Toward a Standardized Thermal-Optical Protocol for Measuring Atmospheric Organic and Elemental Carbon: The EUSAAR protocol

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SOOT CARBON

combustion-derived particle type, identified as an impure form of near-elemental carbon with a graphite-like-structure

In atmosphere, soot carbon assumes an ample variation in morphology (spherules, clusters, aggregates, etc) and chemistry (C:H:O) depending on sources and combustion conditions

Available techniques are Raman spectroscopy and electron microscopy, but absolutely impractical for routine monitoring of this aerosol component

…HOW TO ADDRESS THIS PROBLEM?

It has been taken advantage of some characteristic properties of soot carbon

↓

Measurements methods for routine quantification of soot

NEW OPERATIONAL DEFINITIONS as

EC and BC

EC: term conventionally used in conjunction with thermal and wet chemistry determinations for the selective measurement of the refractory component

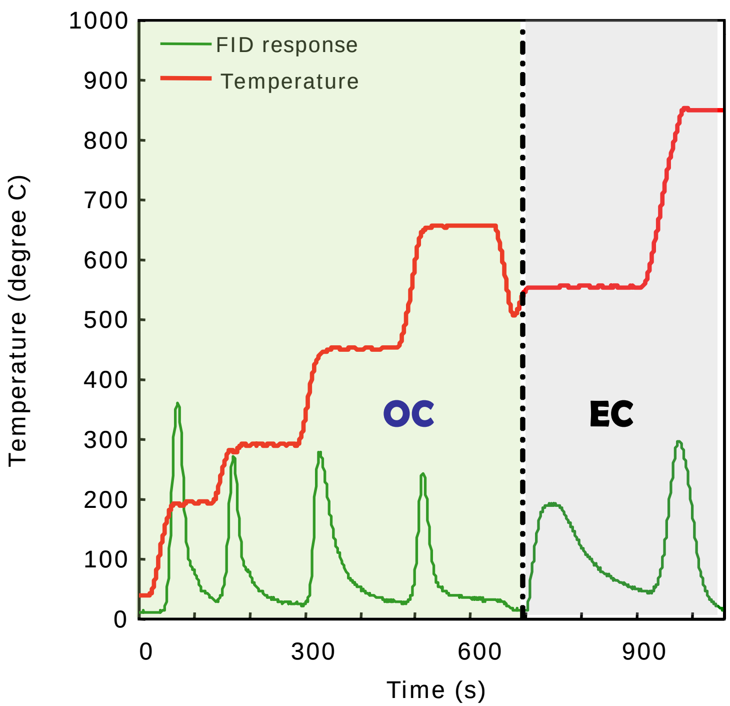
BC: term implies that this component is responsible for the absorption of visible light and generally used when optical methods are applied for its determination

Thermal Optical Method

- controlled heating of aerosol quartz fiber filter samples
- in an inert atmosphere (He-mode) and then in an oxidizing atmosphere (He/O_2-mode)

OPERATIONAL DEFINITIONS:

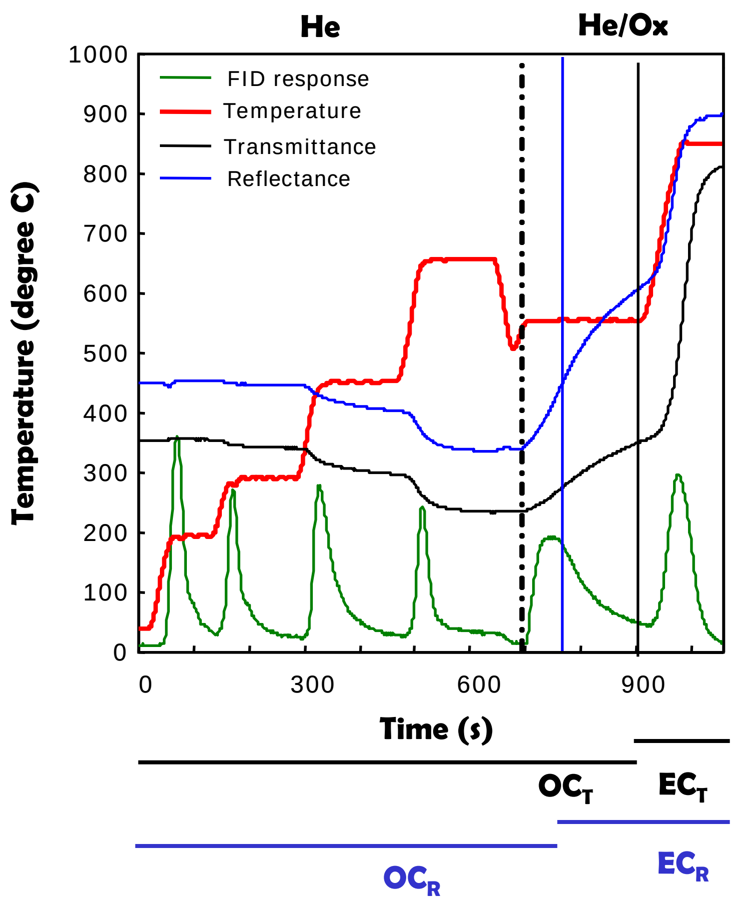
- Carbon desorbing in He mode is OC
- Carbon combusting in He/O_2-mode at high temperature is EC



Ideally, … but

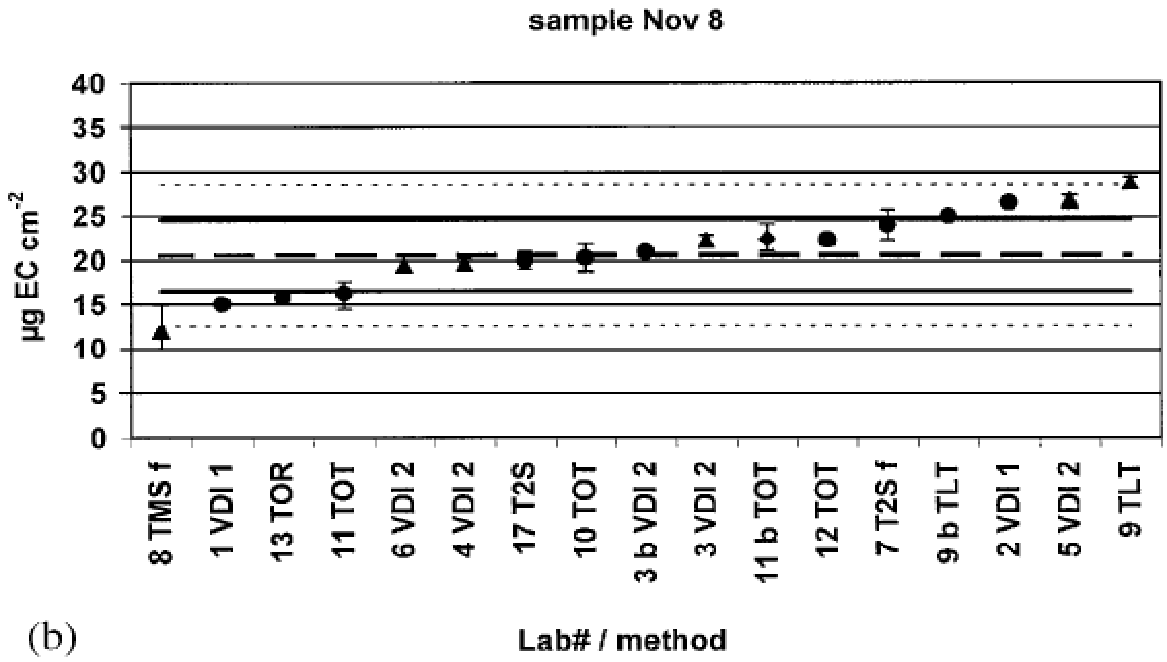
some thermally unstable OC pyrolyses in the He-mode to form pyrolytic carbon, PC, on the filter which behaves like native EC

CHARRING and OPTICAL CORRECTION



Comparability of thermal/thermal-optical methods for measuring the aerosol carbon content:

- TC generally measured with good agreement
- EC highly variable over more than one order of magnitude
  - EC is an operational definition – DIFFERENT METHODS
  - Charring correction – IF and HOW



Results of the "carbon conference" international aerosol carbon round robin test stage I . Schmid et al. 2001, Atmos. Environ. 2111-2121.

Comparability of methods for measuring the aerosol carbon content:

- Importance of a common analytical method
- Importance of a common protocol

to ensure comparability of results

- Importance of definition of an unbiased protocol

to increase accuracy of results

Aim of the project is the harmonization of measurements of aerosol properties of interest to air quality and global climate through coordinated protocols

AIMS

- **Define a standardised protocol for thermo-optical analysis of OC+EC appropriate for variuos sites across Europe**
- **Get the standardised protocol adopted by the EMEP task force on measurements and modelling and WHO Global Atmospheric Watch scientific advisory group**

Method assumptions:

- PC has approximately the same specific cross section as native EC

or

- PC evolves completely before native EC throughout the analysis

BOTH ASSUMPTIONS ARE INCORRECT!

Inherent biases in either direction in the determination of OC and EC

e.g. Subramanian et al. (2006) *Aero. Sci. Tech., 40:763-780*

The optimal thermal-optical protocol should mitigate the occurrence of *events* during the analysis that can magnify biases in the OC/EC split

OPTIMISATION CRITERIA:

1- charring is reduced to minimum levels

2- evolution and/or pyrolysis of OC is completed at the end of the He-mode to avoid that unevolved and uncharred left-behind OC slip into the He/O_2-mode

3- premature evolution of light-absorbing carbon is limited during the He-mode to prevent that the early released light-absorbing species contains native EC

4- multiple desorption steps are designed for the He/O_2-mode to ensure that the position of the OC/EC split point occur where the FID response profile is low

NIOSH and IMPROVE are not satisfactory

The EUSAAR protocol

Key parameters:

- Steps at low temperature
- He-mode maximum temperature
- Residence time of each temperature step
- Temperature steps in He/O_2-mode

Studies performed on aerosol samples collected in Ispra and at various EUSAAR sites

Experiment:

- NIOSH protocol lowest temperature step at 310°C, 60s
- Modifidied NIOSH 200 °C and 300 °C, 120s and 150s, respectively

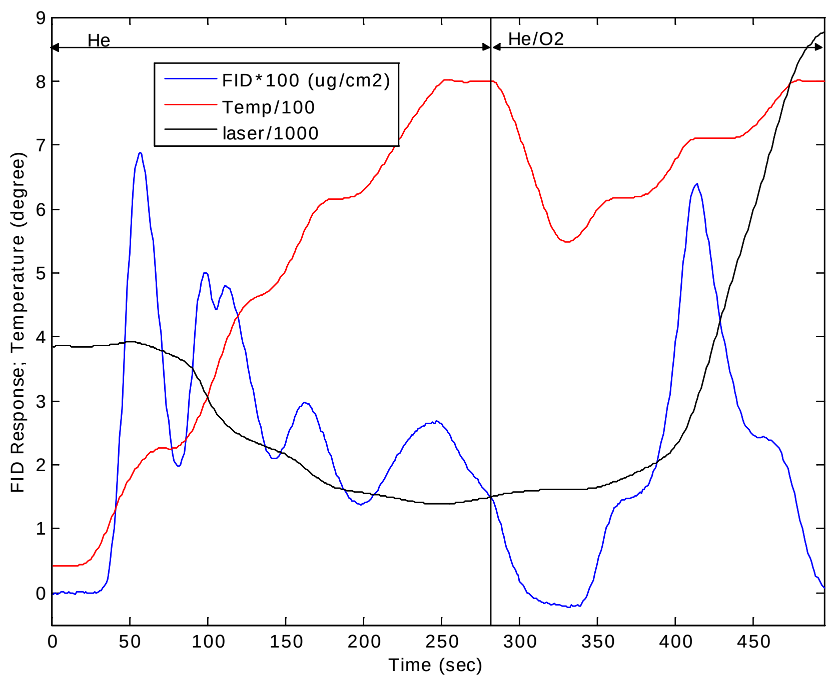
PROTOCOL		TC ug cm-2	OC ug cm-2		PC ug cm-2
			≤ 300 °C	> 300 °C	
NIOSH	1	11.59	2.41	4.27	3.87
Modified NIOSH	1	11.51	2.81	4.20	3.36
NIOSH	2	12.79	2.82	4.54	1.99
Modified NIOSH	2	12.79	3.29	4.60	1.67
NIOSH	3	8.33	1.93	3.05	3.62
Modified NIOSH	3	8.30	2.21	2.98	3.12

PC formed in the modified NIOSH is 85.6 ± 1.4% of that in the NIOSH method

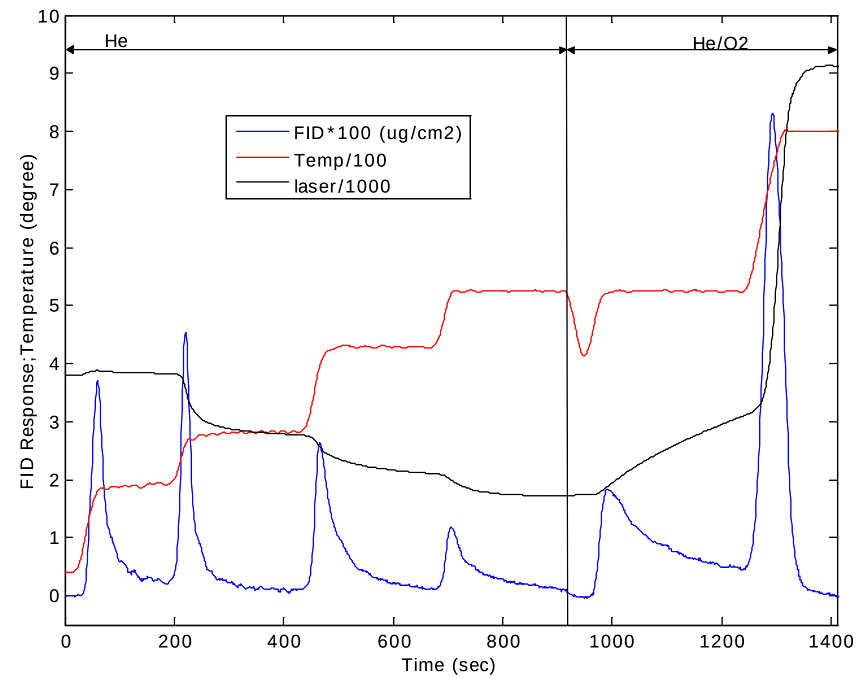
Low temperature steps reduce PC formation in favor of a more complete carbon evolution and improve accuracy of the OC/EC split.

Which type of light-absorbing carbon does prematurely evolve?

EC or PC?



He max Temp 850 °C NIOSH-type protocol



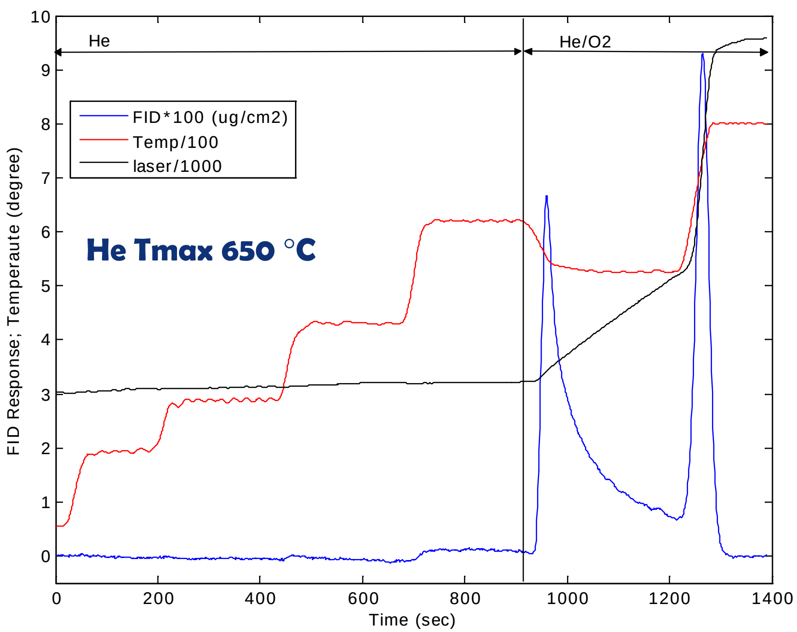
He max Temp 550 °C IMPROVE-type protocol

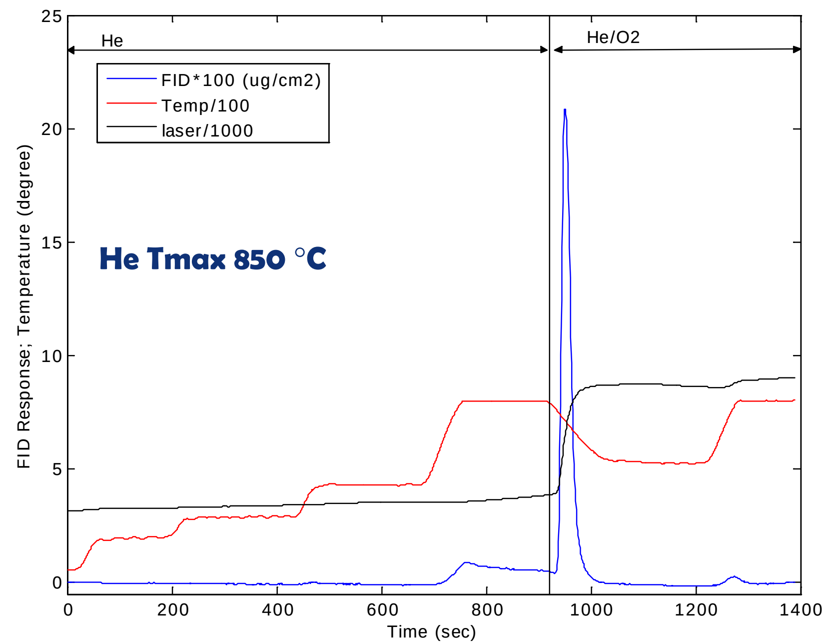
Potential biases in the EC determination

T at which LAC evolution starts and extent of this bias

Experiment::

1. LAC-only samples generation from atmospheric aerosol samples
2. Run using protocols with max T in He of 650 °C, 750 °C and 850 °C





LAC evolved:

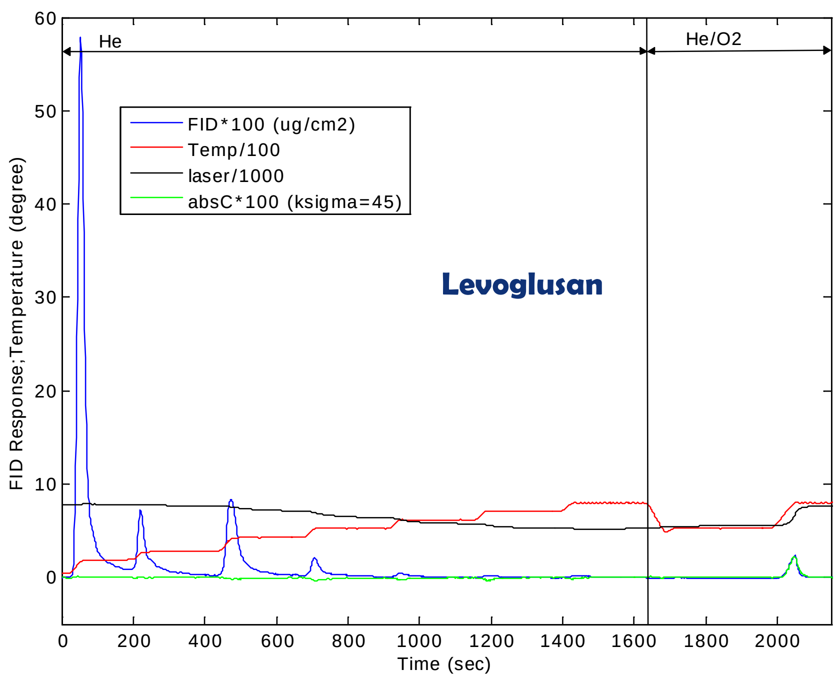
at 650°C 2.5±2.4% **at 750°C 16.2±5.9%** **at 850°C 21.2±4.4%**

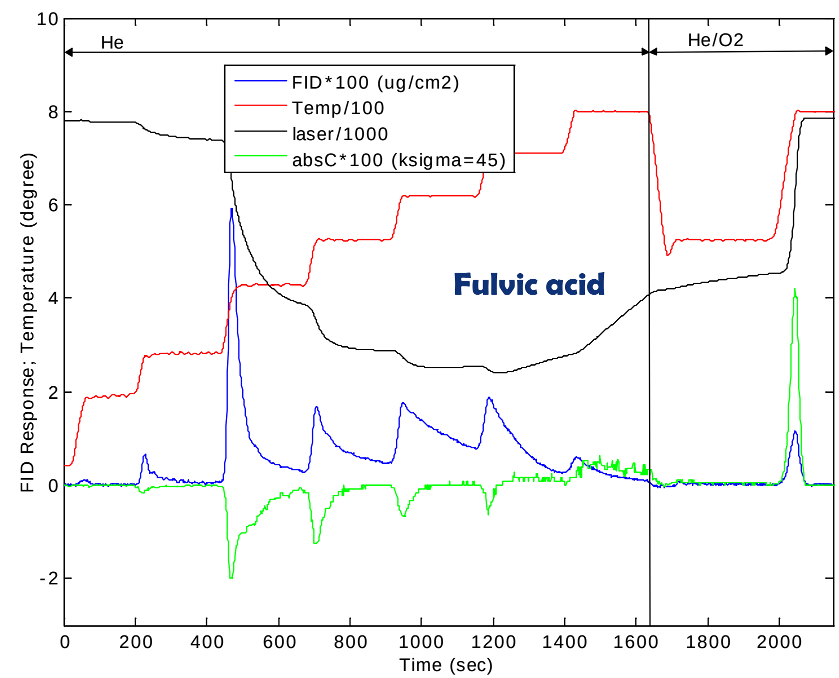
Does OC all volatilize / completely pyrolyse in the He-mode or slip into the He/O_2-mode?

T at which OC completely volitilizes / pyrolyses

Run:

- o Anthropogenic and biogenic SOA
- o Levoglucosan
- o Fulvic acid





The EUSAAR protocol

STEP	T, duration
He1	200°C, 120s
He2	300°C, 150s
He3	450°C, 180s
He4	650°C, 180s
(Helium)	Cool down, 30s
$He/O_2$1	500°C, 120s
$He/O_2$2	550°C, 120s
$He/O_2$3	700°C, 70s
$He/O_2$4	850°C, 80s

- Crucial point is the selection of the maximum He-mode temperature: T = 650°C yielded the best compromise between positive and negative biases
- Temperature plateau durations: FID approaches the baseline before the next set-point; Total analysis time acceptable for routine monitoring applications
- Mutiple desorption step for the He/O2-mode: OC/EC split point occur where the FID signal is low so that uncertainties in the OC/EC split determination is minimum

Conclusions

- We have reviewed the basic assumptions of TOA and the pillar protocols as NIOSH and IMPROVE
- We have developed an optimised thermal evolution protocol: the EUSAAR protocol
- This protocol minimises potential positive and negative biases and hence increases accuracy of OC/EC measurements
- This common analytical protocol represents a relevant step forward for the European atmospheric sciences monitoring communities and Networks:
  - Introduction to the EMEP (European Monitoring and Evaluation Programme) network;
  - Setting-up of a OC/EC working group under CEN, the European Standardisation Committee.