CARBON DIOXIDE IN WORKPLACE ATMOSPHERES

Method Number:	ID-172
Matrix:	Air
OSHA Permissible Exposure Limits Final Rule Limits	10,000 ppm Time Weighted Average (TWA) 30,000 ppm Short-Term Exposure Limit (STEL)
Transitional Limit:	5,000 ppm TWA
Collection Procedure	Each sample is collected by drawing a known volume of air into a five-layer gas sampling bag.
Recommended Air Volume:	2 to 5 liters
Recommended Sampling Rates TWA Determinations: STEL Determinations:	0.01 to 0.05 L/min (4 to 8 h sample) 0.3 L/min (15-min sample)
Analytical Procedure:	A portion of the gas sample is introduced into a gas sampling loop, injected into a gas chromatograph, and analyzed using a thermal conductivity detector.
Detection Limits Qualitative:	200 ppm
Quantitative:	500 ppm
Precision and Accuracy Validation Range:	2,000 to 10,000 ppm
CV_T:	0.026
Bias:	-0.005
Overall Error:	± 5.7%
Special Requirements:	Samples should be analyzed within 2 weeks of collection.
Method Classification:	Validated Method
Chemist:	Rick Cee
Date (Date Revised):	1987 (June, 1990)

Commercial manufacturers and products mentioned in this method are for descriptive use only and do not constitute endorsements by USDOL-OSHA. Similar products from other sources can be substituted.

Branch of Inorganic Methods Development
OSHA Technical Center
Salt Lake City, Utah-84115

1. Introduction

This method describes the collection and analysis of carbon dioxide (CO_2) in workplace atmospheres. Samples are collected in gas sampling bags and analyzed using a gas chromatograph (GC).

1.1 History

In the past, the OSHA Salt Lake Technical Center (OSHA-SLTC) method for analysis of CO_2 consisted of a bicarbonate titration using phenolphthalein as the indicator (8.1). The past method suffered from a lack of specificity, possible contamination from ambient CO_2, and a potentially unsafe collection method. Carbon dioxide was collected in impinger solutions containing sodium hydroxide.

The most recent OSHA method for measuring CO_2 exposures in the workplace required the use of detector tubes (8.2). Because short-term detector tubes offer only spot checks of the environment, another method was needed to determine long-term CO_2 concentrations. Other sources advocated the use of gas chromatography for CO_2 analysis (8.3-8.5). This method is similar to the one proposed by NIOSH (8.3), with some modifications.

1.2 Principle

For time weighted average (TWA) or short-term exposure limit (STEL) determinations, a sampling pump is used to capture a known volume of air into a five-layer gas sampling bag. A GC fitted with a gas sampling loop and a thermal conductivity detector (TCD) is then used to assess sample concentrations of CO_2 .

1.3 Advantages and Disadvantages

1.3.1 The method is specific for CO_2 in industrial environments. Response characteristics and the retention time for CO_2 lead to positive identification. Mass spectrometry can be used if additional verification is necessary.

1.3.2 The method can be used for ventilation assessments in indoor air quality investigations. A CO_2 level of 1,000 ppm is considered a determinant of ventilation system performance.

1.3.3 No impinger sampling is required; however gas sampling bags are used and may be somewhat inconvenient when handling and shipping.

1.3.4 Changes in humidity do not affect sample collection.

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

1.3.6 The gas bags are reusable.

1.3.7 The method requires the use of a GC with a gas sampling valve.

1.3.8 Analytical time required per sample is short; elution of CO_2, using stated GC conditions, occurs within 5 min.

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

1.4 Prevalence and Use

In 1979, CO_2 was the 23rd largest volume chemical produced in the United States (8.6). Potential sources for CO_2 emission and exposure are listed:

carbonated beverage manufacturing
carbonic acid manufacturing
fire extinguisher manufacturing
explosive manufacturing
municipal water treatment facilities
aerosol propellant manufacturing
breweries and fermentation plants
refrigeration units

cloud seeding
greenhouse air enrichment
lime kilns
by-product of ammonia production
product of combustion
anode baking products
fractioning and acidizing of oil wells
bakeries

grain elevators	diving
silos	mining
submarines	wells
	shielded arc welding

1.5 Physical and Chemical Information (8.6, 8.7):

Molecular formula	CO_2
Molecular weight	44.01
CAS No.	124-38-9
Appearance	colorless, odorless gas
Taste	slightly acidic (from reaction with H_2O to form carbonic acid)
Flammability	non-flammable
Boiling gravity	-78.5 °C (sublimes)
Specific gravity (air=l)	1.5240 (0 °C)
Density	1.97 g/L (@ STP)
Synonymns	carbonic anhydride; carbonic acid; gas dry ice

1.6 Toxicology

Information contained within this section is a synopsis of present knowledge of the physiological effects of CO_2 and is not intended as a basis for OSHA policy.

Carbon dioxide is classified as an asphyxiant gas. In the atmosphere, CO_2 normally exists at concentrations between 300 and 700 ppm. Larger gas-phase concentrations of CO_2 may produce signs and symptoms of increased respiratory rate, lassitude, sleepiness, headache, convulsions, dyspnea, sweating, dizziness, or narcosis. Literature citations reveal a wide variation in physiological response to exposures at certain CO_2 concentrations (8.6-8.10). Exposure to CO_2 concentrations above 1O% are generally agreed upon as posing an immediate physiologic threat (8.7-8.10).

Inhalation of CO_2 can produce physiological effects on the central nervous, respiratory, and the cardiovascular systems. Central nervous system (CNS) effects vary with CO_2 concentrations. Signs and symptoms of CNS involvement include lassitude, drowsiness, narcosis, and convulsions. At low levels, inhalation of CO_2 may cause a mild depression of the CNS. At approximately 30% CO_2 a paradoxical CNS stimulation leading to convulsions and coma is seen. Carbon dioxide concentrations above 50% induce an anesthetic effect (8.9).

Carbon dioxide is a potent stimulator of respiration.

Respiration depth and rate is mainly controlled through CO_2 blood levels. Generalized signs of respiratory involvement are displayed by shortness of breath, dyspnea, respiratory acidosis, and a rapid increase in respiratory rate.

Cardiovascular effects of CO_2 are demonstrated by generalized increases in blood pressure, vasodilation, heart rate, and cardiac output. Peripheral and cerebral vasodilation, as demonstrated by signs of sweating and headaches, are usually the first symptoms observed and are prevalent in low concentration exposures (8.7,8.10).

The signs and symptoms of low level CO_2 intoxication are sudden and reversible. Effects of intoxication are usually apparent within seconds of toxic exposure. After discontinuation of exposure, signs and symptoms usually dissipate within a few minutes.

2. Range, Detection Limit, and Sensitivity (8.11)

2.1 The analytical working range is linear from at least 200 to 30,000 ppm. The largest standard used during the study was 30,000 ppm; the response characteristics of the TCD indicate the upper linear limit may be much larger.

2.2 The qualitative detection limit was 200 ppm using a 1-mL sample loop. The quantitative detection-limit is 500 ppm. A lower detection limit for CO_2 can be achieved using a larger gas-sampling loop; however, ambient CO_2 levels are at least 300 ppm. Evaluation below 500 ppm would most likely be unnecessary for workplace atmosphere surveillance.

2.3 The sensitivity of the analytical method (using analytical conditions stated for a Hewlett-Packard 5730A Gas Chromatograph and 3385A Automation System) was taken from the slope of the linear

working range curve (200-30,000 ppm range). The sensitivity is 1.771 area units per 1 ppm. (For the HP 3385A Automation System, 1 area unit = 3.2 microvolt-second.)

3. Method Performance (8.11)

    3.1   The pooled coefficient of variation for the sampling and analytical method was 0.026. The variation was calculated from data within the range of 2,000 to 10,000 ppm.

    3.2   The average recovery of generated samples taken in the 2,000 to 10,000 ppm range was 99.5%. The range of recoveries was from 93 to 104%.

    3.3   Precision and accuracy data are derived from generated samples that were aged less than 2 days. The stability of CO_2 in sampling bags is within precision and accuracy limits up to 14 days after sample collection.

    3.4   Stability tests indicate a significant loss (>10%) of CO_2 when samples are stored longer than 14 days. Samples should be analyzed as soon as feasible to minimize storage losses.

4. Interferences

The gas chromatographic determination of CO_2 is relatively specific; however, any compound having a similar column retention time and response as CO_2 is a potential interference.

    4.1   Potential interferences may be minimized by altering operational conditions such as temperature and column packings or using gas chromatograph-mass spectrometry as a secondary source of confirmation.

    4.2   Using the conditions stated within the method, other common gases and vapors do not present potential interferences. Nitrogen, hydrogen, oxygen, methane, and carbon monoxide retention times are significantly less than that of CO_2. Chromatograms showing the elution of various common atmospheric gases and CO_2 are shown in Figures 1 and 2.

5. Sampling

    5.1   Equipment

        5.1.1   A personal sampling pump capable of delivering a flow rate of approximately 0.01 to 0.05 L/min is necessary for TWA determinations. A larger flow rate pump can be used for STEL assessments. Either pump must have external inlet and outlet ports and hose barbs.

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

        5.1.3   Various lengths of flexible tubing are used to make pump, sampling media, and breathing zone connections.
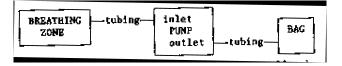
    5.2   Sampling Procedure

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

Flow rate (L/min)	Hours sampled	Total sample volume (L)
0.015	4	3.6
0.022	4	5.3
0.035	2.5	5.3
0.050	1.5	4.5

A large flow rate (0.040 to 0.050 L/min) will require placing new sampling bags into position throughout the day. For TWA determinations, a flow rate of approximately 0.020 to 0.025 L/min is sufficient for a 4 h sample. For STEL samples, calibrate the pump to a rate of approximately 0.3 L/min.

        5.2.2   Evacuate and check gas sampling bags for leaks. The 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, gas sampling bags can be inflated, inspected for leaks, and then evacuated by hand rolling and flattening.

5.2.3 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:

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┌─────────────┐          ┌─────────┐          ┌──────┐
│  BREATHING  │─tubing─  │  inlet  │          │ BAG  │
│    ZONE     │          │  PUMP   │          │      │
└─────────────┘          │ outlet  │─tubing─  └──────┘
                         └─────────┘
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5.2.4 For personal sampling attach the gas sampling bag to any loose fitting clothing on the worker's back or side using tubing clamps.

5.2.5 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. Turn on the pump.

5.2.6 After sampling, rotate gas sampling bag valve clockwise until tight. Record the total air volume taken.

5.2.7 Do not prepare or submit blank samples. Request the laboratory analyze for carbon dioxide.

5.2.8 Wrap an OSHA 21 (or equivalent) seal across the gas sampling bag valve.

5.2.9 When submitting the sampling bags to the laboratory for analysis, pack loosely and apply generous padding to minimize potential damage during shipment. Submit samples as soon as possible after sampling.

6. Analysis

6.1 Precautions

6.1.1 When preparing CO_2 standards, an Ascarite II filter is used to remove CO_2 from the diluent air. Ascarite II contains sodium hydroxide and silica: Avoid contact with skin and mucous membranes. Wear gloves and safety glasses when handling Ascarite II.

6.1.2 The preparation of CO_2 standards should be performed in a hood. Avoid breathing in any toxic concentrations of CO_2.

6.2 Equipment

6.2.1 A gas chromatograph fitted with a 1-mL stainless steel gas sampling loop, sampling valves, and a TCD are used. Loops larger than 1-mL can also be used.

6.2.2 Standard preparation (8.11):

Due to stability considerations, use only five-layer aluminum gas sampling bags for standard generation. Gas sampling bags composed of Tedlar or saran can be used for standards provided they are prepared and analyzed within 24 h.

6.2.3 Columns:

Chromosorb 102, 6 ft x 1/4 in. stainless steel, 80/100 mesh. Similar results were obtained using a 5 ft x 1/4 in. stainless steel, 80/100 mesh, Porapak QS column.

6.2.4 Data reduction:

An electronic integrator is used to calculate peak areas.

6.2.5   Standard generation:

Certified CO_2 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.

6.2.6   Gases:

a)   If certified standards are not available, undiluted, bottled CO_2 ($\geq$99.8% purity) or pre-diluted CO_2 can be used to generate gas standards. If pure liquid CO_2 is used, a heating tape and variable transformer are necessary for regulator heating.

b)   Filtered, compressed, CO_2-free air is used for dilutions. Ambient CO_2 is removed from the compressed air using an Ascarite II/Drierite in-line trap. (See Precautions in Section 6.1 before handling Ascarite) Other methods, such as slaked lime traps, can also be used for removal of ambient CO_2. A diagram of the Ascarite II trap and further information can be found in reference 8.11.

c)   Helium (purified) is used as the carrier gas.

6.2.7   Additional accessories:

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

6.3   Standard Preparation

6.3.1   Prepare standards by either calibrated syringe or metered injection of pure or diluted CO_2 into the dilution medium. Please see precautions in Section 6.1.2 before preparing.

6.3.2   Completely evacuate and flush the gas bags used for standard preparation with CO_2-free air (Note: The in-line trap with an Ascarite II/Drierite bed is used to remove any CO_2). Use a soap bubble flowmeter to measure air flow rates immediately before and after diluent air addition.

A standard dilution scheme using pure CO_2 is listed for 5-L gas bags:

ppm Standard	CO_2 volume (mL)	Air volume (mL)
Blank	0	4000
1248	5	4000
2494	10	4000
4975	20	4000
9901	20	2000
19608	40	20000

Always prepare a blank standard from the compressed air to account for potential CO_2 contamination. Other dilution schemes using smaller or larger gas bags and gas volumes can be used. Standards should be prepared in concentrations that bracket the sample concentrations.

6.3.3   For concentrations other than those listed above, use the following equation when using pure or pre-diluted CO_2:

$$\text{ppm } CO_2 = \frac{(\text{mL } CO_2)(10^6)(A)}{\text{mL Diluent air} + \text{mL } CO_2}$$

where:
A =   mole fraction or decimal per cent concentration of the pre-diluted mixture (i.e., for 1.93% CO_2 stock standard, A = 0.0193. For pure CO_2, A = 1).

6.3.4   If a metered generation of standards is desired, use a mass flow controller or calibrated rotameter to verify and control the CO_2 delivery rate from a gas cylinder. Use a soap bubble flowmeter immediately before and after the standard generation to verify the CO_2

flow rate. Meter a known amount of CO_2 into a bag already containing a known volume of CO_2-free air. Use a stopwatch to determine the volume of CO_2 delivered over time.
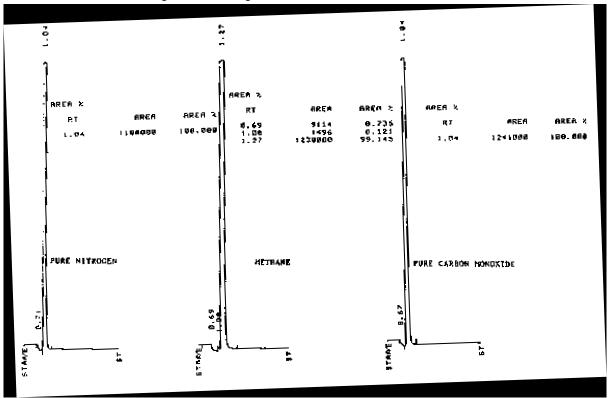
6.3.5 If using calibrated syringe injection, fill a gas sampling bag with concentrated CO_2 or use syringe extraction from an in-line gas cylinder septum. Most gas bags have injection ports or septa for gas syringe withdrawal or injection. Fill and flush a previously calibrated gas-tight syringe with pure CO_2. Then withdraw and inject the required volume of CO_2 into a gas bag already containing a measured amount of diluent air.

6.4 Analytical Procedure

6.4.1 Gas chromatograph conditions:

Helium carrier gas flow rate 15 to 25 mL/min
Reference gas flow rate 15 to 25 mL/min
Detector, manifold, and column
temperature 20 to 25 °C
Retention time 2 to 6 min

6.4.2 Sample and standard introduction:

1) Connect the outlet port of the personal sampling pump to the sampling loop via inert tubing.

2) Adjust the pump to give a suitable flow rate for sample loading from the bag to the sampling loop.

3) Connect a short piece of tubing from the inlet port of the pump to the sample bag. The bag valve is then turned counterclockwise to the open position and the pump is turned on.

4) After the sample is loaded into the loop, turn the pump off 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.)

5) Perform two determinations of each sample and standard.

6.4.3 If present in the sample, oxygen, nitrogen, carbon monoxide, and methane will elute before CO_2. Examples of integrated chromatograms of CO_2 and other common gases are shown in Figures 1 and 2.

7. Calculations

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

7.2 Calculate ppm CO_2 concentrations from a linear least-square regression curve. Establish the regression curve using peak area (or heights) versus ppm. No calculations using air volumes are necessary since gas phase samples are compared directly to gas phase standards. Since the total capacity of the sampling bag is approximately 6-L, field air volumes can be used by the chemist to visually assess any leakage during shipment.

7.3 If necessary, the sample can be analyzed by gas chromatograph-mass spectroscopy to confirm the presence of CO_2.

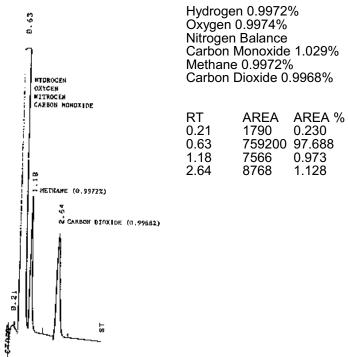7.4 Report results to the industrial hygienist as ppm CO_2.

8. References

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8.3   National Institute for Occupational Safety and Health: NIOSH Manual of Analytical Methods. 2nd ed., Vol. 3 (DHEW/NIOSH Pub. No. 77-157-C). Cincinnati, OH: National Institute for Occupational Safety and Health, 1977. pp. S249-1-S249-6.

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8.11 Occupational Safety and Health Administration Technical Center: Carbon Dioxide Backup Data Report) (ID-172). Salt Lake City, UT. Revised 1990.

Chromatograms of Nitrogen, Methane, and Carbon Monoxide Standards

Figure 1

Chromatogram of a Mixture

Hydrogen 0.9972%
Oxygen 0.9974%
Nitrogen Balance
Carbon Monoxide 1.029%
Methane 0.9972%
Carbon Dioxide 0.9968%

RT	AREA	AREA %
0.21	1790	0.230
0.63	759200	97.688
1.18	7566	0.973
2.64	8768	1.128

Figure 2

T-ID172-FV-01-9006-M

Carbon Dioxide Backup Data Report

This report was revised June, 1990

Introduction

The evaluation of OSHA Method No. ID-172, Carbon Dioxide in Workplace Atmospheres (9.1), was conducted when the time weighted average (TWA) Permissible Exposure Limit (PEL) for carbon dioxide (CO_2) was 5000 ppm (1985). (Note: Some of the data in this report is presented as %CO_2. To convert % to ppm, ppm CO_2 = %CO_2 x 10,000)

1. Experimental Protocol

1. The validation consists of the following experimental protocol:
2. Analysis of 3 sets of 6 spiked samples having concentration ranges of approximately 0.5, 1, and 2 times the PEL.
3. Analysis of 3 sets of 6 dynamically generated samples having concentration ranges of approximately 0.5, 1, and 2 times the PEL.
4. Determination of the qualitative and quantitative detection limit for analysis of CO_2 by gas chromatography.
5. Determination of any variation in results when sampling at high and low humidity levels.
6. Comparison of other methods used for CO_2 workplace determinations with the gas chromatographic method.
7. Determination of the storage stability of CO_2 samples collected in gas sampling bags.
8. Assessment of the performance of the gas chromatographic method and conclusions.

Data for certain experiments were statistically examined for outliers and homogeneous variance. Possible outliers were determined using the American Society for Testing and Materials (ASTM) test for outliers (9.2). Homogeneity of the coefficients of variation was determined using the Bartlett's test (9.3).

2. Analysis

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

2.1. Gas sampling bags were flushed with CO_2-free compressed air [ambient CO_2 and other potential contaminants were removed from the compressed air by using an air scrubber/filtration system (Figure 1) consisting mainly of a Ascarite II/Drierite bed]. A vacuum was then applied to completely evacuate the bags.

2.2. A known amount of CO_2-free air was metered into each sampling bag. Compressed air flow rates were measured immediately before and after each experiment using a soap bubble flowmeter. Air flow was regulated by using a regulator-rotameter system as shown in Figure 1. Blank samples of the compressed air were periodically collected and analyzed along with the samples and standards.

2.3. A known amount of CO_2 was metered into each sampling bag containing diluent air. Carbon dioxide flow rates for the spiked samples were determined immediately before and after each experiment using a soap bubble flowmeter. A gas cylinder containing 1.93% CO_2 in air (Air Products, Long Beach, CA, certified analytical standard) was used for spiking the samples.

2.4. Reference and analytical standards were analyzed along with the spiked samples. The reference standard was purchased commercially (Scott Specialty Gases, Houston, TX, 0.9968% CO_2 in nitrogen, methane, carbon monoxide, oxygen, and hydrogen, certified analytical standard) and analytical

standards were generated by dilution of Bone Dry grade CO_2 (Union Carbide, 99.8% min. purity). Carbon dioxide flow for analytical standards was regulated using a regulator-mass flow controller system as shown in Figure 2.

2.5. Spiked samples, blanks, reference, and generated standards were analyzed by gas chromatography (9.1). Samples were analyzed within 2 days of preparation. Analytical instrument parameters are displayed in Appendix 1.

Results: Spiked sample results were calculated using a linear regression concentration-response curve. Integrated peak areas were used as signal measurement. Spiked sample recoveries are listed in Table 1. All Analysis data passed both the outlier and Bartlett's tests. The data (Table 1) indicates good precision and accuracy. The coefficient of variation for analysis (CV_1) was 0.034 and the average analytical or spiked recovery was 95.2%.

3. Sampling and Analysis

Procedure: Three sets of generated samples were prepared and analyzed by:

3.1. Gas sampling bags were flushed with CO_2-free compressed air. Ambient CO_2 and other potential contaminants were removed from the compressed air by using an air filtration system similar to the one shown in Figure 1. A vacuum was then applied to completely evacuate the bags.

3.2. A dynamic gas generation system was assembled as shown in Figure 2. A humidity, temperature, and flow control system (Miller-Nelson Research Model 301) was used to control and monitor air flow. A dry test meter (Singer Co., Model # DTM 115) was to measure air flow immediately before, during, and after the experiments. The flow control system was calibrated in-house temperature, humidity, and flow prior to use. Calibration of the dry test meter was done using a spirometer as a primary standard.

3.3. Carbon dioxide (Bone Dry grade, 99.8% min. purity) gas was introduced into the flow system via a mixing chamber as shown in Figure 2. Carbon dioxide flow rates were taken immediately before and after each experiment using a soap bubble flowmeter. Flow rates were controlled using mass flow controllers (Tylan Model FC260 mass flow controller).

3.4. Generated samples, blanks, reference, and spiked standards were analyzed by gas chromatography. Reference standards were determined by direct injection of the gas from the canister into the gas sampling valve of the gas chromatograph. Analytical standards were prepared in gas sampling bags and then injected. Samples were analyzed within 2 days of preparation. Instrument parameters used during the analysis are displayed in Appendix 1.

Results: Generated sample results were calculated using a linear regression concentration response curve. Integrated peak areas were used as signal measurement. Generated sample recoveries are listed in Table 2. As shown in Table 2, the gas chromatographic determinations of CO_2 using gas sampling bags are within NIOSH accuracy and precision guidelines (9.3). The CV_T was 0.026 and the overall recovery was 99.5%. The Sampling and Analysis data shows excellent precision and accuracy. All data passed both the outlier and Bartlett's test.

4. Detection Limit

Procedure: The qualitative detection limit for the analysis of CO_2 by gas chromatography was calculated using the Rank Sum Test (9.4). The International Union of Pure and Applied Chemistry (IUPAC) method for detection limit determinations was used to determine the quantitative limit (9.5). The procedure used for sample preparation for determining the detection limit is shown below:

4.1. Same as Section 2.1.

4.2. Blank samples were generated using the flow, humidity, and temperature control system mentioned in [Section 3.2](#).

4.3. Low concentration CO_2 standards were prepared by mixing CO_2 (1.93% in air), via a mixing chamber, with the treated air. Concentrations of 205.1, 398.9, and 662 ppm were used as standards.

4.4. Samples were then analyzed by gas chromatography. Analytical conditions used are given in Appendix 1.

Results: Qualitative and quantitative detection limits are listed in Tables 3 and 4, respectively. The qualitative limit is 200 ppm. The quantitative limit is 500 ppm. A 1-mL sampling loop was used for all analyses. Lower detection limits for CO_2 are possible with larger sampling loops, but should not be necessary for workplace determinations. This assumption is based on the fact that ambient air will always contain a certain amount of CO_2. In well ventilated areas, the level of CO_2 is normally in the range of 300 to 700 ppm.

5. Humidity Study

Procedure: Samples were generated at high (80%), medium (50%), and low (25%) relative humidities using the same equipment and conditions described in [Section 3](#). Samples were taken side-by-side with detector tube samples ([9.6](#)).

Results: Gas sampling bag results at 80 and 25% RH are presented in Table 5. Table 2 contains the 50% RH test. Data from sampling at different humidities displayed no apparent effect on collection efficiency. As shown in Table 5, an analysis of variance (F test) was performed on the data to determine any significant difference among or within the different humidity groups. Variance at each concentration level (0.5, 1, and 2 times the PEL) was compared across the 3 humidity levels (25, 50, and 80% RH). The variance among and within the different concentration groups gave acceptable calculated F values with the exception of the test conducted at the PEL. Recovery at each humidity level was also considered. As also shown in Table 5, no evidence of any constant increase or decrease in average recovery is apparent across the humidity levels. The large calculated F value at the PEL was judged to be due to variation in sample generation and analysis and not to a humidity effect.

6. Comparison Methods

6.1. Detector tubes (in-house study)

A side-by-side (in-house) determination of CO_2 was performed using different types of short-term CO_2 detector tubes and simultaneous gas sampling bag-gas chromatography analysis. Detector tubes were chosen since they were listed as the OSHA sampling method for CO_2 ([9.8](#)). As mentioned in the Introduction of the CO_2 method ([9.1](#)), an alternative titration method ([9.7](#)) was considered unsuitable to use for comparison at the generated concentration levels. Gas chromatographic and detector tube samples were taken at different humidity levels. A synopsis of the side-by-side testing is shown in Table 6. The overall recovery and CV for the gas sampling method displays an improvement over the detector tube technique. Further information regarding the short-term detector tube evaluation can be found in reference [9.6](#).

6.2. "Numbering error. This section contains no data."

6.3. A preliminary evaluation of long-term detector tubes was also performed ([9.9](#)). The Draeger model no. 6728611 long-term detector tube and the Mine Safety Appliance Vaporgard Dosimeter were examined. Preliminary testing revealed the Draeger tube unsatisfactory for CO_2 compliance determinations. Only 10 MSA dosimeters were tested and all were from the first lot of production. Dosimeter results were satisfactory; however, further testing and assessment of lot-to-lot variability are necessary.

6.4. Detector tubes (field study)

A side by side field sampling evaluation was also performed. The sampling was done at a food freezing plant which used liquid CO_2 as the refrigerant. Gas bag samples and detector tubes were taken in various areas around the plant. Detector tubes were taken at random times and in close vicinity to the sampling bags. A log normal distribution was applied to the data to determine TWAs (for a further discussion of grab samples used to determine TWAs, see references 9.10 and 9.11). Detector tube readings were also taken directly from the personal gas bag samples during the gas chromatographic analysis. Results of the field testing are also listed in Table 6.

6.5. Miran 1A

The Miran 1A infrared gas analyzer was also assessed for possible use in CO_2 determinations. As a direct reading instrument, the Miran 1A appeared too sensitive to assess large CO_2 levels sometimes found in industrial settings. An off-scale reading was given when CO_2 concentrations were above 5,000 ppm. However, this response characteristic of the MIRAN appears to make it useful for indoor air quality investigations because CO_2 levels less than 5,000 ppm are normally used to determine ventilation system performance. Carbon dioxide is also used in air quality assessments as a tracer gas to monitor ventilation efficiency. An attempt was also made to use the 5.4-L sampling cell of the gas analyzer as a closed-system analyzer. Samples were collected in gas sampling bags and aliquots were taken from the bags using gas-tight syringes. These aliquots were then injected into the closed system. It was necessary to take 50 to 100-mL aliquots to achieve an adequate signal for CO_2 measurement at the generated levels. The aliquots were considered very large and made accurate and precise analysis difficult.

7. 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 layered, 5-L sampling bags containing generated samples, field samples, and reference standards were used to assess CO_2 storage stability. Samples were analyzed at various times, up to 50 days, after sample collection. A few samples were stored in a refrigerator at 5 °C and analyzed periodically over 31 days. Recovery data are listed in Table 7 and graphically represented in Figure 3.

Results:

Note: Previously, different types of gas sampling bags were evaluated for stability, structural integrity, and compactness. Tedlar sampling bags can be used for standard dilution, provided the standards are analyzed within a 24-h period. A significant loss of CO_2 was noted if Tedlar bag standards were analyzed during longer periods.

The storage ability of the five-layered, 5-L gas sampling bag for CO_2 is unacceptable if stored for a period longer than 14 days. Table 7 individually lists each sample/result. A summary of the stability data per time period is listed below:

Total Samples	Day	Ave % Recovery
10	1-5	95.6
8	9-18	89.7
8	26-31	77.2
7	>31	68.5

Figure 3 graphically depicts the recovery dropping below 90% after 14 days of storage. Sample refrigeration appears to slightly retard CO_2 loss; however, gas bag samples should be sent to the laboratory and analyzed as soon as possible.

8. Method Performance - Conclusions

The data generated during the validation of the method indicate an acceptable alternative for sampling and analyzing CO_2. The gas chromatographic method offers an accurate and precise assessment of CO_2 exposures in the workplace. Although no samples were taken at concentration levels at the 30,000-ppm STEL, the storage stability data at about 20,000 ppm indicates the stability, precision, and accuracy were similar to validation range (2,000 to 10,000 ppm) results. Standards prepared at 30,000 ppm to determine the linear working range displayed excellent linearity with lower concentration standards used to construct the concentration-response curve.

This method should be capable of accurate and precise measurements to determine compliance with the 10,000 ppm PEL and also the 30,000 ppm STEL.

9. References

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Table 1 Analysis

Level	%CO_2 Taken	%CO_2 Found	F/T	n	Mean	Std Dev	CV_1
	0.251	0.248	0.986				
	0.251	0.234	0.931				
0.5 X PEL	0.251	0.236	0.939				
	0.251	0.236	0.939				
	0.251	0.239	0.951				
	0.251	0.236	0.939				
				6	0.947	0.020	0.021
	0.497	0.505	1.016				
	0.497	0.470	0.946				
1 X PEL	0.497	0.467	0.940				
	0.497	0.452	0.909				
	0.497	0.477	0.960				
	0.497	0.452	0.909				
				6	0.947	0.040	0.042
	1.007	1.008	1.001				
	1.007	0.964	0.957				
2 X PEL	1.007	0.995	0.988				
	1.007	0.984	0.977				
	1.007	0.953	0.946				
	1.007	0.911	0.904				
				6	0.962	0.035	0.036

F/T = Found/Taken CV_1(Pooled) = 0.034 Average Recovery = 0.952

Table 2
Sampling and Analysis (50% RH, 25 °C)

Level	%CO_2 Taken	%CO_2 Found	F/T	Airvol	n	Mean	Std Dev	CV_2
	0.270	0.270	0.998	1.7				
	0.270	0.266	0.983	2.1				
0.5 X PEL	0.270	0.269	0.994	2.7				
	0.270	0.275	1.016	3.5				
	0.270	0.274	1.013	3.9				
	0.270	0.269	0.994	2.5				
					6	1.000	0.013	0.013
	0.544	0.563	1.036	3.6				
	0.544	0.560	1.030	3.4				
1 X PEL	0.544	0.565	1.039	3.1				
	0.544	0.560	1.030	1.7				
	0.544	0.546	1.004	2.1				
	0.544	0.556	1.023	4.1				
					6	1.027	0.013	0.012
	1.005	0.981	0.976	3.0				
	1.005	0.935	0.930	3.1				
2 X PEL	1.005	0.975	0.970	1.6				
	1.005	0.969	0.964	3.2				
	1.005	0.961	0.956	3.2				
	1.005	0.952	0.947	4.1				
					6	0.957	0.017	0.018

Airvol = Air volume taken (L)
F/T = Found/Taken
CV_2(Pooled)/FONT> = 0.014
CV_T = 0.026
Bias = -0.005
Overall Error = ±5.7%

Table 3
Determination of Qualitative Detection Limit

ppm	Integrated Area
BLANK	0, 0, 0, 0, 0, 0, 0, 0, 130, 275
205.1	221, 242, 314, 324, 426, 504, 548, 563
398.9	967, 1041, 1075, 1249, 1267, 1268, 1334, 1421
662	2090, 2107, 2335, 2561

Rank Sum Data

a	=	0.01 (two-tailed test)
n_1	=	8 (# of 205.1 ppm determinations)
n_2	=	10 (# of blank determinations)
n	=	$n_1 + n_2 = 18$
R	=	114 (sum of ranks for 205.1 ppm)
R_n	=	$n_1(n+1) - R = 38$
$R_{(table)}$	=	47

Therefore, R_n is not equal to or greater than $R_{(table)}$, and both sample populations are significantly different. Qualitative detection limit = 205.1 ppm

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Table 4
Determination of Quantitative Detection Limit

IUPAC Method

Using the equation: $\qquad C_{ld} = k(sd)/m$

Where:

C_{ld}	=	the smallest detectable concentration an analytical instrument can determine at a given confidence level.
k	=	3, thus giving 99.86% confidence that any detectable signal will be greater than or equal to an average blank reading plus three times the standard deviation (area reading $> Bl_{ave} + 3sd$).
sd	=	standard deviation of blank readings.
m	=	analytical sensitivity or slope as calculated by linear regression.

Minimum detectable signal:

$$C_{ld} = 3(91.97/1.771)$$
$$C_{ld} = 156 \text{ ppm}$$

For k = 10 (Quantitative detection limit, 99.9% Confidence):

$$C_{ld} = 519 \text{ ppm as a reliable detectable signal}$$

Table 5
Humidity Tests 25% RH (25 °C)

Level	%CO_2 Taken	%CO_2 Found	F/T	n	Mean	Std Dev	CV
	0.266	0.293	1.100				
	0.266	0.277	1.040				
0.5 X PEL	0.266	0.266	1.000				
	0.266	0.282	1.060				
	0.266	0.282	1.060				
				5	1.052	0.036	0.035
	0.538	0.483	0.898				
	0.538	0.506	0.941				
1 X PEL	0.538	0.509	0.947				
	0.538	0.499	0.929				
				4	0.929	0.022	0.023
	1.002	1.001	0.999				
	1.002	1.012	1.010				
2 X PEL	1.002	0.957	0.955				
	1.002	0.982	0.980				
	1.002	0.995	0.993				
				5	0.987	0.020	0.021

F/T = Found/Taken CV(Pooled) = 0.027 Average Recovery = 0.989

Table 5 (Cont.)
Humidity Tests 80% RH (25 °C)

Level	%CO_2 Taken	%CO_2 Found	F/T	n	Mean	Std Dev	CV
	0.268	0.300	1.120				
	0.268	0.289	1.080				
0.5 X PEL	0.268	0.281	1.050				
	0.268	0.276	1.030				
	0.268	0.270	1.010				
				5	1.058	0.043	0.041
	0.530	0.493	0.930				
	0.530	0.484	0.912				
1 X PEL	0.530	0.498	0.939				
	0.530	0.483	0.910				
	0.530	0.490	0.923				
				5	0.923	0.012	0.013
	1.002	0.952	0.950				
	1.002	0.908	0.906				
2 X PEL	1.002	0.970	0.968				
	1.002	0.985	0.983				
	1.002	0.954	0.952				
				5	0.952	0.030	0.030

F/T = Found/Taken

CV(Pooled) = 0.030   Average Recovery = 0.978

	F Test Results			Recoveries %			
Level	F(calc)	F(0.99)	df	25%	50%	80%	RH
0.5 X PEL	5.55	6.70	2,13	105.2	100.0	105.8	
1 X PEL	79.4*	6.93	2,12	92.9	102.7	92.3	
2 X PEL	3.73	6.70	2,13	98.7	95.7	95.2	
Average				98.9	99.5	97.8	

df = degrees of freedom * Large F value appears to be due to variability in sample generation and not to any humidity effect.

Table 6
Comparison of Detector Tube and Gas Chromatograph Analyses

In-house Samples - Side-by-Side

Tube Mfg.		**Detector Tube Recoveries**		**Gas Chromatograph**		**Recoveries**
	N	Recovery%	Pooled CV	N	Recovery	Pooled CV
MSA (50% RH)	9	111.8	0.069	5	107.9	0.012
Kitagawa (50% RH)	9	108.0	0.039	8	103.0	0.050
Gastec (25% RH)	18	101.3	0.063	11	98.8	0.031
Gastec (50% RH)	17	109.9	0.058	7	106.5	0.014
Gastec (80% RH)	18	106.2	0.057	13	97.8	0.032
Draeger (50% RH)	9	101.8	0.076	6	100.2	0.010
Totals	80	106.5	0.039-0.076	50	102.3	0.01-0.050

Detector Tube - Gas Chromatography Statistical Summary

Detector Tube Pooled CV_2(all tubes)	=	0.025-0.076
Ave. Recovery, Detector Tubes (all tubes)	=	85.9-111.8%
Gas Chromatograph (CV_2 Pooled)	=	0.014
Gas Chromatograph (CV_T Pooled)	=	0.026
Average Recovery, GC	=	99.5%
Average Recovery, GC (all samples)	=	95-103%

Field Samples

Sample#		**Detector Tube Recoveries**				**GC Recoveries**
	Type	N	AV R%	LAV R%	Bagtube	ppm CO_2
1A	P	7	76	73	104%	11,000
1B	P	7	81	77	93%	15,000
2A	P	6	83	80	86%	8,000
2B	P	7	83	74	83%	7,600
3A	A	5	84	83	--	8,900
3B	A	6	(11000)	(9100)	--	LIS*
4A	A	3	97	96	--	6,800
4B	A	6	72	62	--	5,300
5A	A	4	92	89	--	7,200
5B	A	5	92	84	--	9,700

N   =   Number of tubes or samples taken

*LIS	=	Lost in shipment. Tube results for this sample are, listed in ppm.
AV R%	=	Average recovery in %, normalized to GC results.
LAV R%	=	Log normal average results in %, also normalized (9.10, 9.11).
Bagtube	=	Detector tube sample taken on gas sampling bag prior to gas chromatographic analysis. Bagtube samples were only taken from the personal samples.
P	=	Personal sample
A	=	Area sample

Table 7
Stability Test (Per Sample)

ppm Taken	ppm Found	Recovery %	Day
5260	5150	97.9	5
" "	4760	90.5	18
" "	3980	75.7	29
" "	3650	68.9	50+
5440	4670	85.9	11*
" "	4370	80.4	31+
" "	4840	89.1	11*
" "	4720	86.9	31*+
" "	4990	91.8	11*
" "	5010	92.1	31*+
6770	6550	96.8	5
7210	7020	97.4	5
7570	7140	94.3	5
" "	6880	90.9	18
" "	6060	80.1	29
" "	5730	75.7	50+
7990	7170	89.7	5
" "	6210	77.7	18
" "	5010	62.7	29
" "	4490	56.2	50+
8940	8280	92.6	5
" "	7810	87.4	18
" "	6380	71.4	29
" "	5040	56.4	50+
11010	10420	94.6	5
" "	10750	97.6	18
" "	9550	86.7	29
" "	8850	80.4	50+
14600	14240	97.5	5
" "	13940	95.5	18
" "	12900	88.3	29
" "	12040	82.5	50+
19300	19280	99.9	2
" "	18410	95.4	5
" "	17930	92.9	9
" "	16460	85.3	14
" "	13990	72.5	26
" "	11330	58.7	37

* Samples stored in refrigerator at 5 °C. Data for refrigerated samples is not included in final calculations. All other samples were stored at 20 °C.

+ All samples were analyzed using a 1 mL gas sampling loop, with the exception of the (+) day stability study. On that day, a 5 mL loop was used.

Appendix 1

Analysis Parameters for CO_2 Determinations Gas chromatograph (Hewlett-Packard 5730a gas chromatograph)

Detector	Thermal conductivity
Sensitivity	5
Helium flow rate	15 - 25 mL/min
Column temperature	ambient (20 to 25 °C)
Detector temperature	ambient (20 to 25 °C)
Valve manifold temperature	ambient (20 to 25 °C)
Column	Chromosorb 102 (6 ft X 1/4 in. stainless steel, 80/100 mesh)
Gas sampling loop	1 mL

Integrator (Hewlett-Packard 3385a automation system)

Attenuation	4
Run time	3.5 min
Peak time	2.6 - 2.9 min
External valve switch	0.01 s (from start of integration to valve opening)
Auxiliary signal	a
Chart speed	1
Zero	10
Area reject	0

Generation of Dilution Air (CO₂-free)

| House Air |

↓

| Moisture Trap |

↓

| Regulator |

↓

| Silica Gel Filter |

↓

| Activated Charcoal Filter |

↓

| Ascarite II/ Drierite Filter |

↓

| Rotameter |

↓

| Bubble Meter   or Gas Bag |

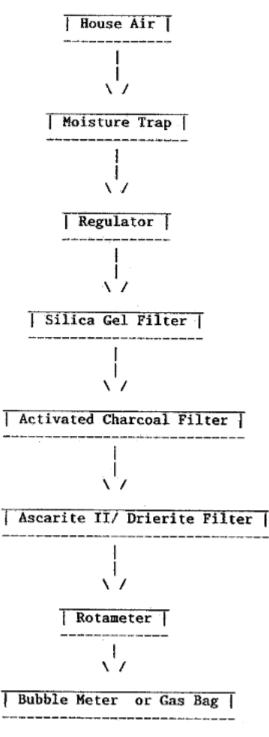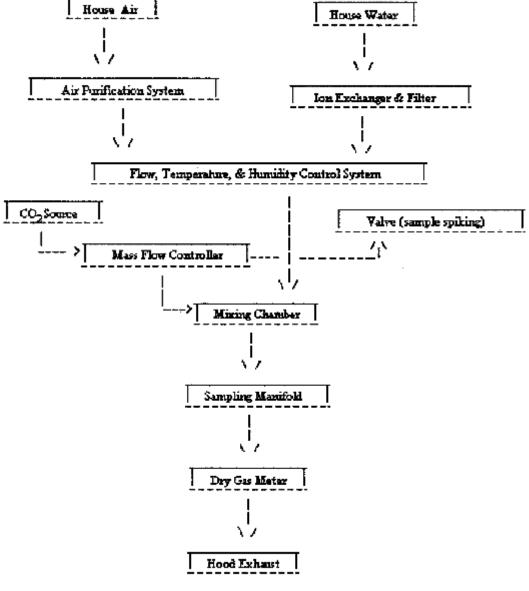**Figure 1**

Carbon Dioxide - Air Flow Generation System

Figure 2

Storage Stability - Carbon Dioxide in Gas Sampling Bags

Figure 3