New **Method** and **Instrumentation** to Measure and Characterize Aerosolized Carbon

6th National Conference on Air and Noise Pollution Management, AQM 2018, Tehran, I. R. Iran, 23-24 January, 2018

Sebastijan Marinič, AEROSOL d.o.o. Slovenia
dr. Martin Rigler, AEROSOL d.o.o. Slovenia

sebastijan.marinic@aerosol.eu
martin.rigler@aerosol.eu

Aerosol

ASA
آزمون صنعت آروین

MAGEE SCIENTIFIC

Introduction

Carbonaceous aerosols account for a large and often dominant fraction of fine particulate matter (PM2.5) and are extremely diverse.

CARBONACEOUS AEROSOL

⇩

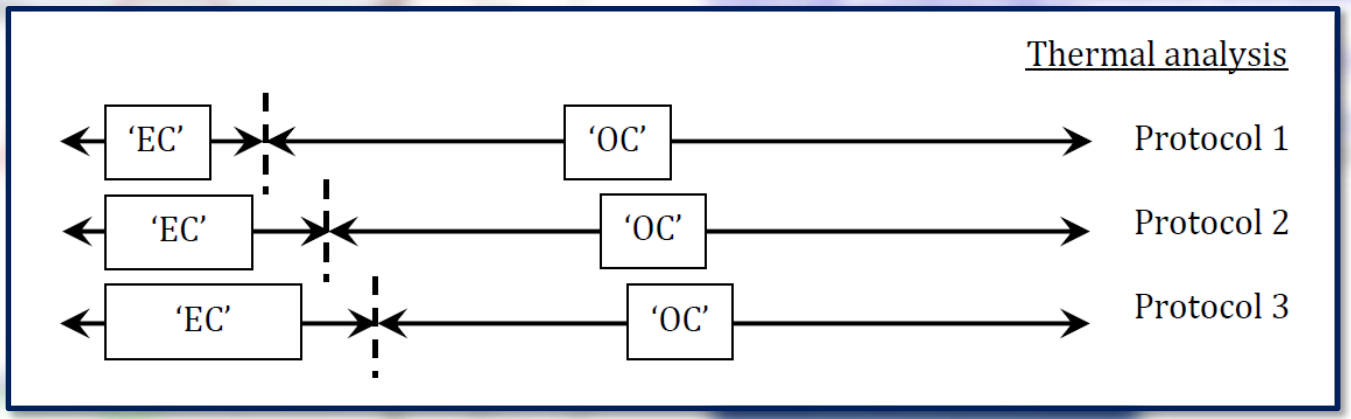
OC ⇦ **TC** ⇨ **EC**

Organic Carbon | Total Carbon | Elemental Carbon

OC/EC determination

Standardized method, EN16909:2017

- Results for **OC** and especially **EC** concentrations vary significantly for different thermal protocols
- Low time resolution (24h filters)
- Sampling artefacts



OC/EC

or

TC-BC

new method
new instrument
equivalence

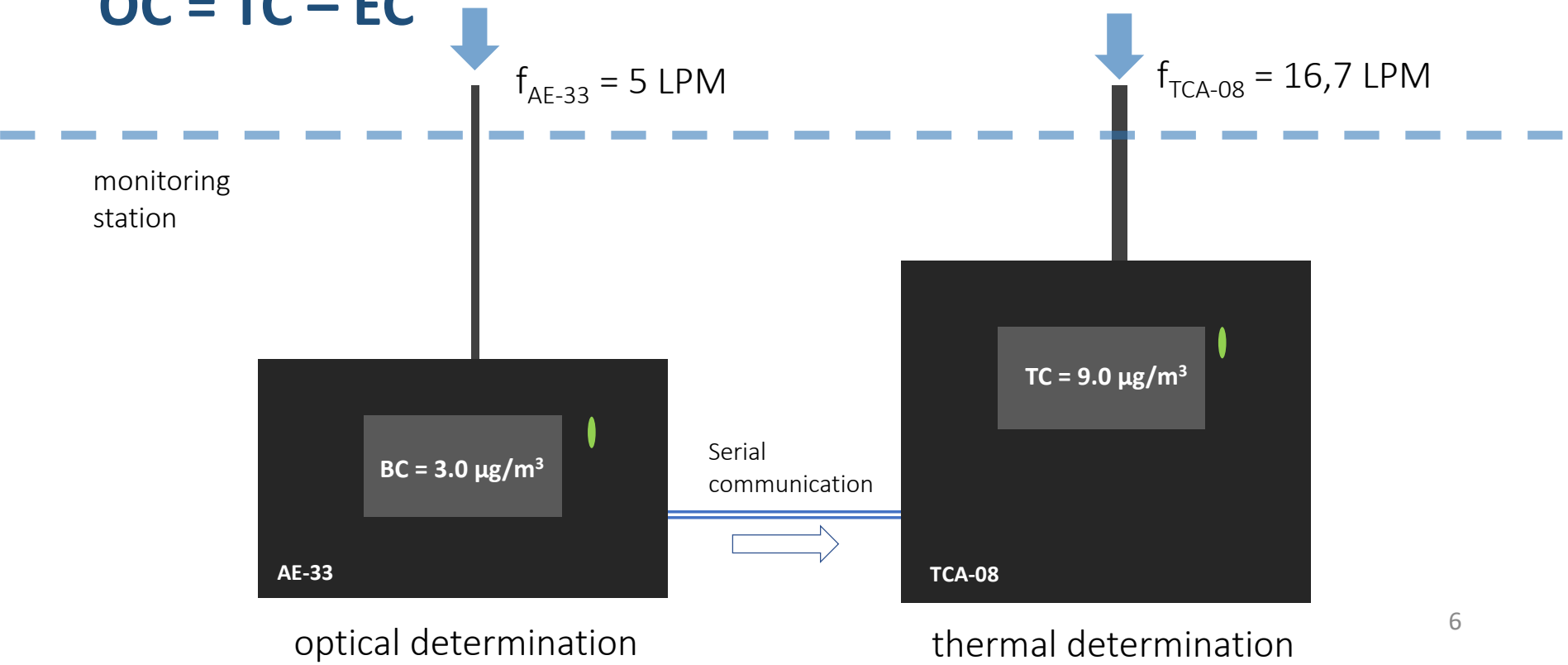
New method

Optical measurement of **BC** in real time with Aethalometer **AE-33**
Thermal measurement of **TC** in real time with **TCA-08**

TC = EC + OC

EC = *bBC**

OC = TC – EC



New instrument

Aerosol

TCA-08

Total Carbon Analyzer

PAUL SCHERRER INSTITUT
PSI

EMPA

LGGE
Laboratoire de Glaciologie et Géophysique de l'Environnement

The Cyprus Institute

AGENCIJA RS ZA OKOLJE

eurostars™

TCA-08 Total Carbon Analyzer

KEY FEATURES

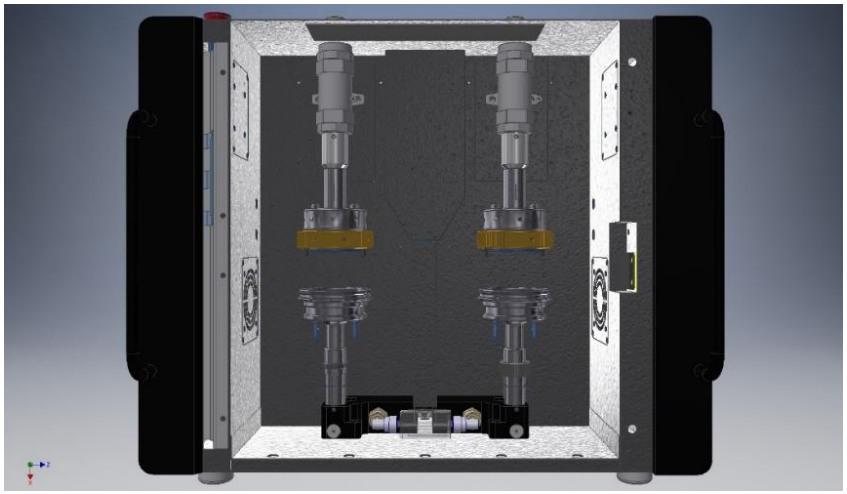
- Continuous analysis of Total Carbon content of aerosol
- Sampling *vs.* analysis switched between 2 channels
- **No carrier gas required**
- **No Glass : Rugged, All-Steel Construction**
- Combine with Aethalometer® for OC = TC – BC
- **Consistent Data**

APPLICATIONS

- Air Quality monitoring
- Health Effects, Climate Change research
- Emissions testing

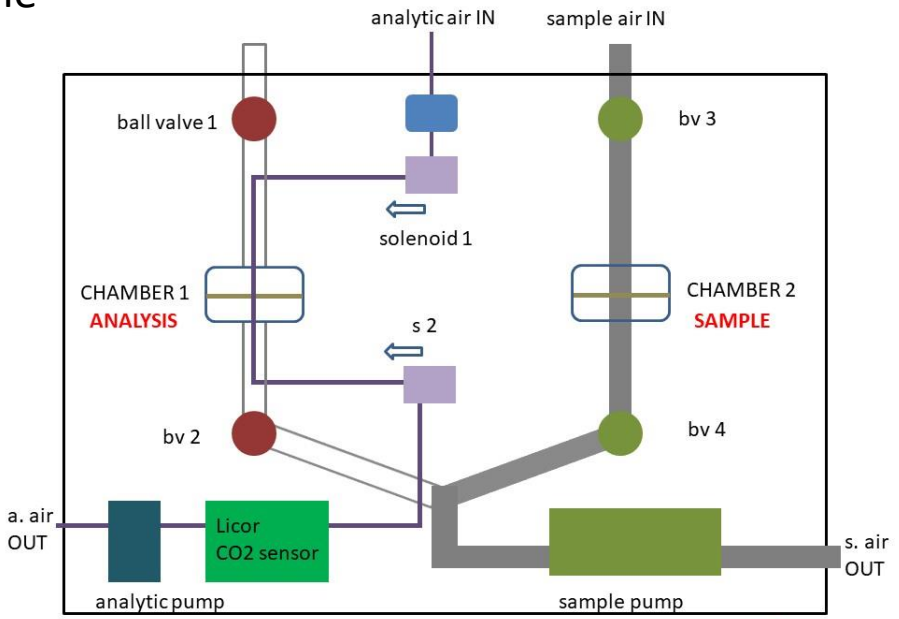
ANALYTICAL PRINCIPLE

- Collect sample on quartz fiber filter
- Flash combustion in ambient air
- **All Carbon converted to CO_2**
- Measure **pulse** of CO_2 over ambient-air baseline
- Quantitate [**C**] component of aerosol



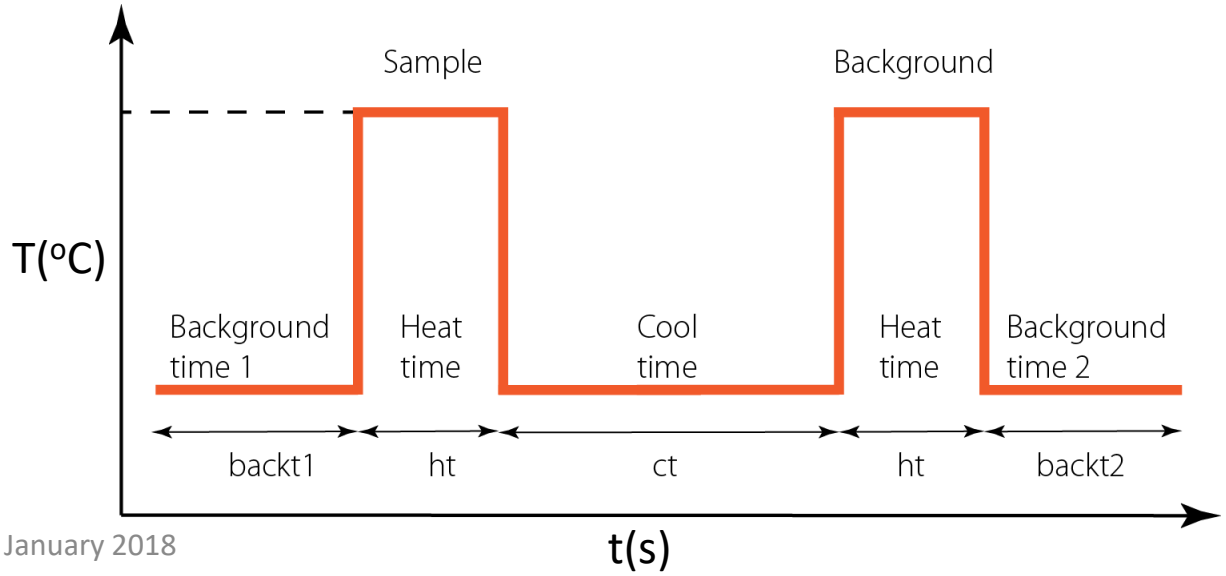
CONTINUOUS PARALLEL CHANNELS

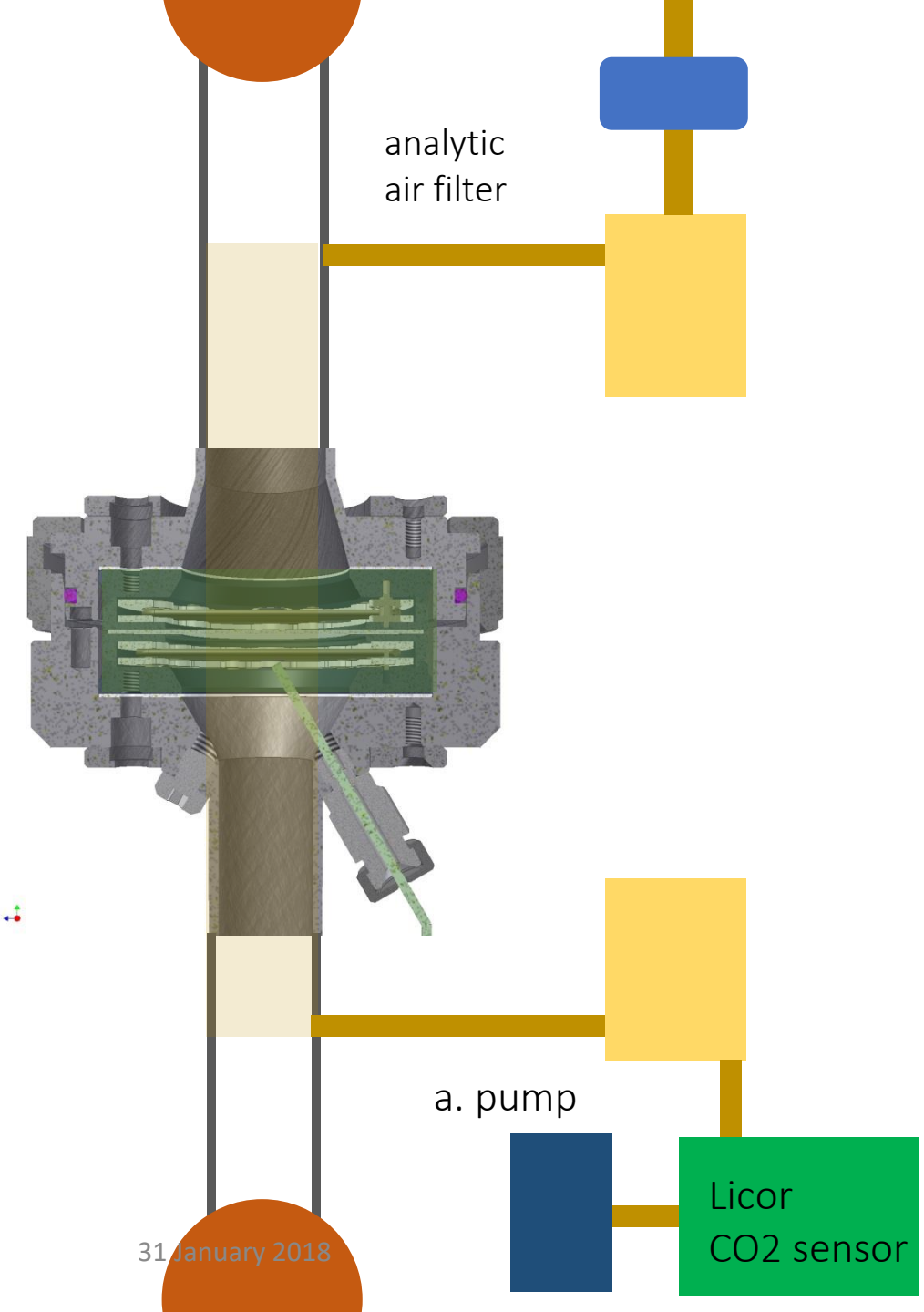
- One channel collecting
- Parallel channel analyzing
- Cool down, switch over
- **Continuous data**

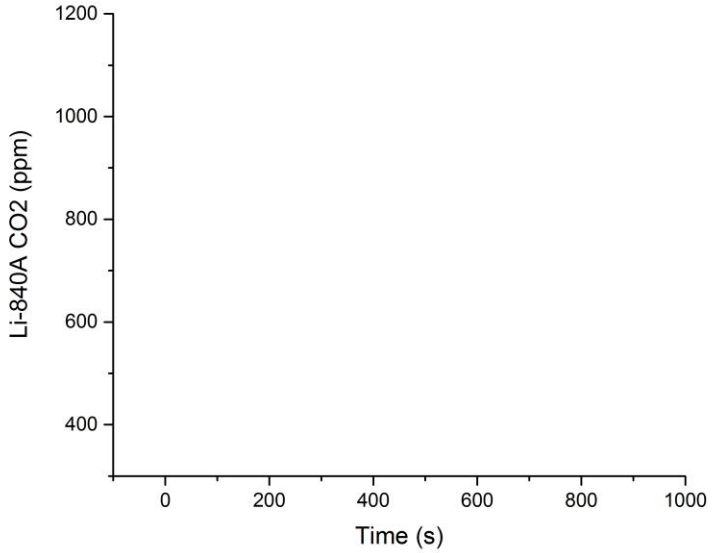


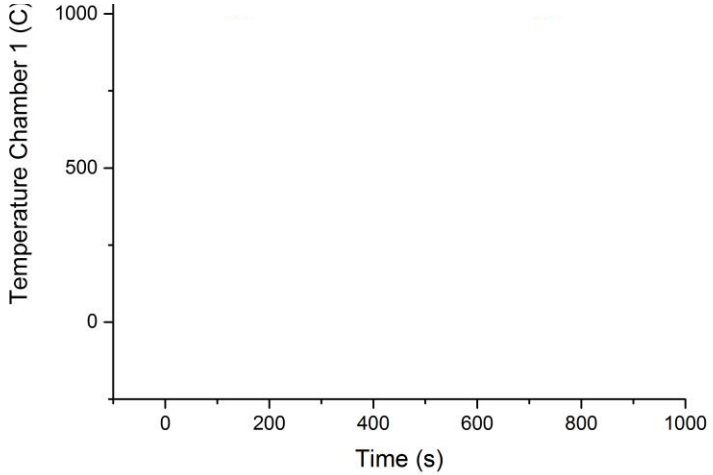
ANALYSIS

- Analytic air:
  - Carrier gas for CO_2 pules
  - Source of O_2 for combustion
  - Must be filtered before entering analysis chamber (free of aerosols, free of OC gases)
- Analytic flow: **0.5 LPM**
- Analysis time: **15 min**
- Thermal protocol:





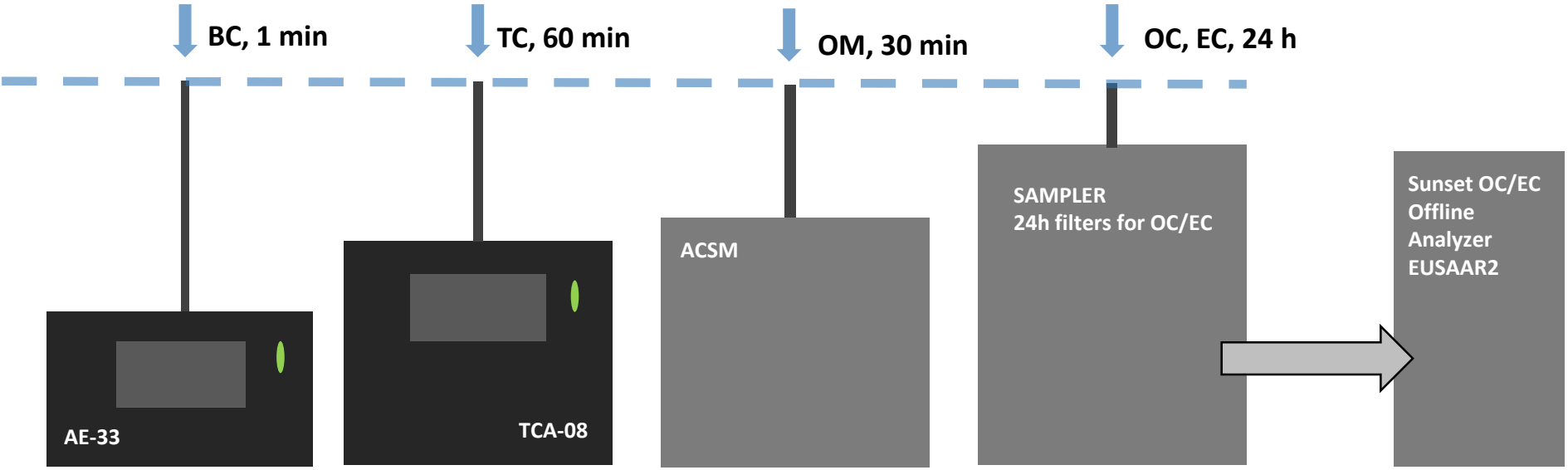




BACKGROUND 1 determination

Campaigns

- Ljubljana basin (SLO), Zürich (CH), Magadino (CH), Beijing (CN)…
- Population 500 000
- Urban background location
- 07 Feb - 10 Mar 2017, 31 days

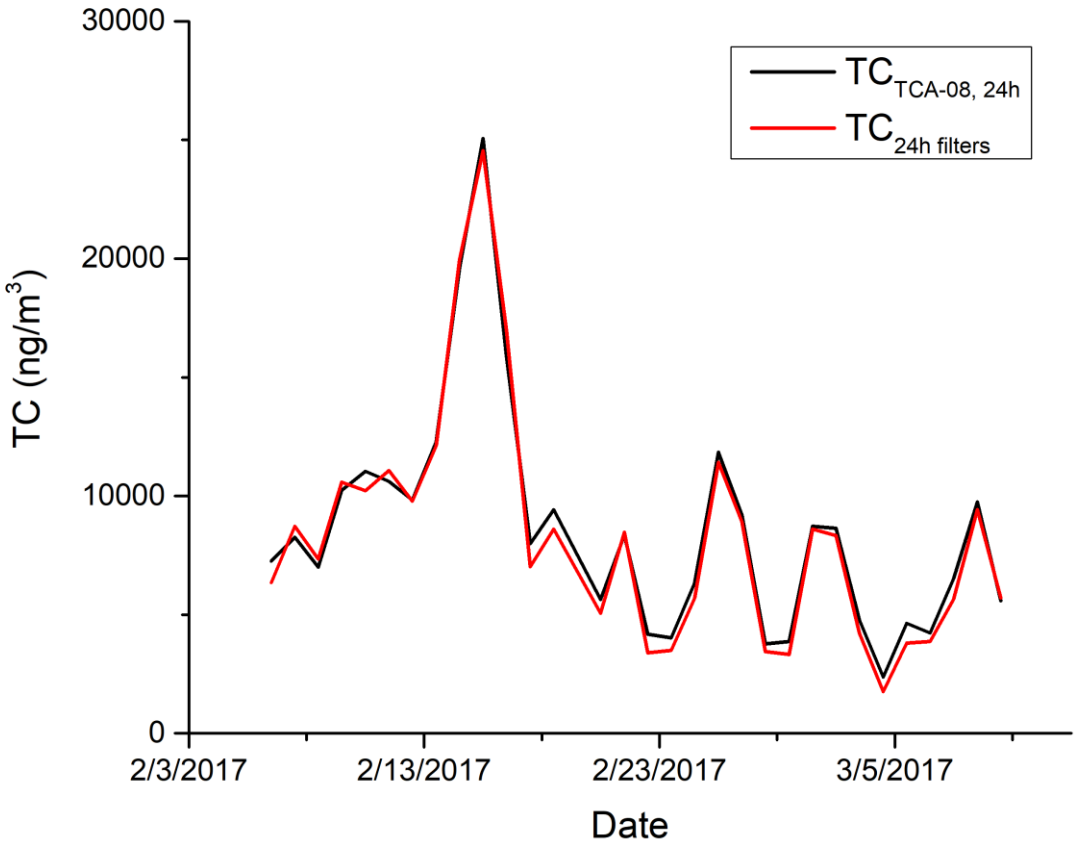


ONLINE/OFFLINE: **TC**

$PM_{2.5}$: TC_{24h}

$TCA\text{-}08_{1h}$ vs TC_{24h}

$TCA\text{-}08_{24h}$ vs TC_{24h}

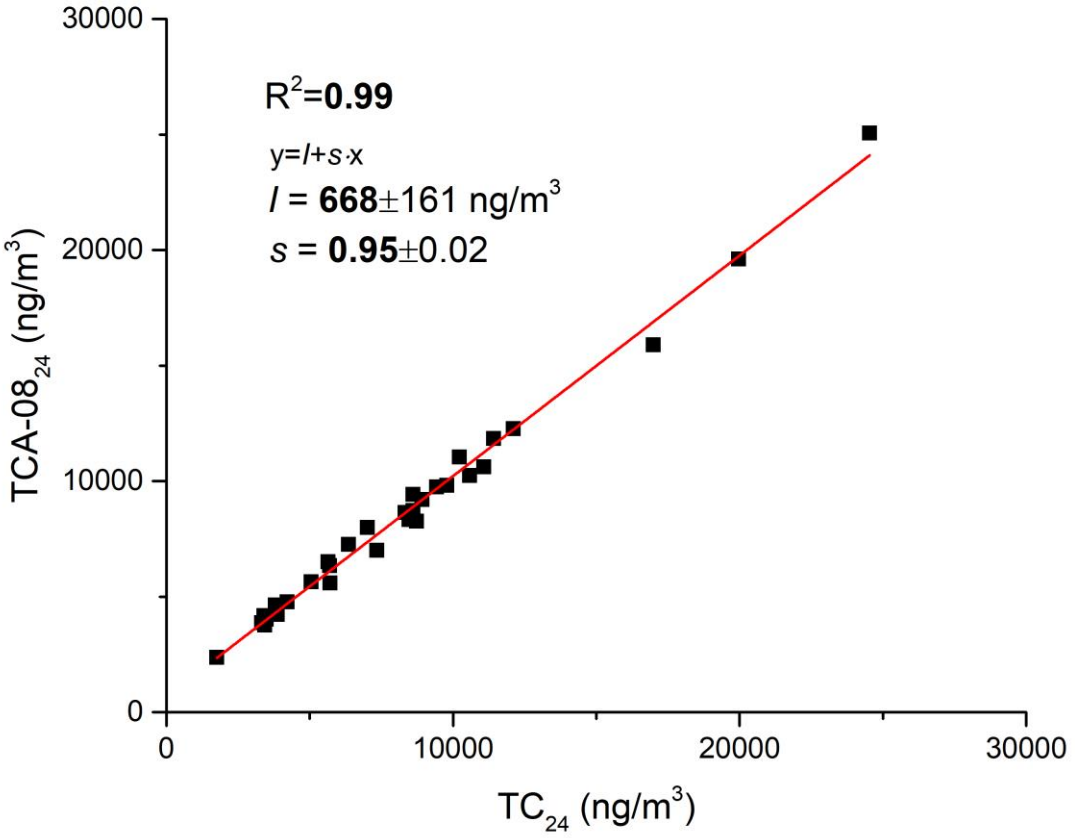


ONLINE/OFFLINE: **TC**

$PM_{2.5}$: TCA-08, AE-33, 24 filters OC/EC

24h timebase equivalency between TC, EC, BC and OC

$TCA\text{-}08_{24}$ vs TC_{24}



ONLINE/OFFLINE: **EC** vs **BC**

$PM_{2.5}$: TCA-08, AE-33, 24 filters OC/EC

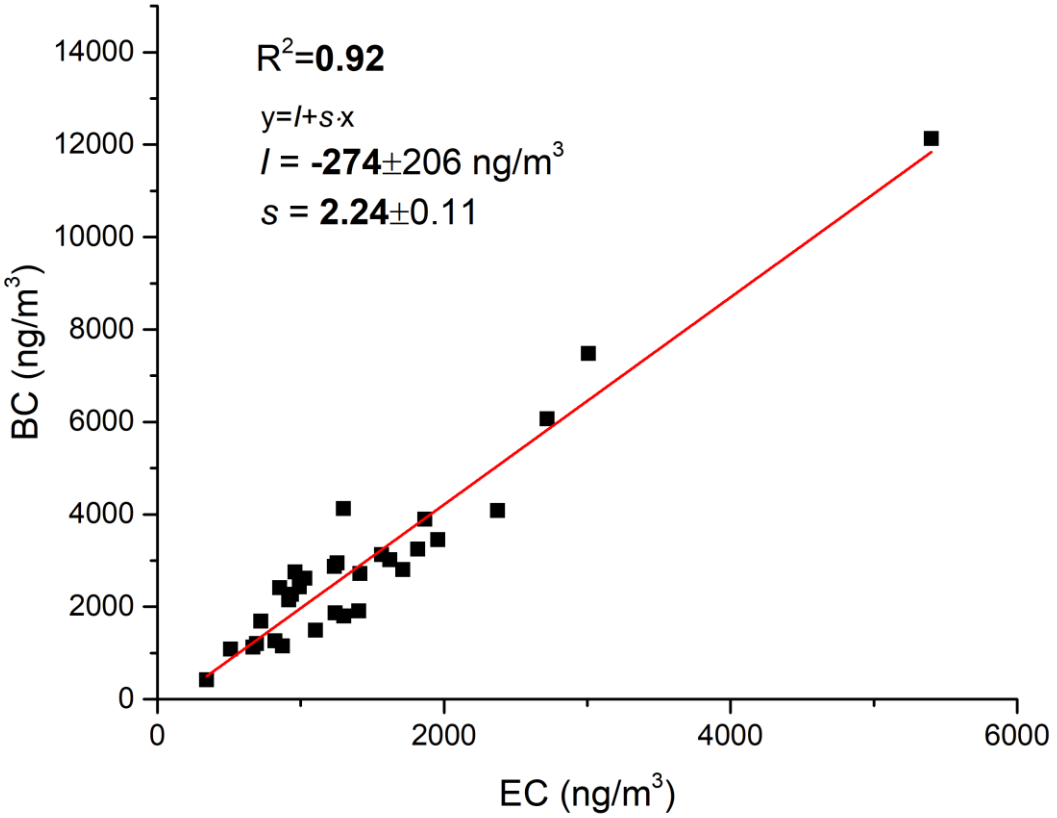
24h timebase equivalency between TC, EC, BC and OC

BC_{24} vs EC_{24}

$OC = TC - (bBC + a)$

$b = 0.45$

$a = 0$

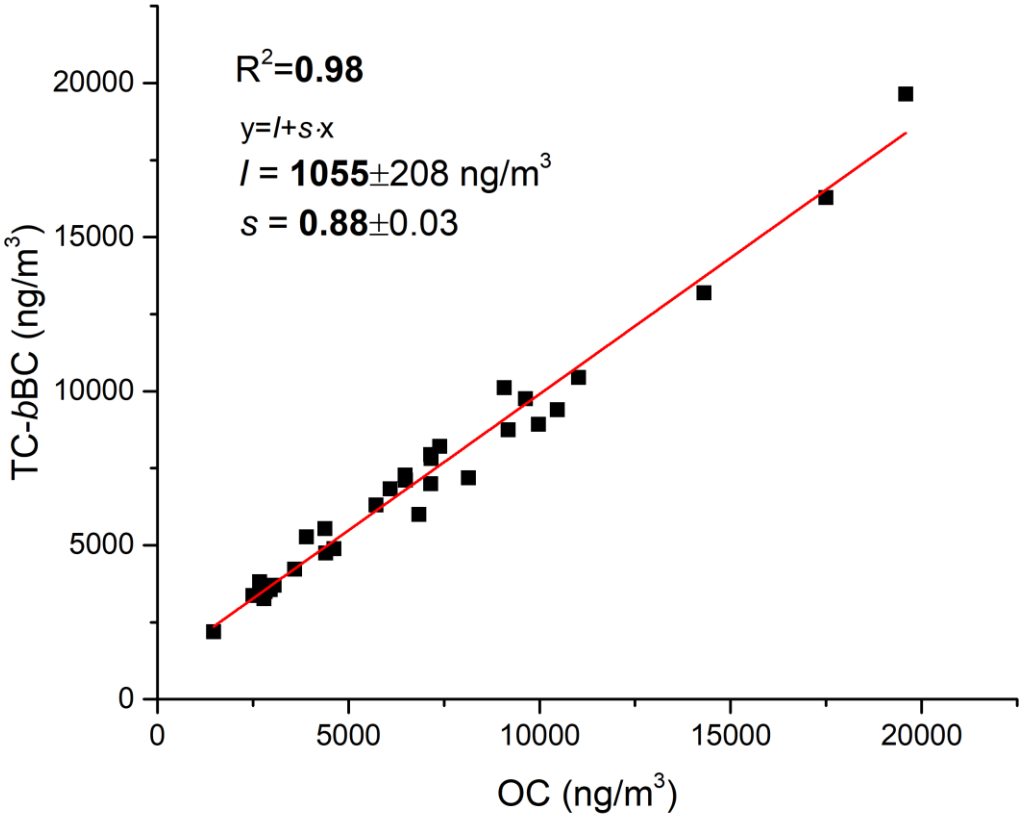


ONLINE/OFFLINE:**OC** vs **TC-bBC**

$PM_{2.5}$: TCA-08, AE-33, 24 filters OC/EC

24h timebase equivalency between TC, EC, BC and OC

OC_{24} vs
TC_{24}-*b*BC_{24}



Equivalence

EUROPEAN STANDARD
NORME EUROPÉENNE
EUROPÄISCHE NORM

DRAFT
prEN 16450

August 2015

ICS 13.040.20

Will supersede CEN/TS 16450:2013

English Version

Ambient air - Automated measuring systems for the measurement of the concentration of particulate matter (PM10; PM2,5)

$$OC = TC - b \cdot BC$$

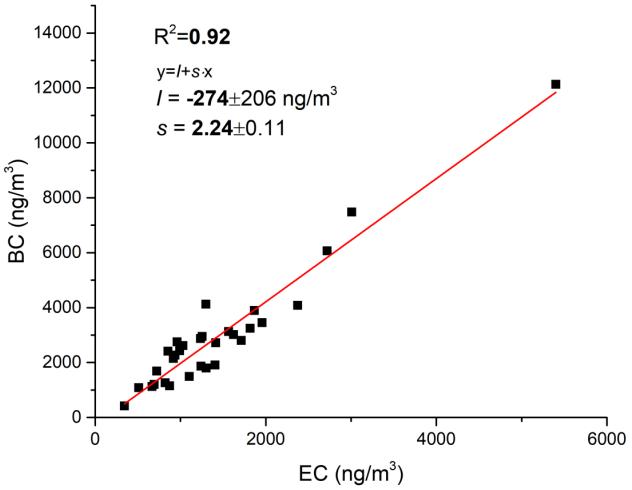


Table 1 — Relevant performance characteristics and criteria

	Performance characteristic	Requirement	Location (Lab/Field)	Clause
1	Measuring ranges	0 µg/m³ to 1 000 µg/m³ as a 24-hour average value 0 µg/m³ to 10 000 µg/m³ as a 1-hour average value, if applicable	L	
2	Negative signals	Shall not be suppressed	L	
3	Zero level and detection limit	Zero level: ≤ 2,0 µg/m³ Detection limit: ≤ 2,0 µg/m³	L	7.4.3
4	Flow rate accuracy[a]	≤ 2,0 % – at 5 °C and 40 °C by default for installation in a temperature-controlled environment – at minimum and maximum temperatures specified by the manufacturer if these deviate from the default temperatures.	L	7.4.4
5	Constancy of sample volumetric flow	≤ 2,0 % sampling flow (averaged flow) ≤ 5 % rated flow (instantaneous flow)	F	7.4.5
6	Leak tightness of the sampling system	≤ 2,0 % of sample flow rate	L	7.4.6
7	Dependence of zero on surrounding temperature[a]	≤ 2,0 µg/m³ – from 5 °C to 40 °C by default for installation in a temperature-controlled environment – at minimum and maximum temperatures specified by the manufacturer if these deviate from the default temperatures.	L	7.4.7
8	Dependence of measured value on surrounding temperature[a]	≤ 5 % from the value at the nominal test temperature – from 5 °C to 40 °C by default for installation in a temperature-controlled environment – at minimum and maximum temperatures specified by the manufacturer if these deviate from the default temperatures.	L	7.4.7
9	Influence of mains voltage on measured signal	≤ 5 % from the value at the nominal test voltage	L	7.4.8
10	Effect of failure of mains voltage	Instrument parameters shall be secured against loss. On return of main voltage the instrument shall automatically resume functioning.	L	
11	Effect of humidity on measured value	≤ 2,0 µg/m³ in zero air when cycling relative humidity from 40 % to 90 % and back	L	7.4.9
12	Zero checks	Absolute value ≤ 3,0 µg/m³	F	7.5.3
13	Recording of operational parameters	Measuring systems shall be able to provide data of operational states for telemetric transmission of – at minimum – the following parameters: – flow rate; – pressure drop over sample filter (if relevant); – sampling time; – sample volume (if relevant); – mass concentration of relevant PM fraction(s); – ambient temperature; – ambient pressure; – air temperature in measuring section; – temperature of sampling inlet (if relevant).	F	7.5.4
14	Daily averages or values	Available with sample change at ≤ 1 % of the day.	F	7.5.5
15	Availability	At least 90 %	F	7.5.6
16	Between-AMS uncertainty	≤ 2,5 µg/m³	F	7.5.8.4
17	Expanded uncertainty	≤ 25 % at the level of the relevant limit value related to 24-hour average results (if required, after calibration, see 7.5.8.5)	F	7.5.8.8
18	Maintenance interval/period of unattended operation	At least 14 d	F	
19	Automatic diagnostic check	Shall be possible for the AMS		

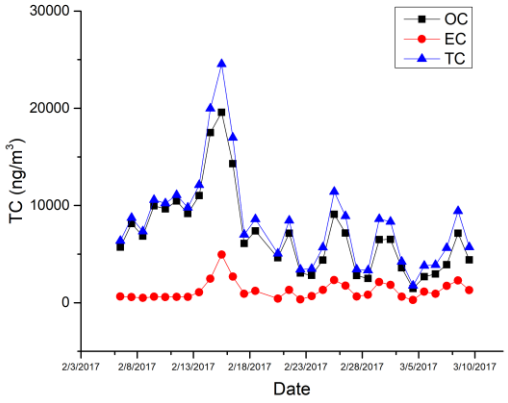
* Limitations, e.g. operation below or above a certain temperature, shall be specified in the type-approval report.

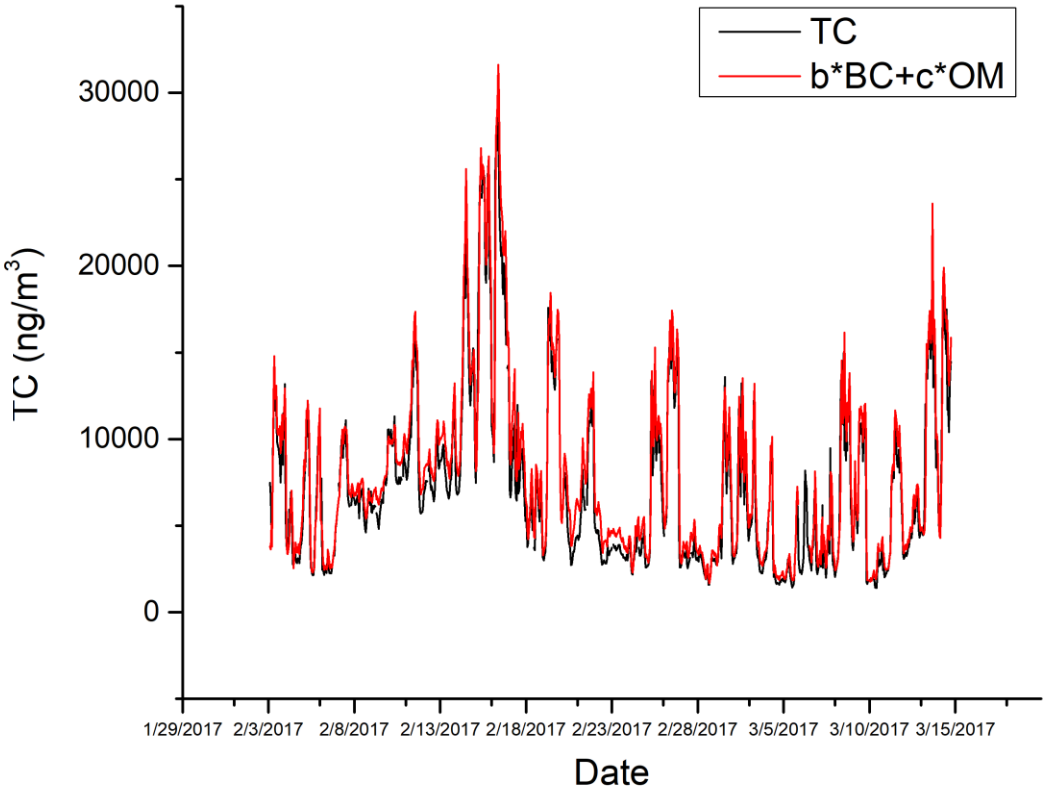
High resolution online TC applications

$PM_{2.5}$: TCA-08, AE-33, ACSM

1h high resolution data comparison

High resolution data





Summary (1)

1. NEW METHOD
   OC = TC - *b*BC
2. NEW INSTRUMENT
   Total Carbon Analyzer **TCA-08**
3. EQUIVALENCE
   SOP: Ljubljana Winter 2017 Campaign
4. HIGH RESOLUTION APPLICATIONS
   ACSM/AMS calibration

NO GAS
NO GLASS
REAL-TIME

Summary (2)

- **No Gas**
  - Great Savings vs. **complexity** and **cost** of gas
- **No Glass**
  - Rugged, reliable, practical for monitoring use
- **High Time Resolution**
  - OC Data to 15 minutes
- Designed for routine, unattended field operation
  - Built to same standards as Aethalometer
- **Consistent Data**

MAGEE SCIENTIFIC

Aerosol

با تشکر از توجه شما

sebastijan.marinic@aerosol.eu
martin.rigler@aerosol.eu

TCA-08
Total Carbon Analyzer

Acknowledgement:

PAUL SCHERRER INSTITUT PSI

EMPA

LGGE Laboratoire de Glaciologie et Géophysique de l'Environnement

The Cyprus Institute

AGENCIJA RS ZA OKOLJE

eurostars™

This work was financed in part by the EUROSTARS grant E!8296 TC-BC.

Appendices

- Sampling
- Analysis
- Analytic air with integrated air buffer
- Accessories
- Maintenance and service
- Filter change procedure
- Heater change procedure
- Offline validation

Accessories

Description	
Quartz Filters, 47 mm, 25 pcs (sample collection)	
Cartridge Filter	
Whatman 7500 Carbon Cap 75 Capsule Filter (analytic air filtration)	
Denuder cartridge (removing OC gases from sample air)	
Denuder cartridge housing	

accessories

Description	
Tube Coupling A and B	
Divider	
Sample line system (different lengths, curvatures)	
Sampler (for denuder efficiency test)	
Sharp-Cut Cyclone Inlet, PM2.5 at 16.7 LPM flow	

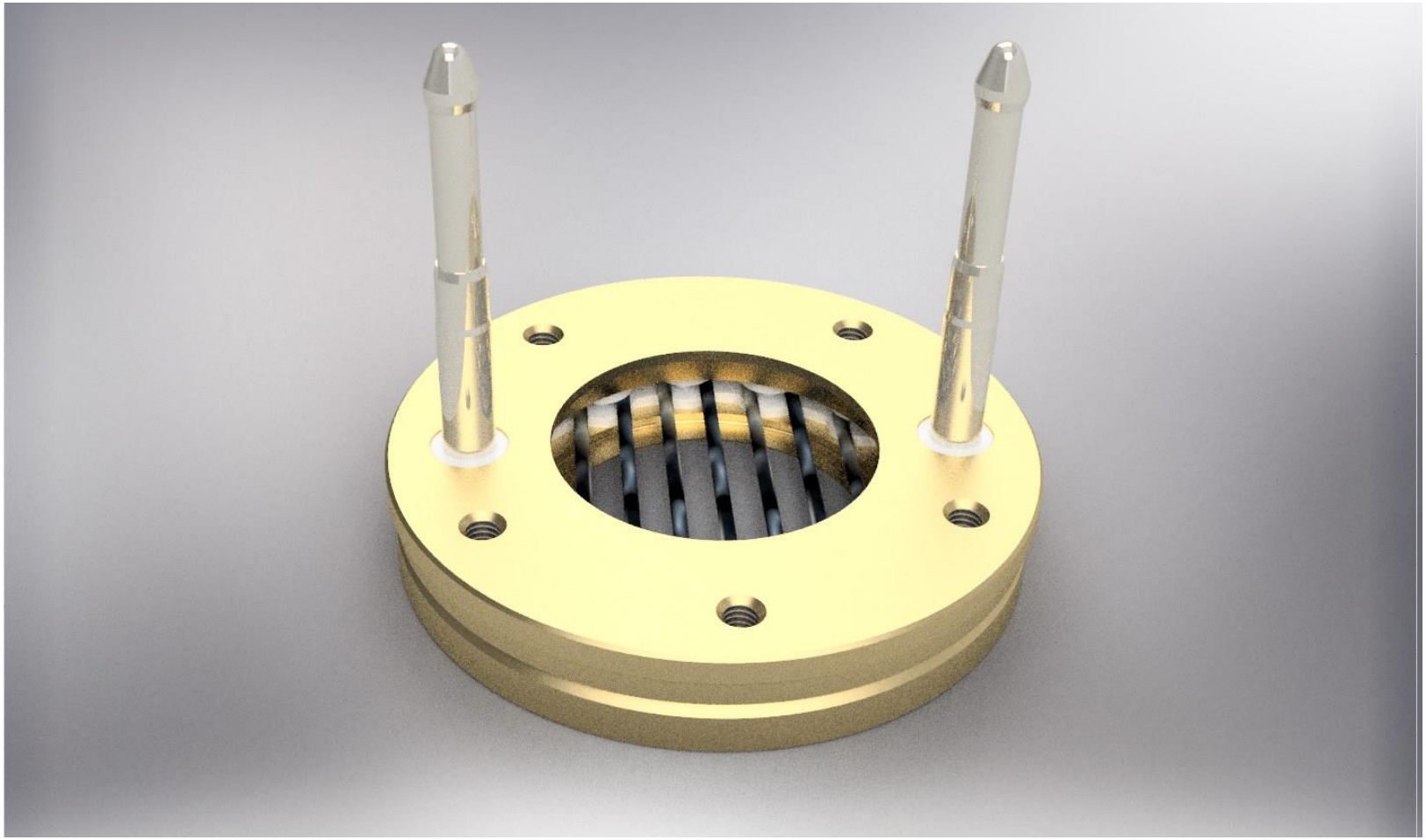
accessories

Description	
Ambient sensor	
BGI TetraCal (0.1 - 30 LPM)	
Certified thermometer	
Pipette	

Maintenance and service

Inspect the sample line tubing	once / month
Inspect and clean the size selective inlet	once / month
Verify date/time	once / month
Verification of analytic/sample flow, calibrate if necessary	twice / year
Quartz filter change procedure	once / month
Leakage test	every chamber opening
Verification of TC thermocouple (temperature), calibrate if necessary	once / year
Verification of TCA with sucrose solution, calibrate if necessary	once / year or after any major maintenance or modification of the system
Clean air test and Denuder efficiency test	once / month
Change chamber	once a year, if needed
Change analytic air filter	twice / year
Change cartridge filter	once / year

chamber change procedure



Offline Validation of the New 'Total Carbon Analyzer'

M. Rigler[1], L. Drinovec[1,2], A. Vlachou[3], A. S. H. Prévôt[3], C. Hüglin[4], J.-L. Jaffrezo[5], A. D. A. Hansen[6] and G. Močnik[1,2]

[1]Aerosol d.o.o., Ljubljana, Slovenia
[2]Jozef Stefan Institute, Ljubljana, Slovenia
[3]Paul Scherrer Institute, Villigen, Switzerland
[4]EMPA, Dübendorf, 8600, Switzerland
[5]Univ. Grenoble Alpes, LGGE, Grenoble, France
[6]Magee Scientific Corp., Berkeley, CA, USA

This work was financed in part by the EUROSTARS grant E!8296 TC-BC.

Introduction

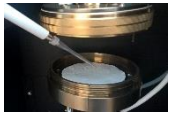
Carbonaceous aerosols are a large and often dominant fraction of fine particulate matter and are extremely diverse. The carbonaceous fractions are frequently separated into organic carbon (**OC**) and elemental carbon (**EC**) using thermal-optical methods. While the results for OC and especially EC concentrations vary significantly for different thermal evolution protocols (Bae, 2009), the total carbon (**TC**) concentration is very consistent between methods (Karanasiou, 2015). We present a new instrument TCA-08 for highly time resolved online measurement of TC concentrations. Combination of the optical method for measuring black carbon (BC) by the Aethalometer AE-33 (Hansen, 1982; Drinovec, 2015) and a thermal method for TC determination by newly developed TCA-08 is a new method (TC-BC) which we show to be equivalent to the standardized OC/EC analysis (EN 16909:2017).

Offline validation

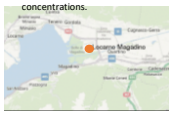
The first step in the validation of the online TC-BC method is to confirm the simplified method of the new instrument and to compare the offline analysis of samples relative to the standardized OC/EC method. For this purpose we used:

(1) A series of different sucrose concentra-tions pipetted on quartz filter.

(2) Punches of 24-h samples of ambient PM, collected by a high-volume PM2.5 sampler (winter campaign in 2013), Magadino (Switzerland), analyzed by two independent laboratories (PSI, Villigen; CRNS, Grenoble) with Sunset offline OC/EC analyzer, using thermal protocol EUSAAR2.



(1) Pipetting different sucrose concentrations.



(2) Location of the measuring station Locarno-Magadino (CH).

Total Carbon Analyzer

The **TCA-08** can operate in both online and offline modes. Quartz filter in the is combusted very rapidly using **filtered ambient air** as the carrier gas. This creates a CO2 pulse which is readily detected as a large transient increase above the ambient CO_2 level. In contrast to conventional OC/EC analyzers, the new TCA method measures TC on the quartz filter without the need for special high purity gases, quartz glass components or specially-prepared catalysts (3).

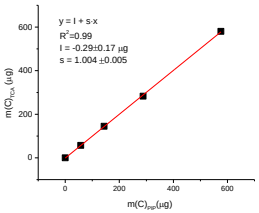
(3) Combustion chamber in TCA-08.

Results

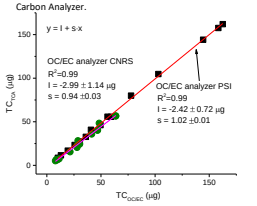
TC concentrations measured by Total Carbon Analyzer in offline mode were compared with known amount of carbon in different sucrose solutions (4) and with TC concentrations of ambient filters obtained by offline OC/EC instruments from two different laboratories (5).

Regression analysis of experiment with sucrose solutions showed excellent consistency between pipetted amount of carbon in sucrose and measured carbon from the CO2 signal with TCA in the range of 5.0 µg to 0.5 mg of carbon. Additionally, adequacy of calibration of TCA with sucrose was confirmed. Comparison analysis on ambient samples with TCA and OC/EC analyzers also showed high correlation but small discrepancy between slopes for OC/EC analyzers CNRS and PSI, which can be explained in terms of the differences in calibrations and the sample composition.

This study confirmed performance of the simplified TCA method. It was a first step in demonstration of the equivalence between TC-BC method and standardized OC/EC method.



(4) Regression analysis of comparison between pipetted mass of carbon ($m(C)_{PIP}$) from different volumes of sucrose solutions and measured mass of carbon ($m(C)_{TCA}$)determined from CO2 signal by Total Carbon Analyzer.

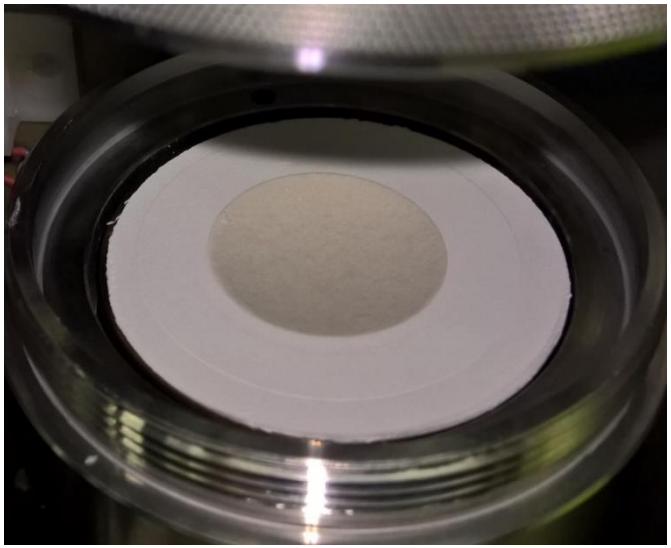


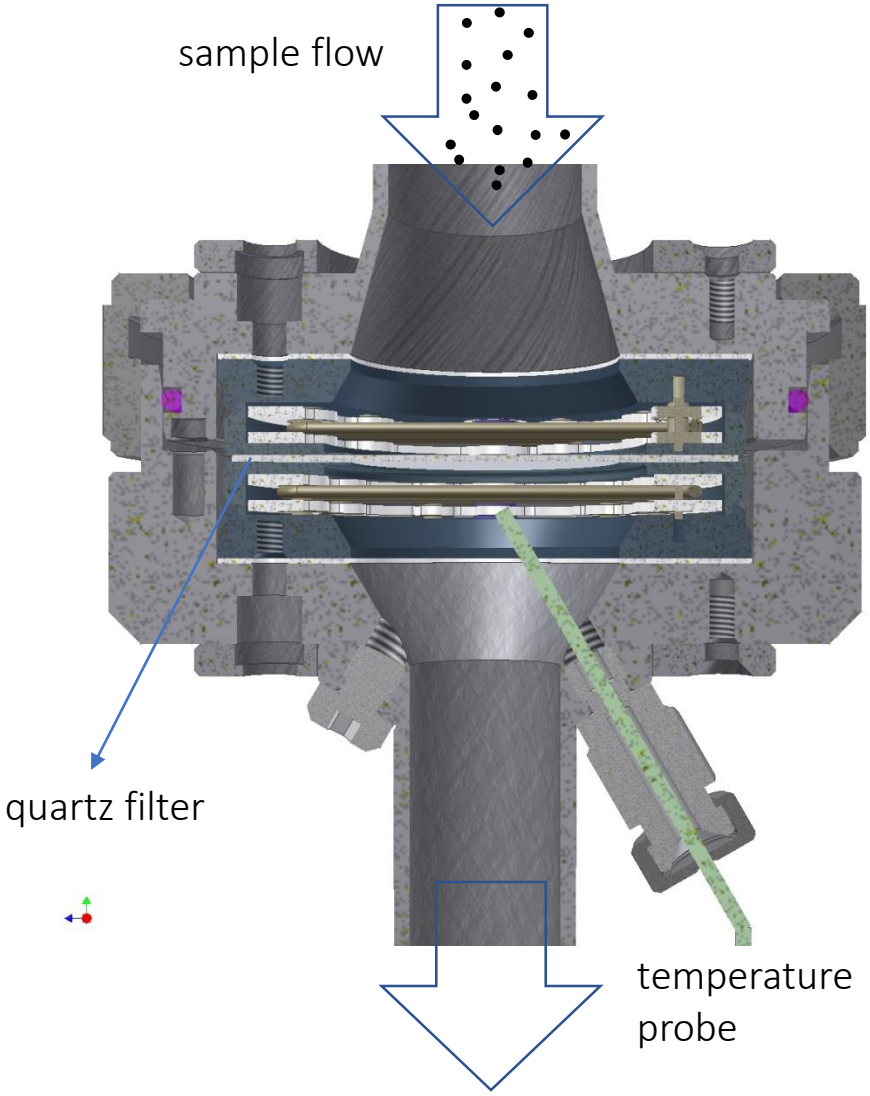
(5) Regression analysis of comparison between TC concentrations of ambient filters obtained by offline OC/EC instruments ($TC_{EC/OC}$) from two different laboratories and TC concentrations measured by Total Carbon Analyzer in offline mode (TC_{ECA}).

combustion chamber = sample chamber

sampling

- Sample flow: **16.7 LPM = 1 m^3/h**
- Time base: **60 min**
- Face velocity = flow/area = **56.6 cms^{-1}**
  (active area filter diameter = 25 mm)
- Quartz filters, diameter **47 mm**
  (standard size)

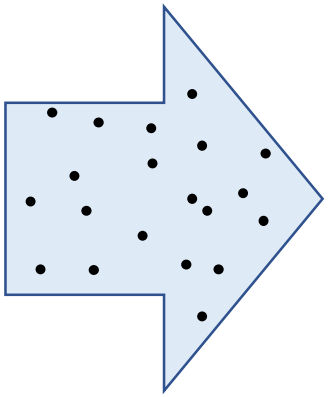




sampling

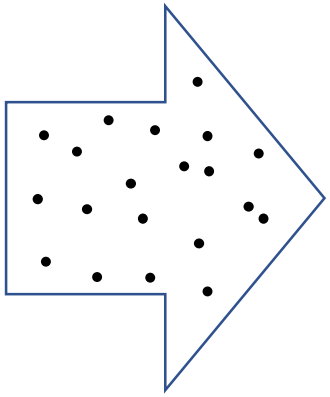
SAMPLING ARTEFACTS: positive artefact = **VOC absorption**

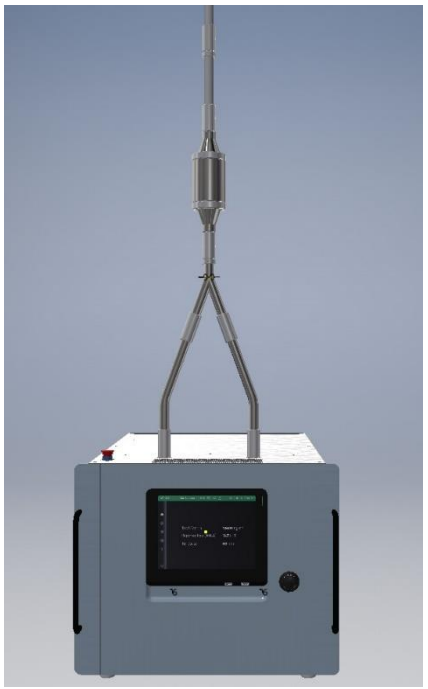
Carbonaceous aerosols
organic gases



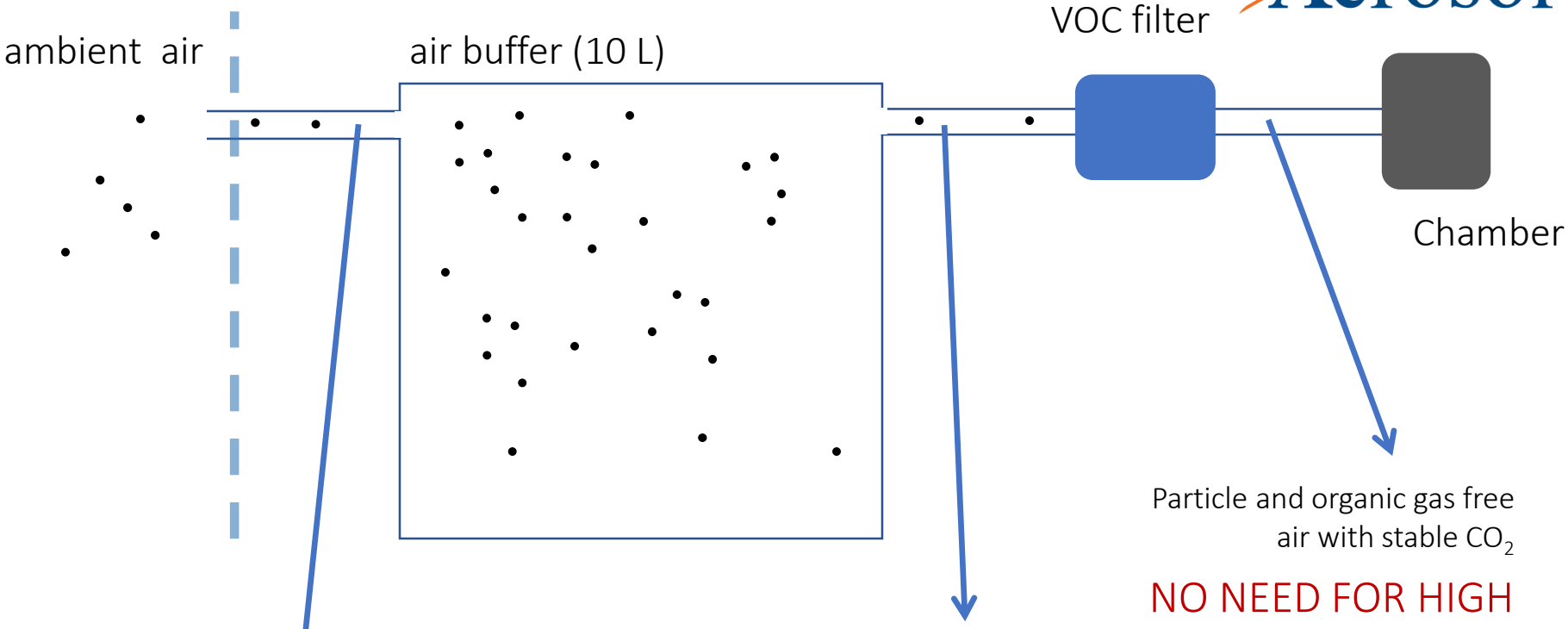
DENUDER

Carbonaceous aerosols





analytic air



Particle and organic gas free air with stable CO_2

NO NEED FOR HIGH PURITY GASES!