

SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

METHOD 10.1

CARBON MONOXIDE AND CARBON DIOXIDE BY GAS CHROMATOGRAPH/NON-
DISPERSIVE INFRARED DETECTOR (GC/NDIR) - OXYGEN BY GAS
CHROMATOGRAPH-THERMAL CONDUCTIVITY (GC/TCD)

OFFICE OF OPERATIONS
TECHNICAL SERVICES DIVISION
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METHOD 10.1

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Section 1 of 3

1. Overview

1.1 Principle

Samples are collected in evacuated 2 liter (nominal) glass bulbs as grab samples or can be collected by pumping the sample into bags to obtain true integrated samples.

Carbon monoxide (CO) and carbon dioxide (CO₂) are fractionated on a chromatographic column, eluting first CO, then CO₂. Carbon monoxide is converted to CO₂, and measured by a non-dispersive infrared detector (NDIR). If low concentrations of CO (in the range of 0-50 ppm) are to be analyzed, the CO is first oxidized to CO₂; then the CO₂ is reduced to methane and measured by flame ionization detector (FID). Oxygen is measured by a gas chromatograph using a thermal conductivity detector (GC/TCD).

1.2 Applicability

This method measures and concentrations between 50 ppm and 100 percent (with dilution) by volume. It has been applied to the quantitative analysis of engine exhausts, vapor recovery systems, and industrial stack effluents. At the South Coast Air Quality Management District, this method applies most specifically to the enforcement of Rule 407 governing the discharge of gaseous air contaminants. This rule requires an integrated gas sample for a minimum period of 15 minutes. Since all CO is oxidized to CO₂, to which the NDIR detector is specifically sensitized, response factors to other compounds need not be determined. The GC/TCD procedure is used to measure the oxygen concentration in the range of 2-25 percent. NDIR detectors specifically sensitized to CO rather than CO₂ may be used for CO measurements, provided that the CO₂/CO interference responses have been adequately characterized.

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2. Field Procedures

2.1 Sampling Apparatus

The nature of the sample, the chemical components of primary interest, and the expected concentrations govern the choice of sampling systems. Procedures for grab sampling and integrated sampling are outlined in Method 3.1.

a. Glass Bulbs

Grab samples may be taken into an evacuated 2 liter glass bulb by opening a pinch clamp attached to a piece of rubber tubing (see Method 3.1).

b. Tedlar Bag

Integrated samples may be taken with a Tedlar bag. (see Method 3.1).

c. Tedlar Bag with Off-Line Pump

Large (to 50 liters) integrated samples may be taken into a Tedlar bag which is continuously evacuated through a pump vented to the atmosphere (Figure 10.1-4). This system has the advantage of integrating samples over longer time periods, reducing the statistical sampling error.

Taking integrated samples by this method requires a Tedlar bag connected in-line to a pump and a probe. Tests on Tedlar bags have shown that the bags are not likely to contribute to negative or positive analytical error from absorption or desorption of these gaseous compounds. Bags may be fabricated of 0.002 inch thick sheets. All seams should be heat-sealed. Flange-and-gasket fittings incorporating an inlet valve for filling the bag and an outlet valve for withdrawing GC

samples are included in the design. Viton is the preferred material for O-rings and gaskets. (Prefabricated bag assemblies are available commercially.)

Connecting tubing should be made of 3/16 or 1/4 in. ID Teflon. One-fourth inch OD stainless steel tubing may be used as a sample probe if the inside surface is free of oil and other residual organic materials. If sections of metal tubing are joined together with flexible plastic or rubber, the joints should be abutted and as closely coupled as possible.

The pump may be any air pump capable of sustaining a pressure differential of 10 mm Hg under sampling conditions.

2.2 Sampling Procedure

2.2.1 Sampling Bulb Evacuation and Leak Check

Either in the laboratory or the field, evacuate the sample bulb to 10 mm Hg absolute pressure or less (measured by a mercury U-tube manometer or mechanical

gauge). Then leak check the sample bulb by isolating the bulb from the vacuum pump and allowing the bulb to sit for 10 minutes. The bulb is acceptable if there is no change in bulb vacuum.

2.2.2 Sample Collection

Collect grab sample or integrated sample in accordance with the procedures given in Method 3.1.

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Section 3 of 3

3. Laboratory Procedures

3.1 Apparatus

3.1.1 Sampling

- a. Glass Bulbs, Tedlar Bags, Tedlar Bags with Off-Line Pump

See Section 2.1.

- b. Vacuum Pump

Capable of producing a vacuum of less than 10 mm Hg.

c. Manometer

Capable of measuring pressures in the
0 to 900 mm Hg range, to ± 1 mm Hg.

3.1.2 Sample Recovery

a. Manometer (see Section 3.1.1).

3.1.3 Sample Analysis

3.1.3.1 CO and CO₂ (GC/NDIR)

a. Chromatograph

Must be capable of resolving
CO, CH₄, and CO₂, separating
them from the higher boiling
organic compounds, and have
backflush capability (see
Section 3.2 for column types).
The chromatograph must have
the capacity to select between
large and small sample loops.

b. Furnace

Capable of oxidizing CH_4 , CO , and organic compounds to CO_2 with at least 95 percent efficiency.

c. Detector

Non-dispersive infrared detector (NDIR) specific for CO_2 .

d. Integrator

To sum area under peaks which cannot be measured using peak height.

e. Syringe

100 ml, gas-tight.

f. Dewar Flask

Capacity to contain the chromatographic columns.

g. Flow Controller (Optional)

A flow controller capable of maintaining constant flow to the NDIR may be necessary.

3.1.3.2 Analysis for Oxygen

a. Gas Chromatograph with Thermal Conductivity Detector

b. Column

Type 316 stainless steel, 4 in. length with a 1/4 in. OD and a 0.028 inch wall thickness, packed with Linde type 5A, 42 to 60 mesh molecular sieve.

c. Syringe

100 ml glass, gas tight.

d. Six Port Gas Sampling Valve

e. Chart Recorder, or Integrator

Set to peak height.

3.2 Reagents

3.2.1 Sampling Preparation

Compressed nitrogen, with total hydrocarbon (THC), CO and CO₂ less than 1 ppm.

3.2.2 Sample Recovery

Compressed nitrogen (See above).

3.2.3 Sample Analysis

3.2.3.1 CO and CO₂

- a. Zero grade air, with THC less than 1 ppm.
- b. Chromatographic columns

The columns used for separating the various carbon compounds are set in series as follows:

- (1) The initial column is 1/8 in. OD, approximately 7 in. long, packed with 10 percent silicone w-98 on chromosorb w, 0 to 100 mesh.
- (2) The second column is 1/8 in. OD, 10 in. long, column packed with Porapak Q, 100 to 200 mesh.

c. Dry Ice

d. 2-Propanol

99.9 percent 2-propanol is needed for the ice bath.

e. Water Baths

Water baths at 0°C (ice water), 20°C (nominal-ambient), and 100°C (boiling water) are required.

f. Calibration Gases

CO₂ in N₂ (approximately 2000 ppm, 6000 ppm, and 1 percent)
CO in N₂ (approximately 2000 ppm), calibrated against a NBS certified CO₂ standard (3.91 percent).

3.2.3.2 Oxygen

a. Calibration Gas

Dry ambient air.

b. Carrier Gas

Argon (99.99 percent
purity).

3.3 Pretest Preparation

Before testing, assemble the required equipment and reagents to check readiness. It is important that analytical, recovery, and sample equipment are all leak-free in order to produce reliable results. Flush sampling flow controllers with clean air or nitrogen between tests. Evacuate the sample tanks and intermediate collection tanks and fill then with nitrogen at least four times before final evacuation in order to flush residual hydrocarbons and CO₂ from the tanks. Maintain the condensate recovery module in the stand-by mode to reduce warm-up time.

3.4 Preparation of Sample Collection Equipment

Fill with nitrogen and evacuate all sampling equipment (bulbs, Tedlar bags) several times to flush out any residual sample. Bulbs may be left clamped with a vacuum of <10 mm Hg, and tested before use for leakage. Bags may be left slightly inflated; a leaky bag generally will deflate within a day. Evacuate the bags before use.

3.5 Leak Check

3.5.1 Sampling Bulb Evacuation and Leak Check

Either in the laboratory or the field, evacuate the sample bulb to 10 mm Hg absolute pressure or less (measured by a mercury U-tube manometer or mechanical gauge). Leak check the sample bulb by isolating the bulb from the vacuum pump and allowing the bulb to sit for 10 minutes. The bulb is acceptable if there is no change in bulb vacuum.

3.5.2 Bag

Inflate the Tedlar bag slightly. If no deflation is found after 24 hours, the bag is leak-free.

3.6 Sample Recovery

If recovering grab samples, allow the sample to equilibrate to room temperature. Using a manometer, measure pressure of each sample to the nearest 1 mm Hg. After recording the initial pressure of the bulb, pressurize with compressed nitrogen to between 860-910 mm Hg. Shut off the pressure, wait until the pressure is stable, record the reading, and seal the bulb until ready for analysis. Tedlar bags do not need to be pressurized.

3.7 Sample Analysis

3.7.1 CO and CO₂

Check the instrument calibration as described in Section 3.9. Equilibrate each of the chromatographic columns (the

silicone oil end column and Porapak Q column) with a dry ice/isopropyl alcohol bath (-80°C). Set flow in the forward direction (from silicone oil to Porapak), and select the large loop if chosen for the initial conditions.

Inject a 50 ml sample into the sample port to flush the loop. Switch the loop valve to the position that flushes the sample into the columns. Under these analytical conditions, CO elutes before CH_4 , and CO_2 is trapped on the Porapak column.

After seven minutes, or when all the CH_4 has eluted, immerse the Porapak column in room temperature water. Under these conditions CO_2 will elute first; followed by ethylene, acetylene, and ethane.

Analyze each sample in duplicate; then calibrate the instrument as described in Section 3.9. Also run the check standard (Section 3.2.3.1 f) after every ten injections, or at the end of a run, whichever occurs first.

3.7.2 Oxygen

The column temperature is 80°C and carrier flow approximately 30 ml/min. Set instrument response to oxygen as described in Section 3.9 as close to maximum as possible (about 90 percent) with ambient air. Obtain an aliquot of the sample in a 100 ml gas-tight syringe and flush it through the sample loop. Inject the sample into the column and allow it to elute. If the sample contains high amounts of hydrocarbons, it will be necessary to increase the analysis time to allow for the elution of these compounds; otherwise, "ghost" peaks may appear after the next injection. Run samples in duplicate. Run duplicate ambient air injections before and after each set or every ten injections, whichever is first. Duplicate determinations must agree within 5 percent.

3.8 Calculations

3.8.1 CO and CO₂

Calculate concentrations of gaseous effluent components present in the gaseous phase as concentrations of carbon in ppm by volume (v/v) using the following equation:

$$C_{sa} = \frac{C_{st} \times A_{sa} \times P_f}{A_{st} \times P_i} \times D$$

where:

C_{sa} = CO, CO₂, or backflush concentration corresponding to peak being measured, ppm v/v

C_{st} = Concentration of CO, or CO₂ in the standard, ppm v/v

A_{sa} = Area of charted response curve for the CO, CO₂, or backflush sample in identical units as A_{st}

A_{st} = Area of charted response curve
for the standard in identical
units as A_{sa}

P_f = The final pressure of the sample
in the tank, Torr

P_i = The initial pressure of the
sample in the tank, Torr

D = Dilution Factor

3.8.2 Oxygen

Calculate percent oxygen by relative peak
heights, and correct for sample
pressurization, as follows:

$$\text{Percent O}_2 = \frac{h_{spl}}{h_{std}} \times 20.95 \text{ percent} \times \frac{P_f}{P_i}$$

where:

h_{spl} = Average peak height of the sample

h_{std} = Average peak height of the
standard

p_f = Final pressure after
pressurization with N_2 , mm Hg

p_i = Pressure of the sample as
received, mm Hg

3.9 Calibrations

3.9.1 CO and CO₂

Before performing any analysis , check the response of the instrument with injections of a check standard. If the response is acceptable, proceed with sample analysis. Each sample component must be immediately calibrated against CO₂ standards that are within 5 percent of the sample peak areas when working in the non-linear range of the NDIR (this must be determined beforehand). Standard injection must be made for every concentration. Follow the last sample analysis with replicate injections of the check standard. A drift

of more than 10 percent invalidates the results and requires sample reanalysis.

3.9.2 Oxygen Calibrations

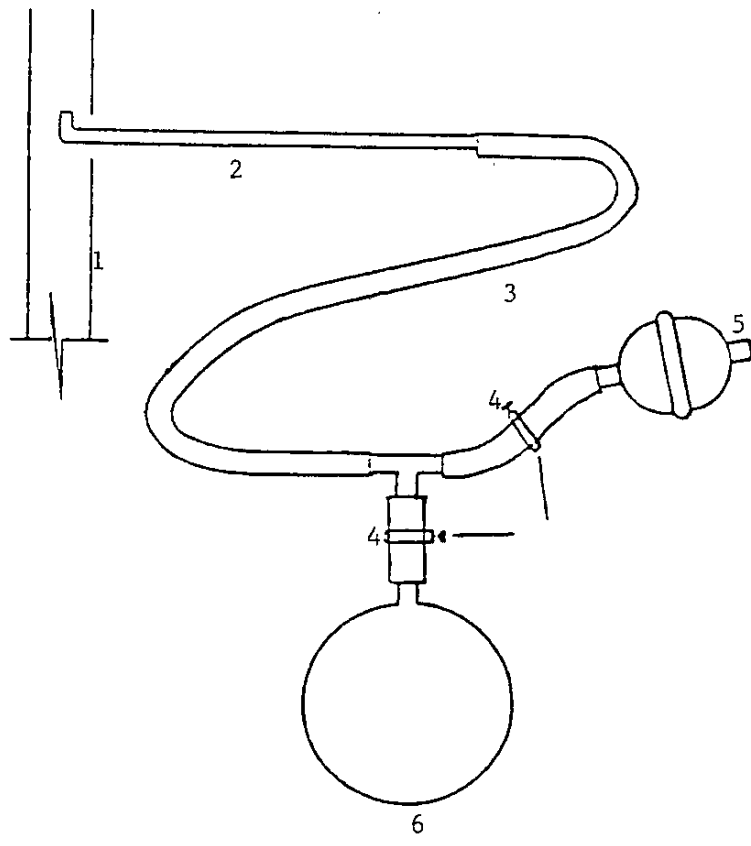
Ordinary room air may be used for oxygen calibrations, and assumed to be 20.95 percent O₂. Room air is passed through a condenser submerged in dry ice-water bath to knock out moisture before injection.

Using room air, set the response of the instrument close to maximum (about 90 percent). Calibrate the instrument twice, at the beginning and end of each set; or every ten injections, whichever is first. Response to the standard must be within 5 percent of average.

3.10 Quality Control

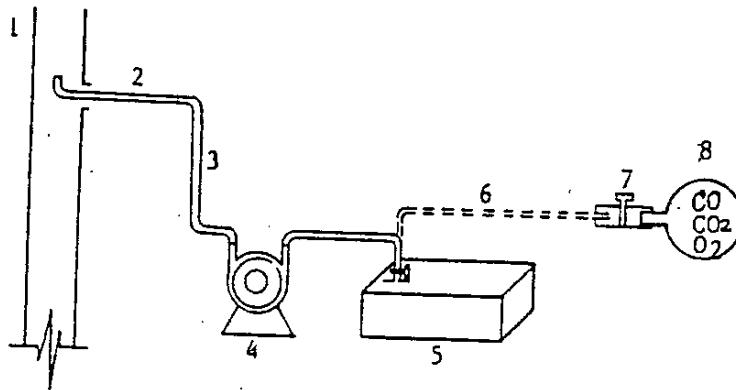
3.10.1 Standard gases must be NBS traceable.

3.10.2 Manometer must be NBS traceable.



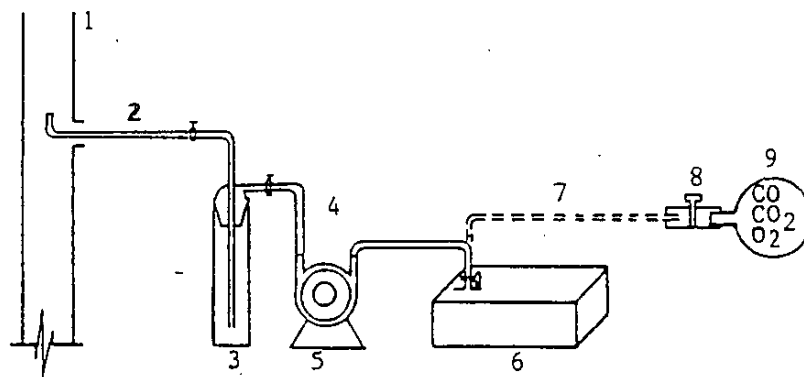
- | | |
|--------------------------|-----------------------------------|
| 1. Stack | 4. Pinch Clamp |
| 2. Stainless Steel Probe | 5. Aspirator Rubber Bulb |
| 3. Teflon Tube | 6. 2-Liter Glass Bulb (Evacuated) |

Figure 10.1-1
Grab Sampling Setup



- | | |
|-----------------------|---------------------------------|
| 1. Exhaust Stack | 5. Sample Bag |
| 2. Sample Probe | 6. Transfer Line |
| 3. Suction Line | 7. Pinch Valve |
| 4. Sealed (Leak Free) | 8. Evacuated 2-Liter Glass Bulb |

Figure 10.1-2
Integrated Gas Sample Collection System



- | | |
|-----------------------|---------------------------------|
| 1. Exhaust Stack | 6. Sample Bag |
| 2. Sample Probe | 7. Transfer Line |
| 3. Moisture Drop-Out | 8. Pinch Line |
| 4. Suction Line | 9. Evacuated 2-Liter Glass Bulb |
| 5. Sealed (Leak Free) | |

Figure 10.1-3

Integrated Gas Sample Collection System with Water and Particulate Dropout

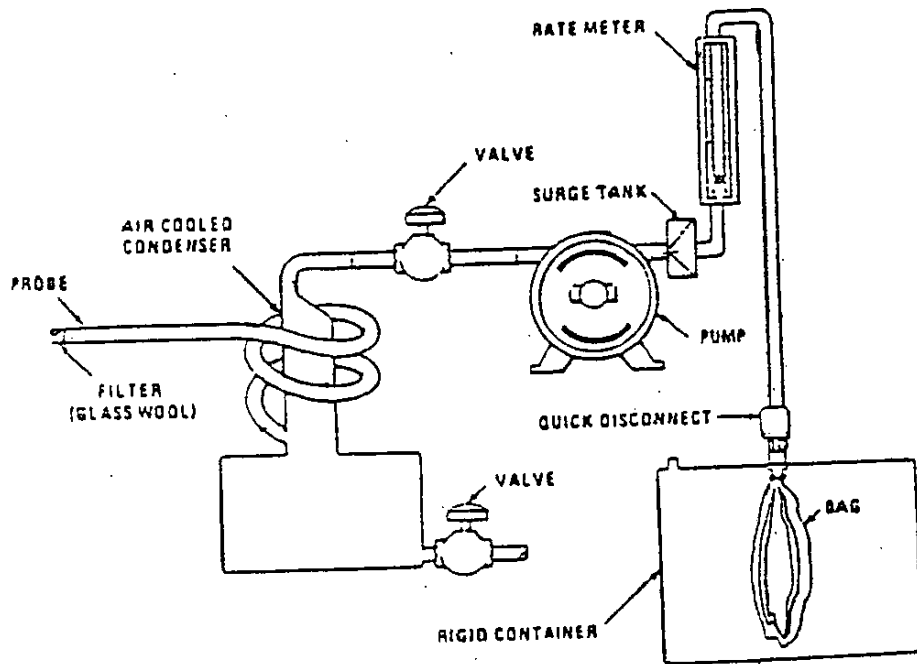


Figure 10.1-4
Integrated Gas Sampling Setup