CARBON DIOXIDE 6603

CO_2 MW: 44.01   CAS: 124-38-9   RTECS: FF6400000

| METHOD: 6603 | EVALUATION: FULL | Issue 1: 15 May 1989 |
| | | Issue 2: 15 August 1994 |

OSHA : 5000 ppm; STEL 30000 ppm
NIOSH: 5000 ppm; STEL 30000 ppm
ACGIH: 5000 ppm; STEL 30000 ppm
(1 ppm = 1.8 mg/m^3 @ NTP)

PROPERTIES: gas; sublimes @ - 78.5 °C

SYNONYMS: carbonic acid; dry ice

SAMPLING	MEASUREMENT
SAMPLER: GAS SAMPLING BAG	**TECHNIQUE:** G A S C H R O M A T O G R A P H Y (PORTABLE), TCD
FLOW RATE: 0.02 to 0.1 L/min; fill bag ≤ 80% of capacity; spot samples (step 2.a.) or TWA samples (step 2.b.)	**ANALYTE:** carbon dioxide
SAMPLE STABILITY: at least 7 days @ 25 °C [1]	**TEMPERATURE-INJECTION:** ambient **-DETECTOR:** 70 °C **-COLUMN:** ambient
FIELD BLANKS: in bag from a non-work area	**CARRIER GAS:** He, 100 mL/min
	COLUMN: 1.5 m x 6-mm ID stainless steel, packed with 80/100 mesh Poropak QS
	DETECTOR: thermal conductivity
ACCURACY	**CALIBRATION:** bag standards or calibrated gas mixtures
RANGE STUDIED: 2270 - 10000 ppm [3] (3.5-L samples)	**RANGE:** 500 - 15000 ppm [2]
ACCURACY: ± 5.3% [1]	**ESTIMATED LOD:** 1 ppm
BIAS: -2.5% [3]	**PRECISION (S̄$_r$):** 0.005 [1]
OVERALL PRECISION (Ŝ$_{rT}$): 0.014 [1]	

APPLICABILITY: The working range is 500 to 15000 ppm (900 to 2700 mg/m^3) in relatively non-complex atmospheres.

INTERFERENCES: Any compound having the same or nearly the same retention time as carbon dioxide on the column in use.

OTHER METHODS: This is method S249 in a revised format [2].

REAGENTS:

1. Carbon dioxide,* 99% or higher purity
2. Nitrogen,* purified
3. Helium,* purified
4. Air*, filtered, compressed

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Portable gas chromatograph (GC), with thermal conductivity detector, column (p. 6603-1), and 5-mL gas sampling loop.
2. Strip chart recorder, if appropriate. (Many GCs have built-in data-handling capabilities)
3. Personal sampling pump, 0.02 to 0.1 L/min or other rate suitable for filling sample bag, with flexible connecting tubing.
4. Sample bags, five-layer, 2- to 20- L, or other appropriate sizes, fitted with a metal valve and hose bib (Calibrated Instruments, 731 Saw Mill Rd., Ardsley, NY 10502, or equivalent).
5. Gas-tight syringes, 10 mL and other convenient sizes for making standards and GC injections if GC is not equipped with gas sampling loop.
6. Calibrated rotameters, for standards preparation.
7. Label tape and marking pens for labelling bags.

SPECIAL PRECAUTIONS: Shipment of compressed must comply with 49 CFR 171-177, DOT regulations regarding shipment of hazardous materials.

SAMPLING AND MEASUREMENT:

1. Start GC and recorder (if applicable) and allow to warm up according to manufacturer's instructions.
    NOTE: A straight baseline should be attained at the highest sensitivity likely to be used.
2. Select one of the following sampling modes:
    a. **Spot sample.** Draw air sample into the gas sampling loop of the GC with the on-board sampling pump, if supplied. Alternatively, inject an aliquot of air to be sampled into the GC with a gas-tight syringe.
        NOTE: A large contributor to random error in the method is imprecision of replicate injections. To improve precision:
        (1) use a gas sampling loop for injections if available;
        (2) make at least three replicate determinations per sample;
        (3) use an injection volume large enough to be precisely readable, and consistent with that used in calibration.
    b. **Integrated air sample for TWA determination.**
        (1) Evacuate a clean sample bag using the inlet port of a personal sampling pump.
            NOTE: To reduce memory effects and contamination, use only previously unused sample bags.
        (2) Attach the sample bag to the outlet port of the personal sampling pump with a minimum length of flexible tubing.
        (3) Pump the air sample into the bag at a rate calculated to fill ≤80% of the sample bag capacity over the sampling period.
            NOTE: The flow rate must be known to ±5% throughout the sampling period.
        (4) Within 24 hours after completion of sampling, introduce an aliquot of the sample into the GC (as in step 2a).
3. Obtain the carbon dioxide peak height of the injected sample.
    NOTE: Under these conditions, carbon dioxide elutes at about 2 min, after oxygen and nitrogen.

CALIBRATION AND QUALITY CONTROL:

4. Perform the following in the laboratory <u>before</u> field work begins:
    a. Establish a laboratory calibration graph with at least three replicate determinations of at least five working standards. Plot peak height vs. mass of carbon dioxide.
    b. Determine detector drift, averaged over the time period(s) expected to be used in the field.
    c. Determine the ability of the GC column to separate the carbon dioxide peak from other substances known or predicted to be present in the field samples.
5. Establish a daily field calibration graph (peak height vs. mass of carbon dioxide with triplicate determinations of working standards under the same conditions as for samples (step 2.a). Alternate analyses of samples and working standards, if possible.

CALCULATIONS:

6. Calculate mass, W (ng), of carbon dioxide in the sample by comparison of the sample peak height with the daily calibration graph (step 5). Determine the concentration, C, of carbon dioxide in the injected sample, V (mL):

$$C = W/V \quad (mg/m^3)$$

NOTE: Some GCs will perform this calculation electronically.

EVALUATION OF METHOD:

This method for carbon dioxide was evaluated in accordance with the criteria for validation described in Reference [3]. Evaluation was over the range 2270-10000 ppm using a Fisher-Hamilton Gas Partitioner Model 29 gas chromatograph with a thermal conductivity detector and a 5-mL gas sampling loop [1,2]. Recovery after storage of CO_2 at 5800 ppm for 7 days was 92.5% (Saran or Tedlar bags), and 99.5% (5-layer bags). Other GCs and columns other than the one used this evaluation are available for use for the determination of carbon dioxide.

REFERENCES:

[1] Documentation of the NIOSH Validation Tests, S249, U.S. Department of Health, Education, and Welfare Publ. (NIOSH) 77-185 (1977).
[2] NIOSH Manual of Analytical Methods, 2nd ed., Vol. 3, S249, U.S. Department of Health, Education, and Welfare (NIOSH) Publ. 77-157-C (1977).
[3] NIOSH Research Report - Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances, U.S. Department of Health and Human Services, Publ. (NIOSH) 80-133 (1980).

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