

Standard Operating Procedures

for thermal–optical analysis of atmospheric particulate organic and elemental carbon

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1. Purpose

This SOP describes the analytical methodology recommended by EMEP for determining the amounts of organic (OC) and elemental carbon (EC) in ambient aerosol filter samples analyzed by thermal–optical analyses. The SOP is based on the “Standard operating procedures for the sampling and thermal-optical analysis of atmospheric particulate organic carbon and elemental carbon” developed within the EU-funded Integrated Infrastructure Initiative project EUSAAR (European Supersites for Atmospheric Aerosol Research, FP6 contract N°R113-GT-2006-026140).

2. Scope and application

This standard operating procedure (SOP) provides detailed instructions for aerosol sample handling and analysis of OC and EC, using the Sunset Laboratory thermal-optical Dual OCEC Lab analyzer. *Trademarks and product numbers are listed for the convenience of users of this SOP.* Equivalent products may be used if they can be shown to lead to the same results. Thus, the recommended thermal protocol,

EUSAAR-2 (See Table 1), can also be used in the Desert Research Institute (DRI) Thermal/Optical Carbon Analyzer; however detailed instructions for analysis of OC and EC using this instrument are not provided in the current SOP.

This SOP is addressed to professionals who know and implement good laboratory practices.

The lower detection limit of the Sunset Laboratory thermal-optical Dual OC EC analyzer is on the order of $0.2 \mu\text{g C m}^{-2}$. The manufacturer of the OCEC analyzer states that the best range for the deposit concentration is $5 - 400 \mu\text{g C cm}^{-2}$ for OC and $1 - 15 \mu\text{g C cm}^{-2}$ for EC. Uncertainties concerning the split between EC and OC can occur within the ranges provided, and is attributed to the instruments ability to separate between absorbing pyrolytic carbon (PC) generated during the He-mode of the analysis and EC, as well as the laser's ability to detect changes in the transmission/reflection of an already severely blackened filter.

3. Safety

All procedures must be conducted in full respect of the occupational health and safety guidelines and regulations in force at the place of work.

Specific safety instructions regarding the use and handling of gas cylinders, inflammable gases, hot surfaces and lasers must be read and understood before any task listed in the present document is performed. Specific safety instructions are listed in the Sunset OCEC Lab Instrument manual (Sections 2 and 3).

4. Description of the method

Both front and back up filters are analyzed by the same thermal-optical method. The carbonaceous material deposited on the quartz fiber filters is thermally desorbed, first in an inert (He) and then in an oxidizing carrier gas (He/O₂). EC evolves in the oxidizing atmosphere only. OC partially chars in the He-mode and forms pyrolytic carbon (PC), which evolve in the He/O₂ mode, along with native EC. To correct for charring, the optical properties of the sample are monitored during the analysis with a laser beam. Light transmission and reflectance decrease while OC chars in the He-mode, and increase again in the He/O₂-mode, as light absorbing carbon (here: EC and PC) evolves. The time when transmission and/or reflectance reach their initial pre-pyrolysis value is defined as the split point between OC and EC. The EUSAAR-2 thermal protocol (Table 1) recommended by EMEP minimizes the biases inherent to this method for separating EC and OC and should be used for OC and EC analyses. Carbonates (CC) can interfere with the split point between OC and EC during thermal-optical

analyses, and should be quantified when its concentration is suspected to contribute by more than 5% to either EC or OC. An analytical protocol for quantification of CC is currently being tested and will be implemented at a later stage.

Table 1: EUSAAR-2 protocol parameters (^a mix of 1-2 % oxygen in UHP helium)

Step	1	2	3	4	5	6	7	8
Carrier gas	He	He	He	He	He/O ₂ ^a	He/O ₂ ^a	He/O ₂ ^a	He/O ₂ ^a
Temperature (°C)	200	300	450	650	500	550	700	850
Duration (s)	120	150	180	180	120	120	70	80

The EUSAAR_2 parameter file to be implemented in a Sunset Laboratory OCEC Lab instrument is shown below:

```
' EUSAAR_2.par
'modified the He/Ox mode
' mode <comma> time <comma> temperature
'n.b. regimen must end 'Offline' mode.
Helium, 10, 1
' start ramping the temperature
Helium, 120, 200
Helium, 150, 300
Helium, 180, 450
Helium, 180, 650
' let the oven cool before starting elemental
Helium, 30, 0
' elemental
Oxygen, 120, 500
Oxygen, 120, 550
Oxygen, 70, 700
Oxygen, 80, 850
CalibrationOx, 110, 0
' All done!
Offline, 1, 0
' end.
```

5. Definitions

5.1. Total carbon – TC: Total quantity of carbon atoms in an ambient aerosol filter sample, whatever the constituent it belongs to. This includes EC, OC and IC.

5.2. Elemental carbon – EC: Fraction of the non-IC total carbon in an ambient aerosol filter sample, characterized by its non-volatility according to a specified thermal-optical protocol. EC evolves from the sample by oxidation only.

5.3. Organic carbon – OC: Fraction of the non-IC total carbon in an ambient aerosol filter sample which is not EC.

5.4. Inorganic carbon – IC: Fraction of carbon belonging to mineral species, including carbonates and other molecules (e.g. carbides).

5.5. Carbonate carbon – CC: Fraction of carbon belonging to a carbonate group. Carbonate carbon (mainly CaCO_3 and MgCO_3) is viewed as the only inorganic carbon fraction being released within the temperature range used in thermal protocols.

5.6. Pyrolytic Carbon – PC: Light absorbing carbon formed by incomplete combustion (pyrolysis) of OC during the Helium mode of the analysis.

5.7. Annealed: submitted to heating at high temperature ($> 800\text{ }^\circ\text{C}$) and slow cooling.

5.8 Charring: process leading to the removal of H and O from organic materials by the action of heat and producing light absorbing carbon (char) .

5.9. FID: Flame ionization detector

5.10. UHP: Ultra High Purity (better than 99.999%)

6. Equipment and supplies

6.1. Sampling

6.1.1.

Particulate matter filter samples should be collected according to, or equivalent to, EN 14907 for $\text{PM}_{2.5}$ and EN 12341 for PM_{10} . Both high volume samplers and low volume samplers may be used. When an automatic sampler is used, filters should not be stored in the sampler for more than 15 days and the filter enclosure has to be kept at a temperature which is $< 5^\circ\text{C}$ higher than the ambient temperature.

6.1.2. Filters

Binder-free quartz fiber filters have to be employed for subsequent thermal-optical analyses. Such filters can be obtained from various manufacturers, including Munktell, Pall, and Whatman.

6.2 Analyses

6.2.1 Sunset Laboratory OCEC Lab instrument

It is recommended to use the "Dual" OCEC instrument, where charring is monitored by both reflection and transmission of the laser beam.

6.2.1 Precision puncher

Use of the 1x1 cm² or 1x1.5 cm² puncher according to the amount of carbon expected on the exposed filter (optimal range 1- 25 µg C per sample).

6.2.3 A quartz boat for 1 cm² or 1.5 cm² square punch

(The punch size should be consistent with the choice of the quartz boat);

6.2.4. Oxygen trap(s)

Oxygen traps (with indicator) are to be inserted in the He line to remove any trace of oxygen from the He carrier gas. It is also advised to use tubing that is impermeable to O₂ for He (i.e. Low Permeation Tubing PTFE, Proprietary Non-Wetted Outer Layer).

6.2.5. Micro-pipette

A high-quality (±1% precision) micro-pipette for sampling 10 µl of aqueous solution is necessary for the daily calibration.

6.2.6 Micro-syringe

The gas syringe should allow precise sampling of 10 – 100 µl of gas (accuracy within ±1% of nominal volume and precision of 1% at 80% of the total volume).

6.2.7. A Swagelok®- compatible stainless steel T

that can accommodate a septum.

6.3 General purpose equipment and consumables

6.3.1 Laminar Flow benches

Filters should be handled under a laminar flow bench in the analytical laboratory, and if possible at the sampling site.

6.3.2 A programmable laboratory furnace

This should be able to reach 950 °C.

6.3.3 Stainless steel tweezers

Tweezers should have the size and shape adapted to the handling of filters.

6.3.4 Dust-free plastic gloves; e.g. polyethylene (PE) gloves

Gloves should be kept clean of any organic or inorganic substance.

7. Gases, standards, and reactants

7.1. Helium (He)

At least 99.999% ultra high purity grade with low (< 0.5 ppm) moisture, hydrocarbon and oxygen background. It is advised to scrub out traces of oxygen from the He carrier gas using an oxygen trap.

7.2. Air or Nitrogen/Oxygen mix 80:20 (N₂/O₂)²

Ultra zero grade with low moisture and hydrocarbon background.

7.3. Hydrogen (H₂)³

99.997% purity or better.

7.4. Helium/Oxygen mix 90:10 (He/O₂)

This is a custom blend gas with 10% oxygen with a helium balance. Purity should be 99.999% or better with low moisture (< 0.5 ppm), hydrocarbon and CO₂ background (< 1 ppm).

7.5. Helium/methane mix 95:5 (He/CH₄)

This is also a custom blend with 5.0% methane with a helium balance. Purity should be 99.999% or better with low moisture, hydrocarbon background and CO₂ (< 1 ppm). [A small cylinder (B5) will last for thousands of analyses].

7.6. Carbon containing standard solution

For instance a sucrose solution with a precisely determined concentration of about 1 to 4 µg C µl⁻¹.

7.7. Pure carbon containing standard gas

For instance, a cylinder of pure CO₂ (purity > 99.999%) for checking the instrument calibration in both He and He/O₂ modes.

^{2,3} ~~Air and Hydrogen can be supplied by Air and Hydrogen generators instead of gas cylinders.~~

8. Procedures

For readability, the various procedures are edited independently from each other, with cross references when necessary. All operations and critical parameters, i.e. gas flows, ovens' temperatures, instrument pressure, baseline FID value, laser transmittance and reflectance values for a blank filter, should be recorded in a paper or an electronic logbook. The various SOPs are sorted according to the index below:

1. Filter cleaning
2. Filter storage
- 3.1. Instrument Start up
- 3.2. Daily calibration with a carbon containing solution
- 3.3. Periodical instrument check from a pure carbon containing gas
4. Analysis of ambient samples
5. Instrument Shut down

SOP 1. Filter cleaning

Cleaning quartz fibre filters ensures a low carbon content for non exposed filters and is thought to enhance the capacity of back up quartz filters in trapping the POC volatilized from the front filter during sampling.

- 1- In order to prevent any contaminations of the filters by the furnace make a carpet in the furnace using organic binder – free filters of large dimensions (e.g. for high-volume samplers) resistant to 950°C, or make use of ceramic stands (e.g. ceramic crucibles).
- 2- Wear dust-free gloves; e.g. polyethylene (PE) gloves.
- 3- Using tweezers, place the quartz fiber filters, one after another, on the filter carpet or on the ceramic stands,,
- 4- Bake the filters at 850°C for a minimum of 3 hours, and let them cool down to ca. 100°C.
- 5- Wear dust-free gloves.
- 6- Place filters into small air tight glass containers or plastic Petri slides.
- 7- Store the annealed filters in a clean place until sampling for ≤ 1 month.

SOP 2 Filter storage

- 1- Keep filters into labeled Petri slides before and after sampling.
- 2- Seal Petri slides tightly.
- 3- Store Petri slides in the refrigerator (ca. 4 °C) before the analysis (for up to 6 weeks).
- 4- Store Petri slides in the freezer (ca. -20 °C) for long term storage.

SOP 3.1. Start-up of the Sunset Laboratory OCEC Lab Instrument

- 1- Ensure that the He, He/O₂, Air and Hydrogen gas cylinder pressures are at least 3 bar. Set gas cylinder delivery pressures to 1.5 bar - 2 bar.
- 2- If the program has been turned off, restart it by double-clicking on the OCECINST icon on the OCEC Instrument computer desktop.
- 3- If the program is in standby mode, click the CONTINUE button.
- 4- Set gas flow rates using the gas valves on the instruments lower control unit according to the user's manual and record flow rates in the logbook. The flow rate of He/O₂ should be as equal as possible to that of He-2.
- 5- In order to ignite the flame of the FID set the H₂ flow to > 100 cc min⁻¹. Once the flame has been lit (usually a little pop can be heard), return the H₂ flow rate back to its operating level. Check that the flame is alight by bringing a cold metallic surface towards the FID exhaust outlet: Condensation of water vapor should be observed when the flame is alight.
- 6- Select the proper PARAMETER FILE (here: EUSAAR_2) to be used and either select the appropriate RAWDATA FILE or enter a new file name into the RAWDATA TEXT BOX.
- 7- Check and record the temperature of the front oven, the back oven and the methanator; instrument pressure; transmittance and reflectance signal with a clean quartz fiber filter punch; transmittance and reflectance dark signal. In the off-line mode:
 - the back oven temperature should be approximately 870 °C
 - the front oven temperature should be approximately < 50 °C
 - the CH₄ oven temperature should be approximately 500 °C
 - the instrument pressure should be in the range 0.5 psi to 4 psi (offline pressure: approx. 1 psi)
 - for a blank filter the transmittance signal should be in the range indicated by the manufacturer and be consistent from a day to another.
 - the FID can only be checked for a signal or a numerical readout when the cycle commences; the peak area for the calibration peak should be in the range indicated by the manufacturer. As this variable varies over a wide range, the range of normal values should be established for each instrument.

SOP 3.2. Daily calibration with an external carbon containing solution

The instrument has to be switched on according to SOP 3.1. first.

- 1- Punch a 1 or 1.5 cm² aliquot from a blank quartz fiber filter.
- 2- When the computer displays in the green message bar:

"SAFE TO PUT IN A NEW SAMPLE"

Open the door to the oven and put it in a safe place (e.g. you can arrange a hook somewhere).

- 3- Pull the quartz boat partially out from the oven using stainless steel tweezers and place it on the instrument boat support arm. Place the filter punch on the 1 cm² or 1.5 cm² boat, according to the size of the punch cut in Point 1-.
- 4- Slide the boat in gently until it stops by the tip of the thermocouple, and then pull it backwards by ca. 1 mm.
- 5- Close the oven door ensuring that the O-ring seals tightly into the front of the oven and lock the door with the clamp.
- 6- Check that the oven pressure is in the range of 0.25 - 4 psi.
- 7- Select CLEAN OVEN from the options menu to clean the filter punch.
- 8- After the CLEAN OVEN CYCLE, open the oven door, pull the quartz boat partially out from the oven using the stainless steel tweezers and place it on the support arm.
- 9- Use a μ -pipette to spike 10 μ l of the calibration standard (containing 1 to 4 μ g of carbon per microliter, i.e. 1 to 4 g of carbon per liter) onto the filter punch
- 10- Put the filter punch back on the quartz boat, push the boat in the oven, and let the filter dry at 50 – 70°C in the oven for ca. 15 minutes (until the laser transmission value returns to the value observed for a dry filter punch).
- 11- Analyse the filter following SOP 4. Points 4- to 8-
- 12- Compare the amount of carbon determined for the external calibration standard with the expected value. If the difference exceeds 10 % or 0.5 μ g C/cm² (if 10% would be less than 0.5 μ g C/cm²), consider the following actions:
 - Perform an additional analysis of the external calibration standard
 - Make a new calibration standard or a new stock solution.
 - Change the calibration constant set in the instrument in the calcpair.txt file.

SOP 3.3. Periodical instrument check with a pure carbon containing gas

An instrument check using external gaseous standards (e.g. CO₂ or CH₄) should be performed at least three times a year, to check the absolute calibration of the whole instrument (back oven excluded if CO₂ is used).

The amount m of C contained in a volume V in the micro-syringe is equal to:

$$m = M \cdot \chi \cdot p \cdot V / (R \cdot T) \quad (\text{Eq. 1})$$

where:

M is the carbon molar mass (12.0 10⁻³ kg mol⁻¹)

χ is the content of the standard gas in the cylinder (if pure gas, $\chi = 1$)

p is the room pressure, in Pascal (normally 101325 Pa)

V is the standard gas volume taken with the syringe, in microlitre (μl)

R is the ideal gas constant ($R = 8,314 \text{ J K}^{-1} \text{ mol}^{-1}$)

T is the room temperature, in Kelvin (normally $T = 298 \text{ K}$)

m is the mass of carbon in volume V into the syringe, in microgram (μg)

In standard conditions ($p = 1013.25 \text{ hPa}$; $T = 298 \text{ K}$), 10 μl of pure CO₂ or CH₄ contain 4.9 μg C.

A known volume of standard gas is injected during each step of the analysis. The amount of carbon detected by the instrument is compared to the amount of C calculated from Equation (1).

- In case the same amount of standard gas are read as different C amounts (> 10%) by the instrument in the He and He/O₂ modes, the carrier gas flow rate calibration (and in particular He-2 and He/O₂) have to be checked.
- If the amount of C detected by the instrument is different from the expected amount (> 10%), the external standard solution has to be replaced, and a new calibration factor should be established.

Procedure 3.3.:

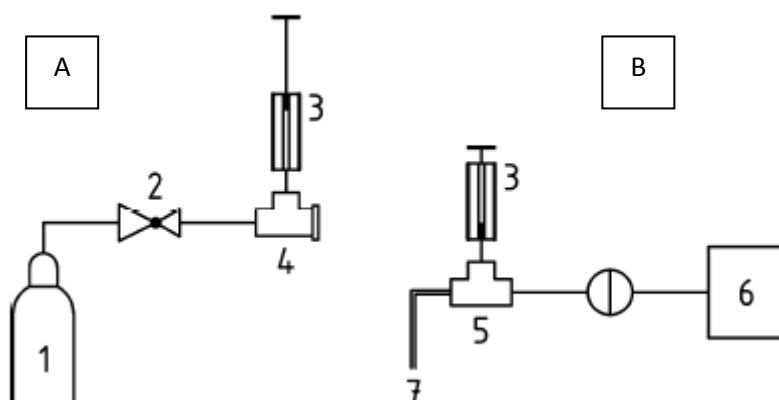
The instrument has to be switched on according to SOP 3.1. first.

- 1- Insert the T with the septum in the carrier gas line just upstream of the point where the sample is usually loaded (see Figure 2).



Figure 2 — Inserting a T with a septum in the carrier gas line of a Sunset Laboratory OCEC Lab instrument.

- 2- Run the analysis protocol with a punch of blank filter 2 to 3 times, until no more C is detected by the instrument (see SOP 4.3.)
- 3- Start a new thermal analytical run.
- 4- Take a precise volume of standard gas from the cylinder through the septum (Fig. 3, step A). The volume of gas in the syringe should be equilibrated to room temperature and pressure. Log the volume injected, and the room pressure and temperature.
- 5- Inject the whole syringe volume (Fig. 3, step B) during the analytical step 1 (e.g. He mode, temperature plateau 200 °C in EUSAAR_2).
- 6- Repeat steps 4 and 5 for each analytical step in the He and the He/O₂ modes.
- 7- Steps 3 to 6 can be repeated e.g. injecting different volumes of standard gas



- 1 standard gas cylinder
- 2 pressure reducer
- 3 gas syringe
- 4 septum holder

- 5 T with septum
- 6 carbon thermal analyser
- 7 carrier gas

Figure 2 — Schematic of procedure 3.3. Points 4 and 5

SOP 4. Analysis of ambient samples

The instrument has to be switched on according to SOP 3.1. first.

- 1- Punch a 1 cm² or 1.5 cm² aliquot from a clean quartz fiber filter.
- 2- When the computer displays in the green message bar:

"SAFE TO PUT IN A NEW SAMPLE"

open the door to the oven and put it in a safe place (e.g. you can arrange a hook somewhere).

- 3- Pull the quartz boat partially out from the oven using the stainless steel tweezers and place it on the instrument boat support arm. Place the filter punch on the 1 cm² or 1.5 cm² boat, according to the size of the punch cut in Point 1-.
- 4- Slide the boat in gently until it stops by the tip of the thermocouple, and then pull it backwards by ca. 1 mm.
- 5- Close the oven door ensuring that the O-ring seals tightly into the front of the oven and lock the door with the clamp.
- 6- Check that the oven pressure is in the range 0.25 - 4 psi.
- 7- Type in the sample identification name and select the sample size according to the actual punch size.
- 8- Click the **START ANALYSIS** button on the computer.
- 9- Repeat steps 1-8 ad libitum.

SOP 5. Instrument Shut down

- If intending to return to the analyser the day after or the following days:
 - 1- Click on the STANDBY button
 - 2- Close **gently** the gas valves on the instruments lower control unit. The back oven will be maintained at a lower than normal temperature, the laser will be shut off and the pressure is close to zero as the flow of helium is kept rather low.
- If not intending to use the instrument for the following 10 days:
 - 1- choose EXIT from the file menu.
This will turn off the power to the instrument, and allow the ovens to cool down.
 - 2- The gas valves on the instruments lower control unit should be tightened **gently**.
 - 3- The gas supply can now be turned off.

SOP 6. Calculation of atmospheric concentrations.

The atmospheric concentration of carbon (i.e. OC or EC) is calculated from the amount of carbon (OC or EC) per square centimeter of filter, as determined from the analysis of a filter punch, and the volume of air sampled through the filter as:

$$[C] = m \cdot S / V \quad (\text{Eq. 2})$$

where:

$[C]$ is the carbon (OC or EC) atmospheric mass concentration ($\mu\text{g C m}^{-3}$)

m is the carbon (OC or EC) amount per surface area of the filter ($\mu\text{g cm}^{-2}$). m should **NOT** be corrected for field blanks values, which should be reported separately

S is the exposed surface area of the filter on which particles are actually deposited (cm^2)

V is the volume of air sampled by the exposed filter area in standard conditions of pressure and temperature (*to be specified*).