Developments and Recommendations for Monitoring Atmospheric Particulate Organic and Elemental Carbon

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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 6

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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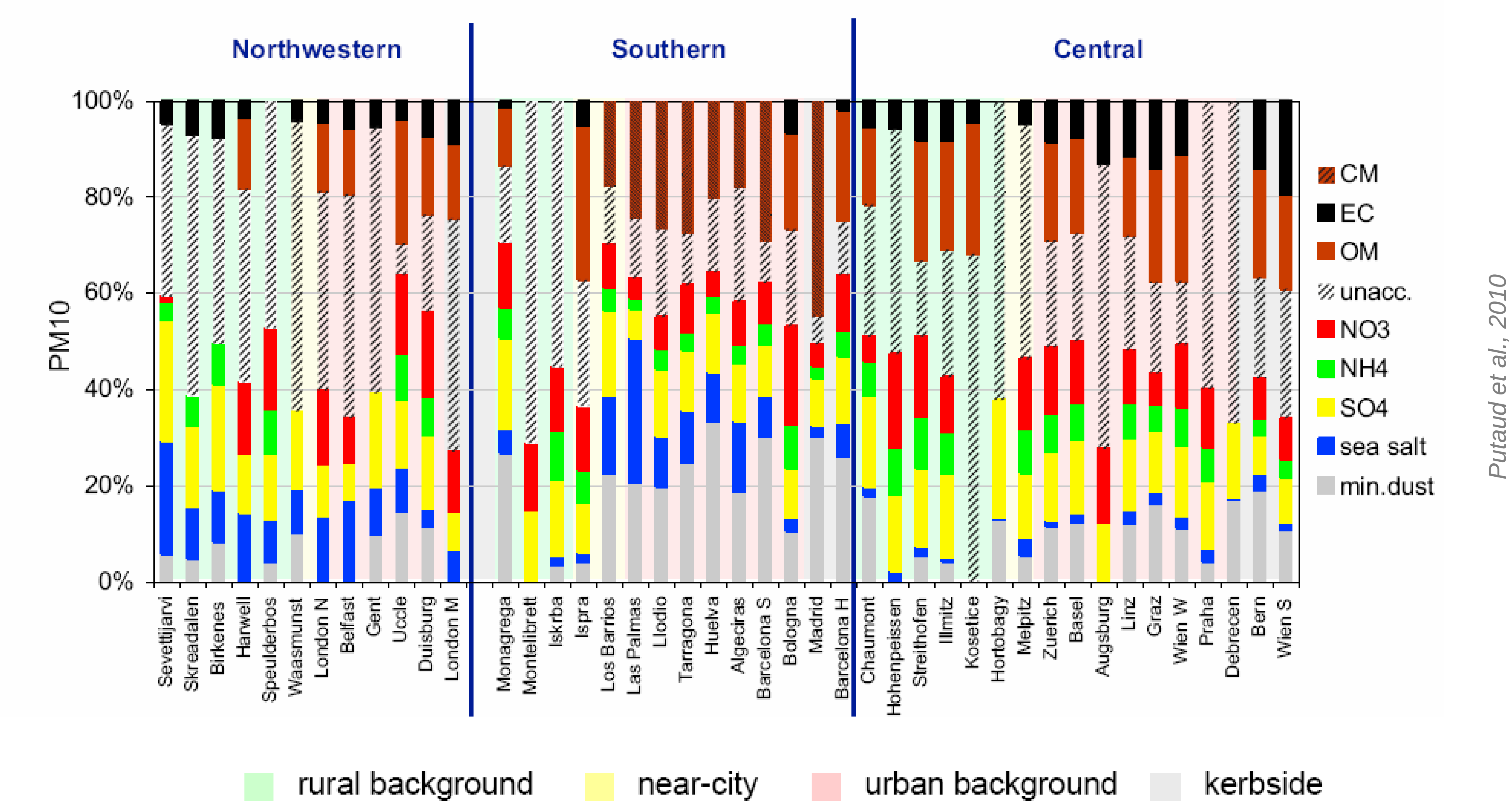
ANNEX IV MEASUREMENTS AT RURAL BACKGROUND LOCATIONS IRRESPECTIVE OF CONCENTRATION

B. Substances - Measurement of PM2,5 must include at least the total mass concentration and concentrations of appropriate compounds to characterise its chemical composition. At least the list of chemical species given below shall be included:

- Major inorganic ions: $SO4^{2-}$, Na^{+}, $NH4^{+}$, Ca^{2+}, $NO3^{-}$, K^{+}, Cl^{-}, Mg^{2+}
- **Organic Carbon (OC) and Elemental Carbon (EC)**

- **Carbonaceous species account for 45 ± 20% of PM2.5**
- **Many sites where carbonaceous species are not measured**



- **Carbonaceous species account for 45 ± 20% of PM2.5**

- **There are many sites where carbonaceous species are not measured yet**

- **The lack of reference methods prevents these measurements from becoming more “popular”**
  - **sampling**
  - **analyses**

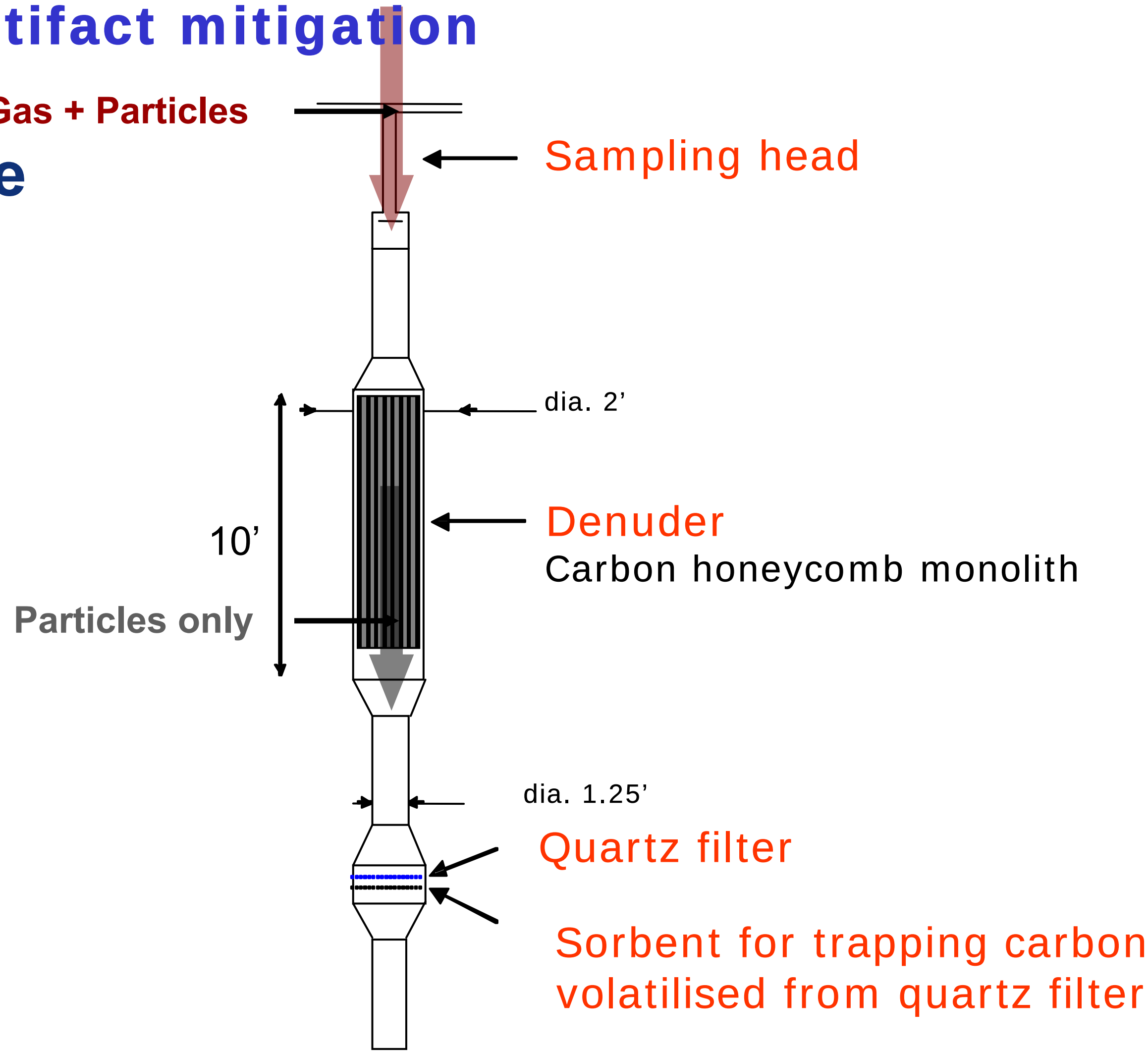
→ Progress (from research) and recommendations (from CEN and EMEP).

1- Sampling

1.1.1 Positive artifact mitigation

The EUSAAR prototype

tested at EUSAAR sites

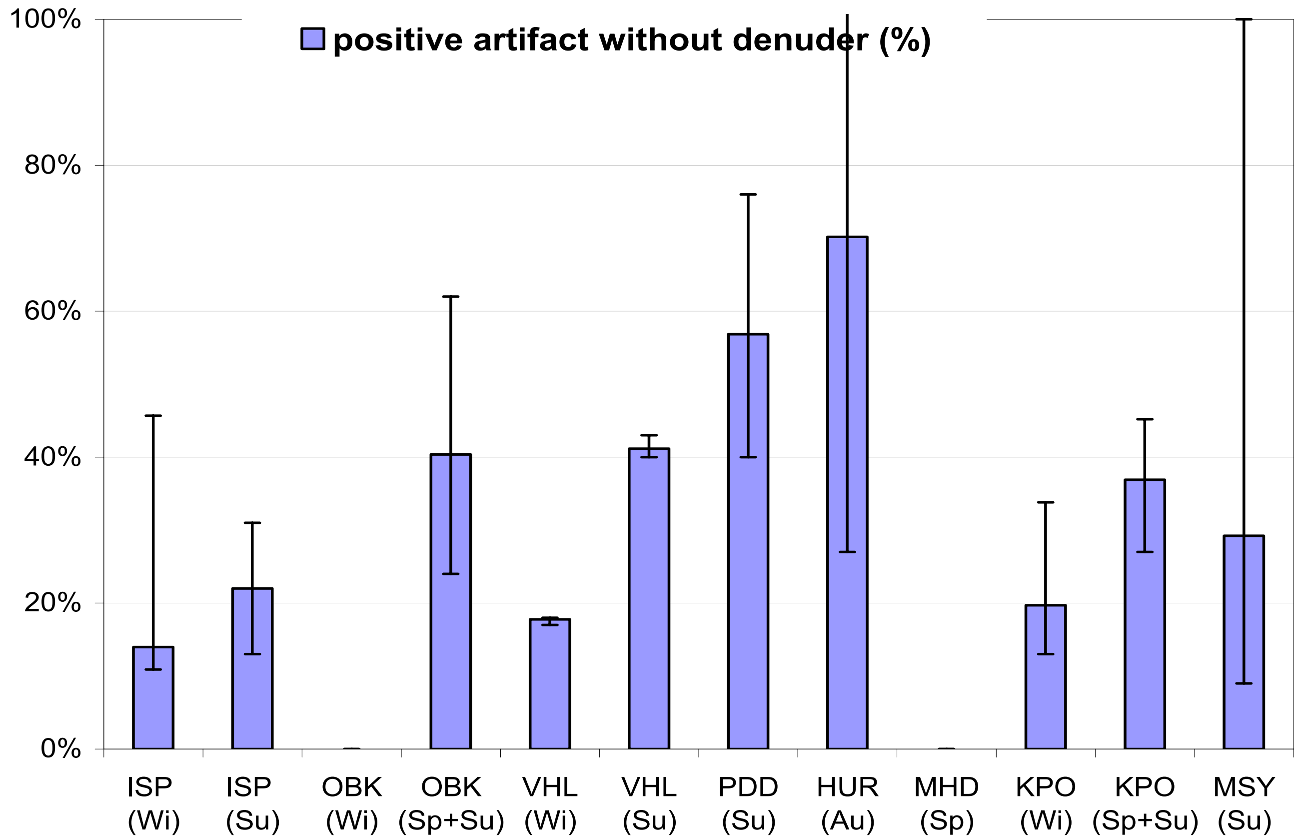


EUSAAR: a EU funded Integrated Infrastructure Initiative project (2006 – 2011)

EUSAAR test sites for positive artifact

1- Sampling

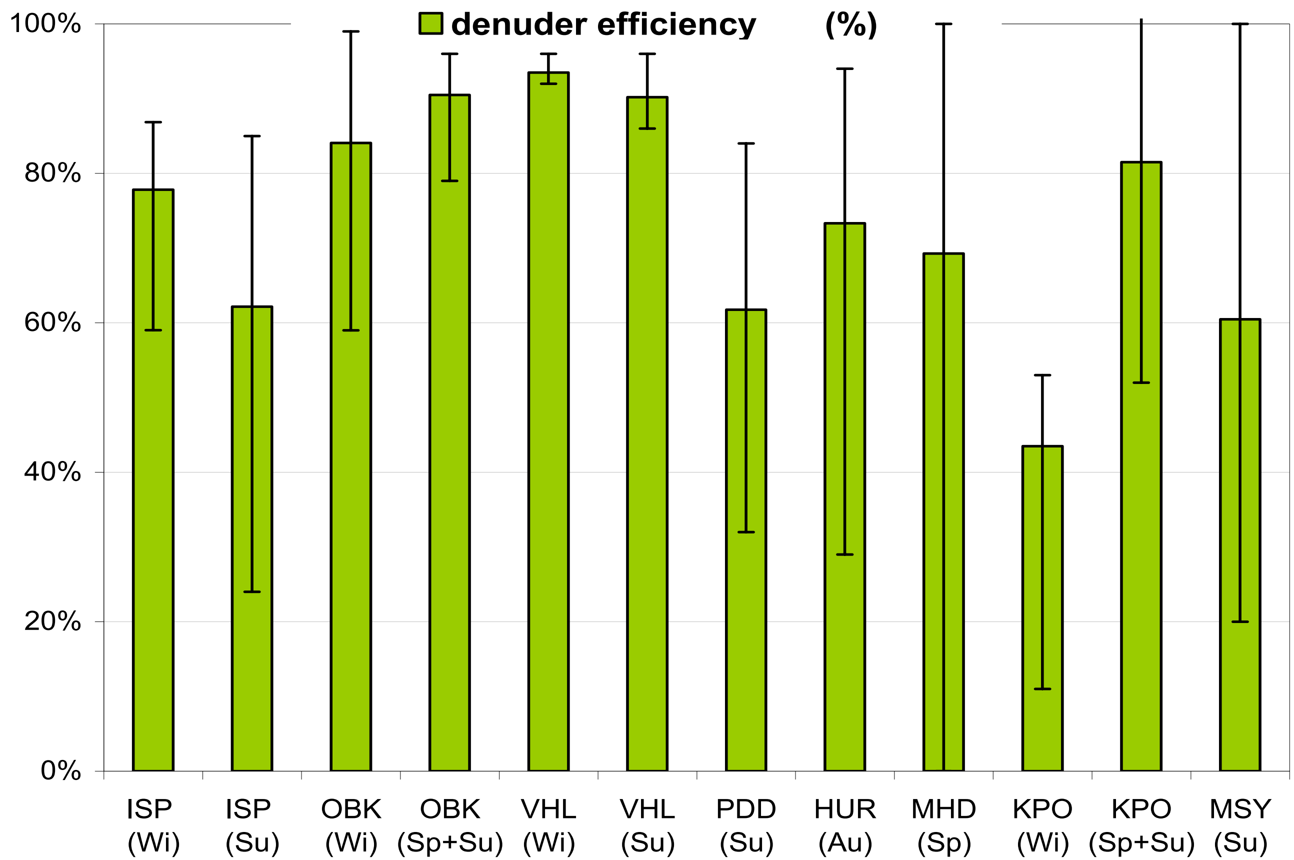
1.1.1 Positive artifact mitigation



Without denuder: 14 – 70 %

1- Sampling

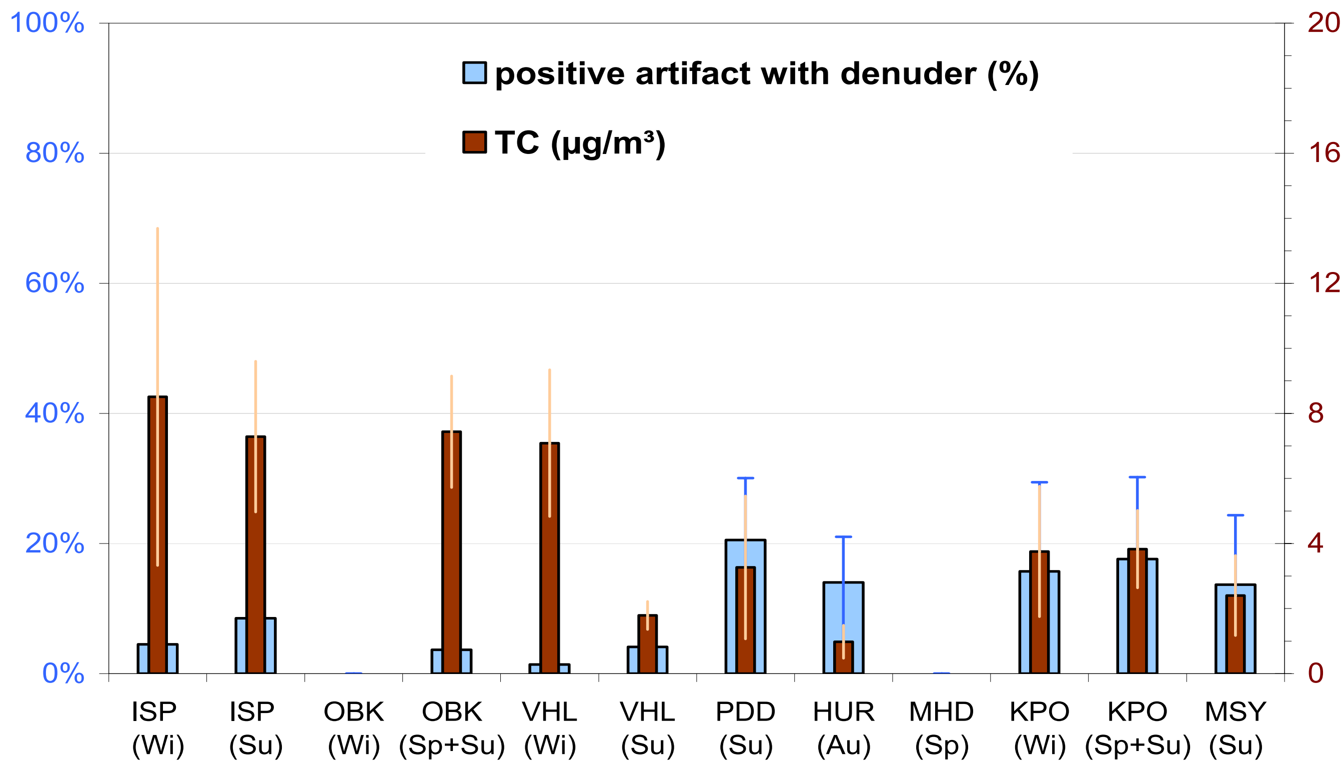
1.1.1 Positive artifact mitigation



Denuder efficiency: 43 – 93 %

1- Sampling

1.1.2 Positive artifact determination



With denuder: 1 -21 %

1- Sampling

1.1.4 Positive artifact: conclusions

- Denuder mean performance ranges from 43 to 93% (site dependent)

- Positive OC artefacts are reduced to 1 – 21 %

  to be compared with 14 – 70 % without denuder

- No decrease in denuder efficiency after 2 months of continuous use (not shown)

1- Sampling

1.2.3 Negative artifacts: back to the future

TECHNICAL PAPER

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Methods to Assess Carbonaceous Aerosol Sampling Artifacts for IMPROVE and Other Long-Term Networks

The SEARCH network uses an OC denuder upstream of the front and backup filters…

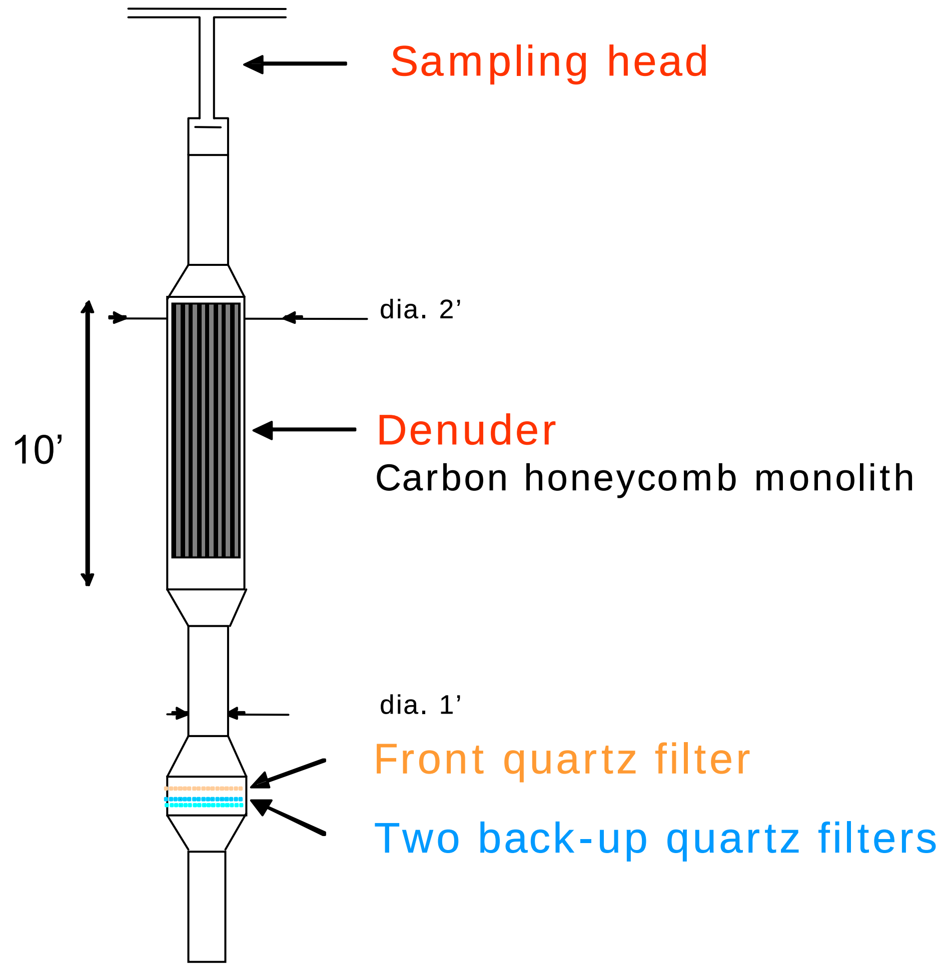
Because the denuder removes most of the organic vapors from the airstream, the backup should consist mostly of material evaporated from the aerosol deposit and be an indication of the negative OC artifact.

This negative OC artifact may be more prevalent in urban than in non-urban areas because of higher SVOCs in the urban areas.

1- Sampling

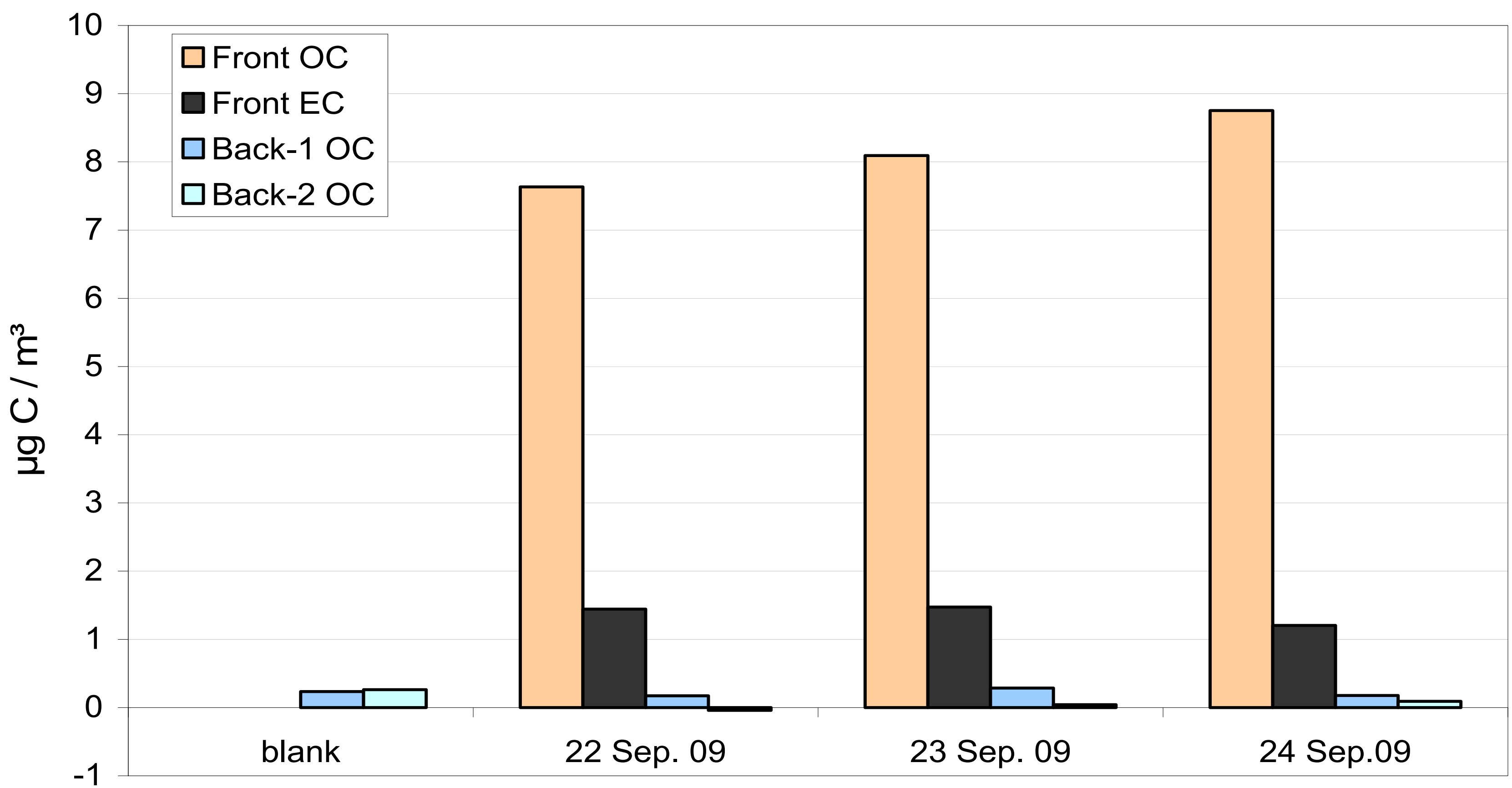
1.2.3 Negative artifacts: 2009’ tests

24-hr sampling
20 cm/s face velocity
14 < T < 28°C



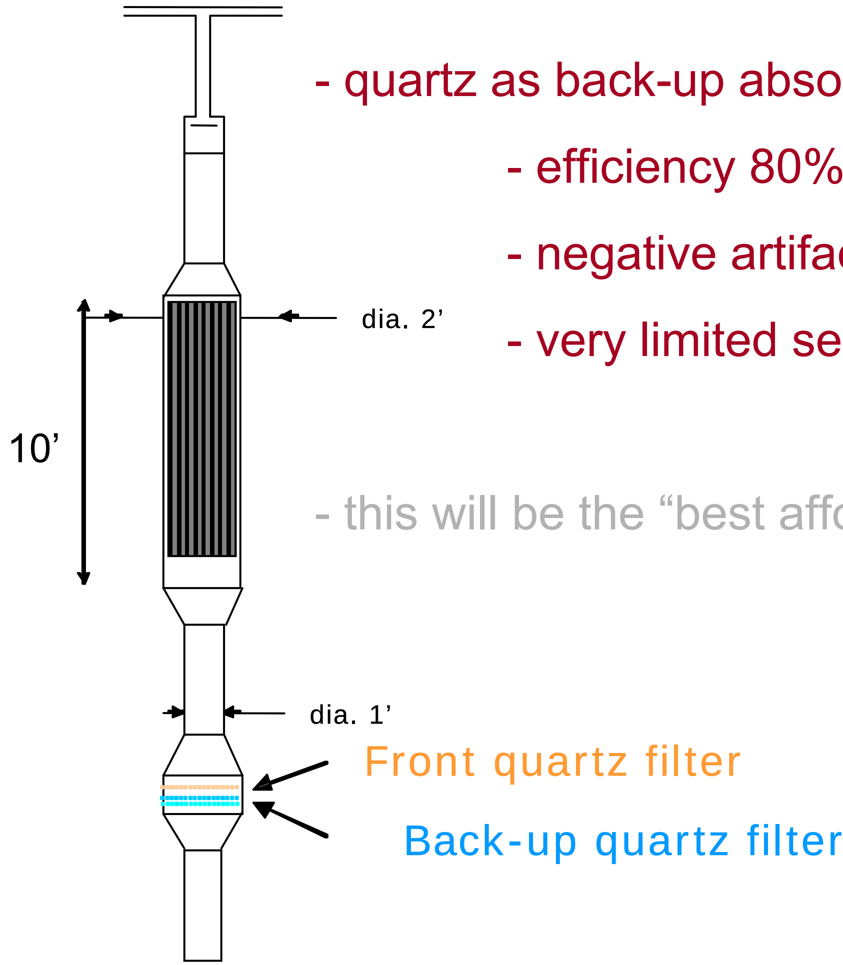
1- Sampling

1.2.3 Negative artifacts: 2009' tests



1- Sampling

1.2.4 Negative artifacts: conclusions



- quartz as back-up absorbent:
  - efficiency 80%
  - negative artifact = only 3% compared to particulate OC
  - very limited set of data

- this will be the "best affordable" EUSAAR sampling train

1- Sampling

1.3 Recommendations ?

- Directive 2008/50/EC:
  - PM2.5 mass concentration (EN 14907: no denuder)
  - PM2.5 speciation (better with denuder)

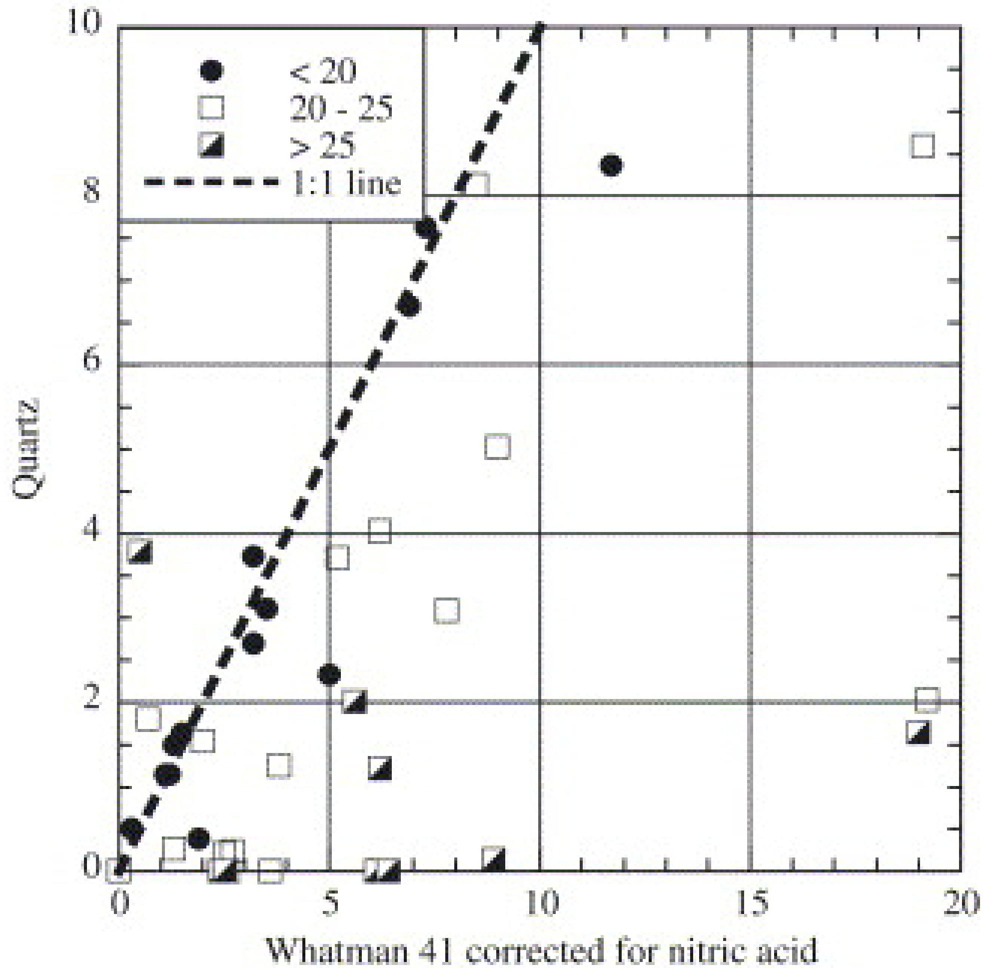
?

- CEN TC264 / WG35 Technical Report

Sampling should be carried out in accordance with one of the standard methods of EN 14907, or an equivalent method. It is acknowledged that the sampling process determines the size fraction of the particulate matter, the retention of semi-volatile material, and ab/desorption of volatile organic compounds on the filter at the time of sampling.

- Same issue as for NH_4NO_3 (see EN12341 & 14907 vs. EMEP manual)

Reminder: also NH_4NO_3 is (partially) lost from quartz fiber filters



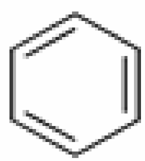
Schaap et al., 2004

Concentration of nitrate (µg m^{-3}) as sampled on a quartz filter compared to that on a Whatman 41 filter (corrected for HNO_3).

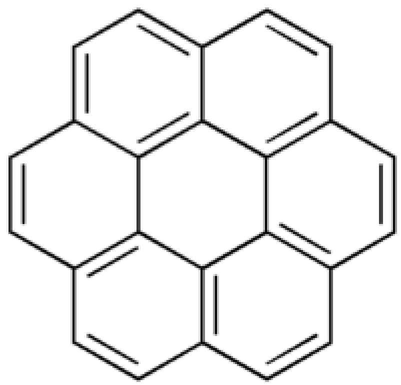
2- Analyses

no clear theoretical split point between highly refractory organic molecules and "infinite" graphitic structure, the model for pure EC.

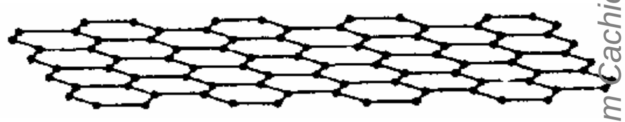
Benzene



Coronene



Graphite



Adapted from Cachier., 1989

	VOC	POC	EC
H/C ratio	1	0.5	≈ 0
Volatility	high	low	≈ 0

2- Analyses

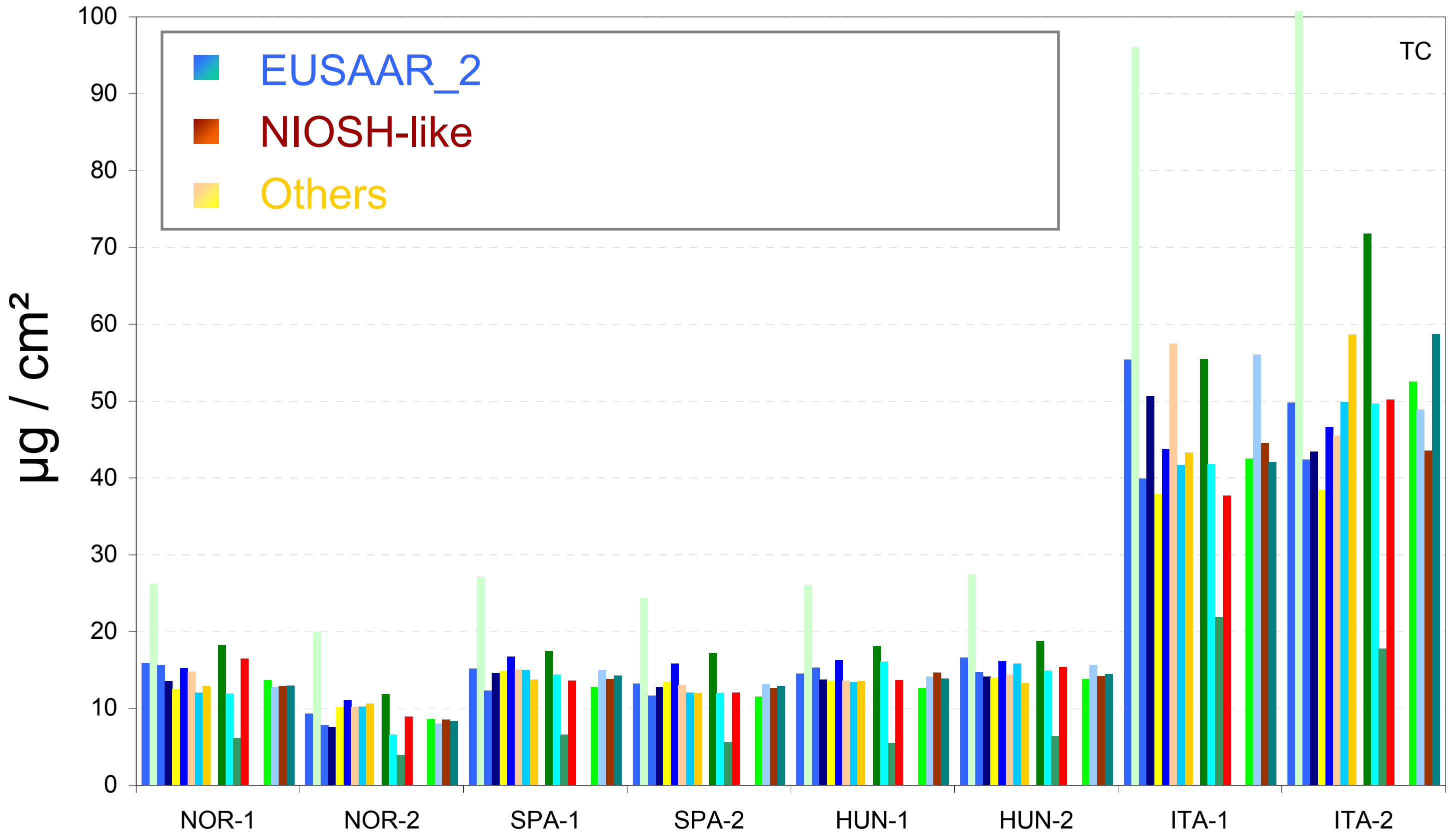
2.0: CEN recommendations

Ambient air quality — Guide for the measurement of elemental carbon (EC) and organic carbon (OC) deposited on filters

(a) ***Prefered method:*** thermal method with optical correction for EC and OC for samples collected on filters

(b) ***Protocols:*** One of the widely used analytical protocols such as NIOSH, IMPROVE, and EUSAAR-2 should be used.

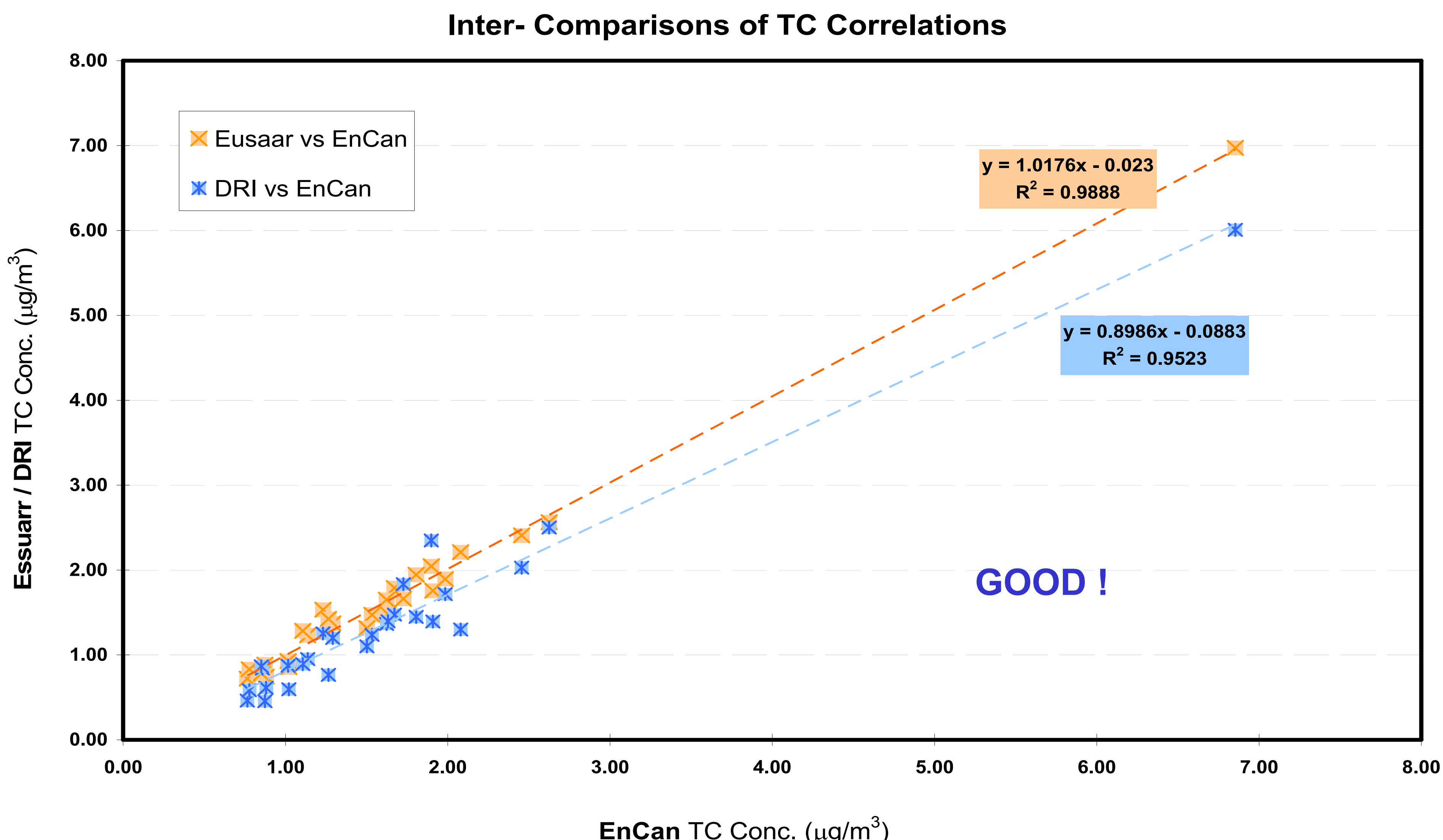
2.1: Thermal methods determine TC with a reasonable reproducibility



EUSAAR 2010 intercomparison

10 among 13 EUSAAR partners determine TC within ±12% on average
14 among 17 EUSAAR + EMEP

Europe – America inter- comparison (2010) confirms



EUROPEAN COMMISSION

2- Analyses

2.2: Speciation of TC.

Distinguish between EC

directly emitted in the particulate form by combustion processes

and OC

from both natural and anthropogenic primary and secondary sources

There are no 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 2.5 ± 24 % of EC evolves in He

min 80% of OC evolves in He

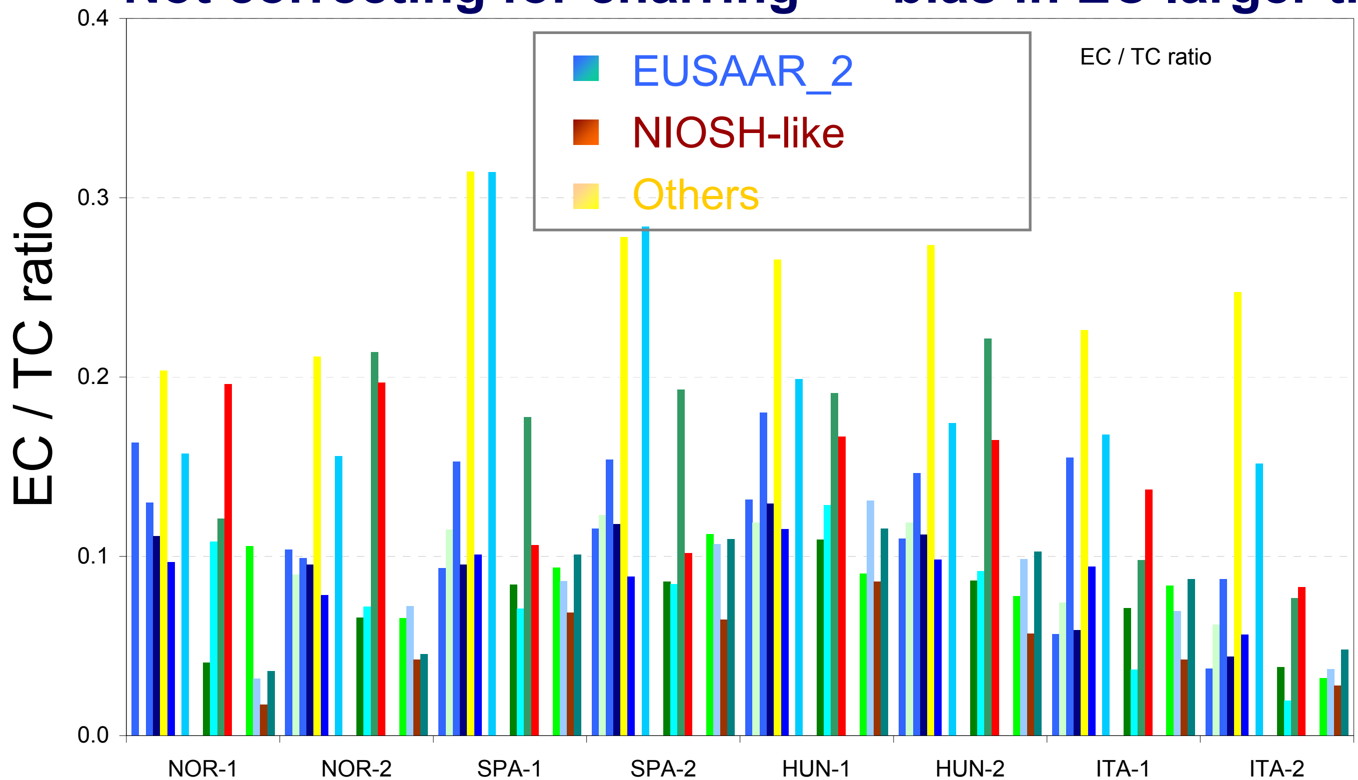
Carrier gas	Temp °C	Time s
OC1_He	200	120
OC2_He	300	150
OC3_He	450	180
OC4_He	650	180
EC1_He / O_2	500	120
EC2_He / O_2	550	120
EC3_He / O_2	700	70
EC4_He / O_2	850	80

2- Analyses

2.3: Charring correction

Pyrolytic carbon (PC) can be detected as EC.

Not correcting for charring => bias in EC larger than 200%.

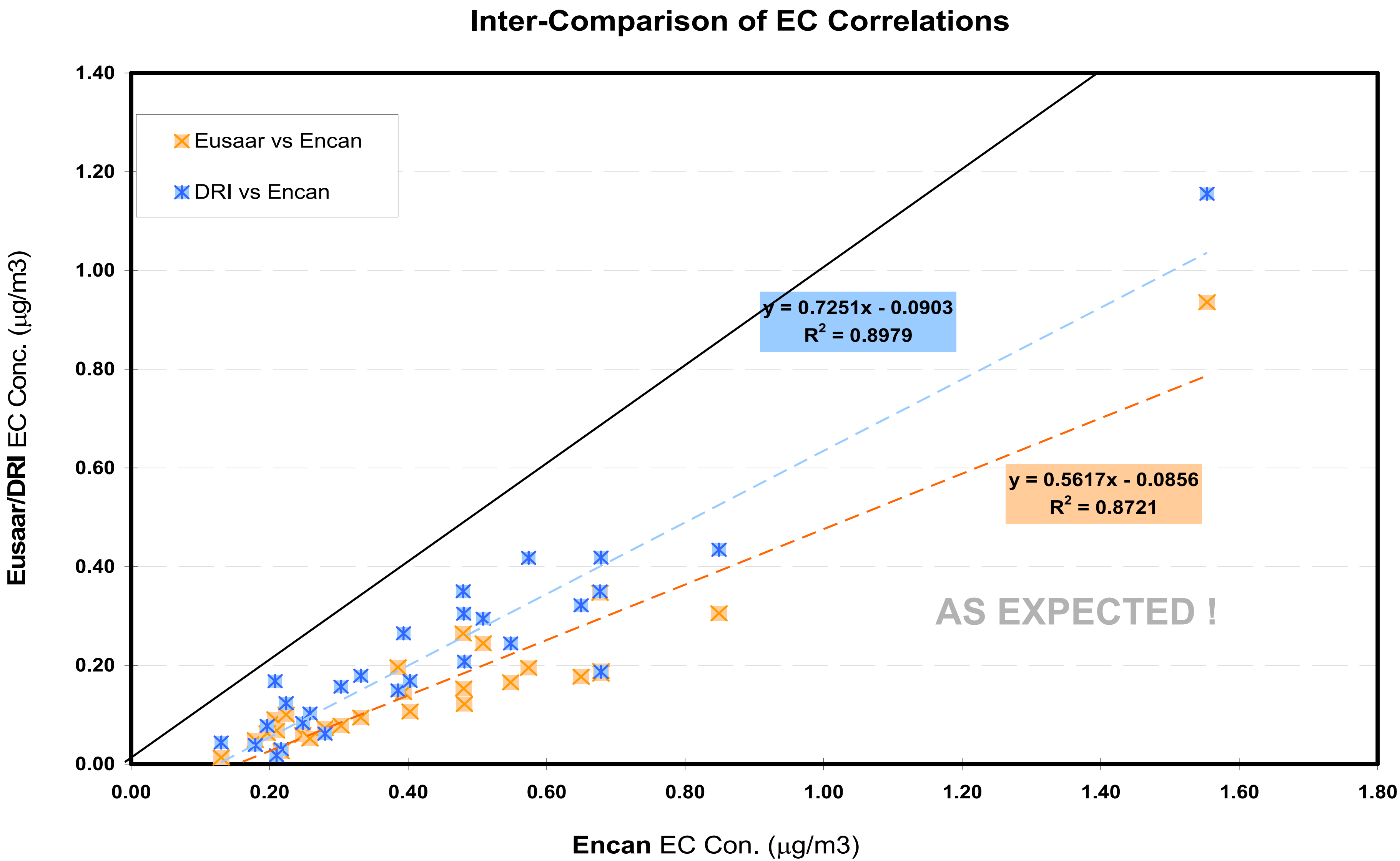


EUSAAR 2010 intercomparison

6 among 15 EUSAAR + EMEP partners determine EC/TC within ±25% on average

9 among 13 using the EUSAAR_2 protocol

Europe – America inter- comparison confirms



2- Analyses

2.4: Charring limitation

Charring correction assumes that:

PC evolves from the filter before EC.

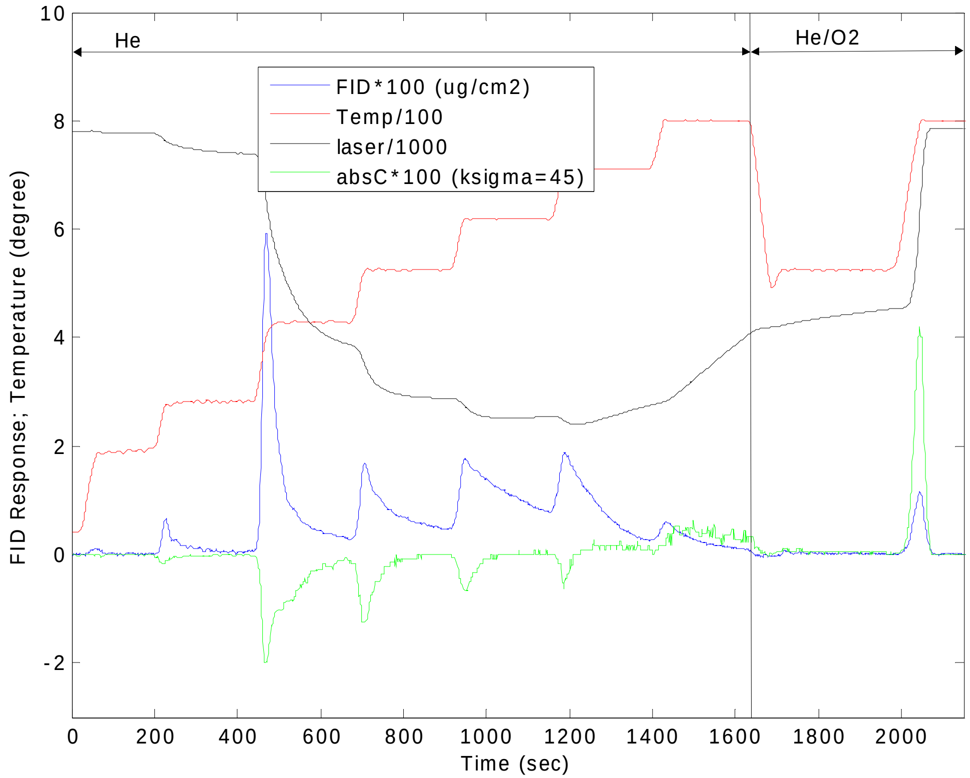
PC has the same specific light absorption cross section (σ) as EC.

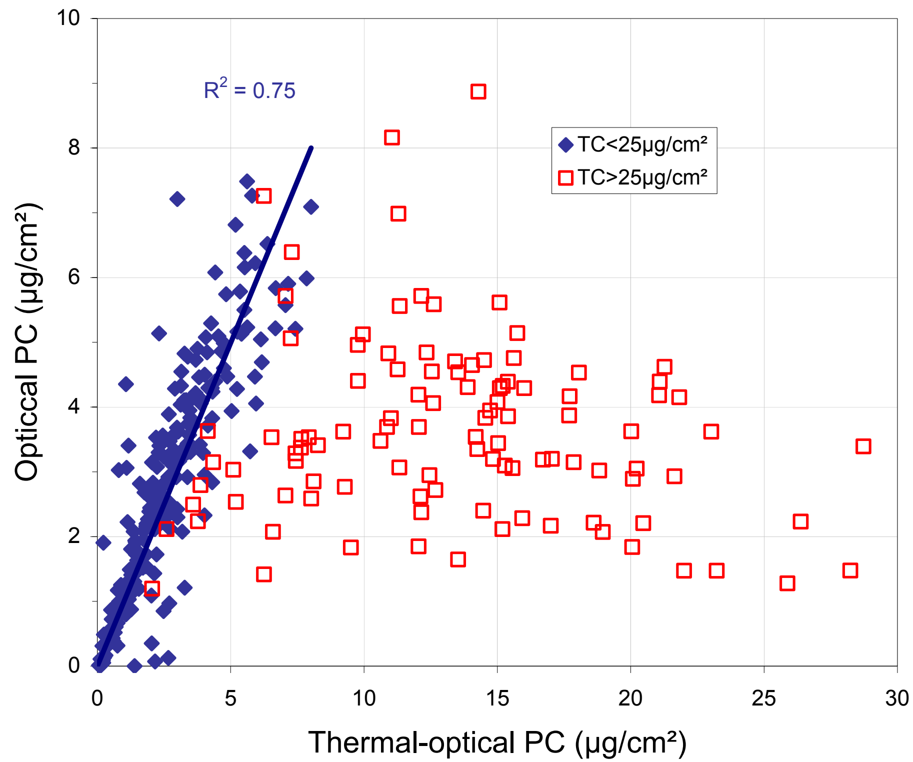
which is not always true

With longer steps at low temp, EUSAAR_2 reduces charring by 16% compared to NIOSH.

The amount of PC determined optically and thermal-optically well agree for a wide range of loads => guarantee for the accuracy of EC

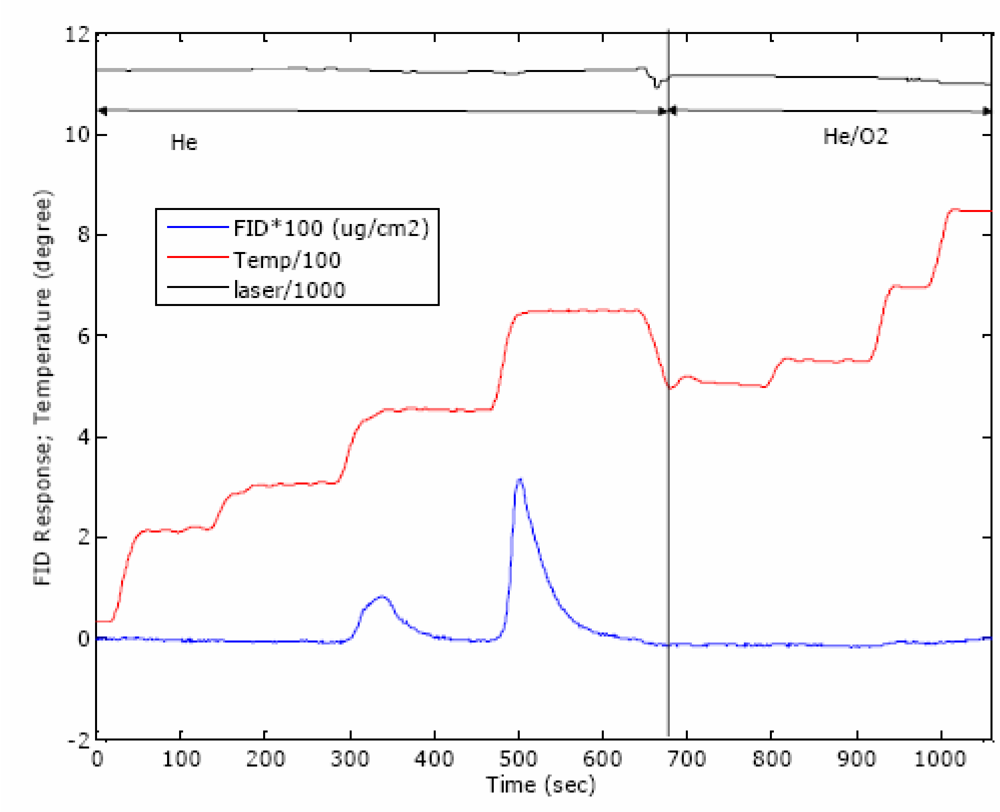
and therefore OC





2- Analyses

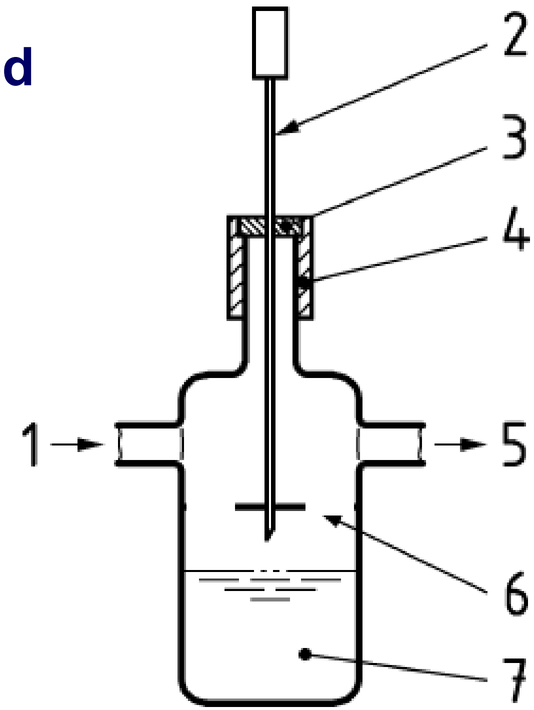
2.5: well understood interference from carbonates



Thermograms from the analysis of natural calcite (1.7 µg CC) with the protocol EUSAAR-2.

2- Analyses (carbonate)

a fast, simple, and quantitative method



Key

1 He or N_2 carrier gas
2 needle
3 septum
4 cap
5 to CO_2 detection
6 filter punch
7 Concentrated H3PO4

2- Analyses

2.6 Progress:

The thermal-optical protocol EUSAAR_2 fulfills a series of requirements for a reference method:

1. Robust determination of TC
2. Sound speciation of TC
3. Minimized biases in OC and EC determination
4. Well characterised interference from carbonates

Conclusion

	Research	Standards
Sampling	Denuder + Sorbent	No Denuder
Analysis	Thermal-optical and limit biases	Thermal-optical (and EMEP advice)

THANKS !

aamg

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