Method 3C—Determination of Carbon Dioxide, Methane, Nitrogen, and Oxygen From Stationary Sources

*1. Applicability and Principle*

1.1  Applicability. This method applies to the analysis of carbon dioxide ($CO_2$), methane ($CH_4$), nitrogen ($N_2$), and oxygen ($O_2$) in samples from municipal solid waste landfills and other sources when specified in an applicable subpart.

1.2  Principle. A portion of the sample is injected into a gas chromatograph (GC) and the $CO_2$, $CH_4$, $N_2$, and $O_2$ concentrations are determined by using a thermal conductivity detector (TCD) and integrator.

*2. Range and Sensitivity*

2.1  Range. The range of this method depends upon the concentration of samples. The analytical range of TCD's is generally between approximately 10 ppmv and the upper percent range.

2.2  Sensitivity. The sensitivity limit for a compound is defined as the minimum detectable concentration of that compound, or the concentration that produces a signal-to-noise ratio of three to one. For $CO_2$, $CH_4$, $N_2$, and $O_2$, the sensitivity limit is in the low ppmv range.

*3. Interferences*

Since the TCD exhibits universal response and detects all gas components except the carrier, interferences may occur. Choosing the appropriate GC or shifting the retention times by changing the column flow rate may help to eliminate resolution interferences.

To assure consistent detector response, helium is used to prepare calibration gases. Frequent exposure to samples or carrier gas containing oxygen may gradually destroy filaments.

*4. Apparatus*

4.1  Gas Chromatograph. GC having at least the following components:

4.1.1  Separation Column. Appropriate column(s) to resolve $CO_2$, $CH_4$, $N_2$, $O_2$, and other gas components that may be present in the sample.

4.1.2  Sample Loop. Teflon or stainless steel tubing of the appropriate diameter.Note:Mention of trade names or specific products does not constitute endorsement or recommendation by the U. S. Environmental Protection Agency.

4.1.3  Conditioning System. To maintain the column and sample loop at constant temperature.

4.1.4  Thermal Conductivity Detector.

4.2  Recorder. Recorder with linear strip chart. Electronic integrator (optional) is recommended.

4.3  Teflon Tubing. Diameter and length determined by connection requirements of cylinder regulators and the GC.

4.4  Regulators. To control gas cylinder pressures and flow rates.

4.5  Adsorption Tubes. Applicable traps to remove any $O_2$ from the carrier gas.

*5. Reagents*

5.1  Calibration and Linearity Gases. Standard cylinder gas mixtures for each compound of interest with at least three concentration levels spanning the range of suspected sample concentrations. The calibration gases shall be prepared in helium.

5.2  Carrier Gas. Helium, high-purity.

*6. Analysis*

6.1  Sample Collection. Use the sample collection procedures described in Methods 3 or 25C to collect a sample of landfill gas (LFG).

6.2  Preparation of GC. Before putting the GC analyzer into routine operation, optimize the operational conditions according to the manufacturer's specifications to provide good resolution and minimum analysis time. Establish the appropriate carrier gas flow and set the detector sample and reference cell flow rates at exactly the same levels. Adjust the column and detector temperatures to the recommended levels. Allow sufficient time for temperature stabilization. This may typically require 1 hour for each change in temperature.

6.3  Analyzer Linearity Check and Calibration. Perform this test before sample analysis. Using the gas mixtures in section 5.1, verify the detector linearity over the range of suspected sample concentrations with at least three points per compound of interest. This initial check may also serve as the initial instrument calibration. All subsequent calibrations may be performed using a single-point standard gas provided the calibration point is within 20 percent of the sample component concentration. For each instrument calibration, record the carrier and detector flow rates, detector filament and block temperatures, attenuation factor, injection time, chart speed, sample loop volume, and component concentrations. Plot a linear regression of the standard concentrations versus area values to obtain the response factor of each compound. Alternatively, response factors of uncorrected component concentrations (wet basis) may be generated using instrumental integration.  Note:  Peak height may be used instead of peak area throughout this method.

6.4  Sample Analysis. Purge the sample loop with sample, and allow to come to atmospheric pressure before each injection. Analyze each sample in duplicate, and calculate the average sample area (A). The results are acceptable when the peak areas for two consecutive injections agree within 5 percent of their average. If they do not agree, run additional samples until

consistent area data are obtained. Determine the tank sample concentrations according to section 7.2.

## 7. Calculations

Carry out calculations retaining at least one extra decimal figure beyond that of the acquired data. Round off results only after the final calculation.

7.1 Nomenclature.

A=average sample area

$B_w$=moisture content in the sample, fraction

C=component concentration in the sample, dry basis, ppmv

$C_t$=calculated NMOC concentration, ppmv C equivalent

$C_{tm}$=measured NMOC concentration, ppmv C equivalent

$P_{bar}$=barometric pressure, mm Hg

$P_{ti}$=gas sample tank pressure after evacuation, mm Hg absolute

$P_t$=gas sample tank pressure after sampling, but before pressurizing, mm Hg absolute

$P_{tf}$=final gas sample tank pressure after pressurizing, mm Hg absolute

$P_w$=vapor pressure of $H_2O$ (from table 3C–1), mm Hg

$T_{ti}$=sample tank temperature before sampling, °K

$T_t$=sample tank temperature at completion of sampling, °K

$T_{tf}$=sample tank temperature after pressurizing, °K

r=total number of analyzer injections of sample tank during analysis (where j=injection number, 1 . . . r)

R=Mean calibration response factor for specific sample component, area/ppmv

Table 3C–1—Moisture Correction

| Temperature °C | Vapor Pressure of H₂O, mm Hg |
|---|---:|
| 4 | 6.1 |
| 6 | 7.0 |
| 8 | 8.0 |
| 10 | 9.2 |
| 12 | 10.5 |
| 14 | 12.0 |
| 16 | 13.6 |
| 18 | 15.5 |
| 20 | 17.5 |
| 22 | 19.8 |
| 24 | 22.4 |
| 26 | 25.2 |
| 28 | 28.3 |
| 30 | 31.8 |

7.2 Concentration of Sample Components. Calculate C for each compound using Equations 3C–1 and 3C–2. Use the temperature and barometric pressure at the sampling site to calculate Bw. If the sample was diluted with helium using the procedures in Method 25C, use Equation 3C–3 to calculate the concentration.

$$B_w = \frac{P_w}{P_{bar}} \qquad 3C\text{-}1$$

$$C = \frac{A}{R(1 - B_w)} \qquad 3C\text{-}2$$

$$C = \frac{\dfrac{P_{tf}}{T_{tf}}}{\dfrac{P_t}{T_t} - \dfrac{P_{ti}}{T_{ti}}} \quad \frac{A}{R(1 - B_w)} \qquad 3C\text{-}3$$

8. Bibliography

1. McNair, H.M., and E.J. Bonnelli. Basic Gas Chromatography. Consolidated Printers, Berkeley, CA. 1969.