CARBON MONOXIDE IN WORKPLACE ATMOSPHERES

Method Number:	ID-210
Matrix:	Air
OSHA Permissible Exposure Limits	
Final Rule Limits:	35 ppm Time Weighted Average (TWA) 200 ppm Ceiling (5-min sample)
Transitional Limit:	50 ppm TWA
Collection Procedure:	Each sample is collected by drawing a known volume of air into a five-layer aluminized gas sampling bag.
Recommended Air Volume:	2 to 5 liters
Recommended Sampling Rates	
TWA Determination:	0.01 to 0.05 L/min
Ceiling Determination:	1 L/min
Analytical Procedure:	A portion of the gas sample is introduced into a gas sampling loop, injected into a gas chromatograph, and analyzed using a discharge ionization detector.
Detection Limits (TWA, Ceiling)	
Qualitative:	0.12 ppm
Quantitative:	0.40 ppm
Precision and Accuracy	
Validation Range:	17.2 to 63.6 ppm
CV_T(pooled):	0.025
Bias:	+0.058
Overall Error:	±10.8%
Special Requirements:	Samples should be sent to the laboratory as soon as possible and analyzed within two weeks after collection.
Method Classification:	Validated method
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1. Introduction

1.1 History

The recent change in the TWA Permissible Exposure Limit (PEL) for carbon monoxide (CO) from 50 to 35 ppm (5.1) and the inclusion of a Ceiling of 200 ppm (5-min sample) (5.2) stimulated a review of the methods used for the analysis of CO in workplace atmospheres, including both direct-reading and classical (TWA) collection procedures. In the past, the OSHA sampling and analytical method for CO required the use of direct-reading procedures for monitoring (5.3). One direct-reading procedure involved the use of CO short-term detector tubes (5.4), and a recent evaluation at the OSHA Salt Lake Technical Center (OSHA-SLTC) has been carried out on several of these tubes (5.5). Short-term detector tubes offer only spot checks of the environment, and sampling procedures capable of determining long-term CO concentrations are preferred. A long-term direct-reading method for compliance determinations was performed by OSHA compliance officers using an electrochemical detector (Ecolyzer, Energetics Science, Inc., Elmsford, NY). However, this instrument required constant calibration, readings were subject to drift and were difficult to assess for TWA determinations, and personal samples were difficult to take without using gas sampling bags. It was for these reasons that the current study was undertaken.

Previous classical methods found in the literature for the analysis of CO have consisted of the collection of air samples in gas bags or canisters with analysis either by infrared absorption spectrophotometry (5.6), electrochemical means (5.7), or gas chromatography using a flame ionization detector (5.8).

Gas chromatography (GC) offers many advantages for CO analysis (5.4, 5.9); however, because the sensitivity for CO by a flame ionization detector (FID) is extremely low, it is necessary to react hydrogen with CO on a catalyst such as heated nickel to produce methane before FID analysis can be performed at the levels of interest (5.5, 5.8). This methanization procedure introduces an additional step, since it is necessary to identify any methane in the sample, and makes the analysis more complex. Also, the hydrogen gas used in the conversion of CO to methane is sometimes contaminated with methane.

With the recent development of the discharge ionization detector (DID) for use with GC analysis, it is possible to measure CO concentrations directly at very low levels (5.10). Helium is generally used as the sample carrier gas and as the ionized species. In the detector, helium is passed through a chamber where a glow discharge is generated and high-energy photons are produced. These pass through an aperture to another chamber where they ionize the gas or vapor species in the sample stream. The resulting electrons are collected for quantitative determination by a standard electrometer. This is the method of detection employed in the current method.

1.2 Principle

1.2.1 A low-flow rate sampling pump is used to capture a known volume of air in a five-layer gas sampling bag (5-L).

1.2.2 A GC fitted with a gas sampling loop and a DID is used to assess CO sample concentrations.

1.3 Method Performance

1.3.1 Range, detection limit, and sensitivity:

a) The upper analytical range used during the evaluation of this method was about 430 ppm; the upper linear range for CO may be much larger than this concentration.

b) The qualitative detection limit was 0.12 ppm for a 1-mL gas sample (size of GC gas sampling loop). The quantitative detection limit was 0.40 ppm. If necessary, a larger sampling loop can be used to achieve a lower limit of detection.

c) The sensitivity of the analytical method [using analytical conditions stated for a Tracor 540 GC (Tracor Instruments Austin, Inc., Austin TX) and Hewlett-Packard 3357 Laboratory Automation System, Revision 2540 (Hewlett-Packard Co., Avondale PA)] was taken from the slope of the linear working range curve (1.70 to 63.6 ppm range). The sensitivity is 1,970 area units per 1 ppm. (For the HP 3357 Automation System, 1 area unit = 1 µVs.)

1.3.2 Precision, accuracy, and stability:

a) The pooled coefficient of variation for the sampling and analytical method from 17.2 to 63.6 ppm was 0.025.

b) The average recovery of generated samples taken in the 17.2-63.6 ppm range at 50% RH was 105.8%. The range of bias was -0.01 to +0.10. The Overall Error (OE) was ±10.8%.

c) Precision and accuracy data were derived from generated samples and prepared standards that were aged 4 days or less. The stability of CO in sampling bags is acceptable up to 2 weeks after sample collection.

d) Stability tests indicated that significant scatter in the results and lower recoveries tended to appear after prolonged storage. Use of new bags free of small leaks and internal deposits may prolong sample stability. Samples should be analyzed as soon as possible to minimize storage problems.

1.4 Advantages and Disadvantages

1.4.1 The method is specific for CO. The method is also applicable in measuring compliance to Indoor Air Quality Standards for CO [9 ppm (8 h), 35 ppm (1 h)] (5.11).

1.4.2 Using similar procedures, sampling and analysis for carbon dioxide (CO_2) is also possible provided the molecular sieve column is eliminated from the gas stream during CO_2 analysis.

1.4.3 Gas sampling bags are employed and may be somewhat inconvenient to use.

1.4.4 Changes in humidity do not affect sample collection.

1.4.5 The bulk of the sample is not destroyed during analysis. Other potentially toxic gases may also be analyzed from the same sample.

1.4.6 The gas bags used as sample collection media are reusable.

1.4.7 The method requires the use of a GC equipped with a DID.

1.4.8 Analytical time required per sample is within 20 min when using the conditions specified.

1.4.9 Gas bag samples are stable for approximately 2 weeks. Samples should be analyzed as soon as possible.

1.5 Physical Properties of CO (5.12, 5.13)

Molecular weight	28.01
Molecular formula	CO
Appearance	Colorless, odorless gas
Explosive limits in air	12.5 to 74.2% (v/v)
Autoignition temperature	651 °C
Melting point	-207 °C

Boiling point	-191.3 °C
Specific gravity (air = 1)	0.968
Density, gas*	1.250 g/L
Density, liquid	0.793
Solubility	
At 0 °C	3.54 mL/100 mL water
At 25 °C	2.14 mL/100 mL water

*Value indicated is at 0 °C, 101.3 kPa (760 mmHg)

1.6 Carbon Monoxide (CAS No. 630-08-0) Prevalence and Use With the single exception of CO_2, the total yearly emissions of CO exceed all other atmospheric pollutants combined (5.13). Some of the potential sources for CO emission and exposure are listed (5.13, 5.14):

- Foundries
- Petroleum refineries
  - Fluid catalytic crackers
  - Fluid coking operations
  - Moving-bed catalytic crackers
- Kraft pulp mills
- Carbon black manufacturers
- Steel mills
  - Coke ovens
  - Basic oxygen furnaces
  - Sintering operations
- Formaldehyde manufacturers
- Coal combustion facilities
  - Utility and large industrial boilers
  - Commercial and domestic furnaces
- Fuel oil combustion operations
  - Power plants
  - Industrial, commercial, and domestic uses
- Charcoal manufacturers
- Meat smokehouses
- Sugarcane processing operations
- Motor vehicles

1.7 Toxicology

(Information contained within this section is a synopsis of present knowledge of the physiological effects of CO and is not necessarily intended to be used as the basis for OSHA policy.)

Carbon monoxide has over a 200-fold greater affinity for hemoglobin than has oxygen (5.15, 5.16). Thus, it can make hemoglobin incapable of carrying oxygen to the tissues. Also, the presence of CO-hemoglobin interferes with the dissociation of the remaining oxyhemoglobin, further depriving the tissues of oxygen (5.12, 5.13).

The signs and symptoms of CO poisoning include headache, nausea, weakness, dizziness, mental confusion, hallucinations, cyanosis, and depression of the S-T segment of an electrocardiogram. Although most injuries in survivors of CO-poisoning occur to the central nervous system, it is likely that myocardial ischemia is the cause for many CO-induced deaths (5.15).

The uptake rate of CO by blood when air containing CO is breathed increases from 3 to 6 times between rest and heavy work. The uptake rate is also influenced by oxygen partial pressure and altitude (5.17).

Carbon monoxide can be removed through the lungs when CO-free air is breathed, with generally half of the CO being removed in one hour. Breathing of 100% oxygen removes CO quickly.

Acute poisoning from brief exposure to high concentrations rarely leads to permanent disability if recovery occurs. Chronic effects from repeated exposure to lower concentrations have been reported. These include visual and auditory disturbances and heart irregularities. Where poisoning has been long and severe, long-lasting mental or nerve damage has resulted (5.12).

The following table gives the levels of CO-hemoglobin in the blood which tend to form at equilibrium with various concentrations of CO in the air and the clinical effects observed. (5.18):

Atmospheric CO (ppm)	COHb in Blood (%)	Symptoms
70	10	Shortness of breath upon vigorous exertion; possible tightness across the forehead.
120	20	Shortness of breath with moderate exertion; occasional headache with throbbing in the temples.
220	30	Decided headache; irritability; easily fatigued; disturbed judgment; possible dizziness; dimness of vision.
350-520	40-50	Headache; confusion; collapse; fainting upon exertion.
800-1220	60-70	Unconsciousness; intermittent convulsions; respiratory failure; death if exposure is prolonged.
1950	80	Rapidly fatal.

Adults (non-smokers) normally have about 1% CO-hemoglobin in the body. Cigarette smokers generally have blood levels of 2 to 10% CO-hemoglobin (5.17).

In examining the CO levels in an occupational environment, consideration may also need to be made for CO generated from tobacco smoking. These amounts may ordinarily be small, but when added to the amounts generated by occupational activities, may aggravate conditions from an already existing high concentration of CO (5.19, 5.20).

1.8 Other Hazardous Properties

Carbon monoxide is flammable and is a dangerous fire and explosion risk. The flammable limits in air range from 12 to 75% by volume (5.16).

2. Sampling

2.1 Safety Precautions

2.1.1 Attach the sampling equipment to the worker in such a manner that it will not interfere with work performance or safety.

2.1.2 Follow all safety practices that apply to the work area being sampled.

2.2 Equipment

Note: The gas sample taken will contact the pump and tubing during collection. The filter (if available) of the pump should be clean and chemically inert to CO as well as any material inside the pump that the sample comes in contact with. Pumps used to evaluate the method were: Du Pont Model No. P-125 pumps [E. I. Du Pont de Nemours and Co. (Inc.), Wilmington, DE] for the TWA portion, and SKC Model No. 224-30 pumps (SKC Inc., Eighty Four, PA) for the Ceiling studies. The tubing also must not affect the CO concentration. Tygon tubing was used for method validation and therefore is specified to be used in this procedure.

2.2.1 Use a personal sampling pump capable of delivering a flow rate of approximately 0.01 to 0.05 L/min for TWA PEL samples. Use a larger flow rate pump (1 L/min) for Ceiling PEL measurements. Either pump must have an external inlet, an outlet port, and hose barbs.

2.2.2 Use five-layer aluminized gas sampling bags (5-L) as the collection media (the bags can be obtained from the OSHA-SLTC or Calibrated Instruments Inc., Ardsley, NY).

2.2.3 Make pump, sampling media, and breathing zone connections with various lengths of flexible Tygon tubing.

2.3 Sampling Procedure

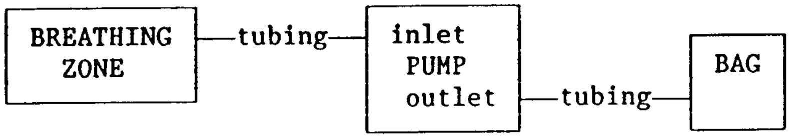
2.3.1 Calibrate the personal sampling pumps. Since the sampling bags have a total volume capacity of approximately 6 L, a sampling scheme for TWA PEL measurements is shown:

Flow Rate (L/min)	Sampling Time (h)	Sample Vol (L)
0.015	4	3.6
0.022	4	5.3
0.035	2.5	5.3
0.050	1.5	4.5

Take as large a sample as possible (<6 L) during the time frame used for sampling. A large flow rate (0.04-0.05 L/min) will require replacing sampling bags throughout the day. For TWA PEL determinations, a flow rate of approximately 0.020-0.025 L/min is sufficient for a 4-h sample. For Ceiling PEL samples, calibrate the pump to approximately 1 L/min.

2.3.2 Evacuate and check the gas sampling bags for leaks. Each sampling bag can be evacuated and leak tested by applying a vacuum to the bag. If a vacuum is applied to a leaky sampling bag, the bag will not fully collapse. If a vacuum pump is not available, inflate the gas sampling bags with nitrogen (N_2), let them sit overnight, inspect for leaks, and then evacuate by hand rolling and flattening.

2.3.3 Label each sampling bag. Attach one end of a piece of flexible tubing to the inlet hose barb of the pump, and place the other end in the breathing zone of the worker. Use another piece of tubing to connect the metal valve sampling bib of the sampling bag to the outlet hose barb of the pump. A graphic representation of the pump set-up is shown:



2.3.4 For personal sampling, attach the gas sampling bag to any loose fitting clothing on the worker's back or side with tubing clamps.

2.3.5 When ready to sample, open the gas sampling bag valve by rotating the metal valve counter-clockwise until fully open. Attach the free end of the tubing connected to the bag to the outlet hose barb of the pump. Turn on the pump. For Ceiling PEL determinations, sample for 5 min; for TWA measurements, sample up to 4 h.

Note: If the employee being monitored is smoking a tobacco product during sampling, a positive contribution of CO from the combustion of tobacco may occur for personal samples. Ask the employee to refrain from smoking during sampling so that only the occupational exposure is measured.

2.3.6 After sampling, rotate the valve clockwise until tight. Place an OSHA-21 seal over the metal valve. Record the total air volume taken.

2.3.7 Prepare samples and paperwork for submission to the laboratory. Do not prepare any blank samples. Request analysis for carbon monoxide.

2.3.8 When submitting sampling bags for analysis, pack loosely and pad generously to minimize potential damage during shipment. Submit samples to the laboratory as soon as possible after sampling.

3. Analysis

3.1 Safety Precautions

3.1.1 Refer to instrument manuals and operating procedures for proper operation of the instruments.

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3.1.2 Observe laboratory safety regulations and practices.

3.1.3 Prepare all CO standards in a well ventilated exhaust hood. AVOID inhaling CO.

3.2 Equipment

3.2.1 Instruments

A GC fitted with a 1-mL stainless steel gas sampling loop, sampling valve, and DID is used. Loops other than 1 mL can also be used.

3.2.2 Standard media:

Five-layer aluminized gas sampling bags are used.

3.2.3 A 4-foot × 1/8-inch stainless steel, 60-80 mesh, Hayesep Q column and a 12-foot × 1/8-inch stainless steel, 60-80 mesh, molecular sieve 5A column (in this order) are used.

3.2.4 Data reduction:

An electronic integrator is used to calculate peak areas.

3.2.5 Standard generation:

Certified CO standards can be used or standards can be prepared using any combination of: Calibrated gas-tight syringes or calibrated rotameters, mass flow controllers, or soap bubble flowmeters. A stopwatch is also necessary.

3.2.6 Additional accessories:

A personal sampling pump, with inlet and outlet ports and hose barbs, is used to load the gas sampling loop (loop loading can also be manually performed by squeezing the sampling bag).

3.3. Reagents (Gases)

3.3.1. A commercially prepared, bottled mixture of CO diluted with either air or N_2 is suitable for generating gas standards. The CO concentration must be certified. If a soap bubble flowmeter (~1 L/min) is used for standard preparation, a mixture containing 100 ppm CO is convenient. If a gas-tight calibrated syringe (~0 to 30 mL) is used, a mixture containing 5,000 ppm is suitable.

3.3.2. Filtered, compressed, CO-free air is used for dilutions when necessary. A convenient source of pure air is a cylinder of USP (United State Pharmacopeia) grade air. Small amounts of CO can be removed from the air by using a catalytic filter unit containing hopcalite to convert any CO to CO_2.

3.3.3. Helium (research grade, $\leq$1 ppm impurities) is used as the carrier gas.

3.4. Standard Preparation

Prepare standards by either using a calibrated syringe or metered delivery of CO using flow measurement. When a soap bubble flow meter is used for gas flow measurements, apply water vapor corrections if necessary, since the gas flowing through the meter expands somewhat upon saturation with water vapor. As an example, consider the case where dry gas at 101.3 kPa pressure (760 mmHg) enters a flow meter and is saturated with water vapor [vapor pressure = 2.9 kPa (22mmHg)]. In this case the gas volume (and therefore the gas flow rate) will be measured at (104.2/101.3 = 1.029) times the actual values. Specific cases of whether or not to use vapor corrections are given below.

Note: Commercially prepared standards in gas cylinders, if available, can be used in place of laboratory-prepared standards. It is recommended to use at least two standards to prepare a concentration-response curve. One of the commercial standards should be above the anticipated concentration of the samples.

A standard generation scheme using 100-ppm CO with metered delivery is proposed as follows:

Standard (ppm)	100-ppm CO Volume (L)	Volume of Air (L)
Blank	0.00	4.00
10	0.40	3.60
17	0.68	3.32
35	1.40	2.60
70	2.80	1.20
100	4.00	0.00

Other dilution schemes with different size gas bags and gas volumes can be used. For other concentrations of CO, use the following equation:

$$\text{ppm CO} = A \times \frac{B}{B + C}$$

where:
A = CO concentration (ppm) in the pre-diluted mixture,
B = Pre-diluted CO mixture volume (L),
C = Diluent air volume (L).

Note: % CO = ppm/10,000; i.e., if starting with a 0.50% CO mixture, A = 5,000 ppm.

Pure CO ($A = 1\times10^6$) can also be used for standard preparation. Prepare standards in concentrations that bracket the sample concentrations. Always prepare a blank standard to assure that the diluent air is not contaminated with CO. Completely evacuate and flush the gas bags to be used for standard preparation with CO-free air into the bag. Add the certified CO mixture to the gas bags by either of the following two procedures:

Note: All mixtures should be prepared within the confines of an exhaust hood.

3.4.1 Metered generations: Use a mass flow controller or calibrated rotameter to verify and control the CO mixture delivery rate from a gas cylinder. Use a soap bubble flowmeter before and after the standard generation to verify the CO mixture flow rate. Meter a known volume of CO-free air. Use a stopwatch or programmed valve to determine the volume of CO mixture delivered over time. If a soap bubble flowmeter is used to measure both the CO gas mixture and the diluent air volumes, any vapor effect is canceled out, and vapor corrections are not necessary.

3.4.2 Syringe injections: Use a calibrated gas-tight syringe to obtain a known volume either from an in-line cylinder septum or from a separate gas sampling bag filled with the concentrated CO mixture. Most gas bags have injection ports or septa for gas syringe withdrawal or injection. Fill and flush the gas-tight syringe with the concentrated CO mixture. After flushing, withdraw the required volume of the CO mixture and inject into a gas bag already containing diluent air. If a “dry” CO gas mixture is injected with a syringe into a gas bag containing air in which the diluent air flow has been measured with a soap bubble flowmeter, the diluent air volume must be corrected for water vapor effect.

3.5 Sample Preparation

No special preparations are necessary; however, the analyst should visually inspect the volume of the bags upon receipt and compare with the field air volumes in order to assess the possibility of leaks.

3.6 Sample Analysis

3.6.1 Recommended GC conditions:

Settings for a Tracor Model No. 540 GC and Model No. 706 DID are given in Appendix 1. Other settings may apply to different GCs.

3.6.2 Sample and standard introduction:

a) Connect the outlet port of the personal sampling pump to the sampling loop via inert tubing.
b) Adjust the pump to give a suitable flow rate for sample loading from the bag to the sampling loop.
c) Connect a short piece of tubing from the inlet port of the pump to the sample bag. Turn the bag valve counterclockwise to the open position and turn on the pump.
d) After the sample is loaded into the loop (which is vented to the atmosphere), turn off the pump to allow the loop sample to return to atmospheric pressure. Wait 1 to 2 min for pressure equalization and then open the gas sampling valve. Carrier gas flow is now directed through the sampling loop to the column and detector.

Note: Samples and standards can be introduced into the loop without a pump by simply squeezing a sufficient amount of sample from the bag into the loop. The sampling bag must be released for loop sample pressure normalization before opening the gas sampling valve.

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e) Perform two determinations of each sample and standard.

3.6.3 Depending on column and GC flow characteristics, CO retention times are in the range of 12 to 14 min.

3.7 Interferences

The GC determination of CO is relatively specific; however, any compound having a similar column retention time as CO is a potential interference. Interferences can be minimized by altering operational conditions such as oven temperature and column packings. Using the conditions stated within this method, other common gases and vapors do not present serious potential interferences. Carbon dioxide is adsorbed on the molecular sieve column and does not interfere. Hydrogen, oxygen, nitrogen, methane, and carbon monoxide will elute in the order listed (5.10). However, the CO peak will normally appear on the shoulder of the N_2 peak for air; therefore, GC conditions should be set so that a distinct CO peak is obtained. A chromatogram showing the elution of CO in N_2 is shown in Figure 1.

If necessary, the sample can be analyzed by GC-mass spectrometry to confirm the presence of CO; however, since CO has nearly the same molecular weight as N_2, low resolution mass spectrometry may not distinguish the two if the peaks are not well separated.

3.8 Calculations

3.8.1 If blank correction is necessary for the standards, subtract the blank peak area from the standard area readings before constructing the concentration-response curve. No blank correction is necessary for the samples.

3.8.2 Calculate CO concentrations from a least-squares regression curve. Establish the curve with peak area or peak height versus ppm. Results are calculated in units of ppm. No calculations using air volumes are necessary since gas phase samples are compared directly to gas phase standards.

3.8.3 Report results to the industrial hygienist as ppm CO.

4. Backup Report

Experimental Protocol

The validation of the method consists of the following experimental protocol:

1) Analysis of three sets of six spiked carbon monoxide (CO) samples having concentration ranges of approximately 0.5, 1, and 2 × TWA PEL.
2) Analysis of three sets of six dynamically generated CO samples having concentration ranges of approximately 0.5, 1, and 2 × TWA PEL. Also, analysis of six generated samples having a concentration close to the Ceiling PEL value.
3) Determination of the storage stability of CO samples collected in gas sampling bags.
4) Determination of any variation in results when sampling at low and high humidity levels.
5) Determination of the qualitative and quantitative detection limits for the analysis of CO.
6) Comparison with a previous GC method used for CO determinations in which the CO was reduced to methane and analyzed with a flame ionization detector (FID).
7) Assessment of the performance of this method and conclusions.

All samples, blanks, and standards used for validation were analyzed by direct injection into a 1-mL gas sampling valve in the GC as mentioned in the method. A Tracor Model No. 540 GC equipped with a Model No. 706 DID was used. Integrated peak areas were used as a measure of instrument response. Analytical parameters used during these experiments are listed in Appendix 1. All results were statistically examined for outliers and, when necessary for pooling results, for homogeneous variance. Possible outliers were determined by using the American Society for Testing and Materials (ASTM) test for outliers (5.21). Homogeneity of the coefficients of variation (CV) was determined using the Bartlett's test (5.22). Overall Error (OE) (5.23) was calculated as:

$$OE_i = \pm [|\text{mean bias}_i| + sCV_i] \times 100\%$$

where i is the respective sample pool being examined

4.1 Analysis (spiked samples)

Procedure: Three sets of spiked samples were prepared and analyzed as follows:

4.1.1. Samples were prepared according to the following procedure:

a) Gas sampling bags were flushed several times with N_2. A vacuum was then applied to completely collapse the bags.

b) Air (USP grade) was used as a diluent after flowing through an Ecolyzer No. 7915 Zero Air Filter. A known amount of air was metered into each sampling bag. Compressed air flow rates were measured before and after each bag filling using a soap bubble flowmeter (Model M-5, A. P. Buck, Inc., Orlando, FL). Air flow was regulated with a regulator-rotameter system. Blank samples of the compressed air were periodically collected and analyzed along with the samples and standards.

c) A known amount of CO was injected into each sampling bag containing diluent air using a calibrated gas syringe. A gas cylinder containing 0.50% CO in N_2 (certified, Linde Div., Union Carbide Corp., Denver, Colorado) was used as the CO source.

4.1.2. Analytical standards were prepared according to the following procedure:

a) Standards were prepared by dilution of 104-ppm CO in N_2 (certified, Airco, Inc., Murray Hill, NJ) with USP grade air.

The CO content of the cylinder was confirmed by employing a simplified modification of a method used by Grant, Katz, and Haines (5.24). A known volume of the 104-ppm

CO was passed through iodine pentoxide contained in a glass tube at about 150 °C. The resulting iodine was collected in an aqueous solution of potassium iodide. The amount of iodine formed was determined by titration using standard thiosulfate solution with starch as the indicator (5.25). Two samples were collected. Carbon monoxide concentration determinations of 99.4 and 95.4 ppm (95.6% and 91.7% recovery respectively) were obtained. Previous work had demonstrated that the results for this procedure tend to be slightly lower than expected (5.24). For the present work, the given concentration of 104 ppm was used.

b) Known amounts of CO and air were metered into gas sampling bags as described in Section 4.1.1 above.

4.1.3 These samples and standards were analyzed within 4 days of preparation.

Results: Spiked sample recoveries (found/taken) are listed in Table 1. All analysis data passed the ASTM outlier test. The Bartlett's test valve (13.73) was high, most likely because the mean and standard deviation values at 1 × TWA PEL were exceptionally better than the other levels tested.

Note: When a set of results fails the Bartlett's test, possible options are to reject the results as being derived from significantly different sample populations, or adopt the CV at the PEL as the "Pooled CV". In this case the CV_1 (Pooled) result was used instead. This appears more conservative since CV_1 (Pooled) > CV_1 (TWA PEL).

The data (Table 1) indicated good precision and accuracy. The CV_1 was 0.038 and the average analytical recovery was 98.1%.

4.2 Sampling and Analysis (Generated samples)

Procedure: Three sets of generated samples at 0.5, 1, and 2 × TWA PEL were prepared and analyzed.

4.2.1 Samples were prepared according to the following procedure:

a) Gas sampling bags were flushed several times with N_2. A vacuum was then applied to completely collapse the bags.

b) A dynamic gas generation system was assembled as shown in Figure 2. Moisture and other contaminants were removed from the diluent air by using a charcoal/Drierite/silica gel filtering system. A humidity, temperature, and flow control system (Model HCS-301, Miller-Nelson Research Inc., Monterey, CA) was used to treat the diluent air to produce the stated RH at 25 °C. Diluent air flow was measured before and after each experiment using a dry test meter (Model DTM-115, American Meter Co., Philadelphia PA). The flow control system was calibrated in-house for temperature and humidity prior to use.

c) The CO (0.5% in N_2) was introduced into the flow system via a glass mixing chamber. Gas flow rates were taken immediately before and after each experiment using a soap bubble flowmeter (Model 823-1, Mast Development Co., Davenport, IA). Flow rates were controlled using a mass flow controller (Model FC-261, Tylan Corp., Torrance, CA).

To assure continuous generation of controlled concentrations of CO and provide an additional verification of concentrations, the flow system was continuously monitored during each test with a direct-reading instrument [Model 7140 (for CO), Interscan Corp., Chatsworth, CA] connected to the flow system. Calibration of the instrument was performed with a 40-ppm calibrating gas (certified, Alphagaz, Cambridge, MD).

4.2.2 Samples were analyzed within 2 days after preparation; standards were used within 4 days after preparation.

4.2.3 Six samples with a CO concentration near the Ceiling PEL (200 ppm) were also generated using the system described above. Standards were prepared by injection of CO (0.5% in N_2) using a calibrated gas syringe into a gas bag containing a known volume of USP grade air. Samples and standards were analyzed 4 days after preparation.

Results: Recoveries for generated samples at 0.5, 1, and 2 × TWA PEL are listed in Table 2a. The Sampling and Analysis date showed good precision and accuracy. All data passed the outlier test. The Bartlett's test value (9.92) was slightly higher than the critical value (9.23), again probably due to greater precision for the TWA PEL results. The data were pooled, since it was felt a significant amount of error would not be introduced by pooling. The CV_2 (Pooled) value is similar to that found during the humidity studies (Section 4.4).

Recoveries for the samples generated at the Ceiling PEL level are given in Table 2b. These results showed excellent recovery.

The results are summarized as follows:

PEL	Ave. Recov. (%)	CV
TWA	105.8	0.020
Ceiling	100.0	0.025

4.3 Stability Test

Procedure: A long-term evaluation of sample media stability was performed to determine any potential problems if delays in sample analyses occur. Five-layer aluminized gas sampling bags (5-L) containing generated samples were used to assess CO storage stability. Samples were generated at 1 and 2 × TWA PEL and 80% RH. Samples were analyzed at various times up to 39 days after sample collection.

Samples were also generated at 0.5 × TWA PEL and 80% RH; however, a few of the bags used for this experiment appeared to have some leakage and technical problems occurred during analysis.

Results: Recovery data are listed in Table 3 and graphically represented in Figure 3 (normalized data). One result for 1 × PEL at 8 days of storage is not included in Figure 3 since it appeared to be unrealistically high; The GC appeared to display some instability on the day these samples were analyzed.

Previously, different types of gas sampling bags were evaluated for stability, structural integrity, and compactness. The five-layer aluminized bag (5-L) was considered more durable than Tedlar or Saran. The storage stability of CO using this sampling bag was acceptable for up to two weeks. In this time frame, average sample recoveries were within 10% of what was found at the beginning of each experiment. Significant problems occurred when samples were analyzed after two weeks. Results displayed significant scatter and low recoveries were noted after prolonged storage. Storage stability was enhanced if a large gas sample (4 L or more) was taken. Thus, it is possible that a small surface to volume ratio may contribute to storage stability. It is also possible that storage stability may be improved if newer bags are used which are free of small leaks and internal deposits. A preliminary study in which CO samples in new gas bags were analyzed over a 2-week period with an Ecolyzer electrochemical detector verified this. Recoveries averaged about 100% even after 17 days of storage.

A summary of the stability data from the GC analysis is shown below:

80% RH and 25 °C

1× TWA PEL			2× TWA PEL		
Day	Recovery*	CV	Day	Recovery*	CV
1	100.0	0.023	2	100.0	0.041
8	103.5	0.161	15	89.6	0.108
21	80.9	0.135	22	75.9	0.136
29	81.9	0.141	32	79.0	0.211
39	79.9	0.176			

* Normalized to 100%

The slope of the plotted normalized 1× PEL data is 0.00597 days^{-1} and of the 2 × PEL data is 0.00781 days^{-1}. The slope of the combined data for 1 and 2 × PEL, as plotted in Figure 3, is 0.00648 days^{-1}.

4.4 Humidity Study

Procedure: Samples were also generated at 25-28% and 80% RH using the same equipment and conditions described in Section 4.2.

Results: The results of the gas sampling bags collected at the three RH are presented in Tables 2 (50% RH) and 4 (25-28%, 80% RH). The RH level displayed no apparent effect on recovery, except possibly at the 25-28% RH level. As shown in Table 4, an analysis of variance (F test) was performed on the data to determine any significant difference among or within the various RH groups. Variance at each concentration level (0.5, 1, and 2 × TWA PEL) was compared across the three RH levels (25-28%, 50%, and 80% RH). The variance among and within the different concentration groups all gave high calculated F values. However, as is also shown in Table 4, no trends are apparent when generation recovery data are compared at different RH levels for each concentration level, with the exception of the data at 0.5 × TWA PEL, where increased recoveries at low humidity were indicated. The large calculated F values appear to be mainly due to variation in sample generation and analysis. The data indicate no apparent significant humidity effect on recovery which would require corrections. It is known as to why the recoveries were enhanced at the 0.5 × TWA PEL, 25% RH test level.

4.5 Detection Limits

Procedure: Both qualitative and quantitative limits for the analysis of CO by GC were calculated using the International Union of Pure and Applied Chemistry (IUPAC) method for detection limit determinations (5.26). The procedure used for determining the detection limits is as follows:

4.5.1 Gas bags were prepared as described in Section 4.1.1, Step 1.

4.5.2 Blank samples were generated using the flow, humidity, and temperature control system mentioned in Section 2.

4.5.3 Low concentration CO samples were prepared by mixing CO (0.50% in N_2), via the mixing chamber, with the treated air. Concentrations of 1.70, 2.62, 5.13, and 10.16 ppm were used.

Results: Detection limit results are listed in Table 5. The qualitative detection limit was 0.12 ppm. The quantitative detection limit was 0.40 ppm. A 1-mL sampling loop was used for all analyses. A larger sampling loop should allow for a lower limit of detection; however, lower limits at this time are not necessary for workplace determinations. Ambient air, especially around combustion sources, will probably have CO levels comparable to or above the levels quoted as detection limits.

4.6 Comparison Methods

The results obtained in the present study were compared with those obtained during the CO detector tube evaluation study (5.5). For the detector tube study, the CO atmospheres generated were sampled side-by-side using five-layer aluminized gas sampling bags (5-L) and detector tubes. A sample of the gas from each gas bag taken was chromatographed using a 5A Molecular Sieve column. It was then passed with H_2 carrier gas through a nickel catalytic methanizer to convert the CO to methane (CH_4) before analysis with a flame ionization detector. Further details are described in reference 5.5. Peak heights were used for sample measurement and fewer gas samples were taken than in the present study. The results are reported in Table 6, along with a summary of the present results for comparison purposes. The results tend to indicate that the mean recoveries for the individual RH and concentration level determinations are less precise in the present study. The Overall Error (Total) (OE_T) values obtained indicate the amount of error is similar for either analytical technique. Either approach gives acceptable results. The DID method is more direct, is simpler to use, and does not involve as much auxiliary equipment as the methanizer/FID method.

4.7 Method Performance - Conclusions

The data generated during the validation of the method indicate an acceptable method for sampling and analyzing CO. The GC-DID method offers an accurate and precise assessment of CO exposures in the workplace. The data are summarized in Table 7. The GC-DID CO determinations near the TWA PEL were within NIOSH and OSHA accuracy and precision guidelines (5.22, 5.23). The total coefficient of variation (CV_T) was 0.025, and the overall recovery was 105.8%. The data obtained in the Ceiling PEL studies showed an average recovery of 100.0%.

Obtaining good analytical results appears to be contingent on analyzing the samples within two weeks, and preferable as soon as possible after collection. Storage stability appears to be enhanced if a large gas sample (4 L or more) is taken. It is also possible that storage stability may be improved if newer bags are used which are free of small leaks and internal deposits. Gas bag samples should be sent to the laboratory and analyzed as soon as possible.

This method is capable of accurate and precise measurements to determine compliance with the 35-ppm TWA PEL and 200-ppm Ceiling PEL for CO exposures.

5. References

5.1 "Air Contaminants; Final Rule" Federal Register 29 CFR Part 1910 (19 Jan. 1989). Pp. 2332-2983.

5.2 United States Department of Labor, OSHA: "Memorandum, Updated Changes to 29 CFR 1910.1000, Air Contaminants Standard." by Patricia Clark, Director Designate, Directorate of Compliance Programs. United States Department of Labor, OSHA, Washington, DC, June 1, 1990. [Memo].

5.3 Directorate of Technical Support, OSHA-DOL: Chemical Information File, Online Database-OSHA Information System. Salt Lake City, UT: Occupational Safety and Health Administration Salt Lake Technical Center, 1989.

5.4 Katz, M., ed.: Methods of Air Sampling and Analysis. 2nd ed., APHA Intersociety Committee. Washington, D.C.: Publication Office, American Public Health Association, 1977. No. 132, pp. 368-369.

5.5 Occupational Safety and Health Administration Salt Lake Technical Center: Carbon Monoxide Detector Tubes (Short-Term) (USDOL/OSHA-SLTC PE-11). Salt Lake City, UT: Occupational Safety and Health Administration Salt Lake Technical Center, 1990.

5.6 National Institute for Occupational Safety and Health: NIOSH Manual of Analytical Methods. 2nd. ed., Vol. 1 (Method No. P&CAM 112) (DHEW/NIOSH Pub. No. 77-157-A). Cincinnati, OH: National Institute for Occupational Safety and Health, 1977.

5.7 National Institute for Occupational Safety and Health: NIOSH Manual of Analytical Methods. 2nd. e., Vol. 4 (Method No. S340) (DHEW/NIOSH Pub. No. 78-175). Cincinnati, OH: National Institute for Occupational Safety and Health, 1978.

5.8 Mine Safety and Health Administration: Regular Mine Gas Analysis (MSHA Standard Method No. 1). Denver, CO: MSHA, 1979.

5.9 Guiochon, G. and C. Pommier: Gas Chromatography in Inorganics and Organometallics. Ann Arbor, MI: Ann Arbor Science Publishers Inc., 1973. pp. 79-115.

5.10 Williams, D.M.: "Unique Applications for New Helium Glow Discharge Ionization Detector for Gas Chromatography." Paper presented at the 1988 Pittsburgh Conference, New Orleans, LA, February 1988.

5.11 American Society of Heating, Refrigerating and Air-Conditioning Engineers Inc.: Ventilation for Acceptable Indoor Air Quality. ASHRAE 62-1989. Atlanta, GA: American Society of Heating, Refrigerating and Air-Conditioning Engineers, 1989. pp. 1-26.

5.12 Sax, N.I.: Dangerous Properties of Industrial Materials. 4th ed. New York: Van Nostrand Reinhold Company, 1975. pp. 520-521.

5.13 National Institute for Occupational Safety and Health: Criteria for a Recommended Standard--Occupational Exposure to Carbon Monoxide (DHEW/NIOSH Pub. HSM 73-11000). Cincinnati, OH: National Institute for Occupational Safety and Health, 1972.

5.14 Coburn, R.F., chairman: Carbon Monoxide. Washington, DC: National Academy of Sciences, 1977.

5.15 Proctor, N.H. and J.P. Hughes: Chemical Hazards of the Workplace. Philadelphia, PA: J.B. Lippincott Co., 1978. pp. 151-153.

5.16 Sax, N.I. and R.J. Lewis, Sr.: Hawley's Condensed Chemical Dictionary. 11th ed. New York: Van Nostrand Reinhold Co., 1987. pp. 221-222.

5.17 American Conference of Governmental Industrial Hygienists: Documentation of the Threshold Limit Values for Substances in Workroom Air. 3rd ed. Cincinnati, OH: American Conference of Governmental Industrial Hygienist, 1971. pp. 41-43.

5.18 Ellenhorn, M.J., and D.G. Barceloux: Medical Toxicology. New York, NY: Elsevier Science Publishing Co., Inc., 1988. p. 821.

5.19 Lee, H.K., T.A. McKenna, L.N. Renton, and J. Kirbride: Impact of a New Smoking Policy on Office Air Quality. In Indoor Air Quality in Cold Climates: Hazards and Abatement Measures, edited by D.S. Walkinshaw. Pittsburgh PA: Air Pollution Control Association. pp. 307-322. (NIOSH-00172085).

5.20 Leaderer, B.P., W.S. Cain, R. Isseroff, and L.G. Berglung: Ventilation Requirements in Buildings. II. Particulate Matter and Carbon Monoxide from Cigarette Smoking. Atmospheric Environment 18, No. 1: 99-106 (1984). (NIOSH-00137853).

5.21 Mandel, J.: Accuracy and Precision, Evaluation and Interpretation of Analytical Results, The Treatment of Outliers. In Treatise On Analytical Chemistry. 2nd ed., Vol. 1, edited by I.M. Kolthoff and P.J. Elving. New York, NY: John Wiley and Sons, 1978. pp. 282-285.

5.22 National Institute for Occupational Safety and Health: Documentation of the NIOSH Validation Tests by D. Taylor, R. Kupel and J. Bryant (DHEW/NIOSH Pub. No. 77-185). Cincinnati, OH: National Institute for Occupational Safety and Health, 1977. pp. 1-12.

5.23 Occupational Safety and Health Administration Salt Lake Technical Center: OSHA Analytical Methods Manual. Vol. III (USDOL/OSHA-SLTC Method Validation Guidelines). Cincinnati, OH: American Conference of Governmental Industrial Hygienists (Pub. No. ISBN: 0-936712-66-X), 1985.

5.24 Grant, G.A., M. Katz, and R.L. Haines: A Modified Iodine Pentoxide Method for the Determination of Carbon Monoxide. Can. J. of Technol. 29: 43-51 (1951).

5.25 Skoog, D.A. and D.M. West: Analytical Chemistry: an Introduction. 4th ed. Philadelphia, PA: Saunders College Publishing, 1986. pp. 591-594.

5.26 Long, G.L. and J.D. Winefordner: Limit of Detection — A Closer Look at the IUPAC Definition. Anal. Chem. 55: 712A-724A (1983)

Table 1
Analysis of Spiked CO Samples (OSHA TWA PEL)

0.5× PEL			1× PEL			2× PEL		
PPM Taken	PPM Found	F/T	PPM Taken	PPM Found	F/T	PPM Taken	PPM Found	F/T
17.600	17.741	1.008	35.200	34.619	0.983	70.200	71.064	1.012
17.600	16.274	0.925	25.200	34.353	0.976	70.000	67.827	0.969
17.600	15.691	0.892	25.200	34.523	0.981	69.800	72.870	1.044
17.600	17.889	1.016	35.300	34.346	0.973	70.000	73.249	1.046
17.500	17.326	0.990	35.300	34.080	0.965	70.100	70.539	1.006
17.500	15.684	0.896	35.500	34.254	0.965	70.00	70.405	1.006
N		6			6			6
Mean		0.954			0.974			1.014
Std Dev		0.057			0.008			0.029
CV		0.060			0.008			0.028
OE		16.5			4.2			7.0

F/T = Found/Taken OE = Overall Error (±%)
Bias = -0.019
CV_1 (Pooled) = 0.038
Overall Error (Total) = ±9.6%

Table 2a
Sampling and Analysis - 50% RH and 25 °C (OSHA TWA PEL)

0.5× PEL			1× PEL			2× PEL		
PPM Taken	PPM Found	F/T	PPM Taken	PPM Found	F/T	PPM Taken	PPM Found	F/T
17.200	18.181	1.057	30.800	34.305	1.114	63.600	62.072	0.976
17.200	19.160	1.114	30.800	33.635	1.092	63.600	63.479	0.998
17.200	18.729	1.089	30.800	33.746	1.096	63.600	63.783	1.003
17.200	19.082	1.109	30.800	33.884	1.100	63.600	63.860	1.004
17.200	18.531	1.077	30.800	34.176	1.110	63.600	63.100	0.992
17.200	17.570	1.021	30.800	34.019	1.105	63.600	62.426	0.982
N		6			6			6
Mean		1.078			1.103			0.992
Std Dev		0.035			0.008			0.012
CV		0.032			0.008			0.012
OE		14.2			11.8			3.1

F/T = Found/Taken OE = Overall Error (±%)
Bias = +0.058
CV_2 (Pooled) = 0.020
CV_T (Pooled) = 0.025
Overall Error (Total) = ±10.8%

Table 2b
Ceiling PEL Study
50% RH and 25 °C
(OSHA TWA PEL)

PPM Taken	PPM Found	F/T
197.500	199.565	1.010
197.500	201.207	1.019
197.500	200.182	1.014
197.500	201.349	1.019
197.500	192.328	0.974
197.500	190.057	0.962
N		6
Mean		1.000
Std Dev		0.025
CV		0.025
OE		5.0

F/T = Found/Taken OE = Overall Error (±%)

Table 3
Storage Stability Test
1× TWA PEL, 80% RH

Day 1		Day 8*		Day 21		Day 29		Day 39	
PPM Taken	PPM Found	PPM Taken	PPM Found	PPM Taken	PPM Found	PPM Taken	PPM Found	PPM Taken	PPM Found
31.600	34.718	31.600	43.028	31.600	25.315	31.600	28.268	31.600	25.872
31.600	34.612	31.600	30.718	31.600	25.128	31.600	27.629	31.600	25.789
31.600	32.851	31.600	36.747	31.600	29.057	31.600	29.594	31.600	29.632
31.600	33.680	31.600	26.702	31.600	22.758	31.600	20.039	31.600	18.690
31.600	32.993	31.600	36.089	31.600	28.697	31.600	29.396	31.600	30.118
31.600	33.905	31.600	36.484	31.600	33.142	31.600	31.012	31.600	31.884
N	6		6		6		6		6
Mean	33.793		34.961		27.350		27.656		26.998
Sta Dev	0.785		5.623		3.700		3.910		4.739
CV	0.023		0.161		0.135		0.141		0.176
Recov, %	106.9		110.6		86.5		87.5		85.4
Normalized to 100%	100.0		103.5		80.9		81.9		79.9

* Plot of standards showed more than the usual scatter--GC performance was erratic.

Table 3
Storage Stability Test
2× TWA PEL, 80% RH

Day 2		Day 15		Day 22		Day 32	
PPM Taken	PPM Found	PPM Taken	PPM Found	PPM Taken	PPM Found	PPM Taken	PPM Found
76.200	68.643	76.200	60.295	76.200	47.042*	76.200	45.644*
76.200	68.459	76.200	67.145	76.200	55.069	76.200	59.314
76.200	69.570	76.200	70.047	76.200	65.320*	76.200	69.860*
76.200	74.060	76.200	69.268	76.200	55.451	76.200	67.860
76.200	74.882	76.200	61.652	76.200	54.587	76.200	52.431
76.200	69.094	76.200	51.995	76.200	44.728	76.200	40.675
N	6		6		6		6
Mean	70.785		63.400		53.700		55.964
Sta Dev	2.893		6.862		7.288		11.820
CV	0.041		0.108		0.136		0.211
Recov, %	92.9		83.2		70.5		73.4
Normalized to 100%	100.0		89.6		75.9		79.0

* Bag contents were somewhat low, indicating leakage.

Table 4a
Humidity Study - 25-28% RH and 25 °C (OSHA TWA PEL)

0.5× PEL			1× PEL			2× PEL		
PPM Taken	PPM Found	F/T	PPM Taken	PPM Found	F/T	PPM Taken	PPM Found	F/T
17.700	21.592	1.220	31.100	30.248	0.973	62.900	60.486	0.962
17.700	20.188	1.141	31.100	31.445	1.011	62.900	59.319	0.943
17.700	19.368	1.094	31.100	31.719	1.020	62.900	55.289	0.879
17.700	20.083	1.135	31.100	31.081	0.999	62.900	59.345	0.943
17.700	20.681	1.168	31.100	32.577	1.048	62.900	61.934	0.985
17.700	20.840	1.177	31.100	31.972	1.028	62.900	59.764	0.950
N		6			6			6
Mean		1.156			1.013			0.944
Std Dev		0.043			0.026			0.035
CV		0.037			0.025			0.037
OE		23.0			6.4			13.1

F/T = Found/Taken OE = Overall Error (±%)
Bias = +0.038
CV (Pooled) = 0.034
Overall Error (Total) = ±10.5%

Table 4b
Humidity Study - 80% RH and 25 °C (OSHA TWA PEL)

0.5× PEL			1× PEL			2× PEL		
PPM Taken	PPM Found	F/T	PPM Taken	PPM Found	F/T	PPM Taken	PPM Found	F/T
17.900	18.343	1.025	31.600	34.718	1.099	76.200	68.643	0.901
17.900	18.943	1.058	31.600	34.612	1.095	76.200	68.459	0.898
17.900	18.177	1.015	31.600	32.851	1.040	76.200	69.570	0.913
17.900	18.027	1.007	31.600	33.680	1.066	76.200	74.060	0.972
17.900	18.590	1.039	31.600	32.993	1.044	76.200	74.882	0.983
17.900	17.358	0.970	31.600	33.905	1.073	76.200	69.094	0.907
N		6			6			6
Mean		1.019			1.069			0.929
Std Dev		0.030			0.025			0.038
CV		0.030			0.023			0.041
OE		7.8			11.6			15.3

F/T = Found/Taken OE = Overall Error (±%)
Bias = +0.006
CV (Pooled) = 0.032
Overall Error (Total) = ±7.0%

Table 4c
Humidity Study

	F Test		Recoveries %		
				RH	
Level	F(calc)	F(crit)	25-28%	50%	80%
0.5× PEL	21.44	6.36	115.6	107.8	101.9
1.0× PEL	27.52*	6.36	101.3	110.3	106.9
2.0× PEL	7.02*	6.36	94.4	99.2	92.9
Average			103.8	105.8	100.6

* Large values appear to be due to variability in sample generation and not to any significant humidity effect.

Table 5
Determination of Qualitative and
Quantitative Detection Limits

PPM	Blank*	1.70*	2.62	5.13	10.16
Integrated Area	1746	5281	7992	10213	19305
	1601	5254	6602	11142	22274
	1649	5604	8214	10511	18974
	1769	5659	8032	9054	19903
	1634	5686	8323	10091	18917
	1630		7342	10066	20201
Std Dev	68.8	211.6	658.2	681.9	1256.9

* Manual integration was performed on chromatographic peaks using CPLOT software (Hewlett-Packard Co., Avondale, PA, CPLOT/3350, Rev. 2509).

IUPAC Method
Using the equation: $C_{ld} = k(sd)/m$
where:
C_{ld} = the smallest detectable concentration an analytical instrument can determine at a given confidence level.
k = 3 (Qualitative detection limit, 99.86% confidence).
k = 10 (Quantitative detection limit, 99.99% confidence).
sd = standard deviation of blank readings.
m = analytical sensitivity or slope as calculated by linear regression.

Minimum detectable signal (Qualitative detection limit):
$C_{ld} = 3(68.8)/1718.5$
$C_{ld} = 0.12$ ppm
For k = 10 (Quantitative detection limit):
$C_{ld} = 0.40$ ppm as a reliable detectable signal

Table 6a
Method Comparison
Analysis of Gas Bags Containing CO by GC Using a
Methanizer and Flame Ionization Detector (5.5)

Test		Samples	Mean	CV	OE_T%***
%RH	× PEL	N*	Recov.**		
25-30	0.5	3	0.944	0.004	8.2
	1	4	0.937	0.018	
	2	3	0.993	0.028	
50	0.5	3	0.933	0.006	6.0
	1	3	1.028	0.011	
	2	6	0.987	0.028	
80	0.5	4	1.013	0.007	5.3
	1	6	1.000	0.037	
	2	6	0.988	0.017	

Table 6b
Method Comparison
Analysis of Gas Bags Containing CO by GC in the Present
Study Using a DID

Test		Samples	Mean	CV	OE_T%***
%RH	× PEL	N*	Recov.**		
25-30	0.5	6	1.156	0.037	10.5
	1	6	1.013	0.025	
	2	6	0.944	0.037	
50	0.5	6	1.078	0.032	9.8
	1	6	1.103	0.008	
	2	6	0.992	0.012	
80	0.5	6	1.019	0.030	7.0
	1	6	1.069	0.023	
	2	6	0.929	0.041	

* These samples were collected throughout the detector tube sampling period (5.5).

** Results were compared to standards prepared from 104-ppm CO in N_2. Theoretical concentrations were based on the blending of 0.50% CO in N_2 with purified, humidified air during sample generation.

*** Note: OE_T% (Total Overall Error in %) is the pooled result of all three concentrations at one RH level.

Table 7

Precision and Accuracy Summary

Precision		
	CV_1 (Pooled)	0.038
	CV_2 (Pooled)	0.020
	CV_T (Pooled)	0.025

Bartlett's Test

Level	B(calc)	B(crit)
Spiked (Table 1)	13.73	9.23
Generated (Tables 2 and 4)		
25-30% RH	0.82	9.23
50% RH	9.92	9.23
80% RH	1.51	9.23

Recovery: Average recovery (Sampling and Analysis) = 105.8%
Average recovery (Ceiling PEL study) = 100.0%

Recovery and CV Ranges*

Mean Recovery, present GC method	92.9-115.6%
CV, present GC method	0.008-0.041
Bias	0.006-0.058
CV_2 (Pooled)	0.020-0.034
Mean Recovery, previous GC method**	93.0-102.9%
CV, previous GC method**	0.004-0.037

* Range--includes different RH and concentration levels.

** GC method--methanizer and FID analysis.

Appendix 1
Analysis Parameters for CO Determinations

Gas chromatograph	Tracor Model No. 540 GC
Detector	Discharge ionization detector*
DID power supply	Tracor Model No. 706
Polarizing voltage setting	700
Discharge current setting	700
Electrometer settings	
Input	10
Output	2
GC temperature settings (°C)	
Column oven	90
Valve oven	60
Detector	190*
Flow control	40
Column pressure (kPa)	50-70
Column pressure (psi)	7-10
Time settings (min)	
Run time	20.0
Pre ready	1.0
On event	0.01
Off event	0.30
Columns (in series)	
First	4' × 1/8" SS Hayesep Q 60-80 (Mounted in valve oven)
Second	12' × 1/8" SS Molecular Sieve 60-80 (Mounted in column oven)
Helium flow rates (L/min)	
Through discharge	0.030
Through columns	0.020
Gas sampling loop volume (mL)	1
Integrator	Hewlett-Packard 3357 Laboratory Automation System (Rev. 2540)**
Recorder	Omniscribe Model No. B5218-5
Y1 full scale setting (v)	0.01 (TWA PEL), 0.1 (Ceiling PEL)
Chart speed (in/min)	0.05
CO peak time (min)	12.0-14.6

* When the detector reaches operating temperature after startup, helium should be allowed to flow through the detector for one day before the discharge is started (manufacturer's recommendation).

** Area counts for CO concentrations of <2.5 ppm were not automatically integrated. These areas were determined by manual integration.

Notes:

If instabilities develop in the chromatogram when the first portion of the gas sample (i.e., O_2 and N_2 peaks) pass through the DID, the GC may be programmed so that the gas flow from the columns is temporarily vented to the outside of the GC and does not pass through the DID. This venting would occur for about the first 8 or 10 min of the analysis, since the CO peak would normally occur at 12 to 15 min.

An early model of the DID which was used by our laboratory for this validation was prone to exhibit oscillatory behavior, requiring extensive down time and manufacturer service.

Chromatogram of Elution of 104 ppm CO in N_2

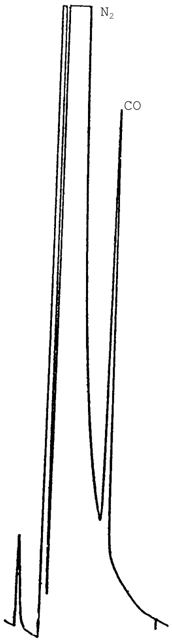

Figure 1

Dynamic Generation System for Production of Carbon Monoxide Atmospheres

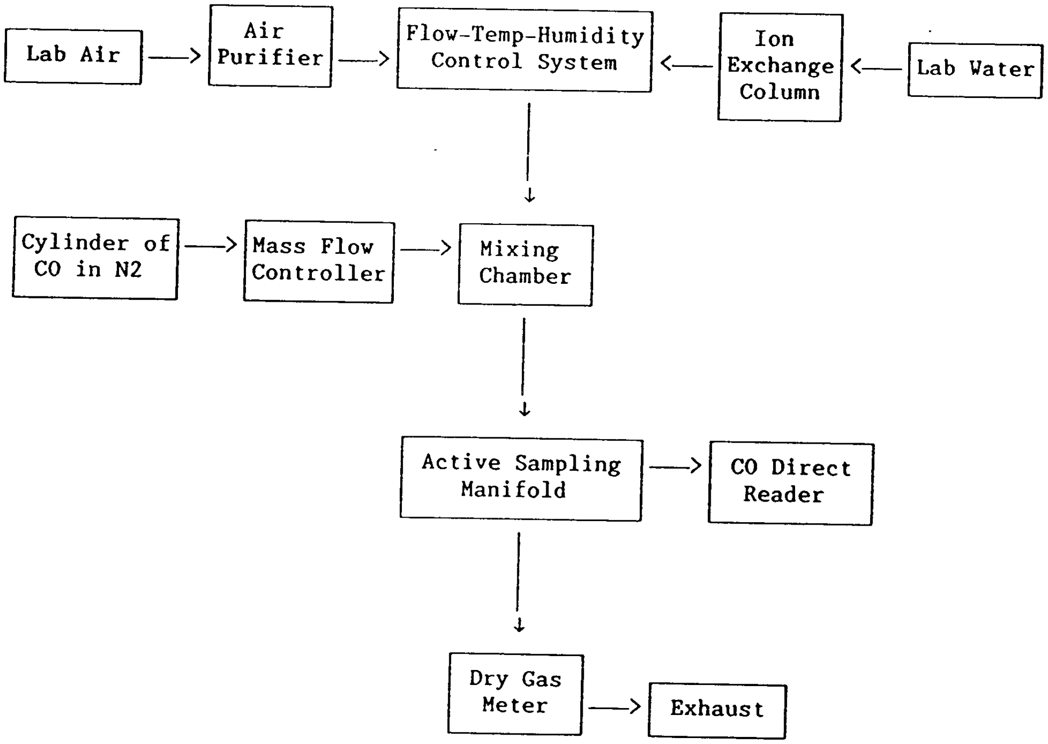

Figure 2

Storage Stability Study of CO in Gas Bags (1,2 × TWA PEL)

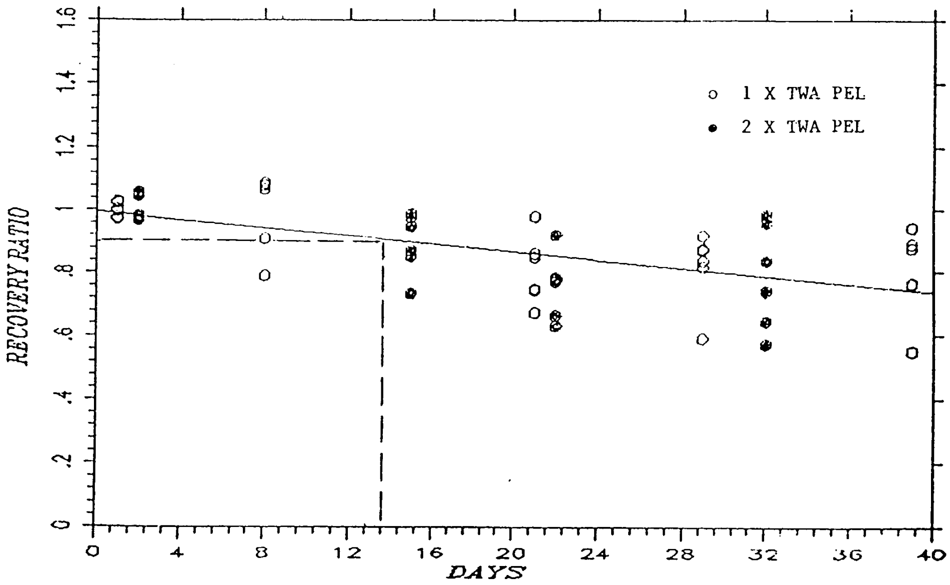

Figure 3