

Occupational Safety and Health Administration

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Sampling and Analytical Methods / Carbon Dioxide In Workplace Atmospheres

Carbon Dioxide In Workplace Atmospheres

OSHA Method ID-172 | 1987, Revised June 1990

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Method no.:	ID-172
Matrix:	Air
OSHA Permissible Exposure Limits	
Limits	10,000 ppm Time Weighted Average (TWA)
Final Rule Limits:	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	0.01 to 0.05 L/min (4 to 8 h sample)
STEL Determinations:	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

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Branch of Inorganic Methods Development
OSHA Technical Center
Sandy, Utah

1. Introduction

This method describes the collection and analysis of carbon dioxide (CO₂) 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 CO₂ 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 CO₂, and a potentially unsafe collection method. Carbon dioxide was collected in impinger solutions containing sodium hydroxide.

The most recent OSHA method for measuring CO₂ 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 CO₂ concentrations. Other sources advocated the use of gas chromatography for CO₂ 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 CO₂.

1.3. Advantages and Disadvantages

- 1.3.1. The method is specific for CO₂ in industrial environments. Response characteristics and the retention time for CO₂ 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 CO₂ 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 CO₂, 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, CO₂ was the 23rd largest volume chemical produced in the United States (8.6). Potential sources for CO₂ 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
silos
submarines
diving
mining
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 ₂ O to form carbonic acid)
Flammability	non-flammable
Boiling gravity	-78.5°C (sublimes)
Specific gravity (air = 1)	1.5240 (0°C)
Density	1.97 g/L (@ STP)
Synonyms	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 CO₂ and is not intended as a basis for OSHA policy.

Carbon dioxide is classified as an asphyxiant gas. In the atmosphere, CO₂ normally exists at concentrations between 300 and 700 ppm. Larger gas-phase concentrations of CO₂ 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 CO₂ concentrations (8.6 - 8.10). Exposure to CO₂ concentrations above 10% are generally agreed upon as posing an immediate physiologic threat (8.7 - 8.10).

Inhalation of CO₂ can produce physiological effects on the central nervous, respiratory, and the cardiovascular systems. Central nervous system (CNS) effects vary with CO₂ concentrations. Signs and symptoms of CNS involvement include lassitude, drowsiness, narcosis, and convulsions. At low levels, inhalation of CO₂ may cause a mild depression of the CNS. At approximately 30% CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ can be achieved using a larger gas-sampling loop; however, ambient CO₂ 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

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 CO₂ 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 CO₂ 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 CO₂ is relatively specific; however, any compound having a similar column retention time and response as CO₂ 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 CO₂. Chromatograms showing the elution of various common atmospheric gases and CO₂ 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.

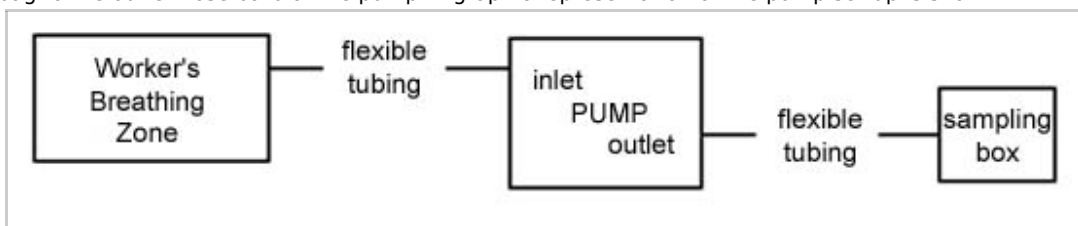
5.2. Sampling Procedure

- 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:



Text Version: The sampler is composed of an appropriate length of flexible plastic tubing attached to the inlet of a personal sampling pump. The other end of this flexible plastic tubing is placed in the breathing zone of the worker. Another appropriate length of flexible plastic tubing is used to connect the outlet of the sampling pump to the inlet of the sampling bag.

- 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

- 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 CO₂ standards, an Ascarite II filter is used to remove CO₂ 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 CO₂ standards should be performed in a hood. Avoid breathing in any toxic concentrations of CO₂.

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 CO₂ 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:

- If certified standards are not available, undiluted, bottled CO₂ (>99.8% purity) or pre-diluted CO₂ can be used to generate gas standards. If pure liquid CO₂ is used, a heating tape and variable transformer are necessary for regulator heating.
- Filtered, compressed, CO₂-free air is used for dilutions. Ambient CO₂ 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 CO₂. A diagram of the Ascarite II trap and further information can be found in reference 8.11
- 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 CO₂ 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 CO₂-free air (Note: The in-line trap with an Ascarite II/Drierite bed is used to remove any CO₂). Use a soap bubble flowmeter to measure air flow rates immediately before and after diluent air addition.

A standard dilution scheme using pure CO₂ is listed for 5-L gas bags:

ppm Standard	CO ₂ volume (mL)	Airvolume (mL)
Blank	0	4,000
1,248	5	4,000
2,494	10	4,000
4,975	20	4,000
9,901	20	2,000
19,608	40	2,000

6.3.3. For concentrations other than those listed above, use the following equation when using pure or pre-diluted CO₂:

$$\text{ppm CO}_2 = \frac{(\text{mL CO}_2)(1 \times 10^6)(A)}{(\text{mL diluent air} + \text{mL CO}_2)}$$

Where:

A = mole fraction or decimal per cent concentration of the pre-diluted mixture (i.e., for 1.93% CO₂ stock standard, A = 0.0193. For pure CO₂, 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 CO₂ delivery rate from a gas cylinder. Use a soap bubble flowmeter immediately before and after the standard generation to verify the CO₂ flow rate. Meter a known amount of CO₂ into a bag already containing a known volume of CO₂-free air. Use a stopwatch to determine the volume of CO₂ delivered over time.

6.3.5. If using calibrated syringe injection, fill a gas sampling bag with concentrated CO₂ 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 CO₂. Then withdraw and inject the required volume of CO₂ 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 CO₂. Examples of integrated chromatograms of CO₂ 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 CO₂ 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 CO₂.
- 7.4. Report results to the industrial hygienist as ppm CO₂.

8. References

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8.9. **Goodman, L.S. and A. Gilman, ed.:** *The Pharmacological Basis of Therapeutics*. 6th ed. New York, NY: Macmillan, 1980. pp. 331-334.

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Chromatograms of Nitrogen, Methane, and Carbon Monoxide Standards

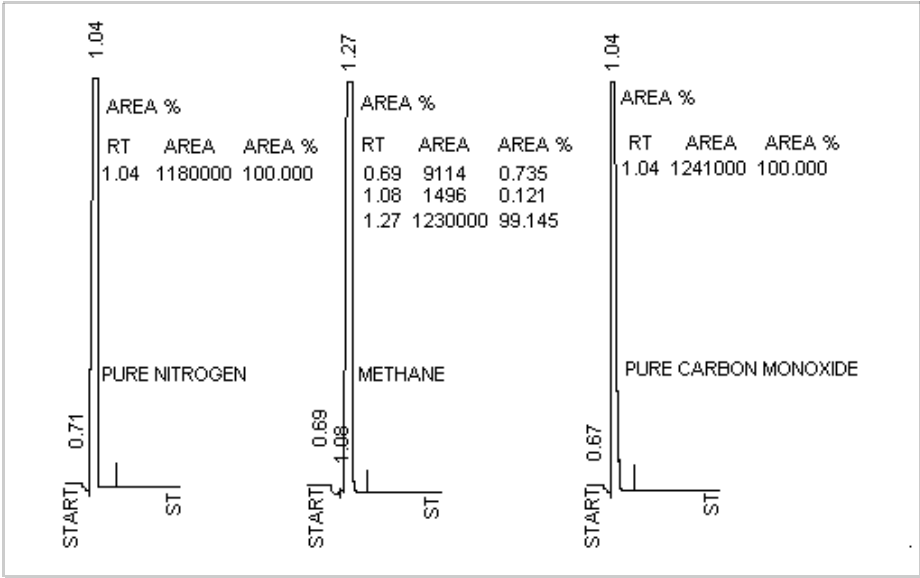


Figure 1

Chromatogram of a Mixture

Hydrogen 0.9972%	RT	AREA	AREA %
Oxygen 0.9974%	0.21	1790	0.230
Nitrogen Balance	0.63	759200	97.688
Carbon Monoxide 1.029%			
Methane 0.9972%	1.18	7566	0.973
Carbon Dioxide 0.9968%	2.64	8768	1.128

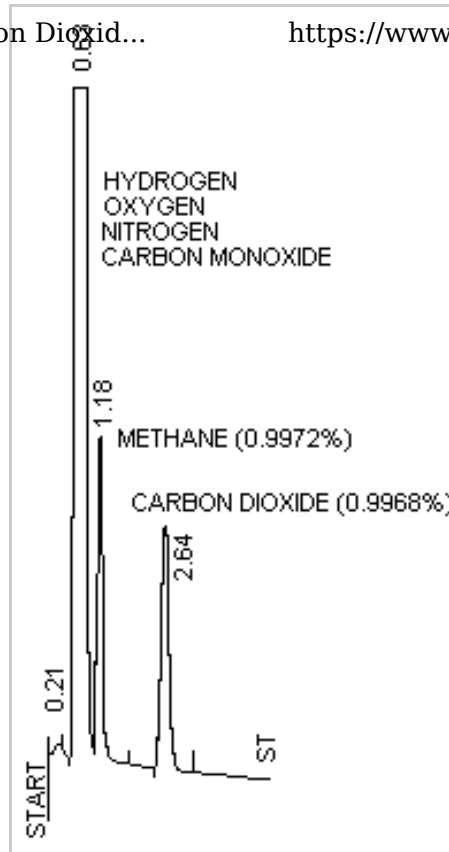


Figure 2

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