeting the following specifications is acceptable:

6.1.1 *Sample Apparatus Hose Fitting*. The sample hose fitting should connect to the wellhead sample fitting firmly and without leaks. Gaskets, O-rings, or other such seals should be replaced if damaged prior to collecting the sample

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

6.1.3 *Breakthrough Indicator Carbon Filter or Equivalent Device*. The external breakthrough indicator and carbon filter or equivalent device that removes H_2S and indicates breakthrough by changing color[4] should be replaced when the

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[4] Indicator may be a separate device from the filter media or a single integrated component.

media has changed color and regularly based on manufacturer specifications or if conditions exceed the interference limits noted by the manufacturer. This is optional for instruments that are not impacted by interference of H_2S.

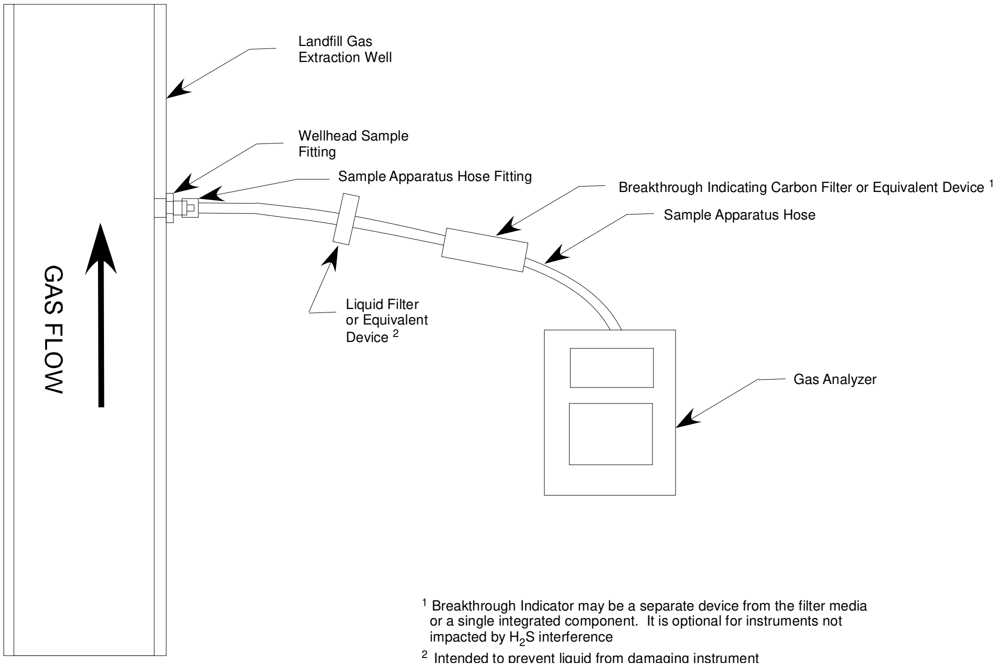
6.1.4 *Liquid Filter or Equivalent Device*. The liquid filter should be replaced regularly based on manufacturer specifications and if abnormal conditions are observed (i.e. excessive moisture). This is intended to prevent liquid from damaging the analyzer but is not required to dry the gas or otherwise remove water vapor.

6.1.5 *Gas Analyzer*. An instrument that measures CO in the gas stream and meets the applicable specifications in Section 13.0. Analyzers operating on other principles may also be used provided the performance criteria in Section 13.0 are met.

6.1.5.1 The gas analyzer should be equipped with a vacuum pump suitable to pull against the wellhead vacuum and to transport gas from the sample point to the analyzer.

6.1.5.2 Internal H_2S filters or other internal systems to address interference are considered part of the gas analyzer and do not require field replacement.

Figure 1 - Sampling System



[1] Breakthrough Indicator may be a separate device from the filter media or a single integrated component. It is optional for instruments not impacted by H_2S interference

[2] Intended to prevent liquid from damaging instrument

7.0 Reagents and Standards

7.1 *Certified Standard Gas. What instrument calibration verification gases do I need?*

Use 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 N.I.S.T weights and/or N.I.S.T Gas Mixture reference materials.

7.1.1 *Low-Level Gas* means a certified standard gas with a concentration that is at least 20 percent less than the 100 ppmv target threshold. This gas may contain zero CO (less than 1 ppmv). Ambient air may be used for this purpose if it is not near a known source of CO e.g. within 50 feet of a combustion device or operating vehicle.

7.1.2 *High-Level Gas* means a certified standard gas with a concentration that is at least 20 percent greater than the 1,000 ppmv target threshold.

7.2 *Interference Check.*

Instrument preventative maintenance, performance inspection and testing must be carried out and documented annually, at a minimum. It should be completed by the manufacturer or a manufacturer designated facility.

For Manufacturers:

The manufacturer should undertake reasonable verification that each make/model CO cell that is used in the instrument's construction conforms with the supplier's specifications. Each individual cell need not be tested in this process.

At a minimum, the manufacturer should:

7.2.1 Select one cell from a batch of cells of the same model and make obtained from a CO cell supplier.

7.2.1.1 Introduce a standard to the selected CO cell at a low, mid, and high concentration within the cell span established by the CO cell supplier.

7.2.1.2 Determine the best fit line between the standard gases. The line should have a R-squared greater than or equal to 0.975 to be considered linear.

7.2.2 Verify the linearity of a specific model/make of CO cell any time a new model/make CO cell is obtained from a supplier or the supplier has changed the specifications of the CO cell.

Manufacturer Documentation

The instrument manufacturer should provide or make available information as follows[5]:

7.2.3 A statement pertaining to the instrument span based on the CO cell supplier's specification.

7.2.4 A statement that the linearity of the CO cell used in the instrument has been verified.

7.2.5 A statement of the interference compensation limit.

7.2.6 A statement certifying that annual instrument performance checks have been conducted and the instrument passes those checks.

8.0 Sample Collection, Preservation and Storage

8.1 Sampling Site and Sampling Points.

Sampling should occur at landfill gas well sampling ports installed into the well casing or wellhead such that gas can be freely extracted when a sample hose is attached. The fitting should allow for the secure connection of the sampling hose.

8.2 *Initial Measurement System Verification Tests. What initial performance criteria must my analyzer meet before I begin collecting samples?*

Before measuring a field sample, perform the following procedures:

8.2.1 Charge instrument battery, if necessary.
8.2.2 Check that the instrument has a valid annual maintenance check certification, if expired, conduct maintenance as per manufacturer procedures.
8.2.3 Check if the scrubbing agent indicates a color change, replace if necessary.
8.2.4 Check that the particulate filter is in place and shows no liquid, replace if necessary.
8.2.5 *Check the calibration gas certificate.*

Obtain a certificate or other similar proof from the gas manufacturer documenting the quality of the gas including a statement that the gas has an analytical uncertainty of at least +/- 2%. Confirm that the manufacturer documentation is current, and the gas has not expired. This documentation should be available on-site for inspection.

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[5] Note that this documentation is intended for the instrument user and is not a required submittal to EPA or an enforceable condition.

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

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 analyzer in accordance with manufacturer recommendations or if conditions indicate that they should be replaced.

1) Apply a calibration gas that contains no oxygen to the meter through the sample apparatus.
2) Close the valve on the calibration gas while the pump is activated.
3) 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.

8.3 Weekly System Verification Tests. What weekly performance criteria must my analyzer meet before I begin collecting samples?

8.3.1 *Measurement System Response Time.*

Observe the time required to achieve 90 percent of the applied standard concentration for both the low-level and high-level standard gases. The longer interval is the response time.

8.3.1.1 The response time test should be conducted at the beginning of a sampling event performed as required by 40 C.F.R. Part 63, Subpart AAAA or if components on the sampling apparatus have changed e.g. liquid or carbon filter or similar device in-line between the extraction well and analyzer replacement.

8.3.1.2 Introduce the high-level standard gas upstream of all sample conditioning components. Record the time it takes for the measured concentration to increase to a value that is at least 90 percent or within 0.5 ppmv (whichever is less restrictive) of the applied standard concentration. Continue to apply the gas standard until it has reached a final, stable value.

8.3.1.3 Next, introduce the low-level gas and record the time required for the concentration response to decrease to a value that is within 5.0 percent or 0.5 ppmv (whichever is less restrictive) of the low-range gas concentration.

8.3.1.4 From this data, calculate the measurement system response time.

8.3.2 *Sensor Stability Check*

8.3.2.1 Introduce the high-level standard gas upstream of all sample conditioning components. Continue to observe the gas concentration reading for up to 300 seconds. Record the value at 240 seconds and again at 300 seconds.

8.3.2.2 The difference between these two values should be less than +/- 2.5%.

8.3.2.3 Use Equation 1 in Section 12.2 to determine sensor stability.

8.3.3 *Instrument Error Test. How do I confirm my analyzer calibration is correct?*

After assembling and preparing the sampling system and analyzer, you must conduct a 2-point instrument error test before the first run and again after any failed drift test. Introduce the low-level and high-level standard gases sequentially. The standard gas must be introduced upstream of all sample conditioning components.

8.3.3.1 Record the analyzer's response to each standard gas on a form like Table 1. An electronic equivalent method of recording the data tabulated in Table 1 is acceptable. For each standard gas, calculate the instrument error using Equation 2 in Section 12.3. The instrument error specification in Section 13.1 must be met for the low-level and high-level standard gases. If the instrument error specification is not met, take corrective action, and repeat the test until an acceptable 2-point instrument error test is achieved.

8.3.4 *Drift Assessment Initial Record.*

Record the analyzer's response to each standard gas on a form like Table 2 as the initial value. An electronic equivalent method of recording the data tabulated in Table 2 is acceptable.

8.4 *Sample Collection.*

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

8.4.2 Purge the system for at least two times the response time before starting the measurement.

8.4.3 If the measurement is not stable[6], repeat the purge procedure. Continue the purge and sample process until a stable measurement is obtained. If a stable measurement cannot be obtained after 3 times, inspect the sample hose and wellhead, replace any components as necessary and try the procedure again.

8.4.4 After the purge, begin sampling. Maintain pump operation and after 1-minute store a record of the concentration. Continue with sampling for another minute. Repeat until a total of 5 records have been stored.

8.4.5 Average the 5 stored records to establish the concentration for the well.

8.4.6 If the sensor response exceeded 80% of instrument range, conduct an Instrument Error Check and determine drift using the procedures in Section 8.5.

8.4.7 If the well results are the last test for the week, conduct an Instrument Error Check and determine drift using the procedures in Section 8.5.

8.5 Drift Assessment. How do I confirm that the samples I collect are valid?

Each week, or more frequently based on analyzer performance, conduct a drift check. Note that for all drift checks, the low-level gas may be injected first and the high-level standard gas last, or vice-versa. A failed drift test will invalidate all samples after the last passed test.

8.5.1 If the drift check did not pass, then the sample is invalid. Diagnose and fix the problem and pass another instrument error test (Section 8.3.3) before repeating the sampling event. Record the results.

8.5.2 Calculate the low-level and high-level standard gas drift, using Equation 3 in Section 12.4. If the low-level and high-level standard gas instrument error checks are passed, but the low-level or high-level standard gas drift exceeds the specification in Section 13.2, the sample data are valid, but an instrument error check must be performed and passed before any more samples are analyzed.

8.5.3 Record the analyzer's response to each standard gas on a form like Table 2 as the initial value. An electronic equivalent method of recording the data tabulated in Table 2 is acceptable.

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[6] A fluctuation greater than 50 ppm over a period of 30 seconds.

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. All the QC data, along with the sample data, must be documented.

QA/QC specification	Acceptance criteria	Checking frequency
Analyzer resolution or sensitivity	<=2% of Instrument Span	Manufacturer design.
Standard gas validity	Valid documentation required with an uncertainty ≤2.0% of tag value	
Data resolution	≤0.5% of full-scale range	Manufacturer design
Instrument error	Within ±2.0 percent of the instrument span of the analyzer for the low-level, and high-level standard gases	Once for each sampling event performed as required 40 C.F.R. Part 63, Subpart AAAA and after a failed drift test
System response time	Determines minimum sampling time per point	Once for each sampling event performed as required 40 C.F.R. Part 63, Subpart AAAA or after replacing any component on the sampling apparatus
Drift	≤3.0% of instrument span for low-level and high-level gases	Once for each sampling event performed as required 40 C.F.R. Part 63, Subpart AAAA or if conditions warrant
Purge time	≥2 times system response time	Each well

10.0 Calibration and Standardization

How do I confirm my analyzer calibration is correct?

After assembling and preparing the sampling system and analyzer, conduct a 2-point instrument error test before the first sample and again after any failed drift test as follows.

10.1 Introduce the low-level and high-level certified standard gases sequentially.

10.2 Record the analyzer's response to each certified standard gas on a form like Table-1.

10.2.1 An electronic record providing information like Table-1 is an acceptable alternative.

10.3 For each certified standard gas, calculate the instrument error using Equation-1 in Section 12. The instrument error specification in Section 13 must be met for the low-level and high-level gases. If the instrument error specification is not met, take corrective action, and repeat the test until an acceptable 2-point verification of calibration is achieved.

10.4 Note the manufacturer's certified accuracy of the standard gases used in the testing as part of the test report.

10.4.1 The analytical uncertainty must be +/- 2% or less and be verified by direct comparison to calibration standards traceable to N.I.S.T weights and/or N.I.S.T Gas Mixture reference materials.

11.0 Analytical Procedures

Because sample collection and analysis are performed together (*See* Section 8), additional discussion of the analytical procedure is not necessary.

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:

ACE = Instrument error, percent of instrument span.

C_{240} = Concentration at 240 seconds

C_{300} = Concentration at 300 seconds

C_{Dir} = Measured concentration of a standard gas (low or high), ppmv.

C_V = Manufacturer certified concentration of a standard gas (low or high), ppmv.

IS = Instrument span, ppmv.

D = Drift assessment, percent of instrument span.

SB_i = Initial Instrument Error, percent of instrument span.

SB_{final} = Final Instrument Error, percent of instrument span.

12.2 *Sensor Stability.*

$$(C_{240} – C_{300}) / C_{240} \times 100 = \text{Sensor Stability} \qquad \text{Eq. 1}$$

12.3 *Instrument Error.*

$$ACE = (C_{Dir}-C_V)/IS \times 100 \qquad \text{Eq. 2}$$

12.4 *Drift Assessment.*

$$D = \left| SB_{final} - SB_i \right| \qquad \text{Eq. 3}$$

13.0 Method Performance

The specifications for instrument error, and drift are as follows:

13.1 Instrument Error. This specification is applicable to the analyzer instrument error test described in Section 8.2.3. At each standard gas level (low and high) the instrument error must be within ±2.0 percent of the instrument span.

13.2 Drift. At no less than the minimum monitoring frequency established for the extraction wells at a site following the requirements of 40 C.F.R. Part 63, Subpart AAAA, the low-level and high-level standard gas drift must be less than or equal to 3.0 percent of the instrument span.

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) National Institute of Standards and Technology (N.I.S.T.), U.S. Department of Commerce

17.0 Tables, Diagrams, Flowcharts and Validation Data

Table – 1 Instrument Error Test

Source Identification: ________________________ Analyzer Model No.: _________________________
Test personnel: _____________________________ Serial No.: __________________________________
Date: ________________ Instrument Span (IS): _________________
Time ________________

	Manufacturer Certified Cylinder Value (A) Units ______	Analyzer Response (B) Units______	Absolute Difference (A-B) Units ______	Instrument Error (Percent of Instrument Span) (A-B)/IS x 100 %
Low Level Standard				
High Level Standard				

Table – 2 Instrument Drift Test

Source Identification: ________________________ Analyzer Model No.: _________________________
Test personnel: _____________________________ Serial No.: __________________________________
Instrument Span (IS): _________________

	Analyzer Response Initial (A) Units ______	Analyzer Response Final (B) Units______	Difference (A-B) Units ______	Drift (A-B)/A x 100 %
Date:				
Time				
Low Level Standard				
High Level Standard				

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

V. Detailed Justification for Alternative Testing Procedure

The following demonstrates that current monitoring instruments and procedures practiced at landfills provide equivalent results with those obtained using EPA Method 10 and would not impact the stringency of the NESHAP final rule or impede EPA's policy of ensuring compliance with environmental and safety standards at municipal solid waste landfills.

Analytical measurement of landfill gas for the purpose of compliance with regulatory requirements has been occurring for more than 20 years. These measurements take place at individual landfill gas extraction wells operated under vacuum in accordance with 40 C.F.R. Part 60, Subparts WWW, Cc, Cf, or XXX. Sample locations for landfill gas extraction wells are unlike those typically found at sources implementing EPA Method 10 for the measurement of CO, which are most commonly positive pressure combustion emission stacks.

In contrast with combustion source stacks, sampling at landfill gas extraction wells occurs at small ports. In most cases, ¼ inch fittings are installed for sampling on 2 to 3-inch manufactured wellheads or into the typical 6 to 8 inch well casings commonly used at landfills. These ¼ inch ports are too small to insert a typical emissions monitoring probe. Consequently, no probe insertion or sample traversing typically used on combustion source stacks is possible without significant modifications. And even if modifications were possible,[7] sample extraction under vacuum[8] would cause air dilution impacting the validity of the sample. In addition, these small ports do not protrude into the gas stream nor do they allow for the insertion of probes into the well casing because many have check valve fittings to prevent air intrusion. To the extent that a typical sample probe necessary to extract a sample in the manner specified by EPA Method 10 is inserted (although this is not possible to do so), it would allow air to enter the well thereby diluting any sample. The vacuum in the well would suck in ambient air past the sample probe because they typically are not sealed. Furthermore, there is no reason to expect that gas composition will vary significantly across the small 6 to 8 inch well casing size. Flow is typically turbulent and there is no mechanism within the landfill to cause disassociation of the mixture. Therefore, the collection of a gas sample from a landfill extraction well is limited to a simple hose connection.

It is important to note that during OTM-38 development, CO electrochemical sensors were determined to be linear over the measurement range for which they were designed. Portable landfill gas analyzers, which utilize this same technology, are similarly linear. There is no substantive difference in CO sensor technology or the CO sensor response for instruments used in the development of OTM-38 or landfill gas analyzers.

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[7] A minimum 1-inch sample port would be required to insert a probe. Most wellheads are either 2 or 3 inches in diameter. The installation of a 1-inch port in a 2-inch wellhead is all but impossible without the complete replacement of the wellhead.

[8] The gas collection systems installed at landfills generate vacuum to extract gas generated from waste decomposition.

Linearity test data for the GEM 5000 instrument is provided in Appendix 1. Seven instruments were tested using certified CO concentrations of 0 ppmv, 504 ppmv and 915 ppmv. The instrument CO sensor cell span is 2000 ppmv. The 915 ppmv concentration standard also contained 851 ppmv hydrogen to ascertain the interference impact on linearity. Table V-1 shows the average and standard deviation of the Instrument Error percentage at each concentration standard. Instrument Error was determined by subtracting the instrument response from the calibration standard concentration and dividing that by the instrument span (2,000 ppmv). The instrument span was based on the CO electrochemical cell specification.

Table V - 1

Certified Standard CO Concentration (ppmv)	Average % Error as a Function of Instrument Span (%)	Standard Deviation (%)
0	0.002	0.028
504	-0.046	0.229
915	0.019	0.417

The average % error as a function of instrument span is -0.008%. This is below both the sensitivity threshold (2% of full-scale range) and allowable analyzer calibration error (2% of calibration span) specified in EPA Method 10. Figure V-1 shows that the CO cell instrument error is less than ±1% at 1 standard deviation of the mean at the instrument span (2,000 ppmv) further demonstrating that the CO electrochemical cells adhere to the performance specifications in EPA Method 10.

Figure V - 1

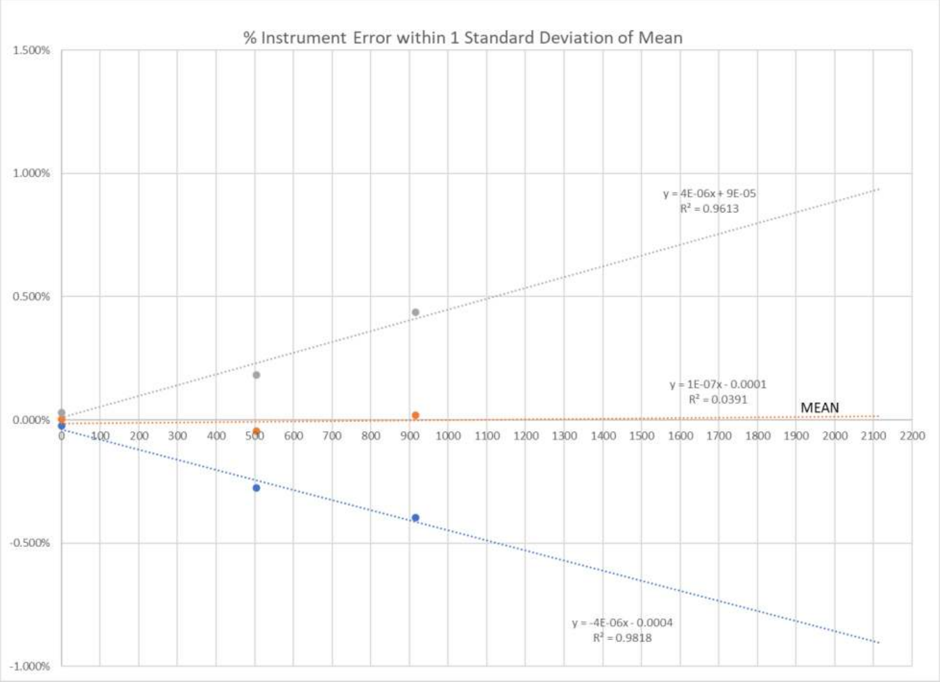

Figure V - 2 Linearity Instrument Response

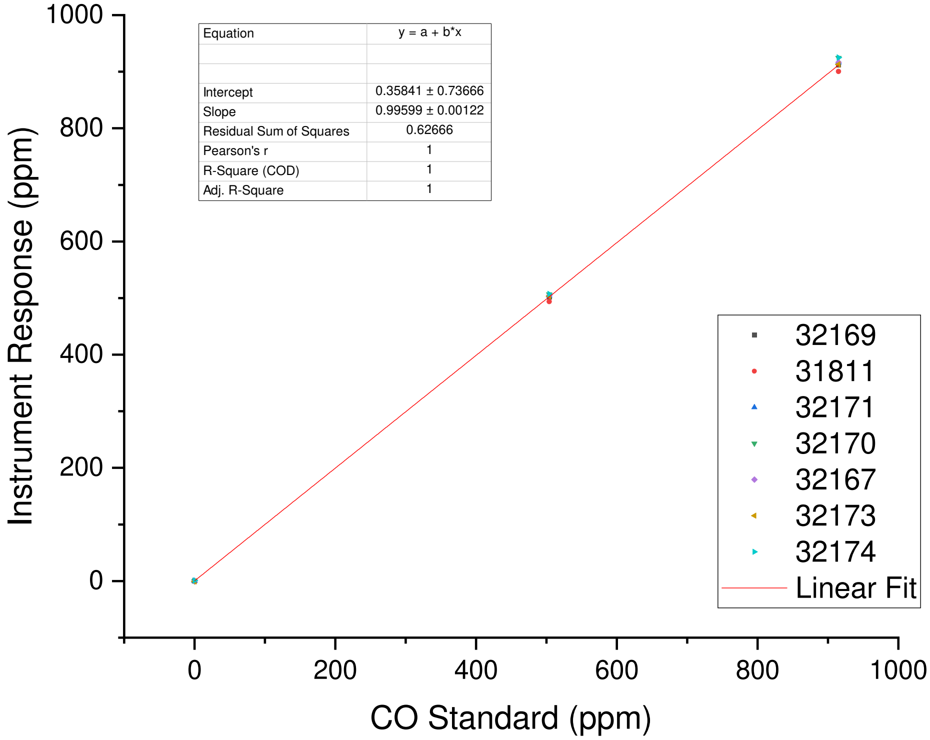

Figure V-2 illustrates the response of the CO cells at the three calibration standards. The best fit line of the data establishes a slope of 0.99599 ± 0.00122 and an intercept of 0.35841 ± 0.73666 with R-squared equal to one (1). Therefore, the proportion of the variance of actual instrument response based on the applied standard is near 100%. In other words, the line represents a good fit of the data. In addition, the mean absolute difference for all sensor data points is 3.1 +/- 4.2 ppm which is below 2.5% of the span gas[9] identified in OTM-38 as the threshold the instrument must meet to qualify as linear.

The sensor data are undeniably linear and, as noted in the OTM-38 development reports, the output remains linear over time even though sensitivity declines[10]. Consequently, this data demonstrates that electrochemical cell technology can be considered viable for landfill gas analyzers.

Consequently, at 100 ppmv, the analyzer would be expected to measure a CO concentration of 99.96 ppmv and at 1,000 ppmv the unit would measure 996.35 ppmv (0.002% and 0.18% of

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[9] Span gas used to develop the landfill gas analyzer curve was 915 ppm although the instrument has a measurement span of 2000 ppm.

[10] A function of the underlying physics related to the sensors.

instrument span respectively). Note that the test deviations at higher CO concentrations were likely the result of hydrogen in the standard mixture, but the unit still performed within the specified performance requirement.

A key limitation of current landfill gas analyzers measuring CO is interference of, specifically hydrogen. EPA allows the use of electrochemical cells,[11] and the current analyzers use this technology, but EPA Method 10 requires a demonstration that the impacts be addressed. The instruments in use at landfills compensate the CO sensor using a mathematical algorithm providing a stable CO response up to 1% hydrogen. Further, the analyzers provide a notification that hydrogen concentrations are approaching the design limits of the instrument or are above 1%. The notifications provide the instrument user a mechanism to respond to those conditions.

The documentation provided indicates that the instrument compensates the results within the acceptable performance limits of the instrument (Appendix 2). Fourteen (14) hydrogen compensated CO cells that are used in the GEM 5000 analyzer were tested. Each cell was exposed to 2,000 ppmv, 5,000 ppmv and 10,000 ppmv hydrogen. This test sought to quantify how the sensor responded to hydrogen and the resultant compensated output. The results show less than 1% cross gas impact on the CO concentration with increasing levels from zero to 1% hydrogen. This indicates that hydrogen impacts the CO cell by increasing amounts as the hydrogen concentration increases but the built-in compensation mitigates those increases. At 2,000 ppmv hydrogen, the cross-sensitivity was approximately -20 ppmv ± 20 ppmv. The cross-sensitivity variability increased to -20 ppmv ± 70 ppmv at 1% hydrogen.

At 100 ppmv CO, the resulting impact would equate to a maximum of 2% of instrument span at 2,000 ppmv hydrogen to approximately 4% at 10,000 ppmv hydrogen. At 1,000 ppmv CO, the resulting impact would equate to a maximum of 0.2% of instrument span at 2,000 ppmv hydrogen to approximately 0.44% at 10,000 ppmv hydrogen. Although the impact of higher hydrogen at lower CO concentrations is more significant than at higher CO concentrations, there is little implication. The 100 ppmv threshold only establishes whether monitoring occurs at a weekly or monthly frequency following the requirements of 40 C.F.R. Part 63, Subpart AAAA. The more significant CO threshold at 1,000 ppmv (significant because a 24-hour notification is required)

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[11] *See* "Frequently Asked Questions (FAQs) for Method 10", U.S. ENVIRONMENTAL PROTECTION AGENCY (Aug. 24, 2016), at https://www.epa.gov/sites/production/files/2016-08/documents/method10_faq.pdf.

> *Q. Does EPA's Method 10 for carbon monoxide (CO) measurements require the use of an NDIR analyzer only, or can an electrochemical CO sensor be used? (This is not explicitly stated in Method 10). Also, is there a minimum measurement range for Method 10?*
>
> A. Yes, an electrochemical analyzer may be used for Method 10. Method 10 refers heavily to Method 7E, which notes that different techniques may be used as long as the performance tests in Section 13 are passed. No minimum measurement range is given for Method 10, since this will depend on the analyzer type used.

would have greater accuracy. Therefore, the hydrogen compensated CO results justify their use and the instrument accuracy is within performance requirements at higher hydrogen concentrations up to the specified instrument limitation.

The other impact of hydrogen is the recovery time (the length of time the sensor takes to return to zero). Sensor recovery results from testing associated with exposure to hydrogen concentrations up to 1% and above are included in Appendix 3.

Spike tests of a hydrogen compensated CO cell to establish the time it took for the sensor to return to zero were conducted. Initially, a 100 ppmv CO standard was introduced to identify the baseline instrument response. This was followed by spiking the cell with 1,000 ppmv hydrogen to confirm that the hydrogen compensation performed as expected. The results showed that the interference was approximately 10 ppmv. This was followed by a 2,000 ppmv hydrogen spike in a 100 ppmv CO mixture. The results showed a 17 ppmv interference response and approximately a 3-minute recovery time. A 20,000 ppmv spike was introduced with a recovery response time measured at approximately 5 minutes. The data shows that even after the introduction of the hydrogen spike, the sensor recovered and showed equivalent results to pre-spike levels.

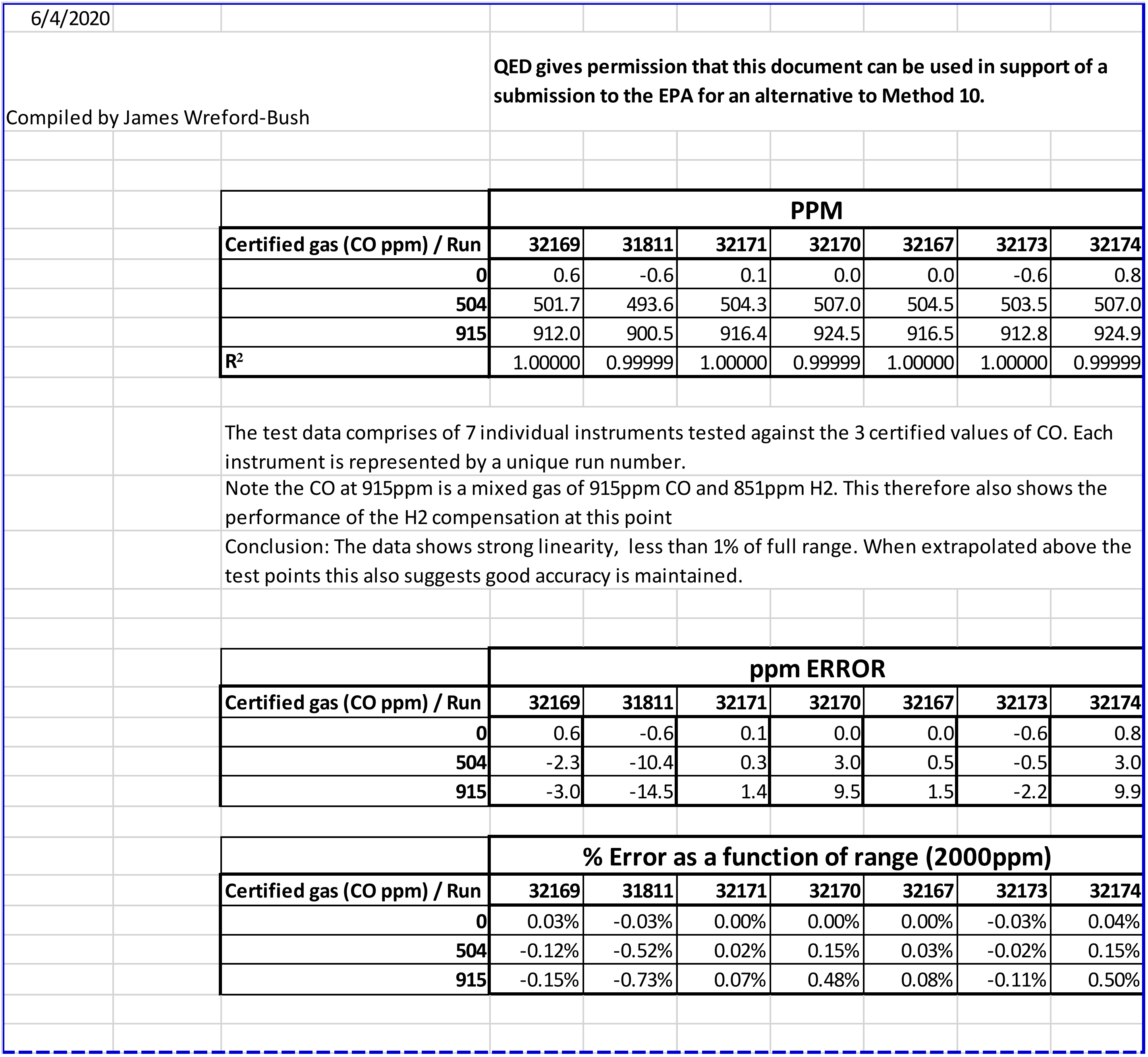
The data shows that hydrogen does influence the CO response, but that the compensation algorithm up to 1% hydrogen keeps the instrument within acceptable norms. Further, to the extent that the unit is exposed to higher concentrations, a warning is provided on the instrument that would allow the user to take corrective measures should conditions warrant. In addition, the alternative method provides a mechanism to conduct additional drift tests to demonstrate that the unit is still performing within the instrument specifications.

As mentioned above, the Solid Waste Working Group researched existing “off the shelf” technology (e.g., FTIR, GC) that follow the procedures and specifications outlined in EPA Method 10 for monitoring CO and determined that none are suitable for raw landfill gas sampling and analysis unless considerable investment or major development is made. Further, none have been demonstrated as viable for portable sampling and analysis of landfill gas at extraction wells in accordance with EPA Method 10.

The gas composition and pressure of those stacks are significantly different than that of raw landfill gas, however, and that difference limits instrument adaptability. For example, the quantity of CO_2 in a combustion stack is nearly half the typical concentration found in raw landfill gas. This impacts analytical measurements that rely on peak separation such as NDIR, FTIR or gas chromatography. Further, the trace compounds have largely been oxidized in combustion stacks, something that has not occurred in landfill gas. This alters the chemical makeup of the gas being measured and consequently the interferences the analyzer experiences. This is readily apparent when looking at the impact on gas interference. NO_2 is found in combustion gas but does not occur in raw landfill gas. Similarly, hydrogen can be found in landfills but is not common in combustion exhaust stacks. Instruments designed to address one interference are not necessarily able to accommodate another. There instruments designed for combustion sources may have different responses in a different gas such as raw landfill gas. No instrument is universally adaptable without undergoing modification. In addition, the presence of vacuum on landfill wellheads significantly alters the sampling method compared with combustion stacks which are performed by inserting a probe into the gas flow stream of the stack. This cannot be accomplished with landfill wellheads. Each well operates with negative pressure that prohibits insertion of a probe and sample traversing as required in EPA's Method 10 direct measurement specifications.

For the above reasons, the procedure and instrument proposed as an alternative to those specified by EPA Method 10 are equivalent and provide results adequate to demonstrate compliance with 40 C.F.R. § 63.1961(a)(5).

APPENDIX 1 Linearity Test Results



6/4/2020

Compiled by James Wreford-Bush

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	PPM						
Certified gas (CO ppm) / Run	**32169**	**31811**	**32171**	**32170**	**32167**	**32173**	**32174**
0	0.6	-0.6	0.1	0.0	0.0	-0.6	0.8
504	501.7	493.6	504.3	507.0	504.5	503.5	507.0
915	912.0	900.5	916.4	924.5	916.5	912.8	924.9
R^2	1.00000	0.99999	1.00000	0.99999	1.00000	1.00000	0.99999

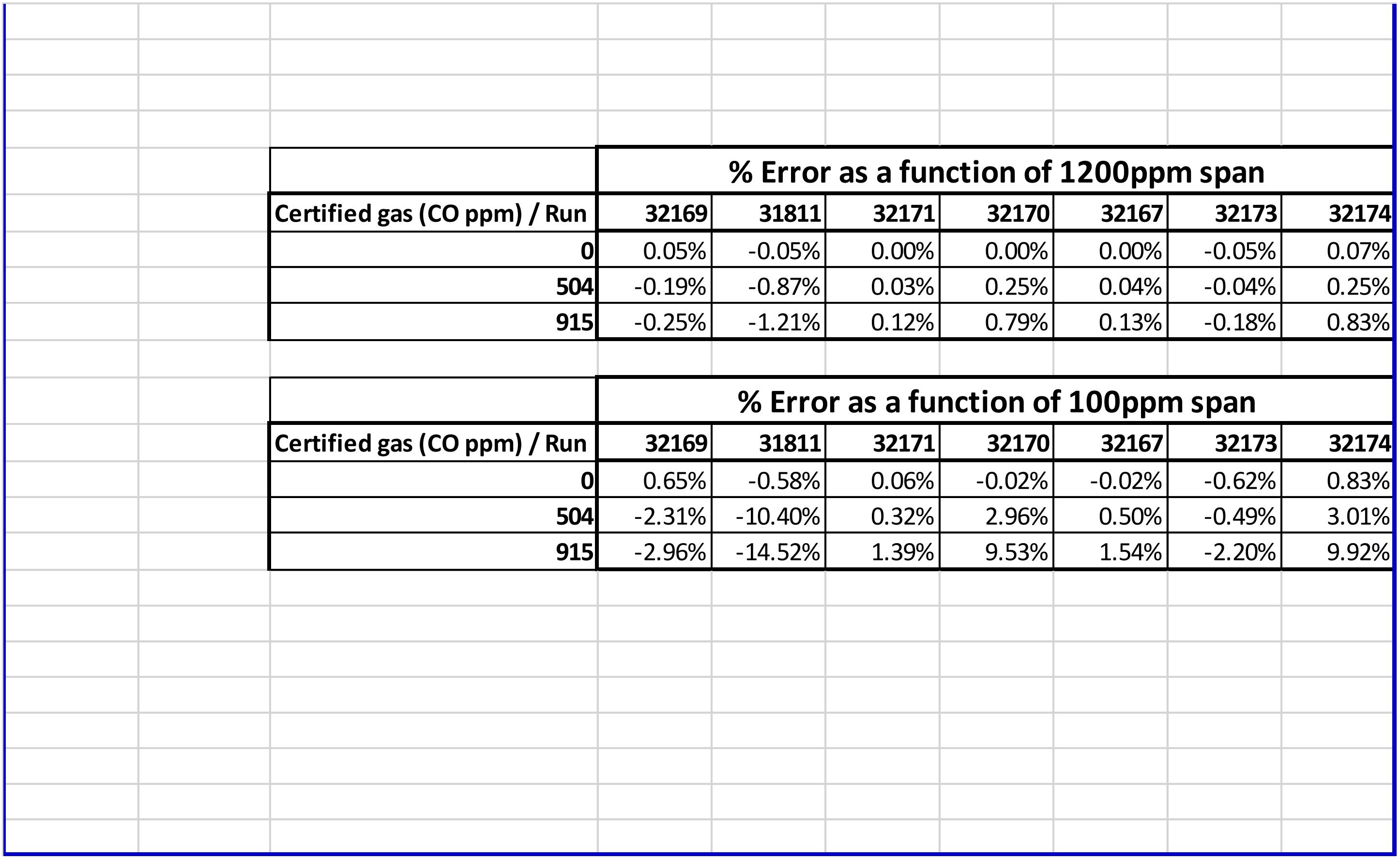
The test data comprises of 7 individual instruments tested against the 3 certified values of CO. Each instrument is represented by a unique run number.

Note the CO at 915ppm is a mixed gas of 915ppm CO and 851ppm H2. This therefore also shows the performance of the H2 compensation at this point

Conclusion: The data shows strong linearity, less than 1% of full range. When extrapolated above the test points this also suggests good accuracy is maintained.

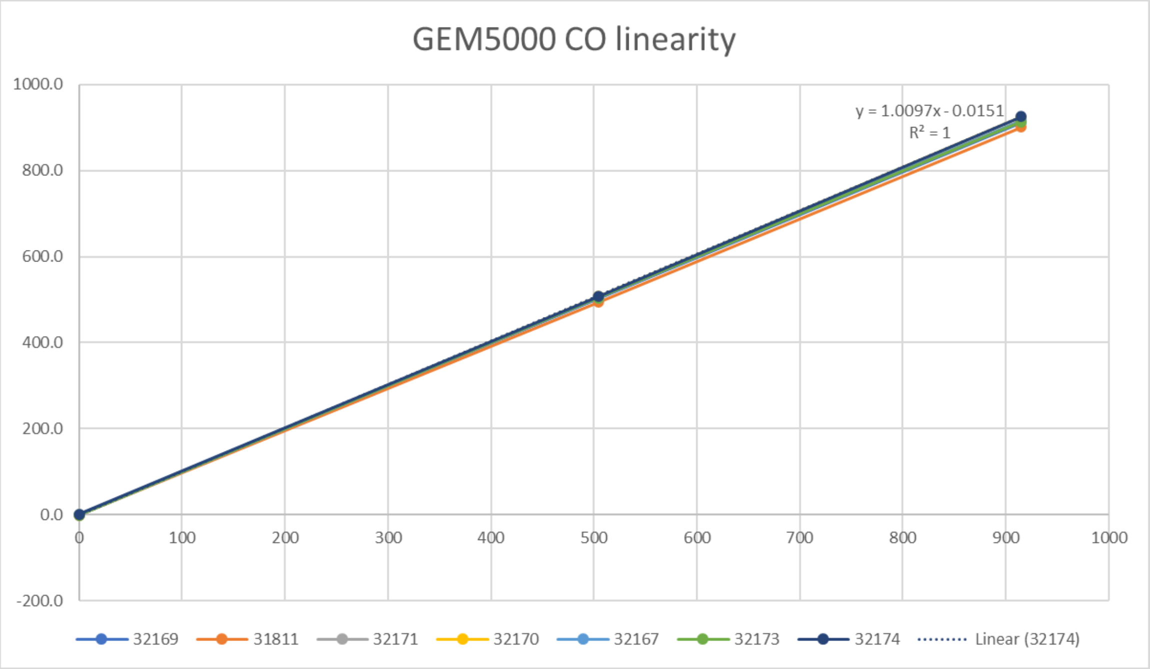
	ppm ERROR						
Certified gas (CO ppm) / Run	**32169**	**31811**	**32171**	**32170**	**32167**	**32173**	**32174**
0	0.6	-0.6	0.1	0.0	0.0	-0.6	0.8
504	-2.3	-10.4	0.3	3.0	0.5	-0.5	3.0
915	-3.0	-14.5	1.4	9.5	1.5	-2.2	9.9

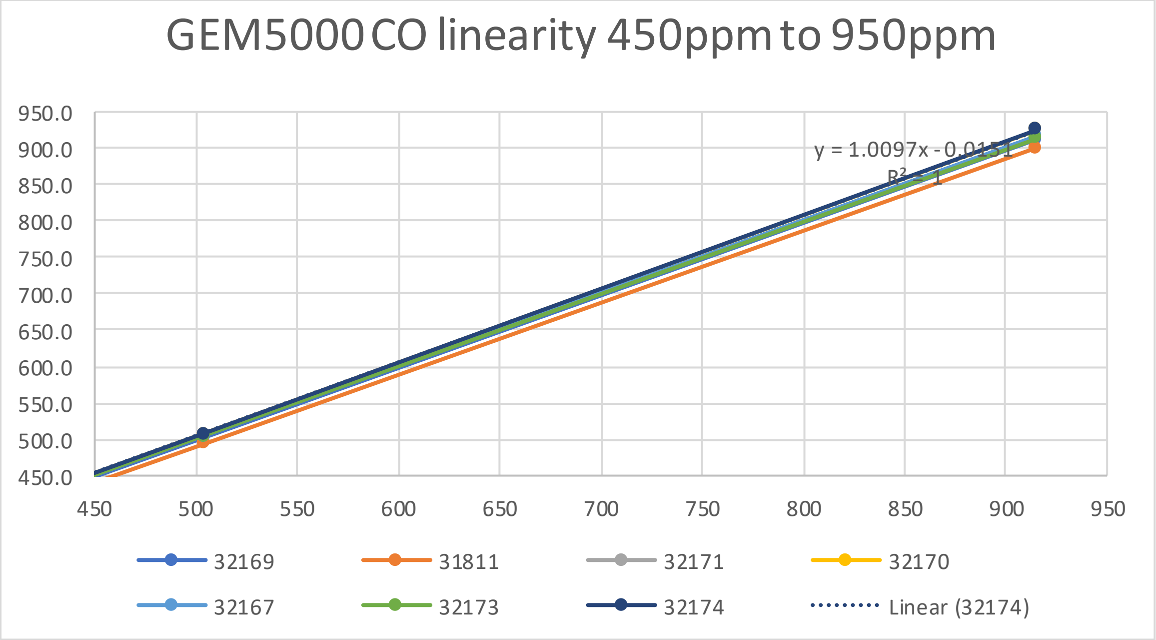
	% Error as a function of range (2000ppm)						
Certified gas (CO ppm) / Run	**32169**	**31811**	**32171**	**32170**	**32167**	**32173**	**32174**
0	0.03%	-0.03%	0.00%	0.00%	0.00%	-0.03%	0.04%
504	-0.12%	-0.52%	0.02%	0.15%	0.03%	-0.02%	0.15%
915	-0.15%	-0.73%	0.07%	0.48%	0.08%	-0.11%	0.50%

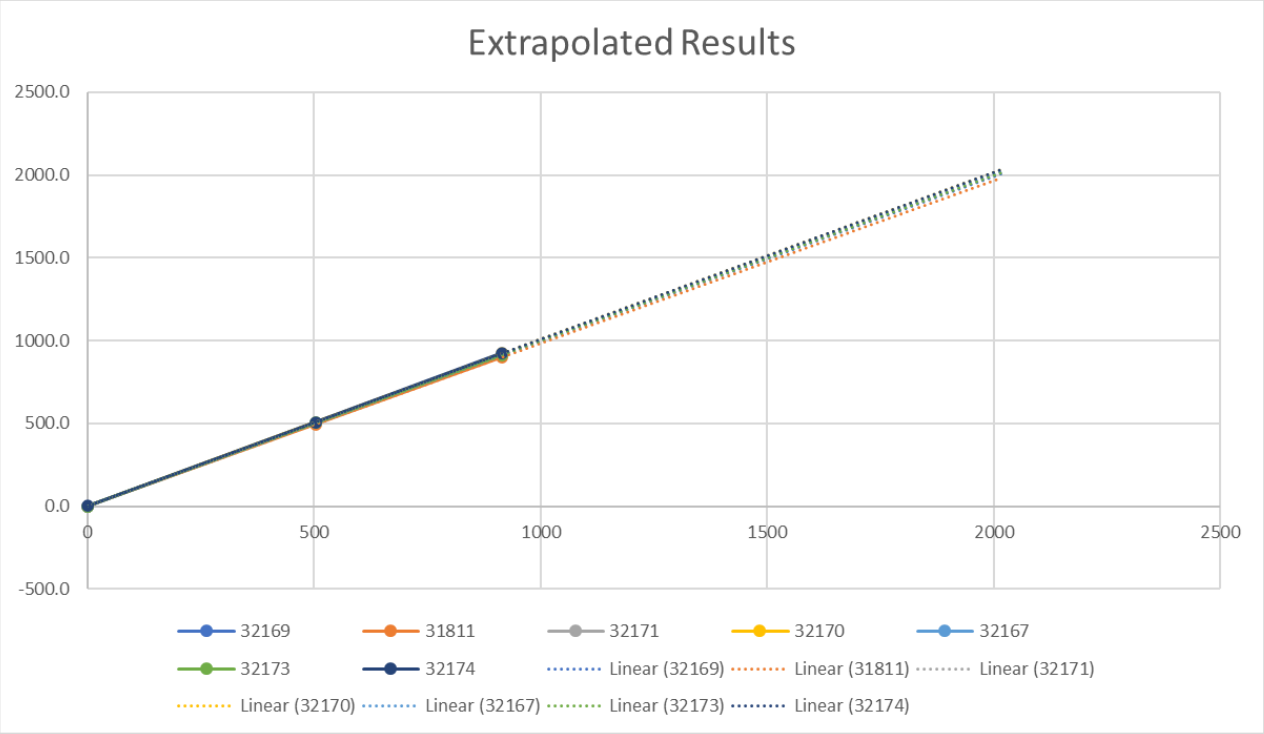


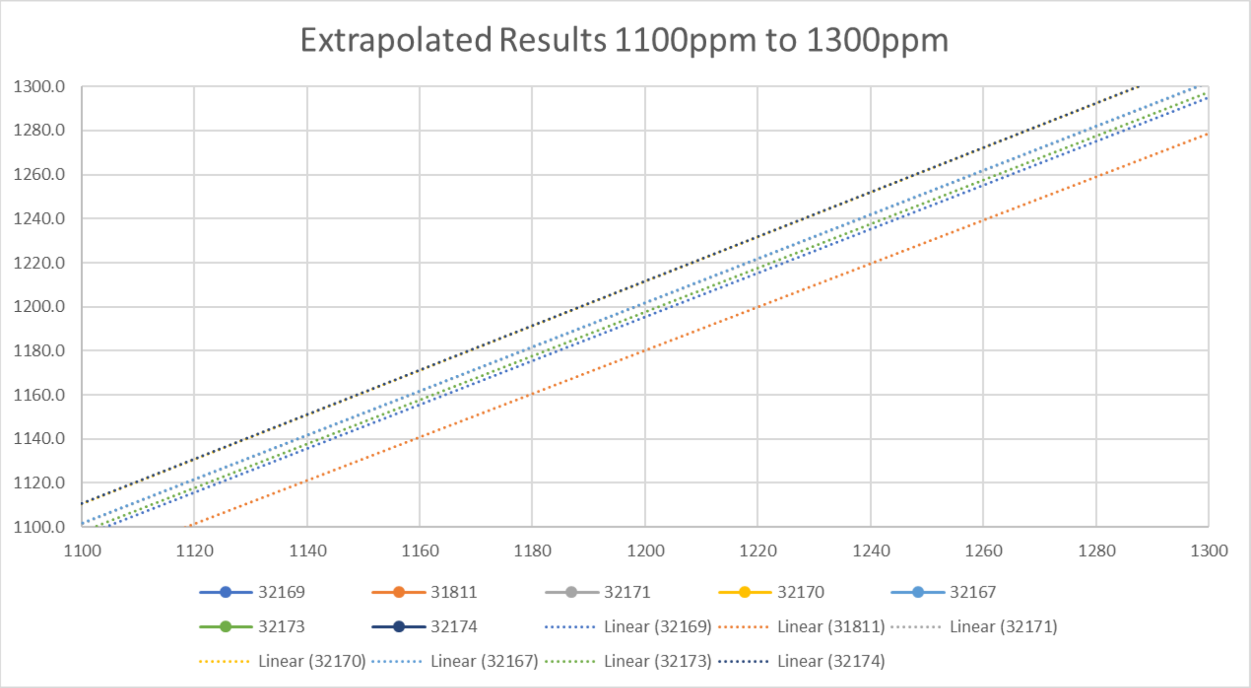
	% Error as a function of 1200ppm span						
Certified gas (CO ppm) / Run	**32169**	**31811**	**32171**	**32170**	**32167**	**32173**	**32174**
0	0.05%	-0.05%	0.00%	0.00%	0.00%	-0.05%	0.07%
504	-0.19%	-0.87%	0.03%	0.25%	0.04%	-0.04%	0.25%
915	-0.25%	-1.21%	0.12%	0.79%	0.13%	-0.18%	0.83%

	% Error as a function of 100ppm span						
Certified gas (CO ppm) / Run	**32169**	**31811**	**32171**	**32170**	**32167**	**32173**	**32174**
0	0.65%	-0.58%	0.06%	-0.02%	-0.02%	-0.62%	0.83%
504	-2.31%	-10.40%	0.32%	2.96%	0.50%	-0.49%	3.01%
915	-2.96%	-14.52%	1.39%	9.53%	1.54%	-2.20%	9.92%


GEM5000 CO linearity
y = 1.0097x - 0.0151
R² = 1
1000.0
800.0
600.0
400.0
200.0
0.0
-200.0
0
100
200
300
400
500
600
700
800
900
1000
32169
31811
32171
32170
32167
32173
32174
Linear (32174)


GEM5000 CO linearity 450ppm to 950ppm
y = 1.0097x - 0.0151
R² = 1
950.0
900.0
850.0
800.0
750.0
700.0
650.0
600.0
550.0
500.0
450.0
450
500
550
600
650
700
750
800
850
900
950
32169
31811
32171
32170
32167
32173
32174
Linear (32174)


Extrapolated Results
2500.0
2000.0
1500.0
1000.0
500.0
0.0
-500.0
0
500
1000
1500
2000
2500
32169
31811
32171
32170
32167
32173
32174
Linear (32169)
Linear (31811)
Linear (32171)
Linear (32170)
Linear (32167)
Linear (32173)
Linear (32174)


Extrapolated Results 1100ppm to 1300ppm
1300.0
1280.0
1260.0
1240.0
1220.0
1200.0
1180.0
1160.0
1140.0
1120.0
1100.0
1100
1120
1140
1160
1180
1200
1220
1240
1260
1280
1300
32169
31811
32171
32170
32167
32173
32174
Linear (32169)
Linear (31811)
Linear (32171)
Linear (32170)
Linear (32167)
Linear (32173)
Linear (32174)

APPENDIX 2 Interference Test Results

GEM5000 CO measurement in the presence of Hydrogen

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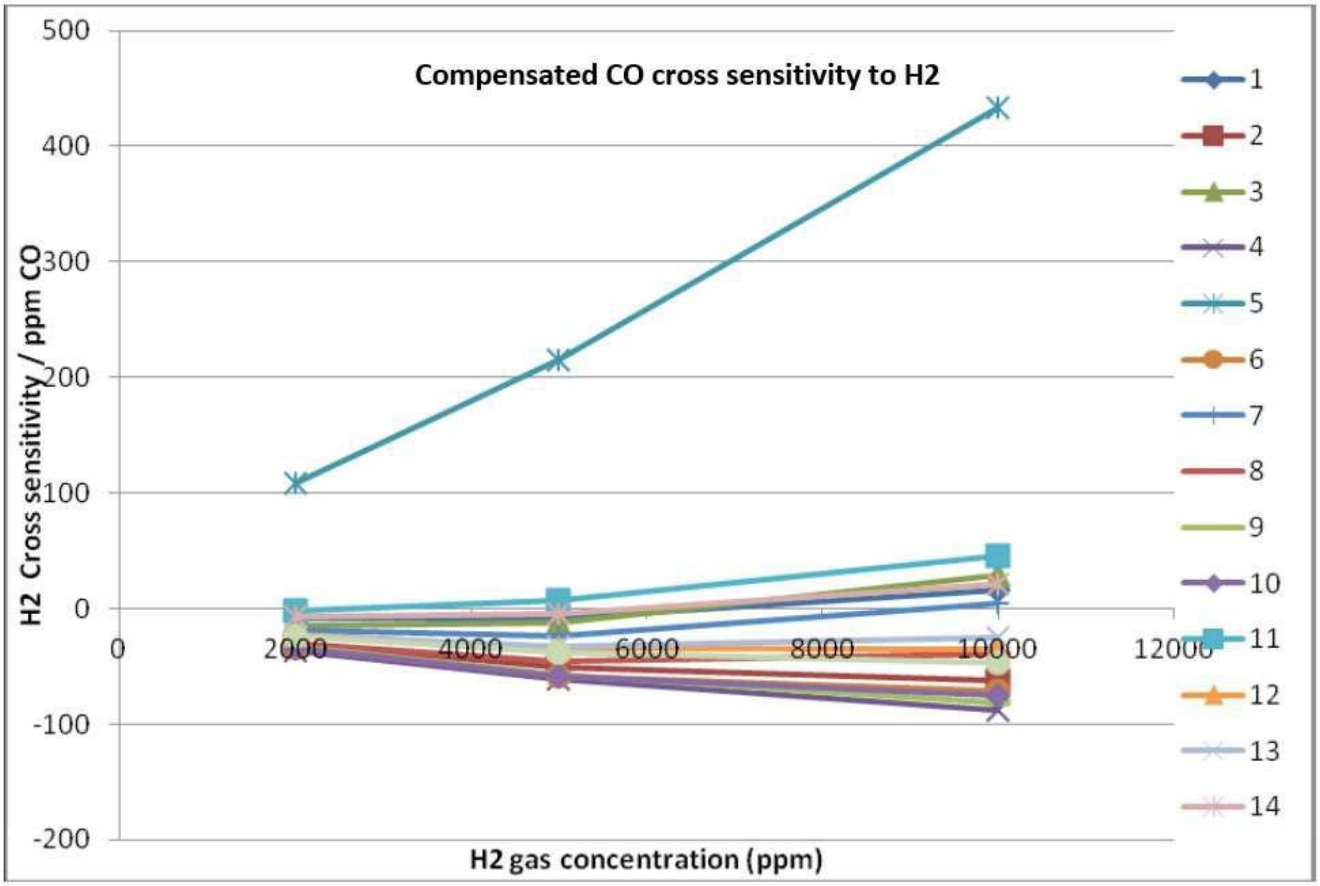
This test data shows the performance of 14 compensated CO cells used in the GEM5000.

This test data was undertaking in conjunction with our chemical cell supplier at their premises.

Each of the cells was exposed to 2000ppm, 5000ppm & 10,000 ppm H2 with the results being recorded. There was no CO present in the applied gas.



CELL number 5 would have failed end of line tests and would have not been built into an analyser. Conclusion: The cross gas sensitivity to H2 is within the stated performance of the GEM5000 datasheet. Hydrogen cross gas effect on carbon monoxide approximately 1%.

Do not use where hydrogen is in excess of 10,000ppm

APPENDIX 3 Sensor Recovery Test Results

Recovery of GEM5000 CO measurement after 20,000 ppm Hydrogen applied

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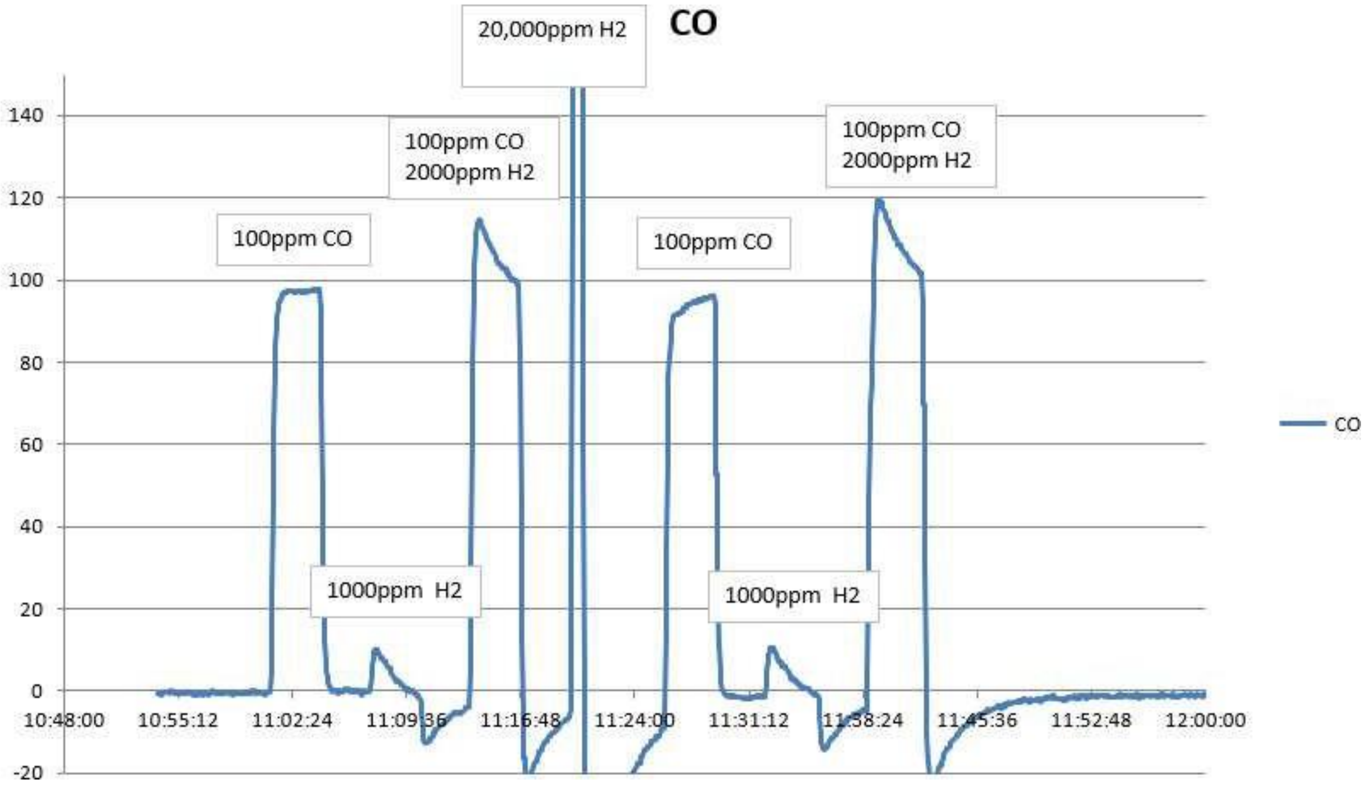
Testing was undertaken to understand the impact of applying a high level of hydrogen to the GEM5000 CO cell. The concentration of Hydrogen applied was twice the recommended concentration the instrument can compensate for.

Before and after performance tests were undertaken. The 20,000ppm H2 was applied until the GEM5000 indicated that the Hydrogen value was excessive.



Test process *Gases applied for 3 mins*

Baseline performance

- Air
- 100 CO
- Air
- 1000H2
- Air
- 100CO 2000 H2
- Air

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20,000ppm (2%) H2 applied: Until the GEM5000 indicates H2 value is excessive (this was approximately 40 seconds)

Air (pumped): Wait for the CO reading to return to within +/-10 ppm then apply the following

Comparative performance

- Air
- 100 CO
- Air
- 1000H2
- Air
- 100 CO 2000 H2
- Air

Purge with air for 20 minutes

Conclusion the GEM5000 continued to perform to datasheet specification after being exposed to 20,000ppm (2.0%) Hydrogen.

This test was performed once on a new CO cell. Results will vary depending upon length and concentration of exposure, age of the cell, and number of times the cell is exposed.

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