# Measuring particulate organic and elemental carbon: challenges and proposed solutions

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**DIRECTIVE 2008/50/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL**

**of 21 May 2008**

**on ambient air quality and cleaner air for Europe**

CHAPTER II

**ASSESSMENT OF AMBIENT AIR QUALITY**

*SECTION 1*

***Assessment of ambient air quality in relation to sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter, lead, benzene and carbon monoxide***

*Article 5*

**Assessment regime**

5. In addition to the assessments referred to in paragraphs 2, 3 and 4, measurements shall be made, at rural background locations away from significant sources of air pollution, for the purposes of providing, as a minimum, information on the total mass concentration and the chemical speciation concentrations of fine particulate matter (PM2,5) on an annual average basis …

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Annex IV: At least the list of chemical species given below shall be included.

| | | | | |
|---|---|---|---|---|
| $SO_4^{2-}$ | $Na^+$ | $NH_4^+$ | $Ca^{2+}$ | elemental carbon (EC) |
| $NO_3^-$ | $K^+$ | $Cl^-$ | $Mg^{2+}$ | organic carbon (OC) |

*The general term "soot" refers to combustion-generated aerosol mixtures of* ***two components****: first, the most thermally refractory and light absorbing byproduct of incomplete combustion, which is commonly referred to as elemental carbon (****EC****; thermal/optical analysis) or black carbon (BC; light absorption methods); and second, organic carbon (****OC****) that can have a wide range of thermal and light-absorbing properties* (Baumgardner et al., 2012).

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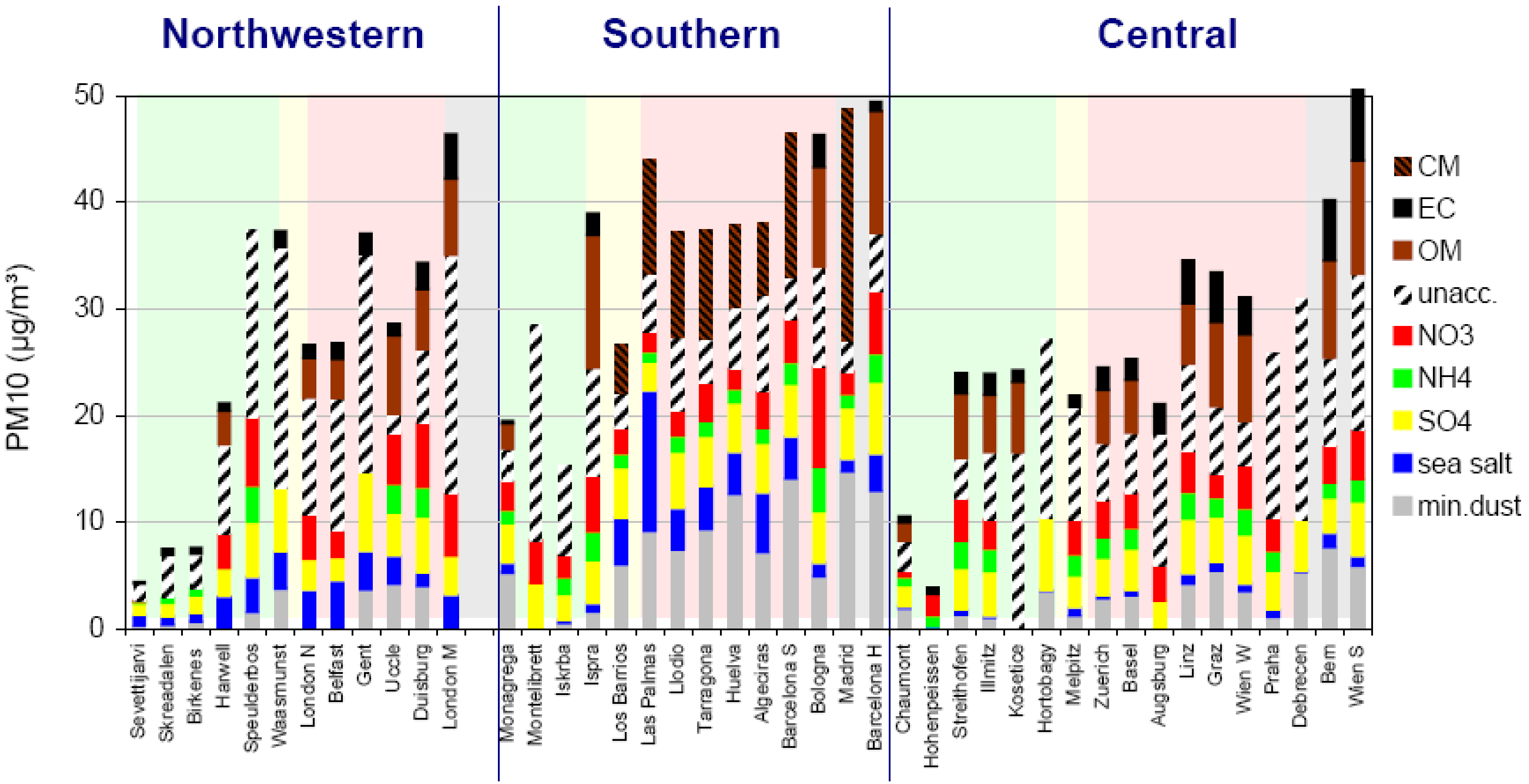
# Chemical characteristics of particulate matter from 43 rural, urban, and kerbside sites across Europe




Putaud et al., 2010

- Carbonaceous species account for a substantial fraction of PM2.5 (& PM10)

- There were many sites where carbonaceous species were not measured

- The lack of reference methods prevents these measurements from becoming more "popular"
    - sampling
    - analyses

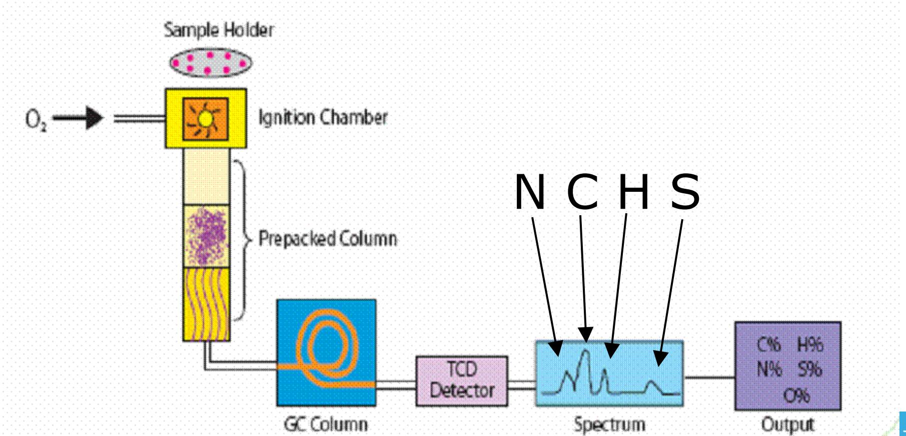
- What challenges should a practicable method for the analysis of particulate carbonaceous matter overcome ?

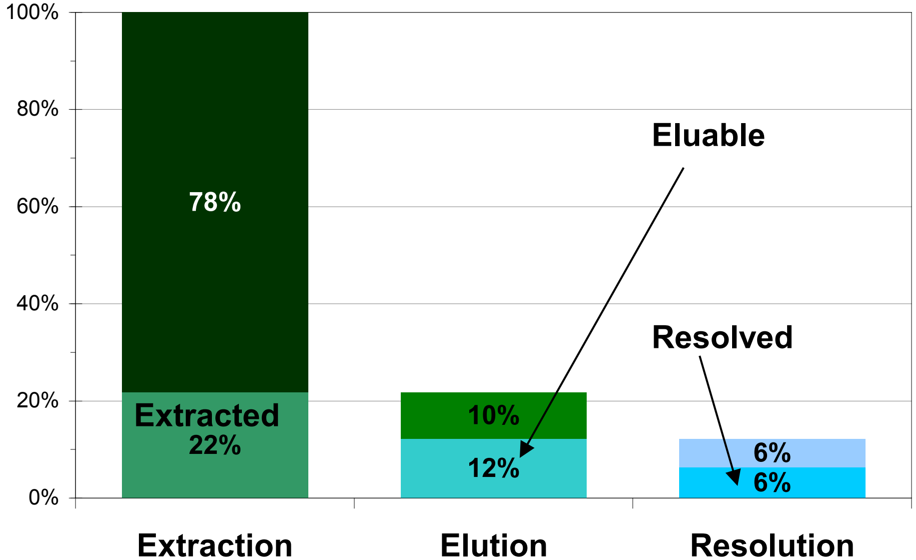
# Carbonaceous atmospheric particulate matter consists of 1000’s of species with very different properties

Atmospheric particulate matter speciation → resolve and quantify up to 10-15% of TC only

Elemental Analysis (CHN)

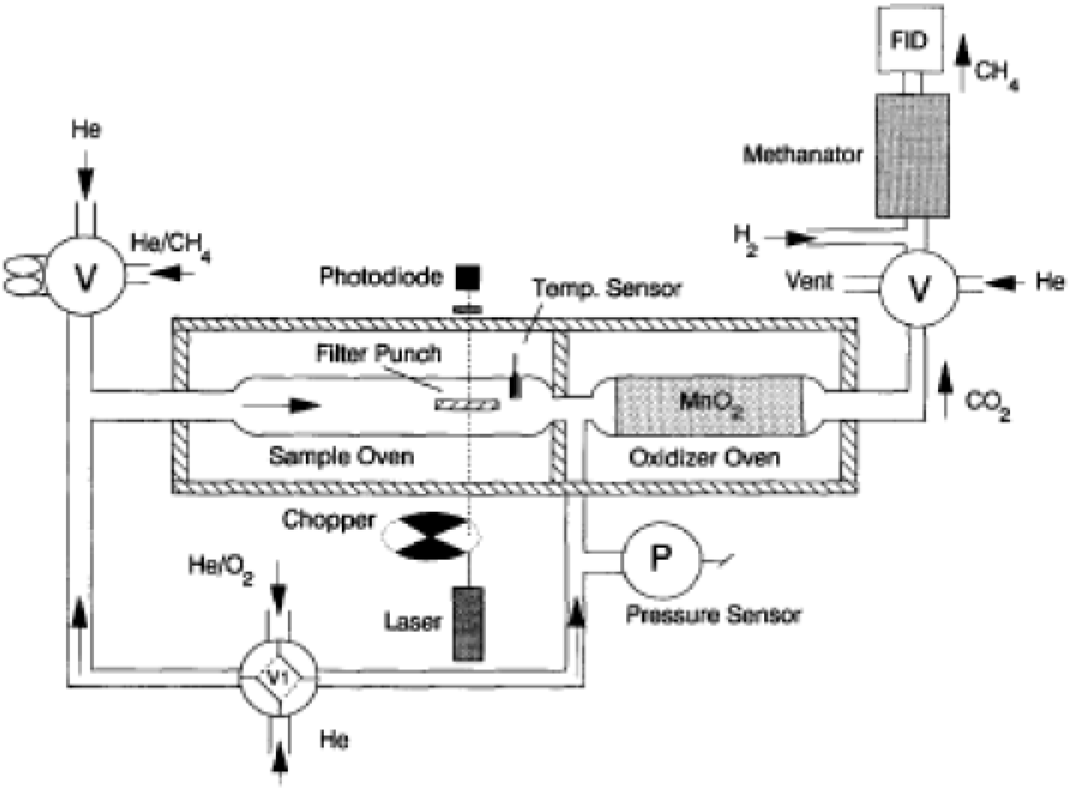
→ get Total Carbon (TC) amount



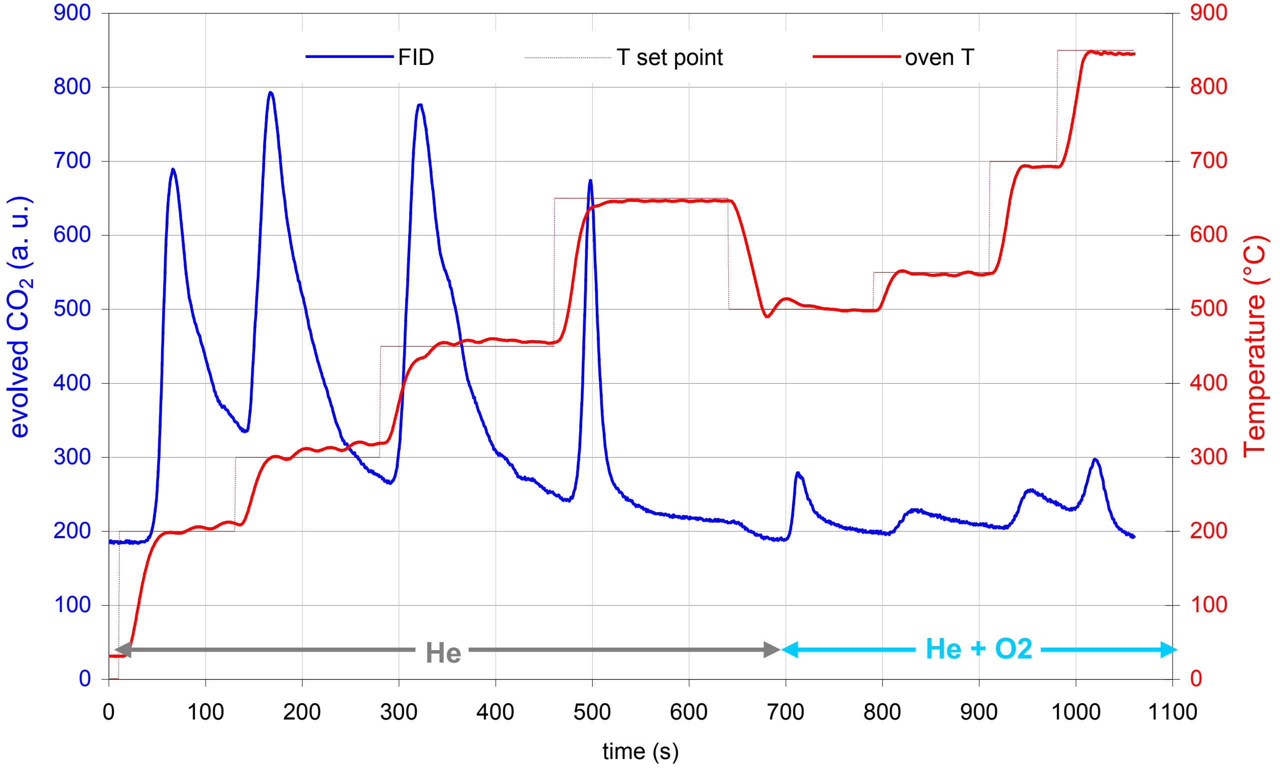




Adapted from Alam et al. (2004) and references therein

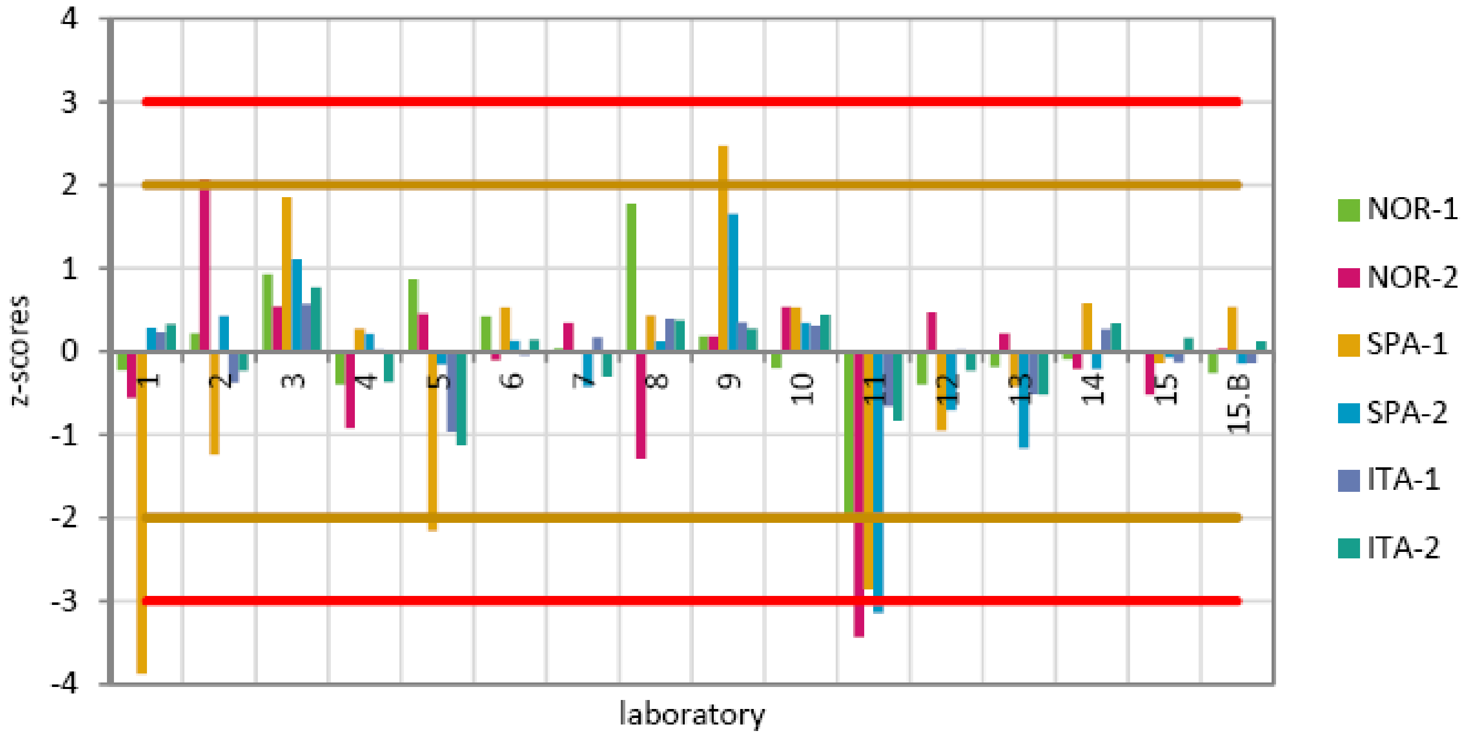
# → Evolved Gas Analysis (EGA):



# Evolved Gas Analysis (EGA):



# EGA methods directly **determine TC** with a reasonable precision



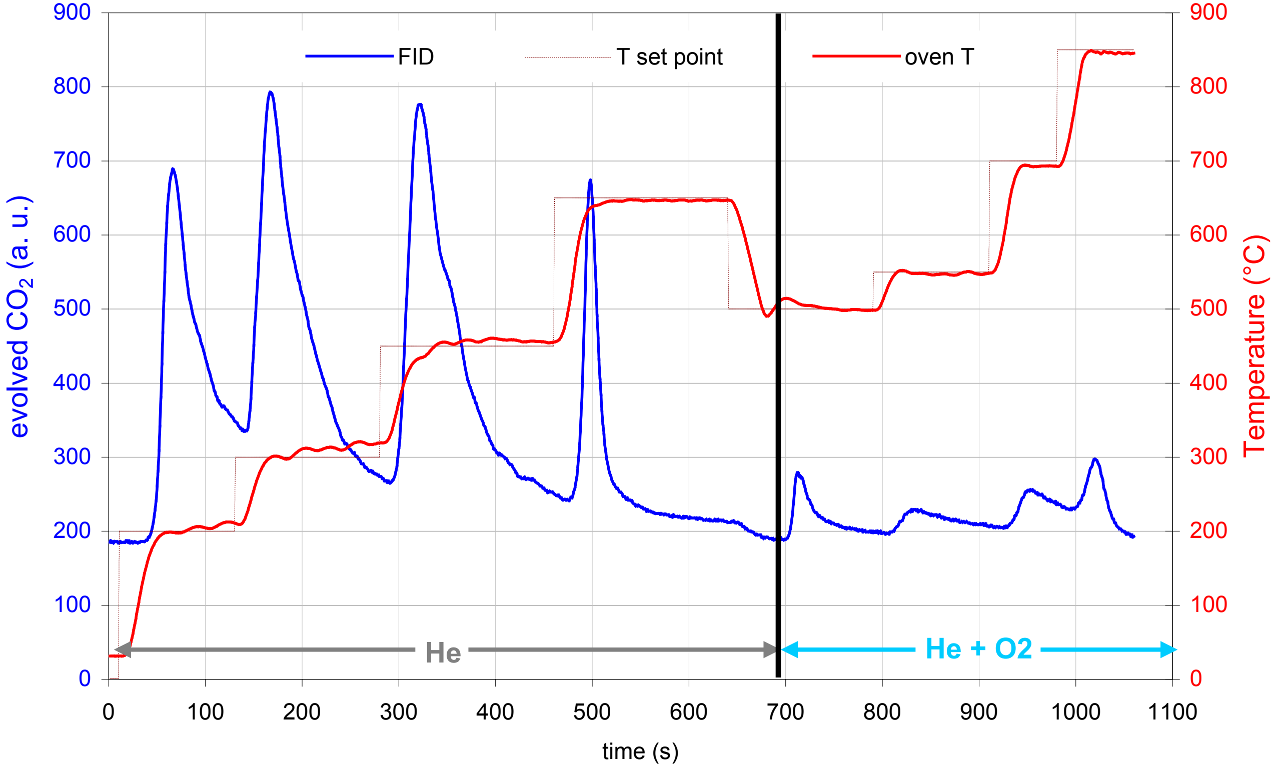

z-scores for TC calculated using a *prescribed* σ* value (25%).

# **Distinguish** between **EC**

directly emitted in the particulate form by combustion processes

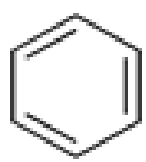
and **OC**

from both natural and anthropogenic primary and secondary sources

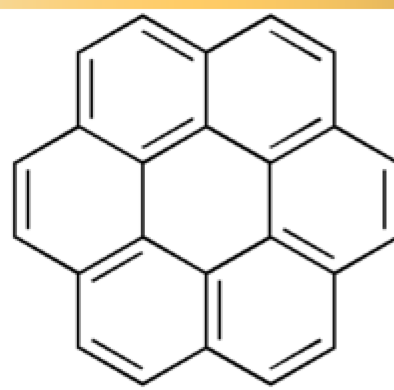


**no clear** theoretical **split point** between highly refractory organic molecules and "infinite" graphene structure, the basic structural element of graphite

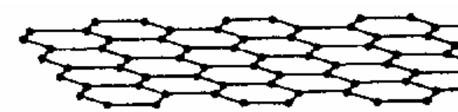
| | Volatile Organic Carbon | Particulate Organic Carbon | Elemental Carbon |
|---|---|---|---|
| H/C ratio | ≈ 1 | ≈ 0.5 | 0 |
| Volatility | high | low | 0 |



Benzene



Coronene



Graphene

**There are currently no suitable standards for atmospheric OC and EC.**

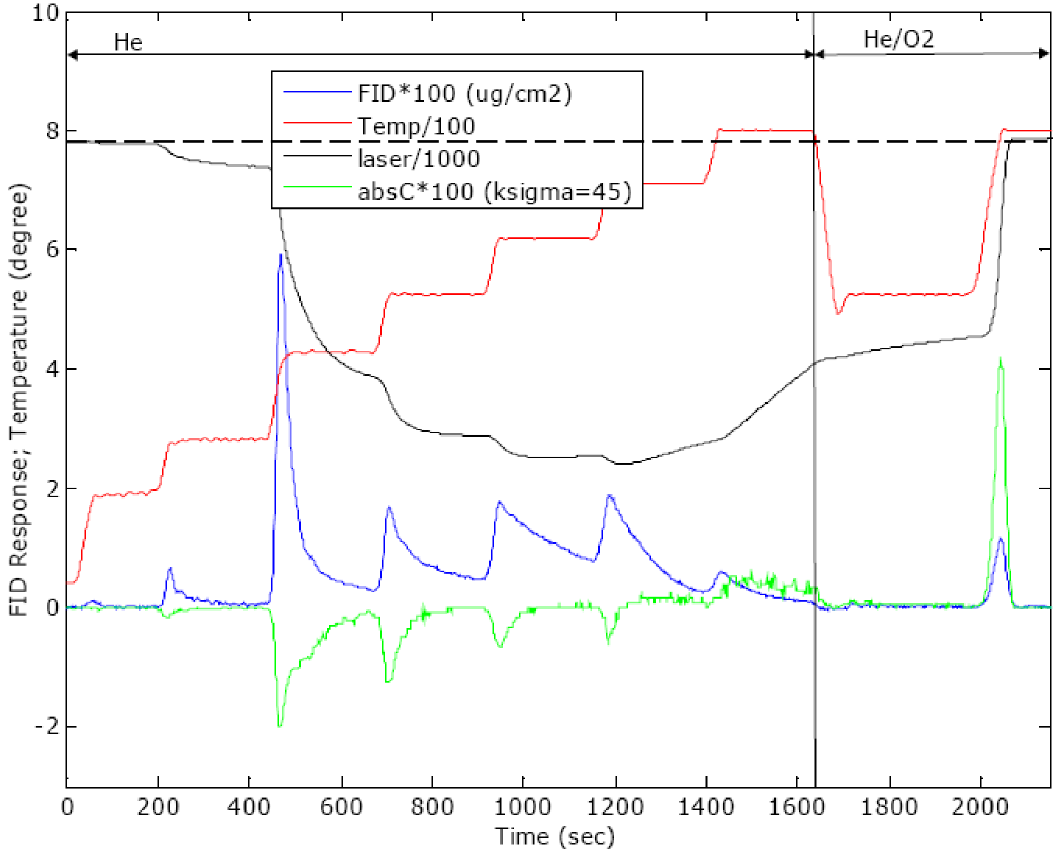
**But at least pure EC should be detected as 100% EC**
**Any organic molecule (or mixture) should be detected as 100% OC**

IMPROVE (up to 550° C): all OC does not evolve during step 1

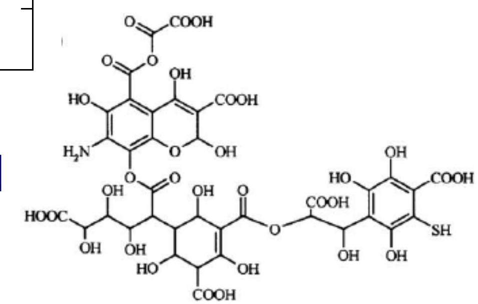
NIOSH (up to 850° C): a fraction of EC can be combusted during the step 1

**EUSAAR_2 (up to 650° C): best compromise**
**max 5 % of EC evolves in He**
**min 80 % of OC evolves in He**

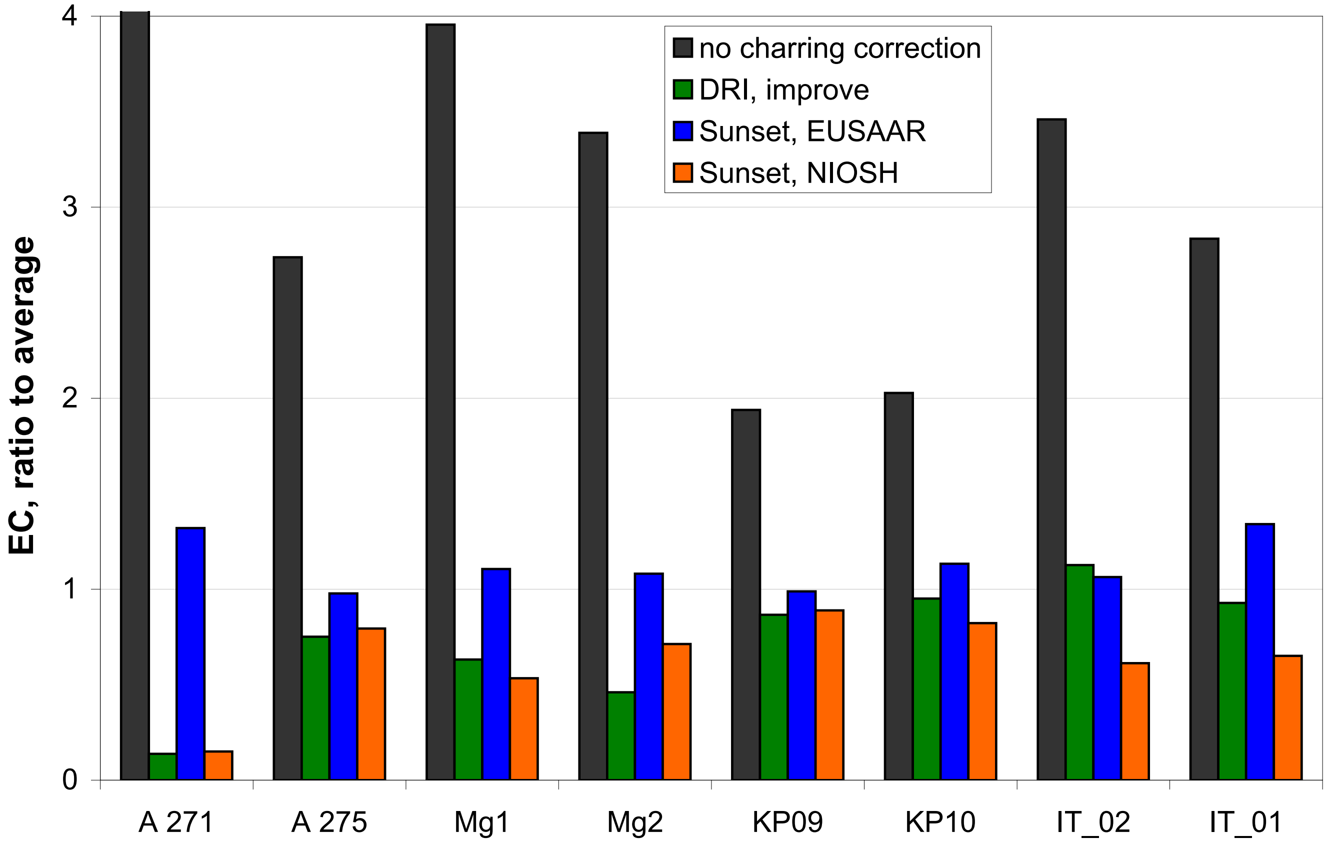
# Pyrolysis produces EC-like species during the analysis (Charring):




Thermal – optical analysis of fulvic acid



Not correcting for charring => error in EC determination larger than 400%.




EUSAAR 2007 intercomparison

EC determined with 4 different thermal methos
in 8 samples collected at various sites in Europe

**Charring must be corrected.**

**The optical correction of charring assumes that:**

PC evolves from the filter before EC.

PC has the same specific light absorption cross section as EC.

**which is not always true**

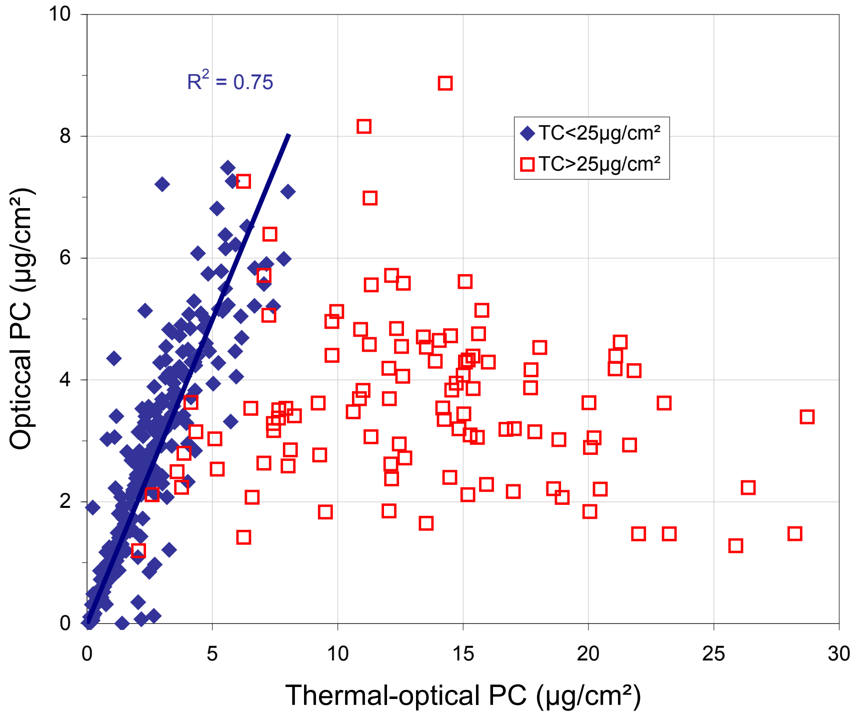
⇒ **Need for charring limitation**

With longer steps at low temperature,

**EUSAAR_2 limits charring**

However,

**charring correction can be inaccurate for loadings > 25 µgC /cm²**



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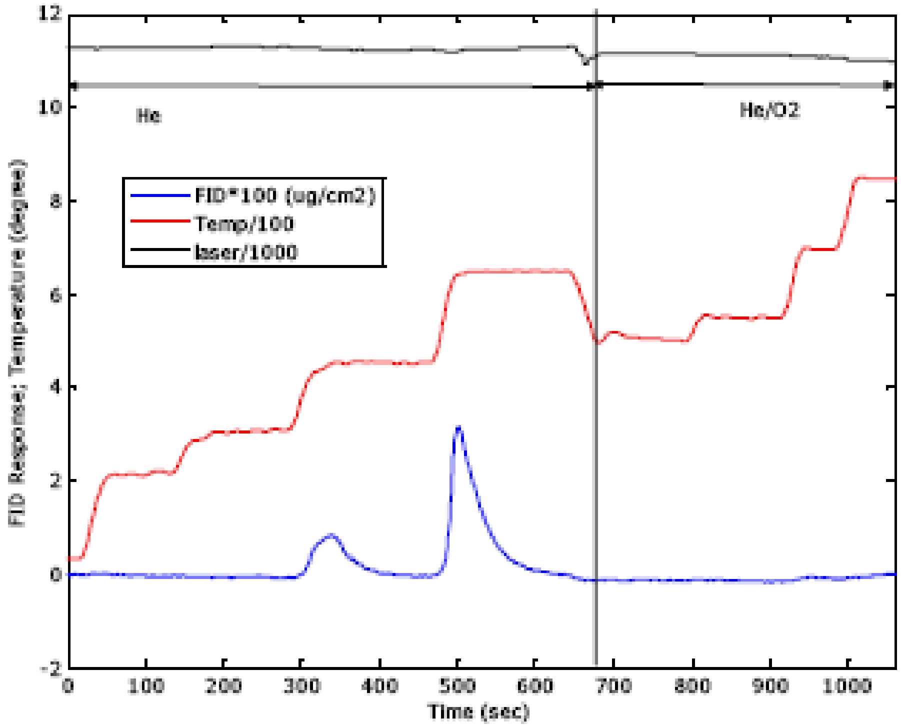
# Carbonate can interfere with the determination of OC and/or EC.

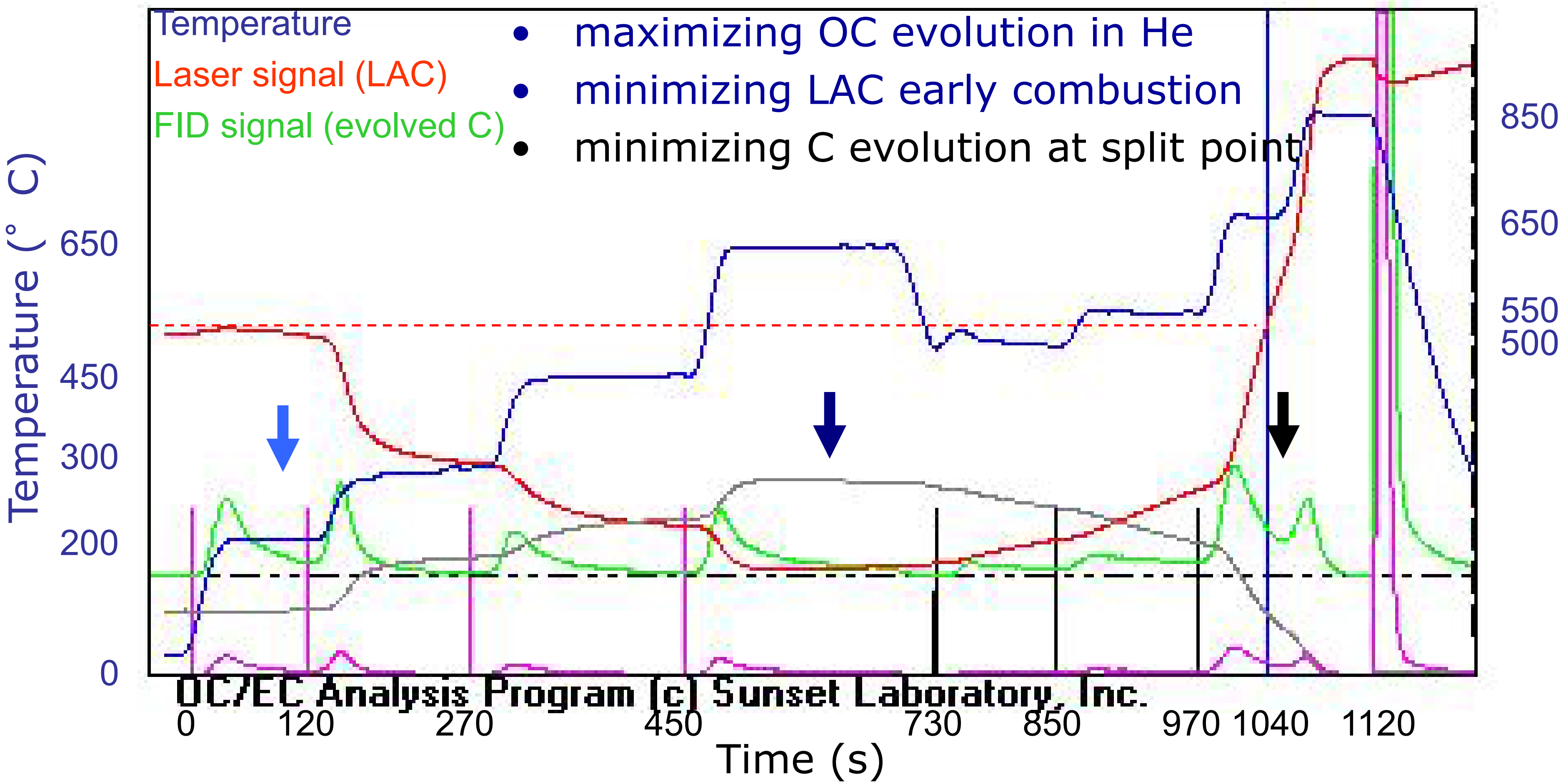



Cavalli et al., 2010

## C from natural calcite evolves in the OC4 fraction with EUSAAR_2
## ⇒ No interference with EC

## Protocol EUSAAR_2

- minimizing charring
- maximizing OC evolution in He
- minimizing LAC early combustion
- minimizing C evolution at split point



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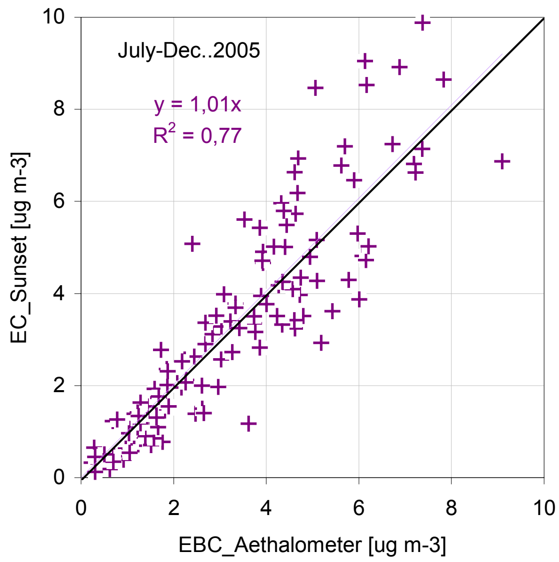
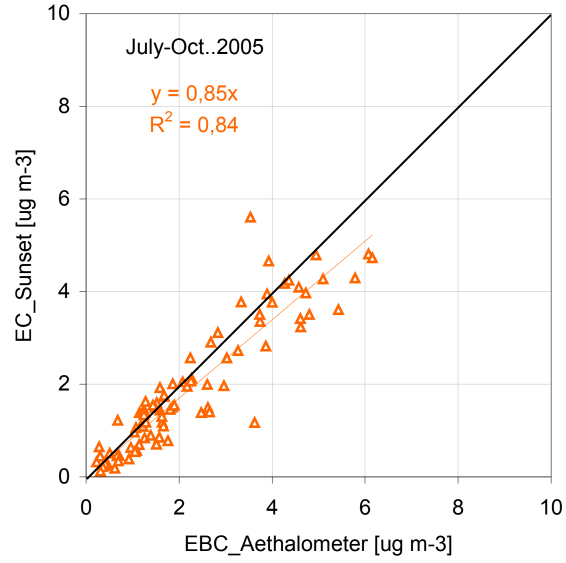
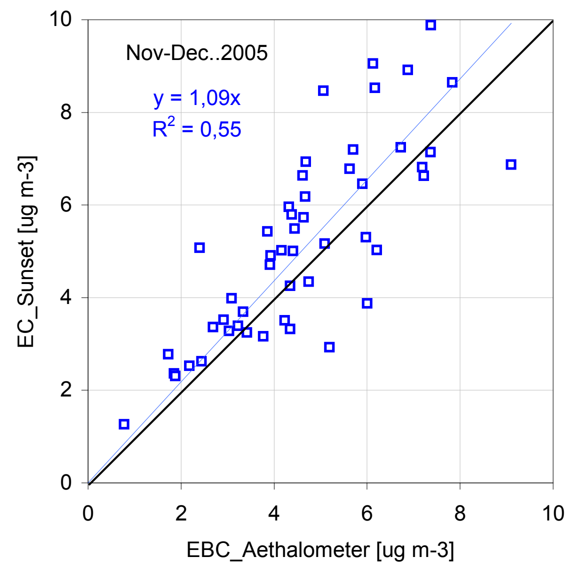
# **Comparison** between Elemental Carbon and Equivalent Black Carbon



## Conclusions:

The thermal-optical protocol EUSAAR_2 overcomes a series of challenges related to the measurement of "soot" in PM:

1. Robust determination of TC
2. Sound speciation of TC
3. Minimized biases in OC and EC determination
4. Enhanced precision and "related" to EBC

Towards a reference method:

1. The thermal – optical method applying the EUSAAR_2 protocol is the **standard for the EMEP network**

2. The thermal – optical method (protocol t.b.d.) will be the **EN standard method**

**The question of sampling artifacts remains more critical.**

**Sampling artifacts affect the determination of PM mass and atmospheric particulate OC concentrations.**

But sampling artifacts are not addressed by the EN standard EN12341:2014 for measuring PM mass concentrations.

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# Danke !

# Additional Material

# EUSAAR-2 protocol

| Carrier gas | Temp °C | Time s |
|---|---|---|
| OC1_He | 200 | 120 |
| OC2_He | 300 | 150 |
| OC3_He | 450 | 180 |
| OC4_He | 650 | 180 |
| EC1_He/$O_2$ | 500 | 120 |
| EC2_He/$O_2$ | 550 | 120 |
| EC3_He/$O_2$ | 700 | 70 |
| EC4_He/$O_2$ | 850 | 80 |

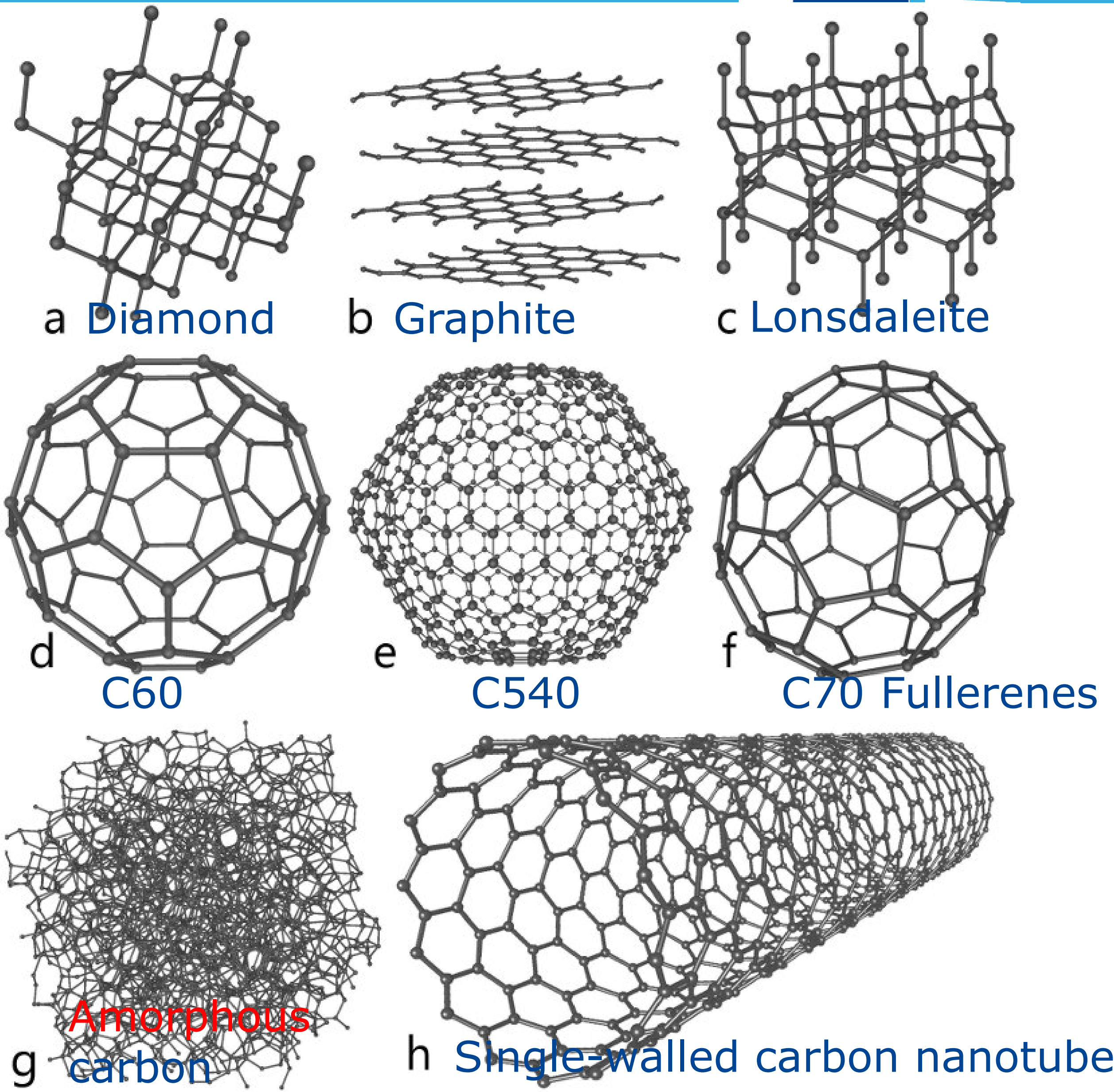
## Sensitivity of the EC value to the position of the split point

The precision of the laser signal measurement translates into uncertainties in EC determination.

The temperature protocol should be such that the slope of the carbon peak evolving at the split point is as small as possible.

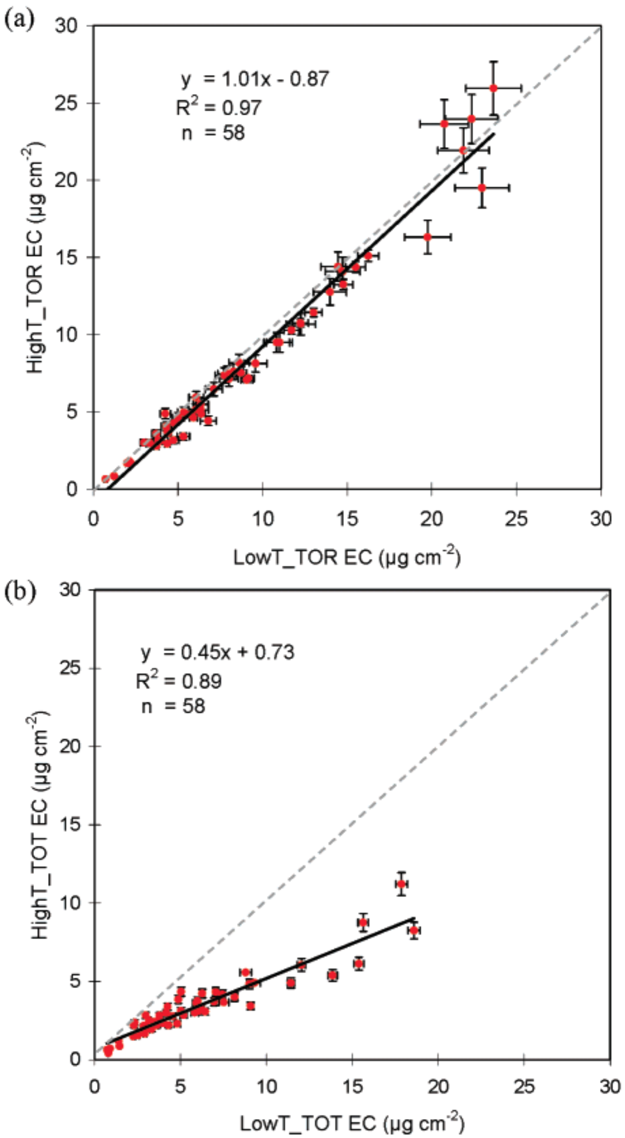
**EUSAAR_2**

**± 3% uncertainty in laser signal => ± 10% uncertainty in EC**




A wonderful image released by Michael Ströck under the GNU Free Documentation License:

The structures of eight allotropes of carbon




Comparisons between determined in samples from Fresno with the LowT and HighT protocols by (a) TOR, and (b) TOT (Chow et al., 2004).