Towards the development of tailored reference materials for black carbon measurements

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Introduction

In order to understand how soot (also called black carbon) impacts the environment, i.e. climate and health, accurate measurements must be made of its properties. There are large uncertainties with respect to how soot evolves with age and is transformed by photochemical and aqueous processes. The uncertainties are largely a result of the paucity of measurements of the physical, chemical and optical properties of soot over sufficiently broad scales in space and time. No single instrument has the capability of measuring all the properties of soot thus requiring various techniques to measure individual characteristics.

A number of potential candidates for soot reference materials have been introduced in recent years[1,2,] however, none have been generally accepted as the standard by those who measure BC properties. The objective of the current work is to introduce the concept of a well characterized, laboratory-fabricated SRM for the purpose of calibrating instruments that measure any soot property. An approach is presented for the manufacture of SRM with precisely controlled mixtures of EC and OC that are representative of compounds found in the combustion of fossil fuel. The validation of this approach is shown with some examples of these SRM samples analyzed with one of the TOA methods.

Methodology and Selected Examples

We assume that laboratory-fabricated soot is representative of ambient soot as long as its physical and chemical structure is similar; however, the complexity of organic species found in combustion particles may significantly restrict the utility of such an approach. To resolve this problem a simplification of the representation of organic components in atmospheric particles has been suggested whereby organic aerosol species are grouped into a relatively small number of representative compounds. In our work we use EC as a basis substrate and deposit organic compounds which are representative of the main classes of organics identified in the surface coverage of soot produced by fossil fuel burning.

The basic carbon substrate, referred to herein as elemental carbon reference material (ECRM), may be produced using a graphitization procedure. The randomly ordered microstructure of technical carbon will undergo graphitization at high temperatures and the amorphous carbon microstructure will change to well-organized crystallites of graphite platelets. The ECRM were heated in an oven with nitrogen at 3000^0 C producing graphitized thermal soot (GTS) with surface areas of 6 and 80 m^2 g^{-1} (GTS-6 and GTS-80), respectively. In our work representative organics were selected from each group of identified compounds. The method of "forced adsorption" is used for producing a coverage by deposition of a given organic species on the EC substrate[3]. A list of GTS-based SRMs that have been created and tested and are listed in

Table 1. Nominal amount of organics which was deposited is given for each sample. Samples with pyrene, octacosane and trimestic acid, deposited on GTS-6, were manufactured with the objective of producing GTS slightly coated with organic compounds (0.1-0.3%). Initially creating an SRM with a very small coating of OC serves to demonstrate the sensitivity of techniques for measurements of the OC fraction in soot. Larger amounts of pyrene and trimellitic acid (up to 5%), deposited on GTS-80 can be used for evaluating those techniques where the thickness of the OC coverage may play a role. A maximum organic coverage of 9% has thus far been deposited on GTS-80 using naphthalene dicarboxylic acid with higher percentages possible.

Figure 1 illustrates how well the a TOA reproduces the nominal OC values. These analyses were made using the TOA implemented by Sunset Laboraties. We see that the agreement is nearly one to one with a correlation coefficient near unity.

Table 1. Soot reference materials: EC basis and organic carbon (OC), nominal and derived by the thermo/optical technique, wt%. Shaded cells indicate differences between the nominal and measured OC that are found to be outside the estimated uncertainty.

Sample #	EC basis	Organic coverage	OC nominal	OC measured
1	GTS 6	**$C_{16}H_{10}$ (Pyrene)**	0.304	0.06±0.05
2	GTS 6		0.152	0.17±0.07
3	GTS 6	**$C_{28}H_{58}$ (Octacosane)**	0.205	0.23±0.08
4	GTS 6		0.102	0.14±0.05
5	GTS 80	**$C_{16}H_{10}$ (Pyrene)**	0.94	0.95±0.01
6	GTS 80		4.55	4.39±0.44
7	GTS 80	**$C_9H_6O_6$**	0.51	0,77±0.14
8	GTS 80		2.57	2.64±0.25
9	GTS 80	**OH [-C_2H_4O-]*n*H** (Carbowax)	0.53	0.60±0.11
10	GTS 80	**$C_{12}H_8O_4$** "NDCA"	6.06	4.90±0.50

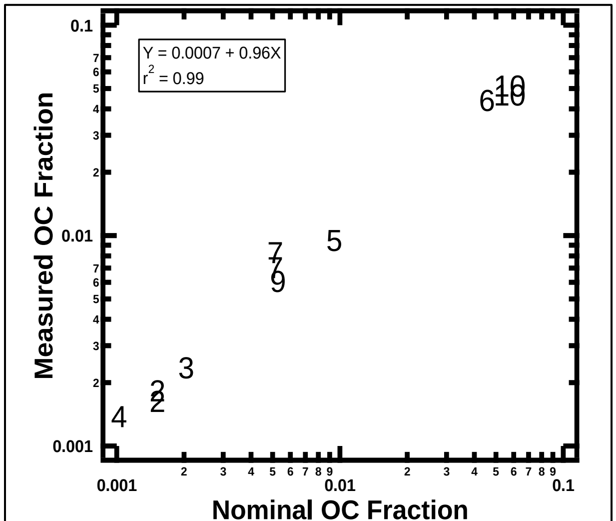

Figure 1. The SRM samples that are listed in Table 1 were analyzed using TOA to derive the weight percent of OC for comparison with the nominal values. The numbers refer to the samples in Table 1. The correlation coefficient is given by r^2.

Summary

Calibration of instruments that measure the properties of black carbon (soot) is a major obstacle to our understanding of how this ubiquitous atmospheric particle is formed, evolves and impacts health and climate. The lack of a reference material whose properties are well characterized has hampered efforts by the atmospheric community to arrive at standard calibration techniques that allow intercomparison of measurement methods and comparison of data sets taken at multiple locations over different periods of time. An SRM is proposed that consists of graphitized thermal soot that can be coated with precise coverings of organic material with different molecular structures similar to those found in the natural environment. A preliminary evaluation has been conducted of ten samples of this ECRM with organic matter from 0.102% - 9.09%. The OC

mass percent was measured with a Sunset Laboratory's EC/OC Thermal/Optical analyzer with a nearly one to one correspondence between the nominal and measured OC percent by weight. Evaluation of the long-term stability of the samples showed negligible change in the chemical or morphological properties after storage for four months. These results suggest that tailored graphitized thermal soot is an excellent candidate as an SRM, for evaluating the sensitivity of thermal/optical analyzers for separating OC from EC as a function of different organic coatings.

Work is now in progress to evaluate these tailored materials for calibrating thermal/optical analyzers and to compare the performance of instruments that measure the optical and hygroscopic properties of soot.

Acknowledgments

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References

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2. Chen, L.-W.A; Chow, J.C.,; Watson, J.G.; Moosmüller, H.; Arnott, W.P. *J. Aerosol Sci.* 2004, *35*, 765–780.
3. Popovicheva, O.B.; Kireeva, E.D.; Shonija, N.K.; Khokhlova, T.D. *J.Phys. Chem.A.,* 2009, *10.1021/jp905522s*

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Monitoring of combustion aerosols in atmosphere:

- **Progress**:

- combustion particles are including into legislation procedure,
- more 5000 instruments operate over the world for monitoring soot mass concentration and OC/EC measurements.

- **Disadvantages:**

Current ability to predict environmental effects of soot emissions is strongly limited

due to:

- a great variety of different sources of original soot ,
- a wide range of soot physico – chemical properties.

A wide variety of methodic is used for various instruments

low accuracy ± 50-100%

problems of comparative analysis,
methodic- dependent results.

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ATMOSPHERIC ENVIRONMENT
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Round robin tests

Results of the "carbon conference" international aerosol carbon round robin test stage I

14 labs

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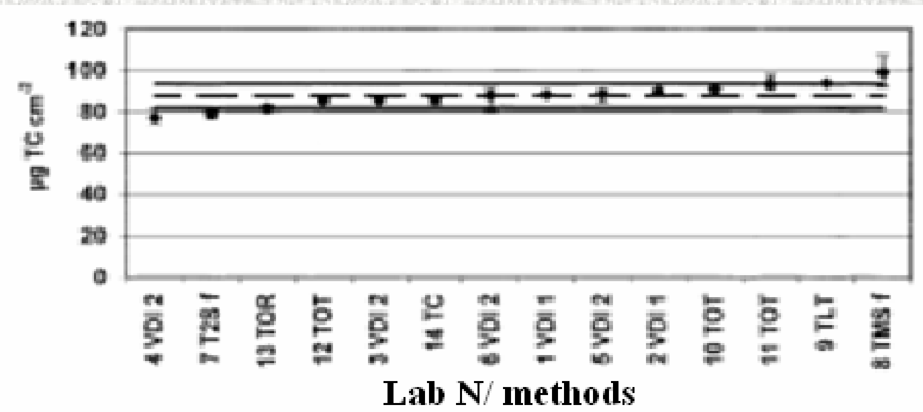
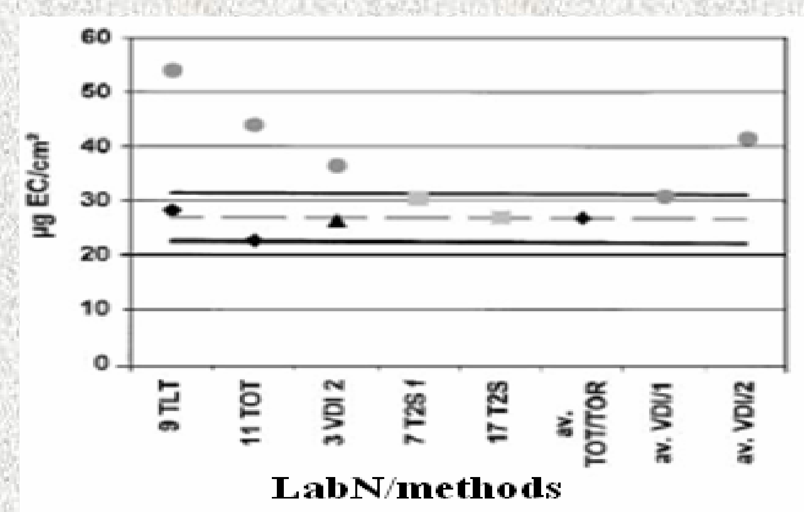
3 urban и 2 rural samples





Comparison of **total carbon** measured by various thermal/optical techniques shows good agreement

TC ~ 79 ÷ 99 µgC cm^{-2} (7%)

Comparison of **elemental carbon** shows
poor agreement

EC ~ 8 ÷ 94 µgC cm^{-2} (46%)

Motivation for production of BC reference materials

- **large discrepancy in** *EC and OC***,**
- **low accuracy** ±50-100% of mass concentration and optical measurements,

derived by different groups and different methods, from samples taken from the same source,

- no calibration standards (*all instruments are calibrated by producers* **)**

lead to the search for a material that could be used as a reference for calibration and validation!

How to produce standard BC reference material?

Characteristics of reference BC materials

- precisely- known properties, especially the content and nature of organic compounds
- reproducibility
- stability
- certification
- comparison Test campaigns

@RM Round Robin Test

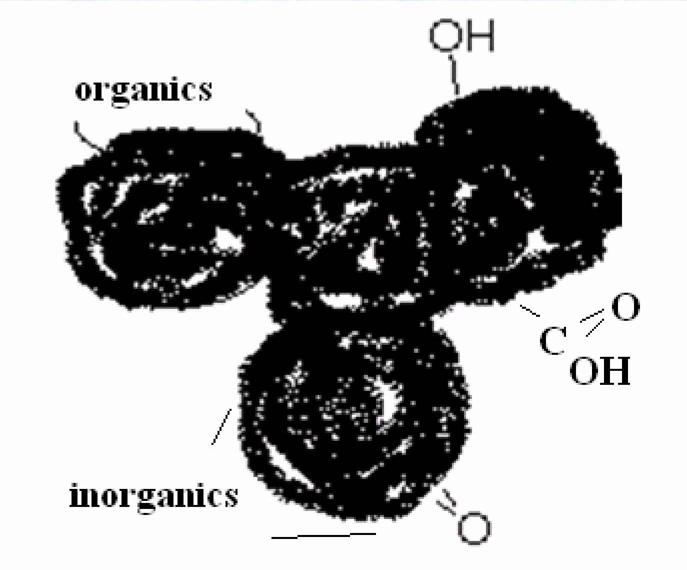
There are currently no controlled methods for producing soot **of precisely-known properties, i.e. size, surface area, composition, organic coverage.**

The *development* of atmospheric representative and accessible BC materials with reproducible "programmable properties" will ensure long-term intra and inter-laboratory *data quality* leading to a great progress of the entire environmental community in the BC measurement and monitoring.

Combustion particles in atmosphere: typical features

Soot is a product of incomplete burning of hydrocarbons

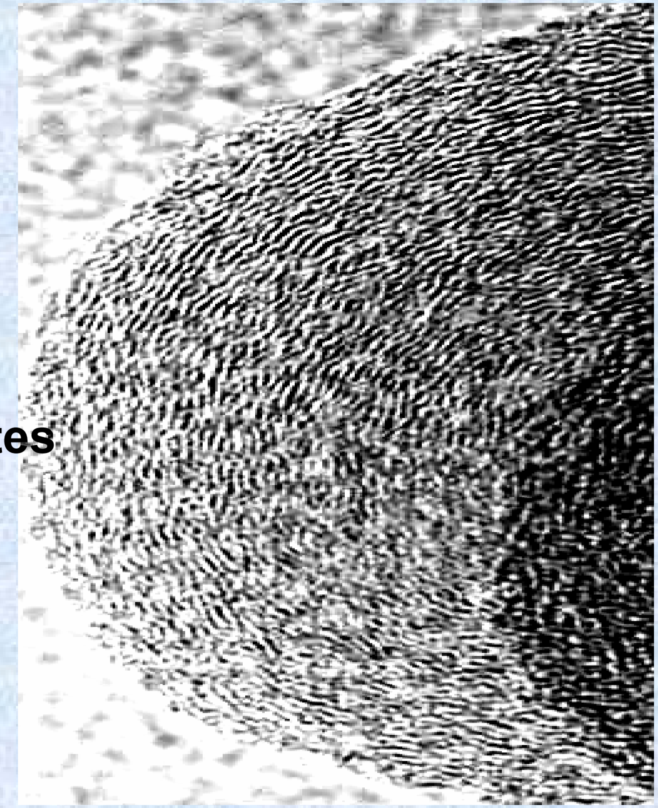
EC, OC + inorganic



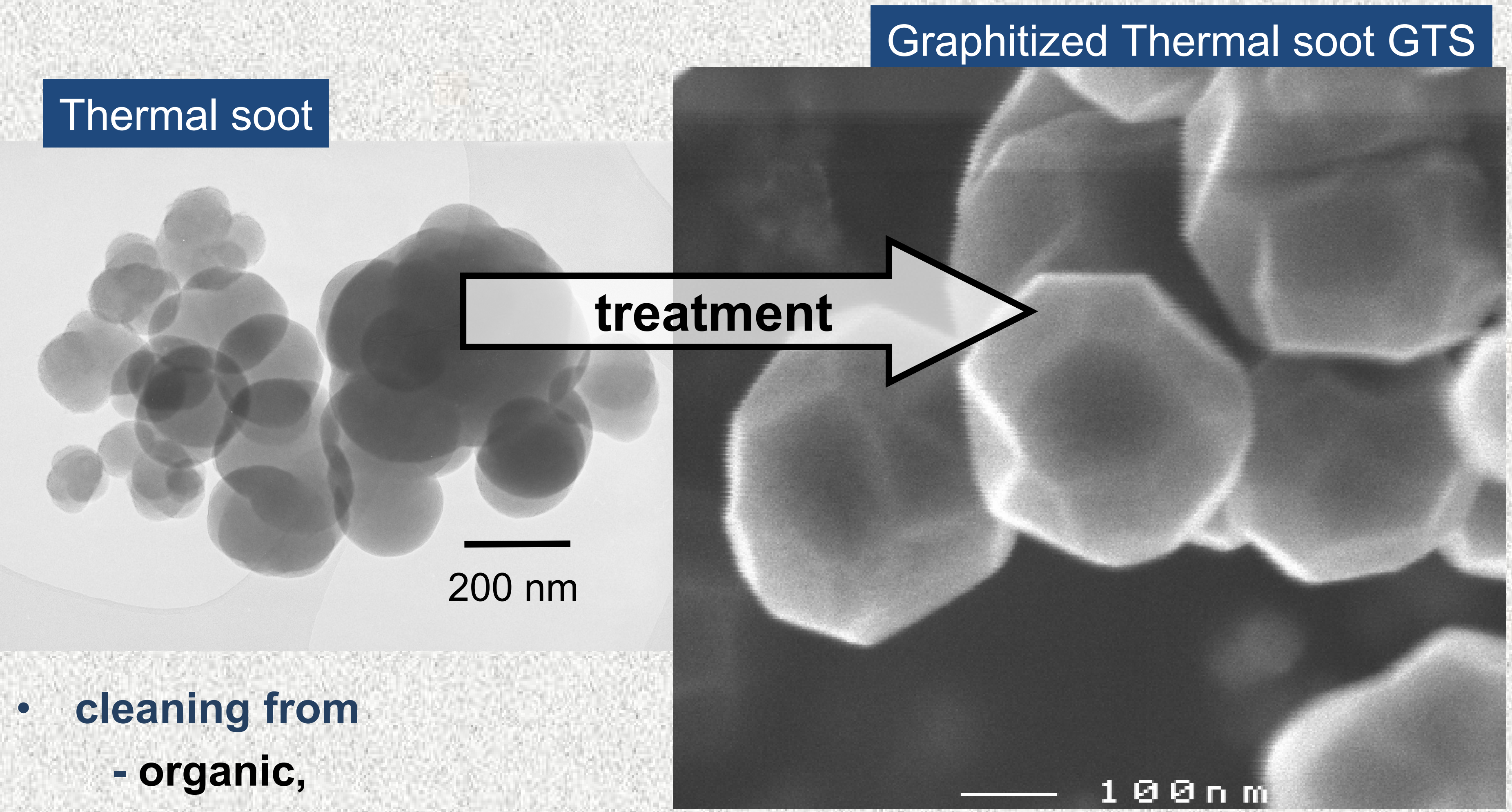
soot agglomerates of primary particles 30-100 нм

morphology

microcrystallites of graphites



Elemental Carbon Reference Material



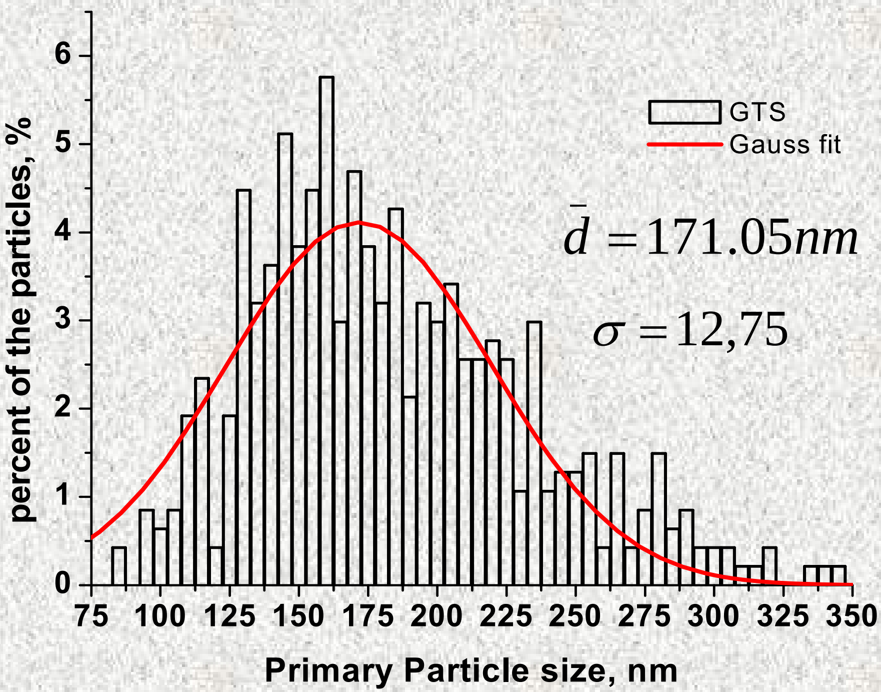
- **cleaning from**
  - **- organic,**
  - **- inorganic and ash.**
- **production of well-graphitized structure,**

  perfect chemically uniform surface.

Elemental Carbon Reference Material: properties

Size distribution

of primary particles GTS-6



GTS - 6 surface area 6 m^2/g

GTS-80 surface area 80 m^2/g

Elemental composition: examination by EDS

$$C = 99,3\% \pm 0,5\%$$

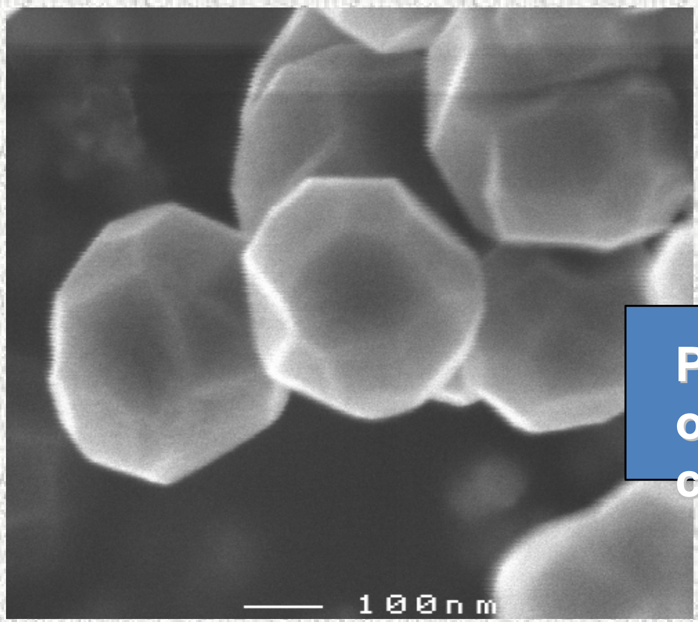
$$O = 0,7\% \pm 0,5\%$$

Elemental composition: examination by AAS

wt%	Si, 10^{-4}	Al, 10^{-4}	Ca, 10^{-4}	Cu, 10^{-4}	B, 10^{-4}	Mn, 10^{-4}	Mg, 10^{-4}	Fe, 10^{-4}	V, 10^{-4}	Ti, 10^{-4}
Thermal soot	5	2,9	7,2	1,4	3,5	4,3	3,6	12	1,1	1,7
GTS	0	1	6,1	0	4	1,1	1,1	1,3	0	0

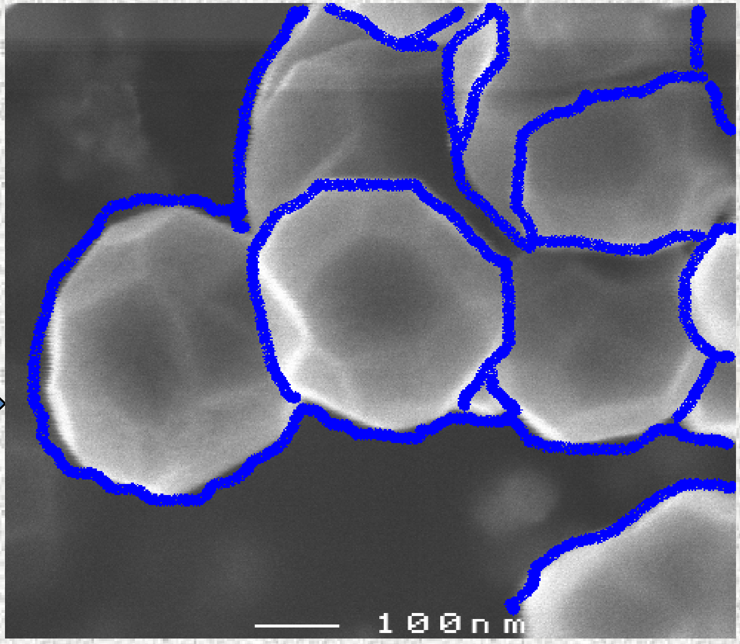
Soot Reference Material

EC RM



PRODUCTION of OC coverage

Soot RM

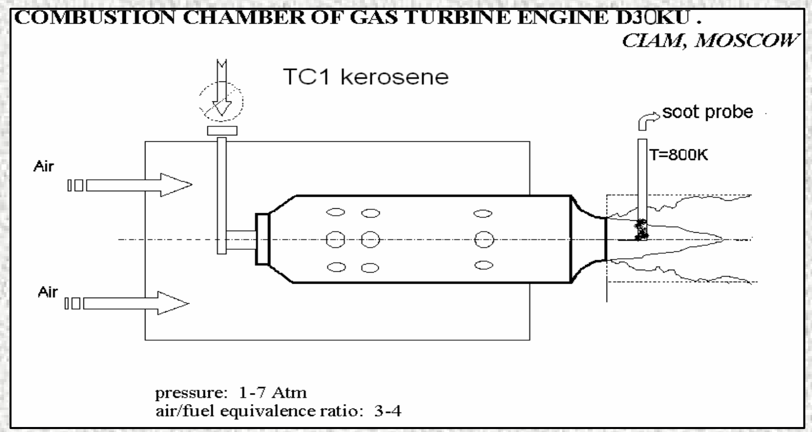


OC coverage on EC basis:
deposition by " forcing adsorption" methodic.

OC coverage correlating with typical composition of combustion particles:

main classes of organics: alkanes, PAHs, organic acids and derivaties.

Aircraft engine soot composition



Gas Chromatography
Mass-Spectrometry

extract by methanol CH_3OH

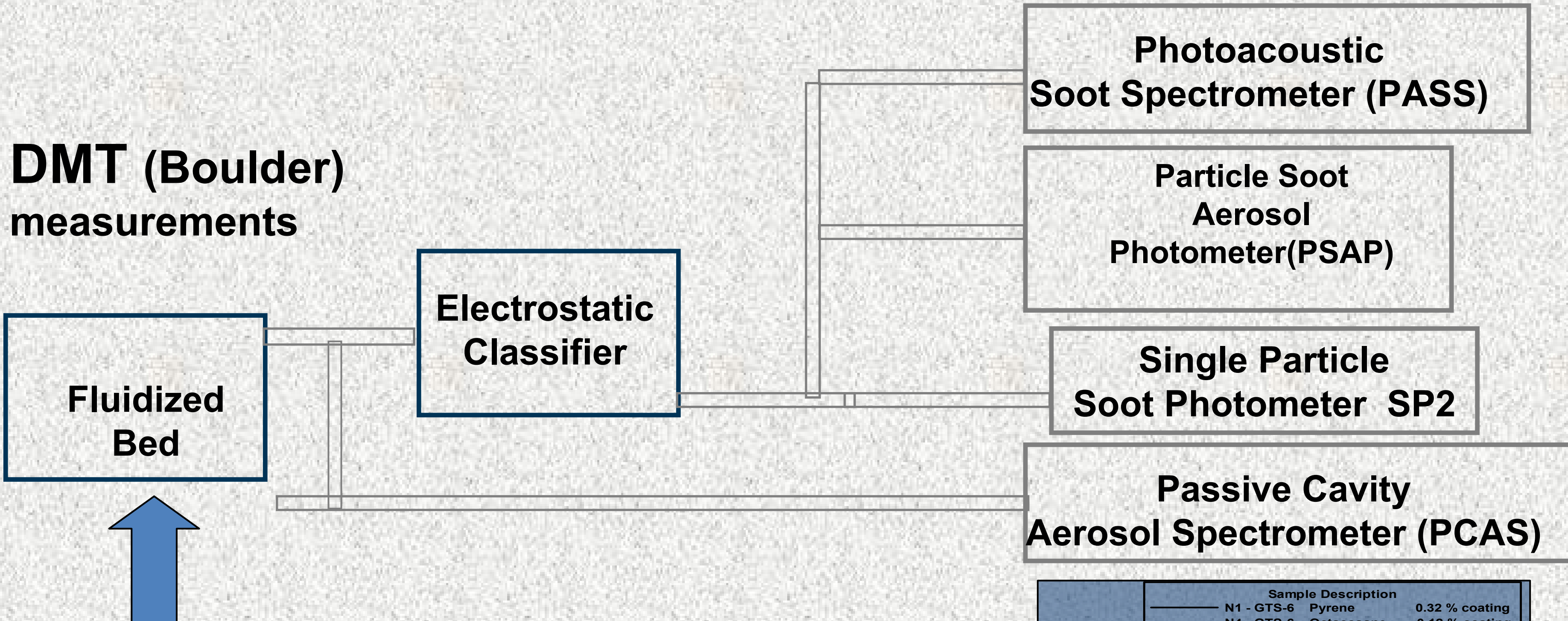
Alken **Cycloalken**	C_nH_{2n} C15H12	$C_{30}H_{50}$ Cyclopropen-diphenyl
Alkanes	C_nH_{2n+2}	CH_3 - $(CH_2)_{n-2}$ -CH_3, n=15,17,19,22,30
Alkilbenzenes	$C_5H_5(C(R)(R_1)$	for R,R_1 C_nH_{2n+1}n=1,10
Polyaromatics:	Phenanthrene Pyrene, Fluoranthene,	Cyclopenta[cd]pyrene, Benzo[a]pyrene Pyrene, 1-methyl
Carboxylic acids	C15H31COOH C17H35COOH	n-hexadecanoic acid Octadecanoic acid
Ketone	C15H10	Cyclopente(def) phehanthrenon
Esters	C_6H14(COOR)(COOR$_1$) $C_{17}H_{35}COOCH_3$	phthalate acid, ester octadecanoic,methyl ester

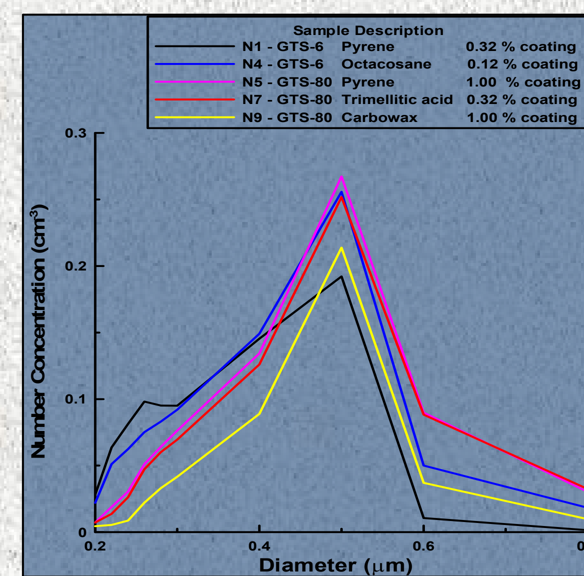
Soot Reference Materials, 10 samples, proposed

№	EC basis	Modificator:	OM
1	GTS-6	Pyrene $C_{16}H_{10}$	0,32%
2	GTS-6		0,16%
3	GTS-6	Octacosane $C_{28}H_{58}$	0,24%
4	GTS-6		0,12%
5	GTS- 80	Pyrene $C_{16}H_{10}$	1%
6	GTS- 80		5%
7	GTS- 80	*1,2,4-Benzenetricarboxylic acid (Trimellitic acid)* ***$C_9H_6O_6$***	1%
8	GTS - 80		4,88%
9	GTS -80	PEG 600 OH [-C_2H_4O-]*n*H Carbowax 600 (M 570-630)	1%
10	GTS - 80	2,6 Naphtalene-dicarboxylic acid $C_{12}H_8O_4$	9.09%

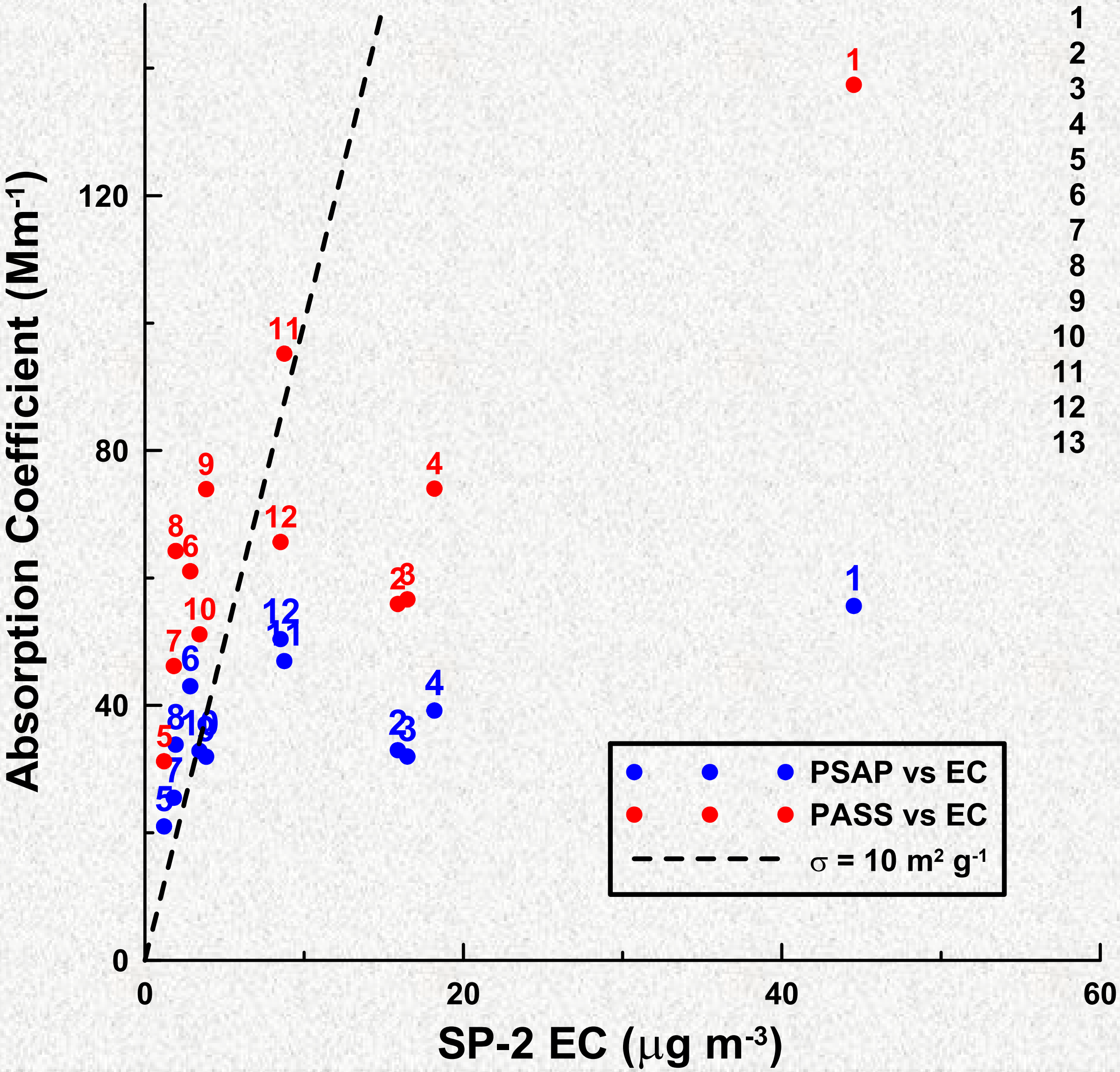
TESTING COMPAIGN: calibration by Soot Reference M

DMT (Boulder) measurements





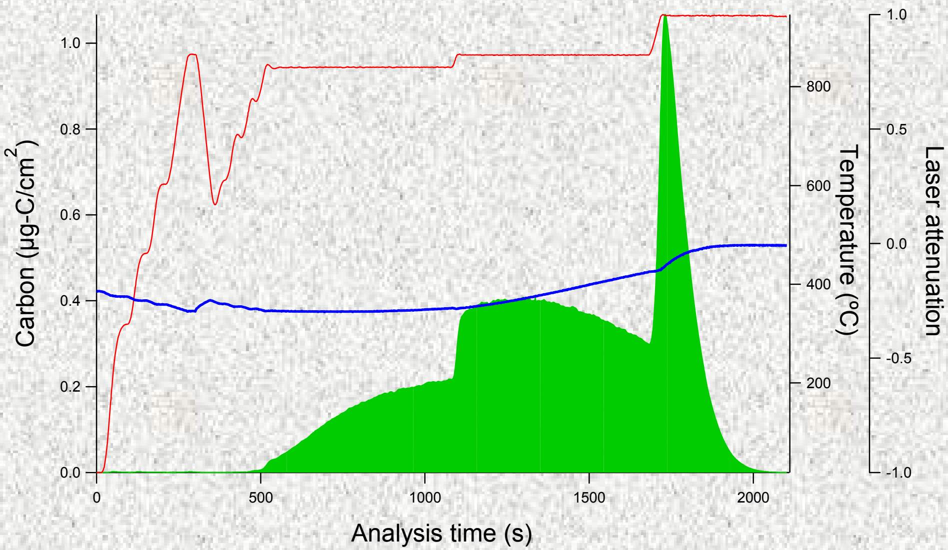
Light absorption measurements PSAP, PASS vs SP2



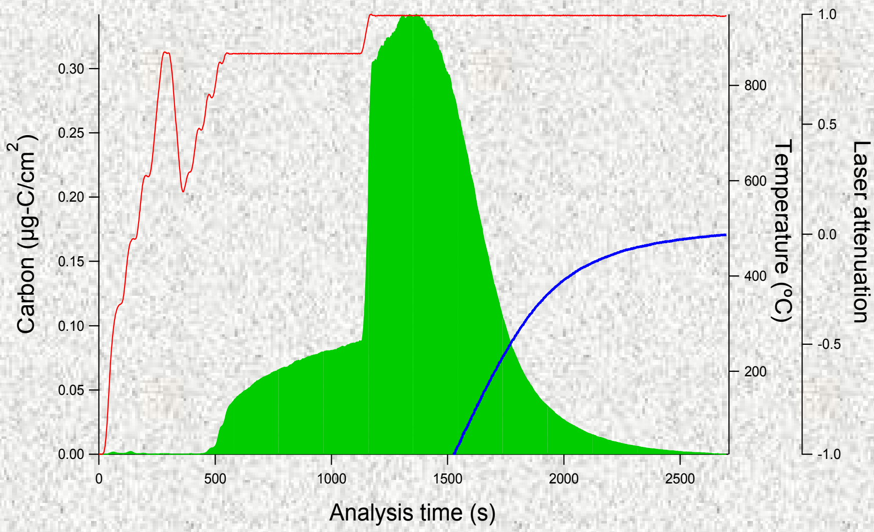
Sample	Description	Coating	Percent
1	GTS-6	Pyrene	0.32
2	GTS-6	Pyrene	0.16
3	GTS-6	Octacosane	0.24
4	GTS-6	Octacosane	0.12
5	GTS-80	Pyrene	1.00
6	GTS-80	Pyrene	5.00
7	GTS-80	Trimellitic acid	1.00
8	GTS-80	Trimellitic acid	4.88
9	GTS-80	Naphtalene	9.00
10	GTS-80	Carbowax	1.00
11	GTS-80	Trimesic acid	0.30
12	GTS-6	Substrate	
13	GTS-80	Substrate	

Thermal/ optical analysis (Sunset) to separate OC and EC

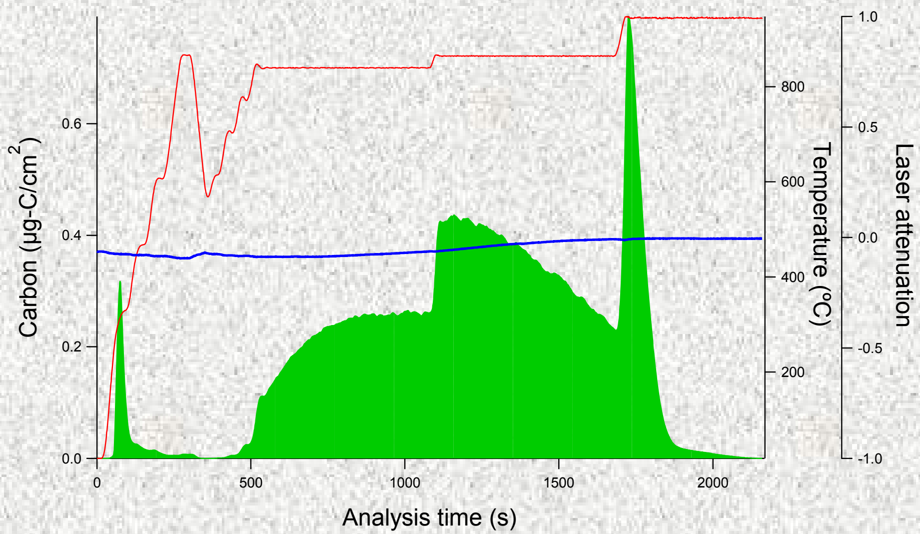
EC RM GTS-80



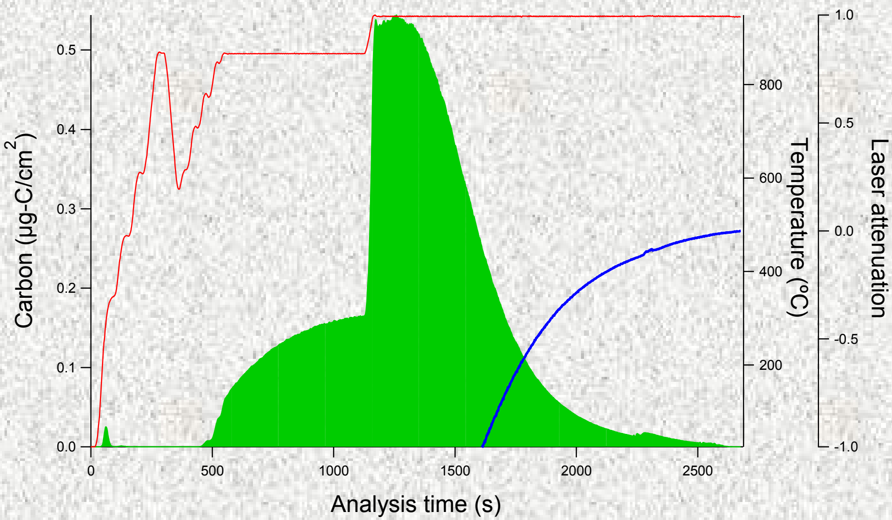
EC RM GTS-6



GTS-80 4.88% 1,2,4- Trimellitic acid



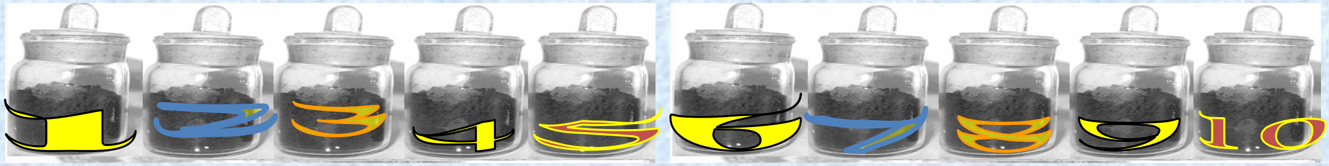
GTS-6 0.16% pyrene



Present points:

1. The **method for production** of standard reference material (SRM) is suggested.

2. The samples for validation , testing and calibration are produced.



3. Production and properties are described in AMTD, 2010

Atmos. Meas. Tech. Discuss., 3, 1743–1773, 2010
www.atmos-meas-tech-discuss.net/3/1743/2010/

Atmospheric Measurement Techniques Discussions

This discussion paper is/has been under review for the journal Atmospheric Measurement Techniques (AMT). Please refer to the corresponding final paper in AMT if available.

Towards the development of standard reference materials for soot measurements – Part 1: Tailored graphitized soot

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Work in progress:

SRM samples are currently being analyzed by DRI (J.Chow), Berkeley (T.Kirschstetter), U.Vienna (H.Puxbaum) and UNAM (D.Baumgardner) using TOA.

Invitation for collaboration!
for evironmental and health studies

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