Other Test Method 48 (OTM-48): Emission Factor Determination by the Carbon Balance Method

Note: Please submit a copy, either electronic or paper, of any test report from application of this OTM to EPA's Measurement Technology Group.

- Electronic copies should be submitted via email with the subject line "OTM-048" to: EMC@epa.gov
- Paper copies should be mailed to:

Measurement Technology Group Office of Air Quality Planning and Standards U.S. Environmental Protection Agency (Mail Code E143-02) Research Triangle Park, NC 27711

Background on OTM-48

This method is a novel approach to emission factor determination, particularly from open are combustion sources. Whereas OTM-32, "Determination of Emissions from Open Sources by Plume Profiling", exists, it is strictly a stationary measurement of time integrated pollutant mass flux, while OTM-48 is not necessarily stationary and uses carbon concentration measurements as opposed to wind speed. Additionally, OTM-48 determines flux at a stationary point, differentiating it from OTM-33 and its sub-methods, which instead determine a flux plane.

The posting of a test method on the <u>Other Test Methods</u> portion of the EMC website is neither an endorsement by EPA regarding the validity of the test method nor a regulatory approval of the test method. The purpose of the Other Test Methods portion of the EMC website is to promote discussion of developing emission measurement methodologies and to provide regulatory agencies, the regulated community, and the public at large with potentially helpful tools.

Other Test Methods are test methods which have not yet been subject to the Federal rulemaking process. Each of these methods, as well as the available technical documentation supporting them, have been reviewed by the EMC staff and have been found to be potentially useful to the emission measurement community. The types of technical information reviewed include field and laboratory validation studies; results of collaborative testing; articles from peer-reviewed journals; peer review comments; and quality assurance (QA) and quality control (QC) procedures in the method itself. The EPA strongly encourages the submission of additional supporting field and laboratory data as well as comments regarding these methods.

These methods may be considered for use in federally enforceable State and local programs (e.g., Title V permits, State Implementation Plans (SIP)) provided they are subject to an EPA Regional SIP approval process or permit veto opportunity and public notice with the opportunity for comment. The methods may also be considered to be candidates to be alternative methods to meet Federal requirements under 40 CFR Parts 60, 61, and 63. However, they must be approved as alternatives under 60.8, 61.13, or 63.7(f) before a source may use them for this purpose. Consideration of a method's applicability for a particular purpose should be based on the stated applicability as well as the supporting technical information outlined in the table. The methods are available for application without EPA oversight for other non-EPA program uses including state permitting programs and scientific and engineering applications. As many of these methods are submitted by parties outside the Agency, the EPA staff may not necessarily be the technical experts on these methods. Therefore, technical support from EPA for these methods is limited, but the table contains contact information for the developers so that you may contact them

directly. Also, be aware that these methods are subject to change based on the review of additional validation studies or on public comment as a part of adoption as a Federal test method, the Title V permitting process, or inclusion in a SIP.

Method History

Final – TBD

EPA advises all potential users to review the method and all appendices carefully before application of this method

Other Test Method 48 (OTM-48): Emission Factor Determination by the Carbon Balance Method

1 Scope and Application

1.1 *Introduction.* This method described herein is applicable to the determination of air emission factors for pollutants from combustion sources using the carbon balance method. Emission factors are defined as the ratio of a pollutant's mass to some quantifiable measure of the process such as mass of particulate matter per mass of fuel burned or mass of particulate matter per acre of forest burned. This method applies to all pollutants, gaseous and particle-related. It is particularly applicable to open area combustion sources where the pollutant flux is difficult to measure in contrast to sampling in stacks or ducts where the gas flowrate can be measured.

1.2 Scope. The carbon balance method measures the mass of the target pollutant while measuring the mass of some conserved element, in this case carbon. With knowledge of the carbon concentration of the fuel, the measured ratio of pollutant mass per carbon mass can be multiplied by the carbon concentration in the fuel to obtain the emission factor. Carbon is considered a conserved element and all forms of carbon species in the pollutants must be measured in order to provide the most accurate emission factor. This OTM covers measurement of major carbon sources from combustion sources; companion measurements of target analytes such as nitrogen oxides (NO and NO_2) are not included in the scope of this OTM. Related OTMs include OTM 32 "Determination of Emissions from Open Sources by Plume Profiling". OTM 32 is a stationary measurement of a time-integrated pollutant mass flux which is the product of pollutant concentration and wind speed. It is distinct from this OTM because it relies on a stationary measurement of concentration and wind speed. This current OTM is not necessarily stationary and relies on carbon concentration measurements rather than wind speed. Other OTMs under development include OTM 33 and its sub-methods C, E, and F, which, like OTM 32, rely on a flux calculation but instead determine a flux plane rather than a stationary point flux. OTM 38 is a method for determination of oxygen, carbon monoxide, and nitrogen oxides from stationary sources using portable gas analyzers equipped with electrochemical sensors. It contains Quality Assurance and Quality Control sections that are applicable to carbon monoxide (CO) measurements and, depending on the user's target analytes, NO and NO₂.

1.3 *Application*. The typical application for this method is for determination of emission factors from open area combustion sources where the total flows from the source cannot be determined because the emissions are not contained in a stack and concentrations are often quite variable due to random dilution. The measured media is air including gases and particles.

1.3.1 *Sources.* This method is applicable to all sources which have a known release of carbon, such as fuel combustion. These may include open combustion sources of obsolete military ordnance, prescribed forest burns, agricultural burns, in situ oil burns, waste burns, biomass pile burns and firing of small arms.

1.3.2 *Pollutant/Measured Parameters*. The method is applicable to criteria pollutants including PM, NO_x, SO₂, CO, volatile organic compounds, lead, and hazardous air pollutants (HAPs), including metals, HCl, Cr VI, semivolatile organic compounds, and carbonyls as well as black carbon, elemental carbon, and energetics.

1.3.3 *Method sensitivity (concentration or mass per unit)*. The method sensitivity is a function of the target pollutant. Differently sampling and analytical methods will have different sensitivities.

1.3.4 Data Quality Objectives. The principal data quality objective is a function of the end-use intent of the data, whether for general information on a source strength or as a prelude to more rigorous source methods. To meet these objectives, the use of National Institute of Standards and Testing (NIST) traceability protocol calibration gases for CO and CO₂ and measurement system performance tests are recommended in accordance with "EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards," September 1997, as amended August 25, 1999, EPA-600/R-97/121 or more recent updates.

2 Summary of the Method

2.1 This OTM describes the carbon balance method for measuring pollutants to determine emission factors. It is particularly applicable to determination of emission factors from open area sources in which a conserved element, in this case, carbon, is co-measured with the target pollutant. The ratio of the measured pollutant and carbon, with knowledge of the carbon content of the fuel, enables determination of an emission factor with units of mass of target analyte/mass of source (fuel) consumed.

2.2 *Sample collection procedures.* Samples are collected from the source plume, either by ground-based (stationary or mobile) or aerial-based collection, such as unmanned aircraft systems (UAS) or "drones". This method is particularly applicable to open area source measurements such as fires.

2.3 The method is not pollutant-specific and can be used for multiple target analyte pollutants. Analytical procedures for collected target analytes are pollutant-specific and not covered herein.

2.4 The method assumes that the target pollutant species is homogeneously mixed with the carbon species being measured such that the target pollutant and carbon species are always in the same mass ratio, at least over the period of the measurements. Likewise, the method assumes that the target pollutant and carbon species are preserved or unreactive over the course of the measurements, again assuming that the ratio is preserved. The method also assumes that the carbon species are all released to the air at a constant ratio with the target pollutant.

There are compelling reasons to support these assumptions. Open combustion events are dominated by turbulent, mixing flow and convective transport forces which render partitioning of the target pollutant and carbon species due to dissimilar diffusivities inconsequential. The reactivity of the target species in the combustion plume will be a function of the source type. The rapid cooling of the plume to ambient temperatures due to air entrainment will slow any reactions to a negligible rate at the point of sampling. Further, fuel carbon is homogeneously associated with other target atoms/molecules so is unlikely to be released from the fuel matrix and times distinct from those of target pollutant.

2.5 This OTM method determines a target pollutant to carbon ratio. If the user desires to relate this value back to the source to determine a pollutant mass per unit measure, such as particle matter mass per kg of fuel burned, then the fuel's carbon content must be known *a priori*. This method then also requires either an assumption regarding completeness of carbon release from the fuel or knowledge of the unreleased carbon in the fuel.

2.6 For example, measurements of PM record 5 mg on a filter; concurrent measurements of carbon amass 100 mg of carbon. The fuel source, containing 60% carbon by mass, is completely burned or consumed. The emission factors is $(5 \text{ mg PM}/100 \text{ mg C}) \times (60 \text{ mg C}/100 \text{ mg fuel}) = 3 \text{ mg PM}/100 \text{ mg fuel}$, or 3% of the fuel mass ends up as PM.

2.7 The method also relies on an ability to sufficiently quantify the carbon released to the degree of accuracy needed for the emission factor. That is, an inability to account for trace carbon in the emissions, such as in PAHs, may not significantly affect the data quality. For example, if the variation in replicate measurements is 5%, an inability to account for 0.1% of the total carbon being in PAH emissions may not have a significant effect

3 Definitions

Air flow calibrator: Instrument measuring the flow of sampling pumps to ensure flow accuracy.

<u>Background-correction</u>: The ambient background concentration of a pollutant is subtracted from the collected plume concentration of the pollutant.

<u>Calibration gas</u>: Gas mixture containing CO_2 or CO at a known concentration mixed in either N_2 or Air.

<u>Calibration span</u>: Calibration span means the upper limit of the sensor's calibration. The calibration span must be within the range of the sensor and at least half of the expected highest concentration to be measured. To the extent practicable, the majority of measured concentrations should be within the selected span.

<u>Elemental Carbon (EC)</u>: Graphitic carbon, ultraviolet absorbing as determined by NIOSH Method 5040 as in Kahn et al. (2012).

<u>Linearity Check</u>: Initial and periodic maintenance linearity check of the sensor's entire measurement range. For sensors with voltage ouput the initial check includes determining the relationship that converts voltage to ppm values (engineering units).

<u>Organic Carbon (OC)</u>: Non-inorganic carbon, as determined by NIOSH Method 5040 as in Kahn et al. (2012).

Particle size separator or Impactor: A particle sampler with a specific PM size cut.

<u>PM_{2.5}</u>: Particulate matter with an aerodynamic size of 2.5 micrometers and smaller.

<u>*PM_{TOT}*</u>: A total measurement of particles of all aerodynamic sizes.

<u>PM System</u>: Equipment used to determine the PM concentration.

ppm: parts per million. Units for measuring CO2 and CO concentrations, a volumetric ratio.

<u>Response time</u>: The time it takes the sensor signal to change after the concentration is altered determined by the time between the first observable measurement response and the measurement response equal to 90% of the final reading.

<u>Sensor:</u> A sensor is defined as the instrument/equipment being measured which produce an output equivalent to the gas concentrations.

<u>Sensor system</u>: A sensor system means all equipment used to determine CO₂/CO concentration which may include filter, micro-pump, tubing, sensor, and data recorder.

<u>Sensor stability</u>: The relative stability (lack of variability or change) of the sensor's signal when injected with calibration gas when the sensor's response exceeds 95% of the final reading.

<u>Total carbon (TC)</u>: The sum of EC and OC from a PM_{TOT} sample.

Upscale calibration checks: Calibration gas at the mid-point or span concentrations.

4 Interferences to the Method

4.1 Potential interferences to this method are background concentrations and handling of sampling media.

4.2 This method background corrects the measurement by subtracting the background concentrations from the measured plume concentration. The most significant correction should be for background carbon concentrations, primarily or exclusively, CO_2 concentrations. For example, measurements upwind of the source record an ambient CO_2 concentration of 405 ppm. Measurements of the source plume record an average CO_2 concentration of 550 ppm. The carbon as CO_2 attributed to the source is 550 ppm – 405 ppm = 145 ppm. Other background corrections for carbonaceous species, for example, methane (CH_4), can be ignored on a case-specific basis, when ambient levels of these species are so low that they would not affect the data quality objectives.

4.3 Collection of filter field blanks will account for the potential interference from sampling media handling. A filter field blank is handled as a routine sample, but no air is pulled through the impactor.

5 Safety

5.1 This method may involve hazardous operations and it is the responsibility of the user to ensure compliance with site entry, health, and safety requirements.

5.2 This method may be used with aerial- or crane-based sampling systems and as such the sampling equipment may be positioned of a height of more than 2 meter (6.6 feet) above ground level. The user (sampling crew) should establish safety procedures before using this method in order to take appropriate precautions with respect to power lines, trees, falling objects and other obstacles.

5.3 This method includes use of compressed gases for calibration of sensors. The user should follow user established safety procedures before using this method as mentioned in section 5.0 of Method 7E. CO is a poisonous, odorless and colorless gas so calibration should take place using proper ventilation. OSHA's permissible exposure limit (PEL) for CO is 50 ppm during an 8-hour time period. Initial symptoms of CO poisoning include headache, fatigue, dizziness, drowsiness or nausea.

6 Equipment and Supplies

6.1 *Note.* As noted in Section 2, this method has the capability to measure and determine emission factors for many pollutants. Details on equipment, supplies, and procedures for measuring the many pollutants not addressed are not part of this OTM; the user is referred to pollutant-specific methods elsewhere for equipment, supplies, and proceedures. The subsequent method sections address determination of a PM_{2.5} emission factor as an example to the OTM user. The same approach can be used for other pollutant measurements. This method includes details for measuring gas- and particle-phase carbon such as, respectively, CO/CO₂ and TC. PM_{TOT} samplers are used in this example to capture particles for carbon determination. For sources in which particulate matter is known to be smaller than 2.5 micrometers, a PM_{2.5} impactor may be used for determining both the PM_{2.5} mass and TC.

6.2 Gas Collection

6.2.1 Sensors for measuring CO₂ and CO capable of meeting performance requirements in Section 8 which are based on Methods 3A and Method 10.

6.2.2 Micro pump for pushing ambient gas through the sensors. The pump should be sized according to required flow as specified in the sensor manual.

6.2.3 Pre-filters for screening particles prior to sensors as specified in the sensor manual.

6.3 PM collection

6.3.1 *Particle size seperator (impactor).* Use a PM impactor with a particle size cut as specified in the user's operating procedure.

6.3.2 *Sample filter for PM mass.* Use a polytetrafluoroethylene (PTFE) filter with support ring as described in 40 CFR Part 50, Appendix L sections 6.2-6.4. Use diameter size as specified in the impactor manual.

6.3.3 *Sample filter for TC*. Use a quartz filters for collection of total carbon as described in NIOSH Method 5040 pages 1 and 2. Use diameter size as specified in the impactor manual.

6.3.4 *Pump and flow measurement.* Pumps should be sized according to the requirements of the specific particle size separator samplers. Use a flow-compensating pump to ensure the correct cut size is collected during the entirety of the collection time as described in 40 CFR Part 50, Appendix J sections 7.1.3 and 8.1.2.

6.4 Sample Recovery – See caveat, section 6.1.

6.4.1 Protective containers (petri dishes) for holding PM and TC samples pre- and post-sampling.

6.4.2 Portable insulated cooled storage container for samples that are susceptible to thermal volatilization or degradation.

6.5 Sample preparation and sample analysis – See caveate, section 6.1.

6.5.1 Analytical balance for weighing PTFE filters as described in 40 CFR Part 50, Appendix L, section 7.5.

6.5.2 Pre-cleaning of quartz filters as described in NIOSH Method 5040, page 2.

6.6 *Reagents and Standards* – See caveat, section 6.1.

6.7 *Calibration gases* should be traceable to National Institute of Standards and Technology (NIST) through use of the EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards. The quality level of the CO₂ and CO gases shall be $\pm 2\%$. The concentration of the calibration gases depends on the users anticipated plume concentration, the range of the sensors, and the selected calibration span. At least three calibration gas concentrations are needed, high-level gas, mid-level gas and a low-level gas, as specified in Section 8 of this method.

6.8 *Flow rate calibration standard.* Certified air flow calibrator traceable to a NIST standard flow rate.

6.9 *Mass working standards for check of microbalance*. Standards verified against NIST traceable primary standards.

6.10 Reagents and standards used to analyze filters for total carbon analysis as specified by NIOSH Method 5040, page 2.

7 Sample Collection, Preservation, Storage, and Transport (PM_{2.5} example)

7.1 Pre-Test Preparation

7.1.1 PM_{2.5} mass sampling filters. Weigh the PTFE sampling filters in a conditioned environment as described in 40 CFR Part 50, Appendix L, section 8.2. Place the pre-weighed sampling filters in labeled protective containers and store them at room temperature. Transport the filters in an insulated container to the sampling site. Load the particle size separators or impactors with filters as described in user's standard operating procedures or the manufacturer's instruction manual.

7.1.2 TC sampling filters. Condition the quartz filters according to NIOSH Method 5040, page 2.

7.1.3 TC sampling filters. Place the cleaned TC quartz filters in protective containers and store them at $<0^{\circ}$ C. Transport the filters in a cooled insulated container below 25°C. Load the particle size separators with filters as described in sampler's standard operation procedures or the impactor's instruction manual.

7.1.4 Perform linearity checks of the CO and CO₂ sensors initially and at least semiannually thereafter by conducting a 3-point calibration error check of each gas sensor. Introduce low-, mid-, and high-level calibration gases sequentially. Record each sensor's response to each of the three calibration gases. For each calibration gas, calculate the sensor calibration error as a percent of the calibration span (see span definition in section 3 of this method). The calibration error specification in section 8 must be met for the low-, mid-, and high-level gases. If the calibration error specification is not met, take corrective action and repeat the linearity check until an acceptable 3-point calibration is achieved.

7.1.5 Immediately before sampling, conduct a 2-point calibration check (zero and upscale) on the CO and CO_2 sensors (see Table 1 and section 8.4.3). For the zero checks, the sensors must show a stable null value. For the upscale calibration checks using a high-level gas, calculate the calibration error for each sensor as a percent of the calibration span; the calibration error specification in section 8 must be met for the upscale gases for each sensor.

7.2 Site Selection Criteria. The site selected should have ease of observation of the source and the sampling instrumentation without obstruction and without jeopardizing safety of personnel and equipment.

7.3 Deployment of Air Sampling Equipment

7.3.1 Samplers, whether ground-based or aerial-based, must be placed in the path of the source plume.

7.4 Operation of aerial or ground samplers. Start all CO and CO_2 pumps. When the sampling platform is in the plume as indicated by the CO_2 concentration rising to levels above ambient background concentrations (e.g., for a fire, this means the sensor is picking up carbon oxidation products), start all PM pumps, and pumps for any other analyte of interest. Sampling should continue until the user assesses that sufficient sample is collected to exceed the analytical detection limits or until the PM pumps can no longer maintain the flow rate specified by the manufacturer of the impactor. In initial sampling cases for an analyte, the user will have to use best judgement as to whether sufficient sample has been collected to exceed analytical limits. Additional trials and analytical results will provide the user with more experience with which to assess sample collection sufficiency. Turn all pumps off when the sampler is no longer in the plume, as indicated by return of the CO_2 concentration to ambient levels. Immediately after each sampling run, conduct 2-point drift checks (zero and upscale) on the CO and CO_2 sensors (see Table 1 and section 8.4.4).

7.5 Data Recording

7.5.1 During sampling, continuously record time-stamped CO and CO₂ concentrations as well as the starting and stopping times for sampling pumps.

7.6 Sample Recovery and Transport.

7.6.1 When the sampling is completed and the sampler is accessible, remove the PM_{2.5} mass filters (PTFE) from the particle size impactors following user's standard operating procedures or manual and place them into labeled protective containers. The filters should be stored in a temperature below the average sampling temperature or at 4°C as described in 40 CFR, Appendix L, section 8.3.6.

7.6.2 Remove the PM_{TOT} TC filters (quartz) from the particle size impactors following user's standard operating procedures or the PM impactor user manual and place them into labeled protective containers and store them as specified in users standard operating procedures.

8 Quality Assurance and Quality Control

8.1 The quality control checks and associated performance criteria are summarized in Table 1 below.

8.2 Performance Audits. Any audits should be conducted by a independent auditor/analyst to demonstrate that sensor and pump calibrations, data processing and sampling are conducted within the acceptance criteria of the methods. Findings that would invalidate a sample include pump stoppage and breaks in the sensor data recording.

8.3 Sample Identification and Traceability. Each sample must be given an identifying code number. Proper application of the code will simplify sample tracking throughout the collection, handling, analysis, and reporting processes.

8.4 Method Accuracy

8.4.1 Response time. Determine the rise time by calculating the time between the first observable measurement response and the response equal to 90% of reading when injecting the span calibration gas. The response time should be less than 2 minute.

8.4.2 Stability check. Determine the stability of the sensor's signal response two minutes after the sensor reaches 95% of reading (when injecting calibration gas) by measuring the change in concentration during one minute. The measured concentration should change less than 1% per minute.

8.4.3 Determine how well the sensor's measured response fits with the injected calibration gases by calculating the calibration error between the sensor's response and the calibration gas concentration; the calibration error must be $\leq 5\%$ of span for linearity checks and $\leq 5\%$ of span for upscale calibration checks performed in the field.

8.4.4 To assess drift, repeat the zero and upscale checks at the conclusion of a sampling run. Determine the sensor drift as described in Method 3A for CO_2 and Method 10 for CO. The zero gas shall yield a stable null value and the upscale calibration error shall be $\leq 5\%$ of the initial calibration values for each point.

8.4.5 *Pump calibration.* The sample flow rate should be within $\pm 2\%$ of the specified flow rate as stated in section 7.3 in 40 CFR Part 50, Appendix J, section 8.2.2.

8.5 Filter blanks

8.5.1 Laboratory PTFE blank. Follow instructions in 40 CFR Part 50, Appendix L, section 8.3.7.2.

8.5.2 PTFE field blank. Handle the field blank filter as a routine sample, but do not pull air through the impactor. Follow instructions in 40 CFR Part 50, Appendix L, section 8.37.1.

8.5.3 Quartz filter laboratory blank. Analyze a pre-cleaned filter for OC contaminants according to NIOSH Method 5040, page 2.

Target Compound	QA/QC Check Frequency	QA/QC Check Procedure	DQI/Acceptance Criteria	Corrective Action	Reference Standard
CO, CO ₂	Initially and semiannually thereafter	3 level calibration error test	< <u><</u> 5% of calibration span	Check for leaks Re-calibrate	See Section 7.1
CO, CO ₂	Daily	2-point calibration check (zero and upscale	<u><5% of</u> calibration span	Check for leaks Recalibrate	See Section 7.1
CO, CO_2	Daily	Stability check	$\leq 1\%$ of calibration value within 1 min	Check for leaks, replace sensor	See Section 7.1
CO, CO ₂	Daily	Response time	≥90% of calibration value within 2 min	Check for leaks, replace sensor	See Section 7.1
CO, CO ₂	After each test run	Drift check	$\pm 5\%$ of initial calibration value	Run is invalid	See Section 7.1

Table 1. Quality control checks and criteria

Method to Quantify Emissions from Open Area Sources

PM Flow	Daily	Flow calibration	±2% of flow rate L/min	Check for leaks, Re-calibrate gas pump	Certified Flow calibration device
PM Mass	Once per weighing session	Field blank	±20 μg of initial weight	Check balance	Certified weights
PM Mass	12-24 h between weighing sessions	Weighing of same filter	$\pm 15 \ \mu g$ of initial weight	Re-weigh filter	Certified weights
PM Mass	Once per weighing session	Laboratory blank	±15 μg between weighings	Check balance	Blank filter, Certified weights
PM TC	One per cleaned filter batch	Analyze for OC contaminants	$<0.1 \ \mu g/cm^2$	Re-clean filters	Analytical

9 Calibration and Standardization

9.1 Sensor Calibration. Warm up the sensors according to the user's standard operating procedures or as described in the sensor's manuals prior to calibration. The sensors should be calibrated against calibration gases (see section 7.1) prior to sampling and checked for drift after after each run as described in Method 3A, section 8.5 for CO_2 and Method 10, section 8.5 for CO.

9.2 *Pump Calibration.* Set the flow rate on the pump to the desired impactor flow as stated in the impactor manufacturer's manual. Calibrate the PM pump flow against a flow calibration instrument (see section 7.2) as described in the pump manufacturer's manual or users standard operating procedures using the same filter type as used during testing. The PM pump system should be calibrated before use as established in the users standard operating procedures.

9.3 *Microbalance Calibration*. The microbalance used for weighing of filters should be calibrated as specified by the manufacturer and checked before each weighing session as described in 40 CFR Part 50, Appendix L, section 8.1.

10 Analytical Procedure

10.1 Filter analysis for gravimetric analyses. Follow the steps as described in 40 CFR Part 50, Appendix L, section 8.3.

10.2 Filter analysis for carbon content. Follow steps in analytical methods which are suited for the open combustion source being sampled such as NIOSH Method 5040, pages 3 and 4.

11 Calculations and Data Analysis

11.1 Carbon Fraction (F_c). The carbon fraction in the fuel has to be known in order to calculate the emission factor in mass per mass fuel burned. The carbon fraction in the fuel can be obtained by either analyzing the fuel for carbon content or by looking up the fuel's carbon content in the literature. The carbon in the fuel will be labeled as mass carbon per total mass of the fuel.

11.2 Matching PM filters time with CO and CO₂ collection. Calculate the carbon mass from the same time interval as the PM filters were collected.

11.3 Nomenclature.

R = 0.082 L atm

T = Sampling temperature in °C

CTC_{PS}	=	TC concentration in the plume sample
CTC _{BS}	=	TC concentration in the background sample
ΔCO_2	=	CO_2 concentration sampled in mg/m ³
ΔCO	=	CO concentration sampled in mg/m ³
ΔTC	=	TC concentration sampled in mg/m ³
M_{C}	=	Molar mass of carbon, 12.0107 g/mol
M_{CO_2}	=	Molar mass of CO ₂ , 44.01 g/mol
$M_{\rm CO}$	=	Molar mass of CO, 28.01 g/mol
PM EF	=	PM Emission factor in g PM/g fuel burned
F _c	=	Carbon fraction in the fuel
C_{PM}	=	PM concentration in mg/m ³
C_{c}	=	Carbon concentration sampled in mg/m ³

11.4 Background corrected concentration of CO_2 and CO_2 and ΔCO_2 respectively. Subtract the measured ambient background concentration from the periodic measured concentration in the plume in ppm.

> $\Delta CO_2 = CO_2$ in the plume $- CO_2$ in the background $\Delta CO = CO$ in the plume - CO in the background

11.5 The concentration measured is calculated from the calibration relationship in ppm. The ΔCO_2 and ΔCO concentration in ppm is converted to mg/m³ by using:

 $\Delta CO_2 \text{ and } \Delta CO \text{ Concentration in } mg/m^3 = \\ = \frac{\Delta CO_2 \text{ and } \Delta CO \text{ Concentration in } ppm \times M_{CO_2 \text{ or } CO}}{R \times (273.15 \text{ K} + T \text{ °C})}$

11.6 Concentration of ΔTC . The concentrations of TC in the plume and in an upwind background sample are calculated from the TC mass on each filter divided by the volume of gas sampled (e.g. mg/m³). Then the upwind background concentration is subtracted from the plume sample concentration to yield the TC concentration, ΔTC :

$$\Delta TC = CTC_{PS} - CTC_{BS}$$

11.7 *Carbon concentration collected*. The carbon concentration collected, in mg/m³, is calculated using the following equation:

$$C_{C} = \Delta CO_{2} \times \frac{M_{C}}{M_{CO_{2}}} + \Delta CO \times \frac{M_{C}}{M_{CO}} + \Delta TC$$

11.8 *Concentration of PM Pollutant*. The PM concentration, C_{PM} , is calculated from the mass particulate on the filter divided by the volume sampled (e.g., mg/m³).

11.9 *Emission Factor*. The PM emission factor (mass PM per mass fuel) is calculated using the following formula:

$$PM \ EF = F_C \times \frac{C_{PM}}{C_C}$$

11.10 Example. The CO₂, CO, and TC background concentrations were measured at 420 ppm, 0 ppm, and 0.015 mg/m³, respectively. The CO₂ and CO average concentrations in the plume during the sampling period was 2,020 ppm and 60 ppm respectively. The TC and PM_{2.5} concentrations in the plume were 50 mg/m³ and 190 mg/m³, respectively. Temperature in the plume was 28°C and the carbon fraction in the fuel 0.5.

Background corrected CO₂ and CO concentrations

$$\Delta CO_2 = 2,020 - 420 = 1,600 \ ppm$$

 $\Delta CO = 60 - 0 = 60 \ ppm$

Concentration of CO₂ and CO

$$\Delta CO_2 = \frac{1,600 \ ppm \times 44.01}{0.082 \times (273.15)} = 2851.51 \ mg/m^3$$
$$\Delta CO = \frac{60 \ ppm \times 28.01}{0.082 \times (273.15+28)} = 68.06 \ mg/m^3$$

Concentration of ΔTC

$$\Delta TC = 50 - 0.015 = 49.985 \, mg/m^3$$

Carbon concentration collected

$$C_C = 2851.51 \times \frac{12.0107}{44.01} + 68.06 \times \frac{12.0107}{28.01} + 49.985 = 857.37 \ mg/m^3$$

Emission Factor (given: C_{PM} *is* 190 mg/m³)

$$PM_{2.5} EF = 0.5 \times \frac{190}{857.37} \times 1000 \ g = 110.80 \ g/kg \ Fuel$$

12 Method Performance

12.1 *Carbon mass balance assumptions.* This method assumes that all carbon from the material burned is emitted to the atmosphere and that the pollutants and carbon emitted are proportionally distributed in the plume (Nelson et al., 1982). It also assumes that the rate of the carbon emitted is proportional to the mass loss rate of the fuel (Nelson et al., 1982).

12.1.1 A waste gasifier/combustor was sampled to determine PM emission factors (PM mass/waste mass) by both the carbon balance method and the waste input method (Aurell et al., 2019). The latter was determined with use of the waste mass input and the volumetric ratio of the sampled duct flow and the total duct flow. The carbon balance method resulted in a PM emission factor of 0.39 (± 0.22) g/kg waste and the waste input method resulted in a value of 0.37 (± 0.19) g/kg waste, a difference of 5%.

12.1.2 Dhammapala et al. (2006) compared PM emission factors determined by direct sampling and by the carbon balance method for biomass burns. Direct sampling used a flow through chamber with measurements of exit concentration, flowrate, time, and mass loss burned to calculate an emission factor for PM mass/fuel mass burned. When the carbon balance method was reported as a percentage of the direct method, three campaigns resulted in values of 94.4 %, 91.1 %, and 110.7 %.

12.2 Due to instrumentation size, and power and weight constraints in sampling emissions from open combustion sources, measurements of methane and total hydrocarbons (THC) which are relatively insignificant have not been addressed in this approach. Depending on the combustion source, the user could also consider ignoring the TC contribution. As such only CO₂ and CO would be used as the carbon source in determining emission factors.

12.2.1 Nelson et al. (1982) found a 5% difference in emission factors when only CO_2 and CO were used as the carbon source and THC and total suspended particles were ignored.

12.2.2 VOC emission factors derived from prescribed forest fires were 2.3% lower using CO₂, CO and CH₄ as a carbon source than using CO₂ alone (Aurell et al., 2015).

12.2.3 A study by Aurell et al. (2017) showed when a plume from jet fuel contained approximately 10% TC the PM_{2.5} emission factor was reduced by 13% when TC was included as a carbon source. The same study also found that a TC fraction of 0.05% in a propane plume reduced the PM_{2.5} emission factor by 0.1% when included in the carbon source.

13 Pollution Prevention

NA

14 Waste Management

NA

15 References

15.1 References that use the carbon balance method

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