BC properties and its measurement techniques

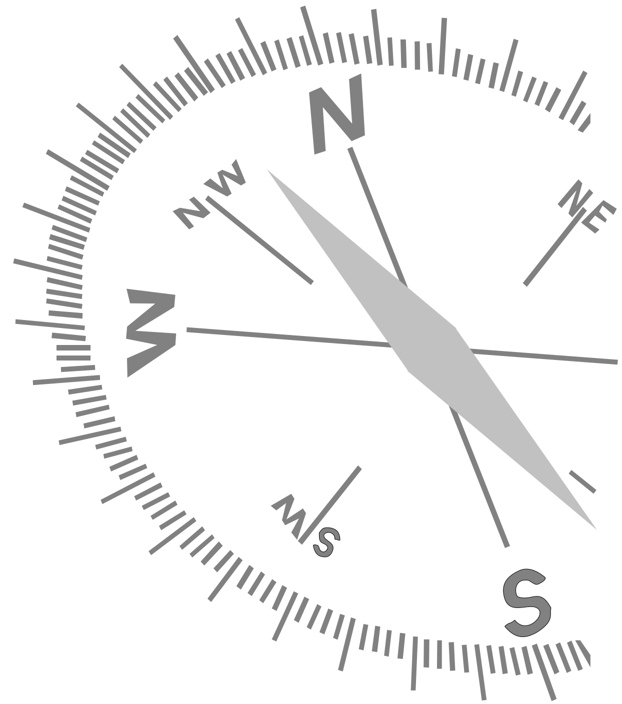
An overview

Navigator

1. Introduction and overview
    - some definitions

2. BC properties and how to measure them
    a. Light absorption
    b. Thermal stability
    c. Insolubility
    d. Morphology

3. Synopsis



EMISSION / IMMISSION DEFINITION

- **Emission:**

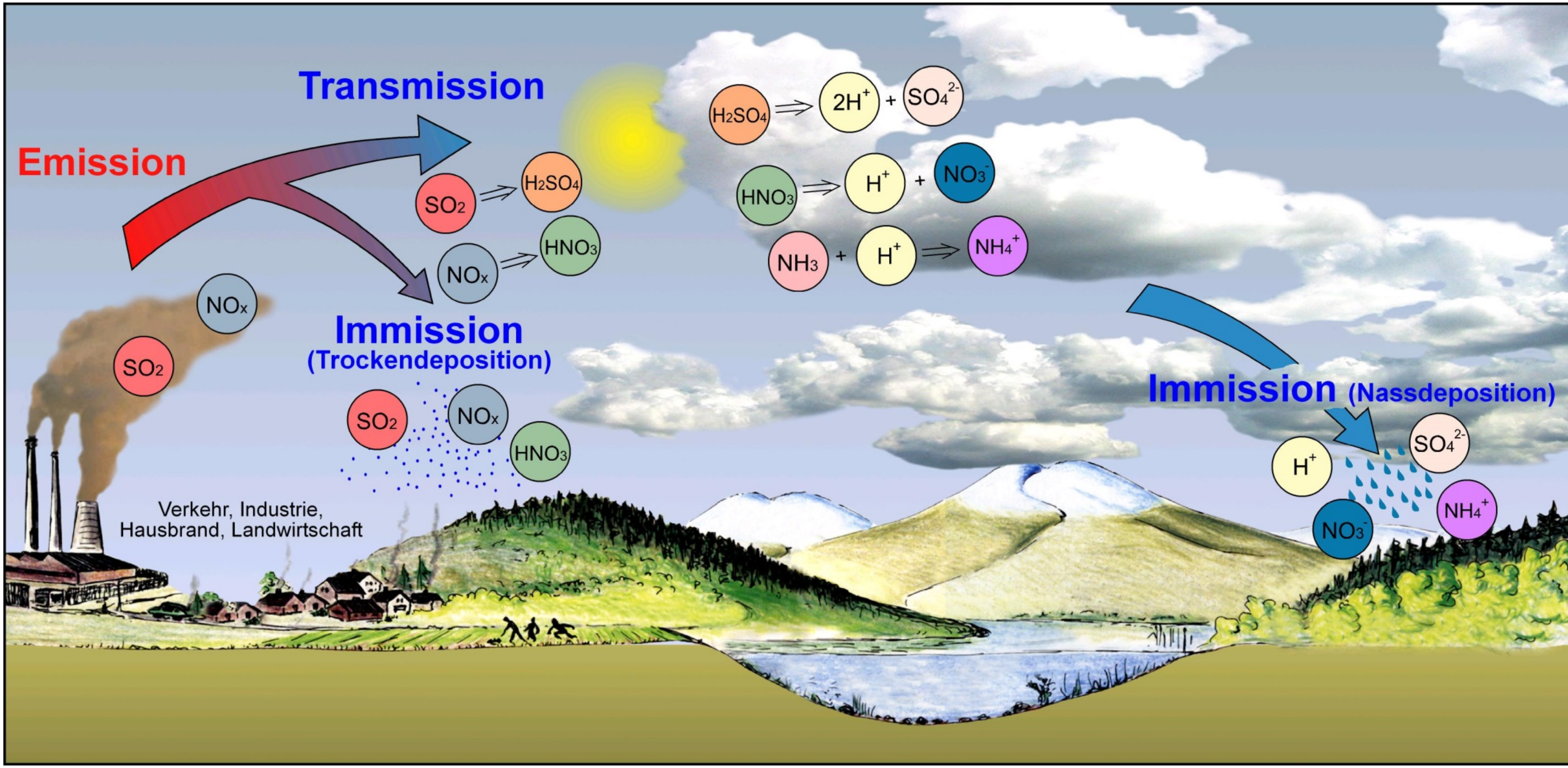
  "Emissions" as used herein shall mean *any air pollution*, noise, vibration, light, heat, radiation and similar phenomena *originating from an installation*.

- **Immission:**

  "Immissions" as used herein shall mean *any air pollution*, noise, vibration, light, heat, radiation and similar effects on the environment *which affect* human beings, animals and plants, soil, water, *the atmosphere* as well as cultural objects and other material goods.

Source: Federal Immission Control Act - BImSchG Section 3 Definitions

EMISSION / IMMISSION ILLUSTRATION



Source: http://www.ubz-stmk.at/

Non-road mobile machinery

- **Definition:**

  “non-road mobile machinery” shall mean any mobile machine, transportable industrial equipment or vehicle with or without body work, *not* intended for the use of *passenger- or goods-transport on the road*, in which an internal combustion engine … is installed.

EU – Nonroad-Directive

97/68/EC (as amended by 2004/26/EC)

Diesel engines

Power P_n kW	NO_x g/kWh	HC g/kWh	CO g/kWh	Particulates g/kWh	Date*
	NO_x + NMHC				
Stage I					
$37 \le P_n < 75$	9.2	1.3	6.5	0.85	Apr 99
$75 \le P_n < 130$	9.2	1.3	5.0	0.70	1999
$130 \le P_n \le 560$	9.2	1.3	5.0	0.54	1999
Stage II					
$18 \le P_n < 37$	8.0	1.5	5.5	0.8	2001
$37 \le P_n < 75$	7.0	1.3	5.0	0.4	2004
$75 \le P_n < 130$	6.0	1.0	5.0	0.3	2003
$130 \le P_n \le 560$	6.0	1.0	3.5	0.2	2002
Stage III A					
$19 \le P_n < 37$	7.5		5.5	0.6	2007
$37 \le P_n < 75$	4.7		5.0	0.4	2008
$75 \le P_n < 130$	4.0		5.0	0.3	2007
$130 \le P_n \le 560$	4.0		3.5	0.2	2006
Stage III B					
$37 \le P_n < 56$	4.7		5.0	0.025	2013
$56 \le P_n < 75$	3.3	0.19	5.0	0.025	2012
$75 \le P_n < 130$	3.3	0.19	5.0	0.025	2012
$130 \le P_n \le 560$	2.0	0.19	3.5	0.025	2011
Stage IV					
$56 \le P_n < 130$	0.4	0.19	5.0	0.025	Oct 2014
$130 \le P_n \le 560$	0.4	0.19	3.5	0.025	2014

* Date for placing the engine on the market, type approval one year earlier

Source: DIRECTIVE 97/68/EC

Source: VDMA, Exhaust emission legislation Diesel and gas engines

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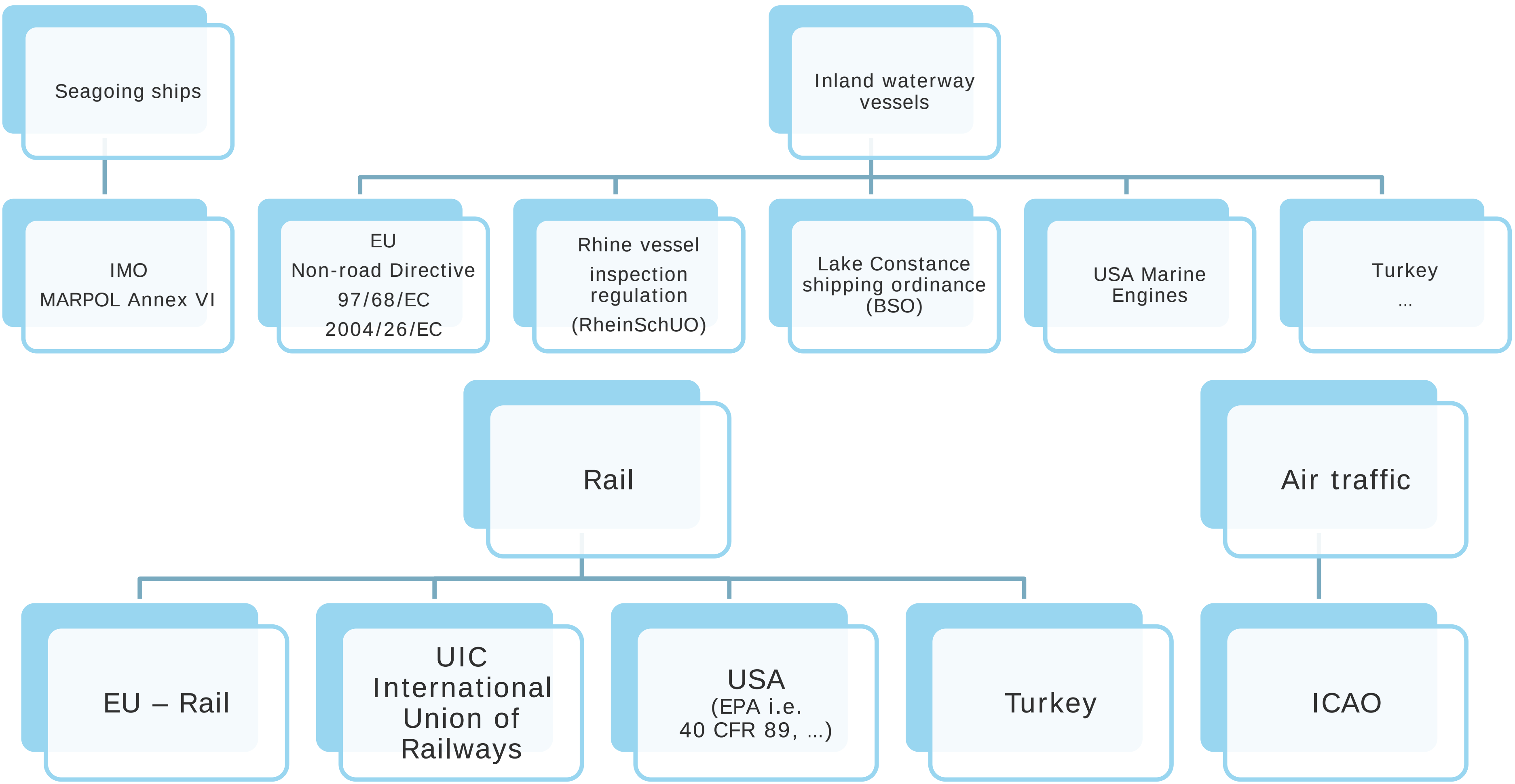
Examples for “non-road” emission regulations



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Various regulations limiting particulate mass

Particle Mass (PM)

Sector	PM regulation
Aviation	no regulations on PM
Seagoing ships	No values required
Inland waterway vessels	EU 0,2-0,5 g/kWh USA 0,04-8 g/kWh (depending on vessel size)
Rail	EU 0,025-0,2 g/kWh UIC 0,25 g/kWh USA 0,022 – 0,19 g/kWh
Road Transport (heavy duty trucks)	EU 0,01 g/kWh PN: 6-8 10^{11}

Source: VDMA, Exhaust emission legislation Diesel and gas engines

Introduction for BC measurement techniques

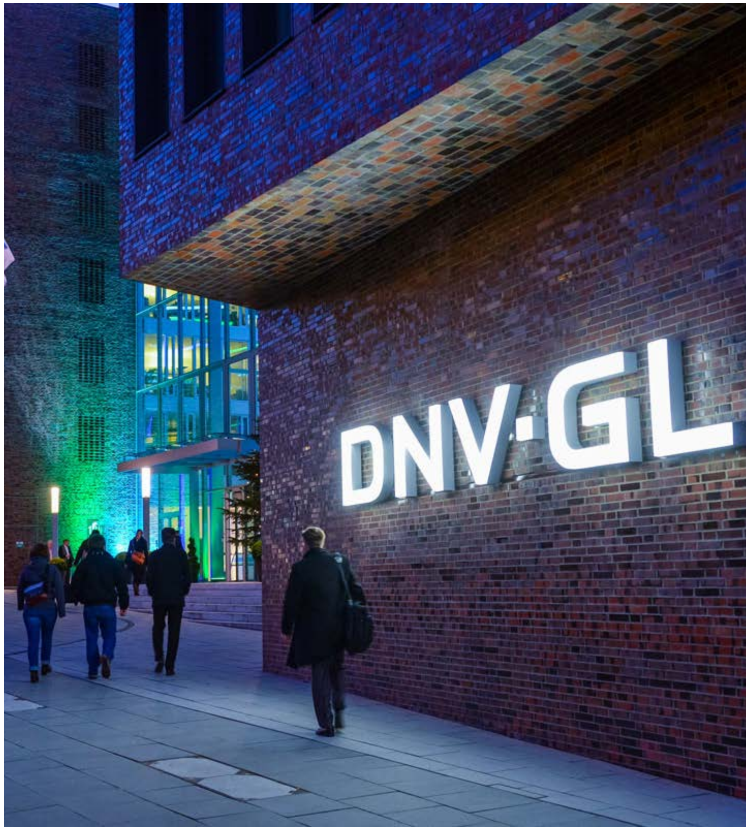
- Black carbon is defined by four properties (Bond et al.), that can not be measured simultaneously by one system
- There are several measurement systems in use and commercial available
- Some techniques can measure continuously (transient),
  others need a sample from a filter
- There are just a few standardised
- Every measurement technique / principal gains other results
- Studies which compare the different measurement principals show a dependency on the analysed aerosols

Basics for BC / PM emission measurements

- The aim of measurements are:
  - Quantify the emission of BC / PM

- Where measurements can be conducted:
  - on engine test bed
  - on-board ships according to standards
    (i.e. ISO 8178, or other defined protocol)
  - analysing ship emission plumes from distance
    (by planes carrying equipment or exhaust plumes reaches shore based equipment)

- Every measurement application has different requirements, challenges and options



The four properties of BC*

- **Light absorption**

„It strongly absorbs visible light with a mass absorption cross section of at least 5 m^2/g at a wavelength of 550 nm."

- **Thermal stability (refractory)**

„It is refractory; that is, it retains its basic form at very high temperatures, with a vaporization temperature near 4000K."

- **Insolubility**

"It is insoluble in water, in organic solvents including methanol and acetone, and in other components of atmospheric aerosol."

- **Morphology**

"It exists as an aggregate of small carbon spherules."

*according to Bond et al. (2013)

Overview on measurement techniques according BC properties

- Property: **Light absorption**
  - Filter-based extinction measurement
  - Extinction-minus-scattering
  - Photo-acoustic technique
  - Interferometric technique

  A Mass Absorption Coefficient (MAC), which is instrument dependent, is applied to obtain *equivalent BC** (*eBC*).

- Property: **Morphology**
  - Raman spectroscopy (*Elemental Carbon**)
  - TEM/SEM (*nano-spherical (NS)-Soot**)
  - Mass spectrometry (*refractory BC or Elemental Carbon**)

- Property: **Thermal stability**
  - Laser induced incandescence (LII) (*refractory BC**)
  - Thermal-optical methods (*Elemental Carbon**)
    - Thermal optical transmittance (TOT)
    - Thermal optical reflectance (TOR)
    - VDI 2465 Blatt 2

- Property: **Insolubility**
  - VDI 2465 Blatt 1 (*Elemental Carbon**)

*recommondations accord. Petzold et al.

Light absorption

Introduction

- Black Carbon consists of small spheres with many delocalized electrons (sp2 orbital hybridization), which leads to a broad-band light absorption.

- Mass absorption/ attuention coeffient (MAC) of black carbon is comparable high. Freshly emitted BC has a MAC of 7.5+/- 1.2 m^2/g at 550 nm.
- Linking BC morphology with optical properties has been a challenge, BC agglomerates do not show simple “Rayleigh” or “Mie” scattering behaviour.
- Overall, Filter-based and in-situ-techniques (for transient measuring) exists.
- Many scientists argue for the declaration of the measurement results in optical units.
- There are many challenges...
  Indications exists that the measurement of fresh combustion products delivers less bias than on aged filter materials.
- Interactions with sulphur!
- No commonly accepted reference material for calibration exists.

Filter-based extinction measurement 1 / 4

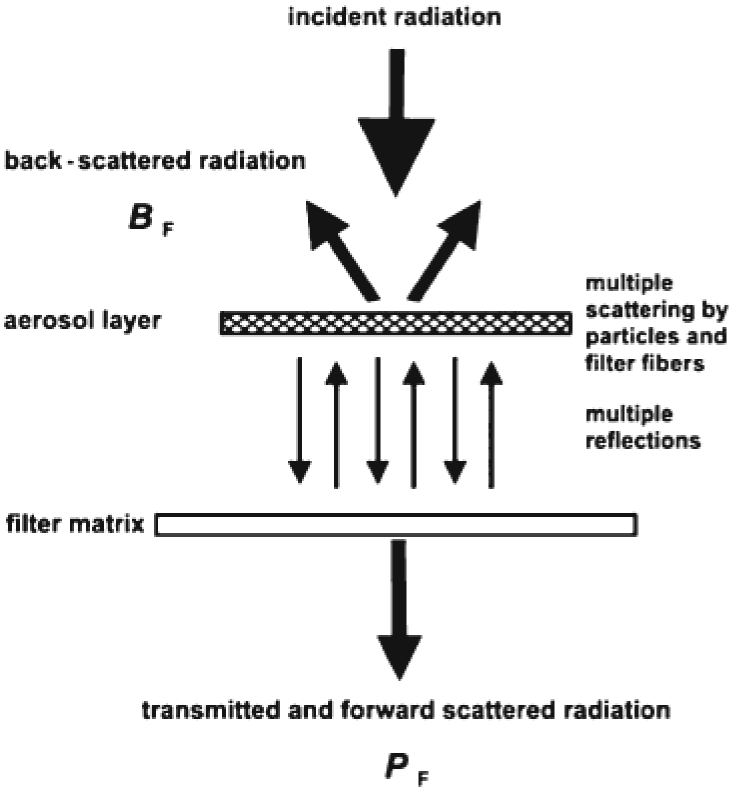
- Most traditional measurement technique
- Sample air flows through a filter
- The particles accumulate on and within the filter
- The light transmission (and attenuation) or reflection of the filter is measured continuously
- Collected black carbon leads to a higher light attenuation

- The mass is calculated with empirical mass attenuation coefficients, which are subject to on-going discussions
- There are some methods in use by the industry, e.g. filter smoke number, which is based on the same measurement principle.

Filter-based extinction measurement 2 / 4

Challenges

- Scattering within the filter
- Differentiate between Black Carbon and other light absorbing aerosols e.g. Brown Carbon
- Filter loading
- Scattering (increase of attenuation by direct scattering and increasing absorption)
- Humidity can alter filter scattering



A. Petzhold et al. (2005)

Filter-based extinction measurement 3 / 4

Challenges

- Scattering within the filter
- Differentiate between Black Carbon and other light absorbing aerosols e.g. Brown Carbon
- Filter loading
- Scattering (increase of attenuation by direct scattering and increasing of absorption)
- Humidity can alter filter scattering

Solutions

- Filter with refractive index close to atmospheric particles
- Measurement at different wavelengths. Black Carbon will absorb light at all wavelengths (Angstrom exponent of 1), other materials will show a wavelength depending absorption.
- Correction factor for scattering and filter loading (Aethalometer, PSAP)
- Measurement of the scattering (MAAP)
- Keep humidity low

Filter transmission measurements for industrial application usually don't cover above mentioned aspects!

Filter-based extinction measurement 4 / 4

- Filter-based extinction measurements for industrial applications are usually not built to cater for above mentioned capabilities / circumstances as they should be:
  - **small, cheap and portable instruments**
  - easy to operate and maintain (automatic filter changes)
  - Resolution time: minutes to seconds
  - There are some doubts regarding the accuracy of differentiating BC from other light absorbing and scattering materials when time for filter loading and extinction measurement is more than days (from loading to analysing), "fresh" combustion particles and direct extinction measurement show improved comparable behaviour.

Extinction-minus-scattering technique

- A light beam is lead through an air sample
- The extinction and the scattering is measured
- The scattering is subtracted from the extinction

- Resolution: seconds
- Would be presumably easy and cheap technology
- Long path ways needed (mirrors) which make it **sensitive towards mechanical vibration**
- No instruments commercially available yet
- Sensitive towards humidity

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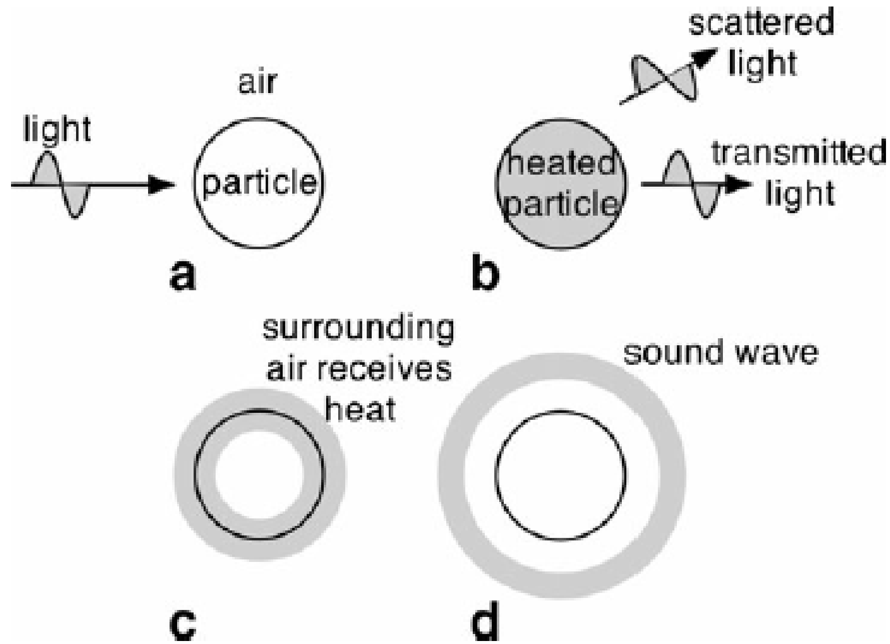
Photo-acoustic techniques

- Photo-acoustic techniques are based on the photo-acoustic effect:
  - Light is send through an air sample
  - The intensity of the light is changed rapidly
  - The air and aerosols are absorbing the electromagnetic energy (light) and are locally heated, depending on their optical properties and the wavelength of the light
  - The local heating and cooling leads to small thermal expansion and constriction, resulting in pressure waves which are detected as sound
  - A photo-acoustic spectrum can be recorded by varying the wavelength



H. Moosmüller et al. (2009)

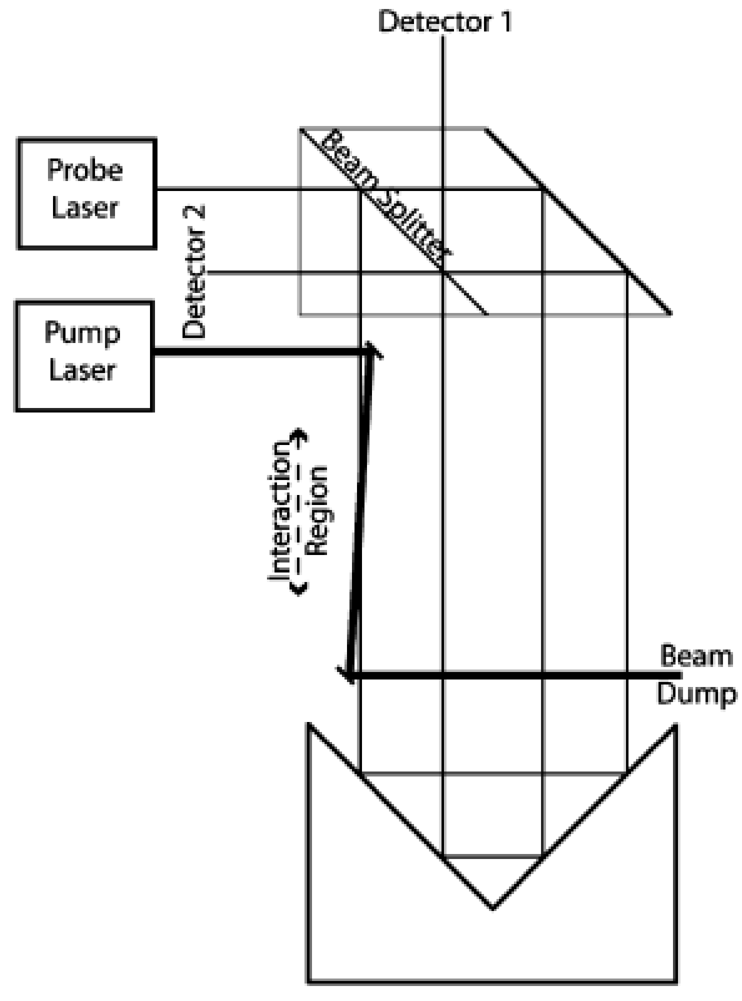
- Corrections for scattering needed, but usually implemented in the measurement system
- Photo-acoustic measurements are used widely e.g. in medical research or to determine concentrations of trace gases (consider wavelength)

Challenges with Photo-acoustic techniques

- Interferences with noise and vibrations from the ship / engine? Although, measurements are conducted.
- Conversion factors to quantify the black carbon, which may no be appropriate due to variable amounts of Organic Carbon (OC)
- Sensitive towards semi-volatile compounds like water and coatings
- It is a „standard“ technique for accurate measurements of aerosol light absorption
- There are several instruments available
- Time resolution: seconds
- BC-particles > 2.5µm would cause challenges

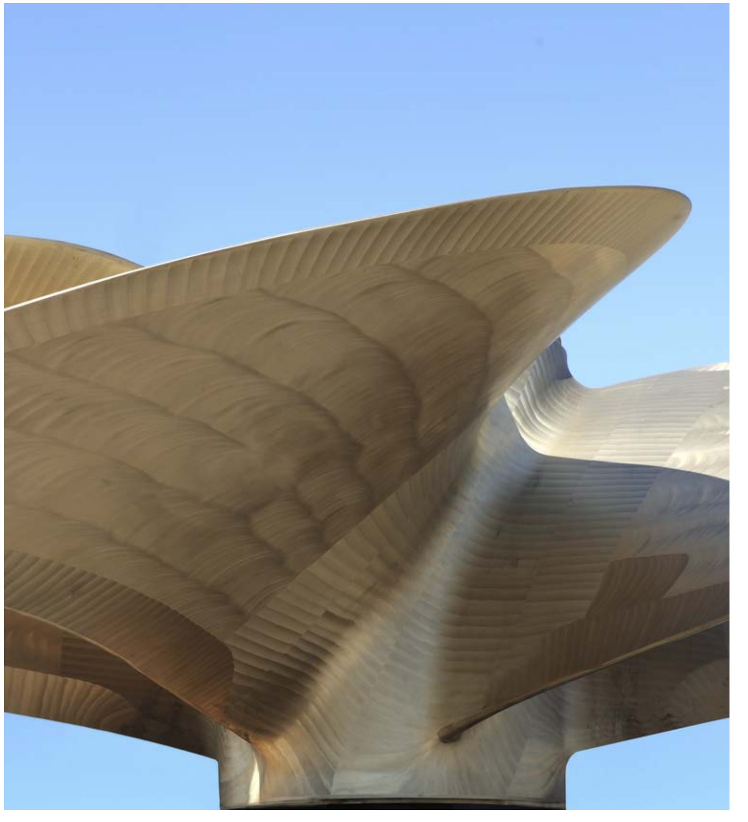
Interferometric techniques 1 / 2

- One probe laser is splitted into two beams, which travel the same path length and are detected afterwards
- One of the beams passes through a sample volume, which is affected by a pump laser
- If there is BC in the sample volume it is heated by the pump laser and will heat the air around, too
- The heated air results in a different refractive index and a short optical path length
- This leads to a observable phase shift between the two beams



Interferometric techniques 2 / 2

- Time resolution: high (seconds)
- Commonly used to measure particle absorption
- Sensitive **towards mechanical vibration**
- Development on-going
- Not really usable today



Thermal stability (refractory)

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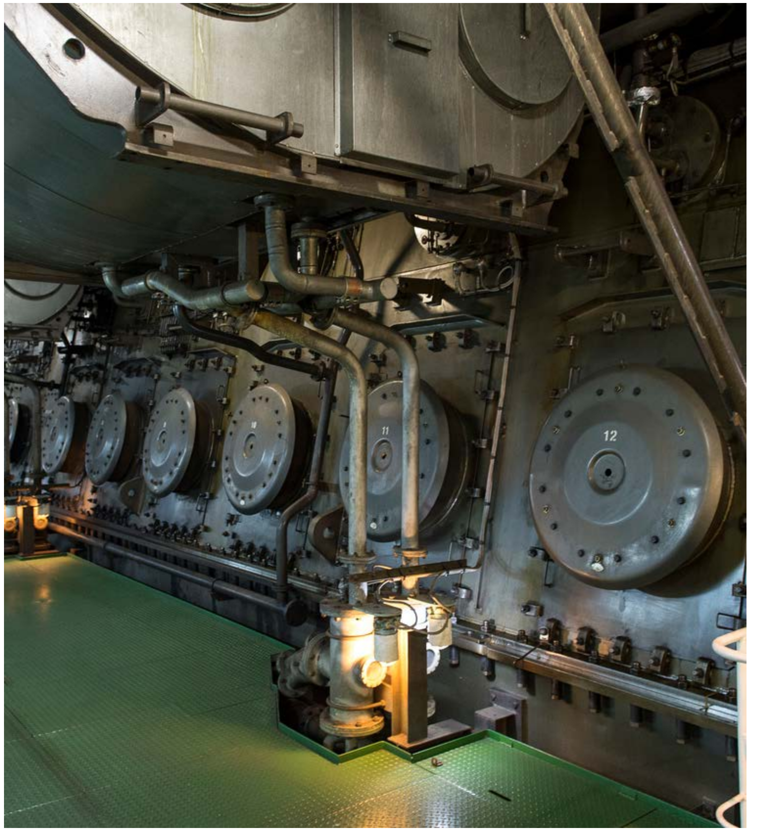
Introduction

- The measurements techniques for the property of thermal stability can be distinguished into two techniques
  - Techniques to measure **refractory black carbon**
  - Thermal-optical methods to measure **elemental carbon**
- The most important difference is the temperature used. For refractory black carbon measurements 4000K are used, while the thermal-optical methods (elemental carbon) use just about 1000K



Refractory Black Carbon (rBC) / laser induced incandescence (LII)

- Developed in the 70es for in situ investigation of soot
- Particles are heated by a high power density laser beam up to 4000k using the light absorbing and refractory properties of black carbon
- Black carbon starts glowing, vaporizes and emits blackbody radiation
- The blackbody radiation is used for identification and its magnitude for mass determination
- This measurement technique is commonly used
- Time resolution: seconds
- It is possible to gain many other information from this process e.g. particle size
- Lower particle size threshold is about 10 nm volume equivalent diameter
- There are two types of laser used:
  - Pulsed laser
  - Continuous laser

Refractory Black Carbon (rBC) / laser induced incandescence (LII)

Pulsed laser

- Measuring a group of particles
- Commonly used in motor engineering
- LII signal is proportional to the volume of BC
- Particle size can be gained by the cooling behaviour

- Measurement systems commercially available* and used for e.g. engine ECU settings (R&D)

Continuous laser

- Measuring single particles
- Determination of particle size by scattering
- Less stringent safety restrictions

- Two measurement system commercially available (SP2, LII 200) and widely used in the atmospheric research

*Commercially available does not imply that it is as well suitable for the purpose !

Thermal-Optical Methods

- PM collected on a filter, heated to a fixed temperature to exhale all volatile components and than the remaining EC is quantified
- There are a lot of different temperature protocols and methods
- Sensitive towards charring (coking)
- Result: Elemental Carbon
- Aging dependence!
- Long-standing reliance on these methods
- Many observational data
- Interferences with metal oxides
- Different methods gain different results, but seems for diesel engine exhaust suitable
- Time resolution: hours

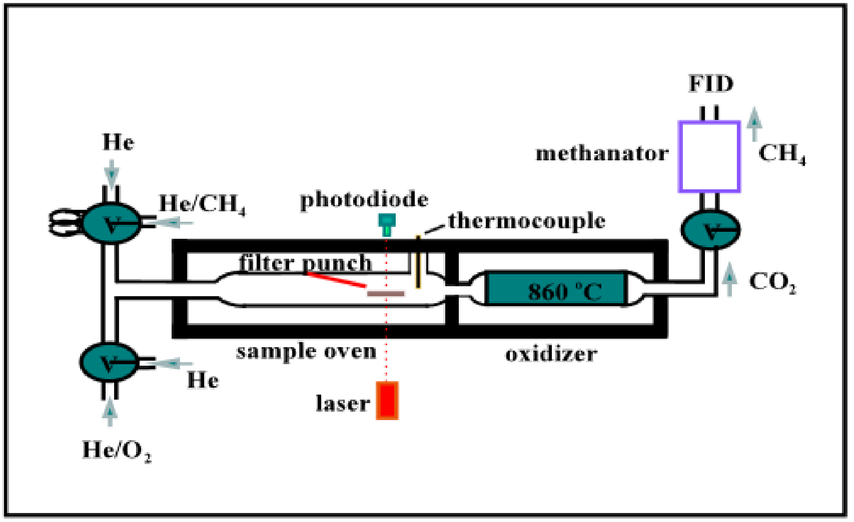
Protocol	Carrier gas for OC	Carrier gas for EC	Temperature plateaus for OC (°C)	Residence time at each temperature for OC (s)	Temperature plateaus for EC (°C)	Residence time at each temperature for EC (s)	Optical charring correction	Converter and detector
IMPROVE[1]	He	98%He 2%O_2	120,250,450, 550	150 – 580[a]	550,700,800	150 – 580[a]	Reflectance	Methanator; FID/CH_4
TMO[2]	He[b]	98%He 2%O_2	525	300[c]	750	180	N/A	Methanator; FID/CH_4
OGI[3]	He[d]	98%He 2%O_2	600	Varies[a]	400, 500, 600	100,120,>200	Reflectance	Methanator; FID/CH_4
NIOSH[4] 5040	He	98%He 2%O_2	250,500,650, 850	60,60,60, 90	650,750,850, 940	30,30,30, >120	Transmittance	Methanator; FID/CH_4
STN[5]*	He	98%He 2%O_2	310,480,615, 900	60,60,60, 90	600,675,750, 825,920	45,45,45, 45,120	Transmittance	Methanator; FID/CH_4
HKGL[6] (Hong Kong)	He	95%He 5%O_2	350,550,850	70,70,110	550,600,700, 750,800,850	10,50,40, 30,30,70	Transmittance	Methanator; FID/CH_4
HKUST-3[7] (Hong Kong)	He	99%He 1%O_2	250,500,650, 850	150,150,150, 150	650,750,850, 890	150,150,150, 150	Transmittance	Methanator; FID/CH_4
CalTech[8] (ACE-Asia)	He	90%N_2 10%O_2	310,450,575, 870	60,60,60, 90	550,625,700, 775,850,900	45,45,45, 45,45,120	Transmittance	Methanator; FID/CH_4
MSC1[9] (Canada)	He	90%He 10%O_2	250,450,550, 900	150,150,180,90	550,700,800	240,210,150	Transmittance	Methanator; FID/CH_4
RU/OGI[10] (Atlanta)	He	90%He 10%O_2	Stepwise to 700[e]	N/A	Stepwise to 850	N/A	Transmittance	Methanator; FID/CH_4
LBL[11]	O_2	O_2	Continuous (25 – 825)[f]	10 °C per minute	Continuous (25 – 825)	10 °C per minute	Transmittance	NDIR/CO_2
CNRS-CEA[12] (France 2-Step)	O_2	O_2	340	7200	1100	~600a	Assume 10% of OC is charred; assume EC decomposition rate of ~0.22% per min during OC analysis.	Coulometric titration/CO_2
U. Berne[13] (Switzerland 2-Step)	O_2	O_2	650[c],340[c]	60, 2520	650	1920	N/A	NDIR/CO_2
BNL[14]	He	90%He 10%O_2	400	300 or 900[g]	700	300 or 900[g]	N/A	NDIR/CO_2
GM[15] Research Laboratory	He[h]	Ambient air	650	~100[a]	650	~120[a]	N/A	NDIR/CO_2
VDI[16] 2465/1 (Germany)	N/A[i]	O_2	N/A	N/A	200,650,200	60,420,120	N/A	Coulometric titration/CO_2
VDI[17] 2465/2 (Germany)	He	80%He 20%O_2	80,350,620, 400	12,72,108, 18	300,700[j]	30,54	N/A	Coulometric titration/CO_2
RCOP[18] (Japan)	N_2	92%N_2 8%O_2	450	600[k]	850	300	N/A	Methanator; FID/CH_4
R&P 5400[19] (continuous analyzer)	Ambient air	Ambient air	340	~600[l]	750	~600[1]	N/A	Low-volume IR CO_2 Meter

J. Watson et al. (2005)

Thermal-optical transmittance (TOT) 1/2

NIOSH* 5040

- Standard for gaining the elemental carbon concentration of diesel particulate matter for occupational health and safety, especially in mining operations
- Filter based
- Used by several atmospheric scientists, too.
- A filter sample is heated to 870°C in helium atmosphere to remove the organic matter
- Filter transmittance is used to correct the charring effect
- The organic matter is catalytically oxidized, reduced to methane and measured with a flame ionization detector (FID)

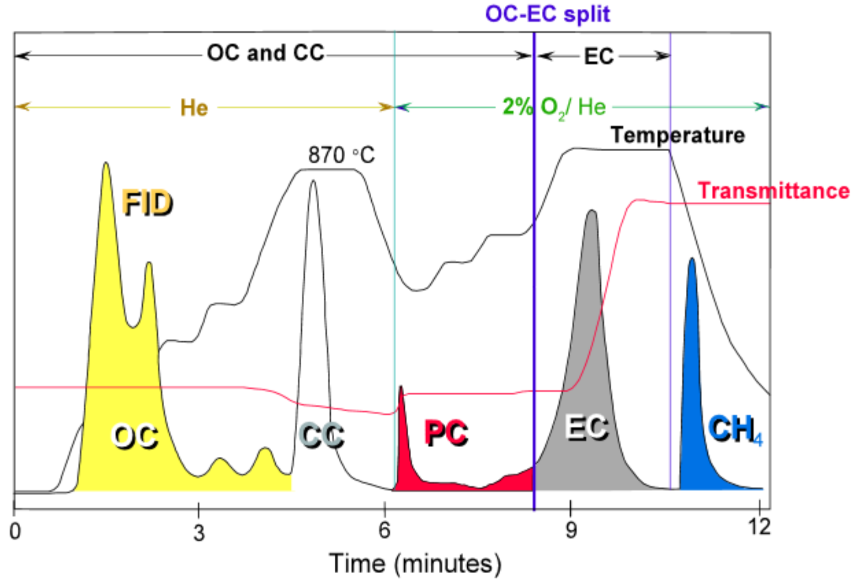


*National Institute for Occupational Safety and Health

Thermal-optical transmittance (TOT) 2/2

- After removal of OC a oxygen-helium-mix is used to burn the remaining material
- The CO_2 is reduced to methane and quantified by the FID

- It is a well-known and commonly used method, but it is just measuring EC and OC and does not fulfil the requirements of the BC-definition
- Measurement system commercially available*
- There are some doubts regarding the correction by laser
- Time-resolution: hours
- Sample will be transferred to shore

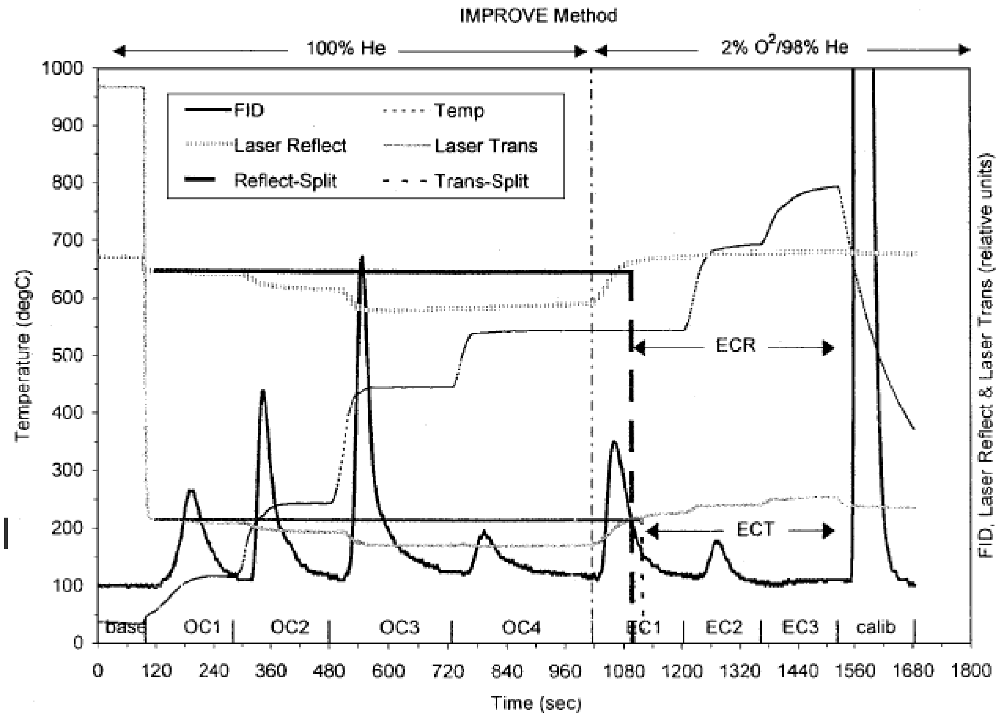


*Commercially available does not imply that it is as well suitable for the purpose !

Thermal-optical reflectance (TOR)

IMPROVE

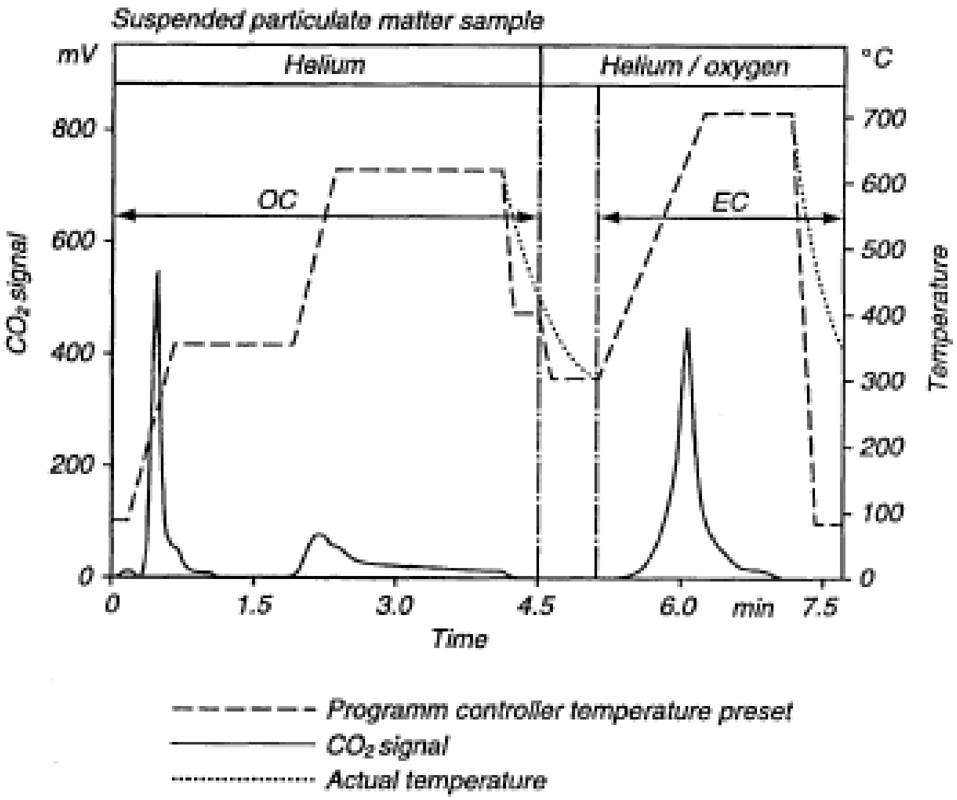
- Interagency Monitoring of Protected Visual Environments (IMPROVE) was developed by several US agencies
- Purpose: Monitoring ambient air quality
- Similar to NIOSH 5040, but other temperature and optical monitoring protocols
- Using Laser reflectance
- Differencing the sample in seven fractions
- The comparability with the TOT-results depends on the analysed material (factor 4) but good for diesel
- There are some doubts regarding the correction by laser



Thermographic – VDI 2465 Blatt 2

- Method for the EC immission quantification
- Filter sample
- Time resolution: hours
- Desorption of OC by heating in an helium atmosphere
- Burning of the EC with helium / oxygen-mixture
- Quantification of CO_2 by a non-dispersive infrared detector (NDIR)

- No correction for charring!

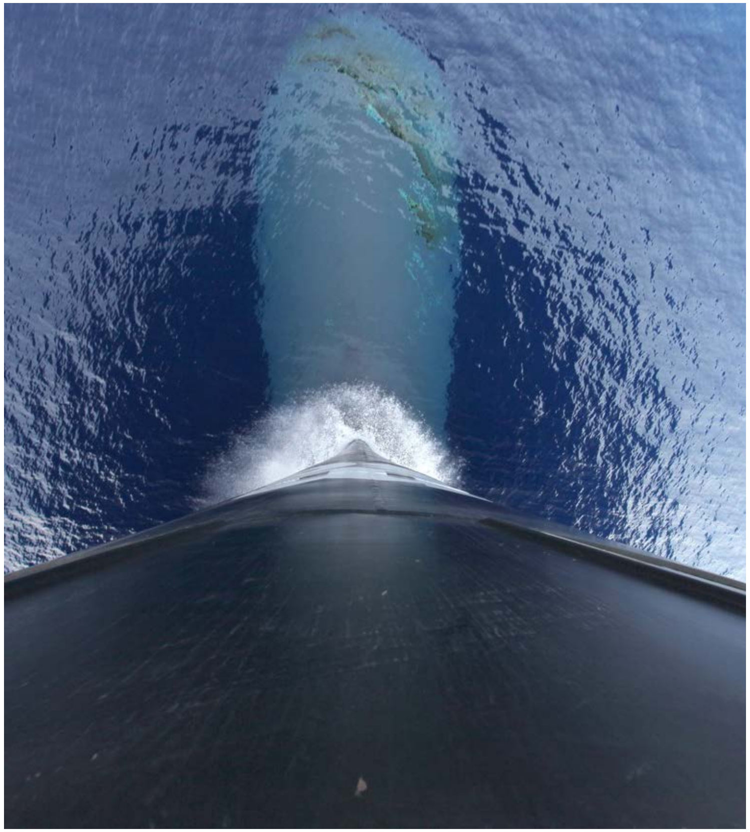


Insolubility

Overview

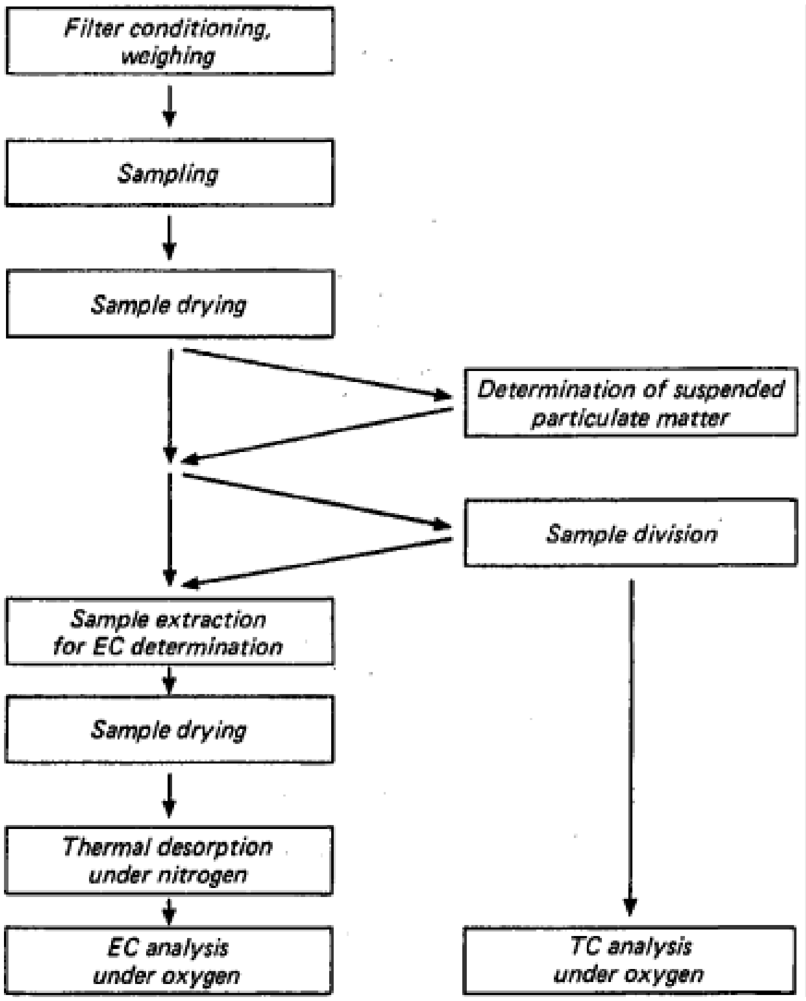
- This property is more or less ignored by the scientific community
- There are some methods to gain OC and the VDI 2465 Blatt 1 for EC
- Apple et al. made one proposal for a two-step extraction process
- Germanischer Lloyd developed a combination of VDI 2465 Blatt 1 and 2

- Filter-based technique
- Time resolution: hours
- Sample will be transferred to shore



Insolubility – VDI 2465 Blatt 1

- Method for the EC immission quantification
- Filter sample
- Liquid extraction by 50:50 vol.% mixture of toluene and 2-propanol
- Heating to 500° C in nitrogen atmosphere and cooling to 200° C
- Burning of the remaining EC by oxygen at 650° C
- Removal of sulphur oxides with silver wool and perhydrit
- Estimation of the produced CO_2 by $Ba(ClO_4)$-solution and titration
- High correlation to results of VDI 2465 Blatt 2



Morphology

Introduction

- Even though the other three properties of black carbon are results of the morphology of black carbon there are just a few techniques to investigate it directly due to several difficulties
- Electron microscopy has shown onion-like layers of graphitic platelets in a disordered and wrinkled structure
- Possibly 'good' instruments and techniques for fundamental research (i.e. combustion optimisation) but not useful for practical / field application
- Three measurement techniques
  - Raman spectroscopy (sometimes referred as regarding the light absorbing property)
  - Transmission / Scanning Electron Microscopy
  - Mass spectrometry

Raman spectroscopy

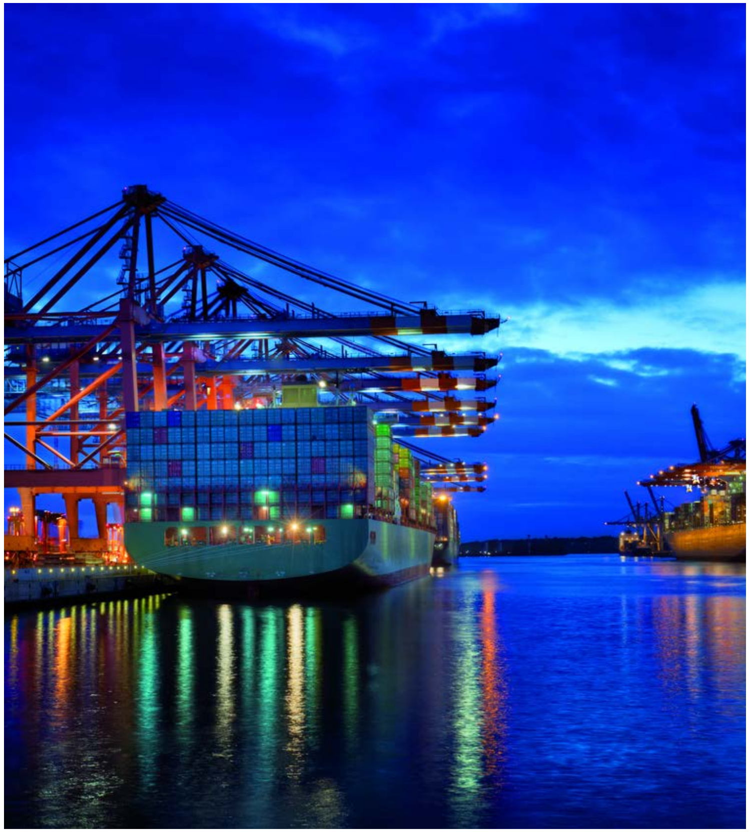
- Raman scattering is the inelastic scattering of a photon
- A small amount of photons are scattered inelastic when interacting with a solid or liquid
- The scattered photons have another frequency

- The Raman scattering depends on several properties of the measuring object, which can be investigated by Raman spectroscopy, e.g. chemical bonds and symmetry of molecules.
- Raman spectroscopy is very selective towards hexagonal lattice structures of SP2- orbital hybridization

- Result: Elemental Carbon!
- It needs a comparable big quantity of sample (filter collection)
- Time resolution: hours

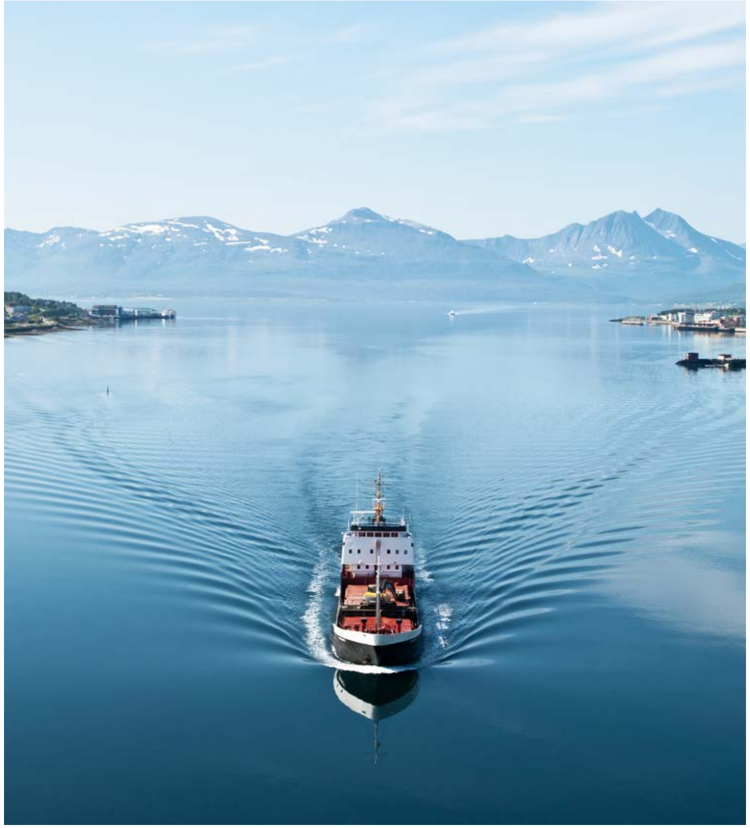
Transmission / Scanning Electron Microscopy

- TEM or SEM images can be used to gain further information about the structure e.g. by the nested square method or the ensemble method
- Expensive and complicated measurement technology
- Not portable
- Filter samples
- Time resolution: hours
- Result: nano spherical-Soot (NS–Soot)



Mass spectrometry

- There are several types of mass spectrometer in use by the atmospheric scientists e.g.
  – Aerosol Mass Spectrometer (AMS / SP-AMS)
  – Aerosol time-of-flight mass spectrometer (ATOMFMS)
- vaporising non-refractory components by heat (LII) and low pressure
- Expensive and not easy to maintain

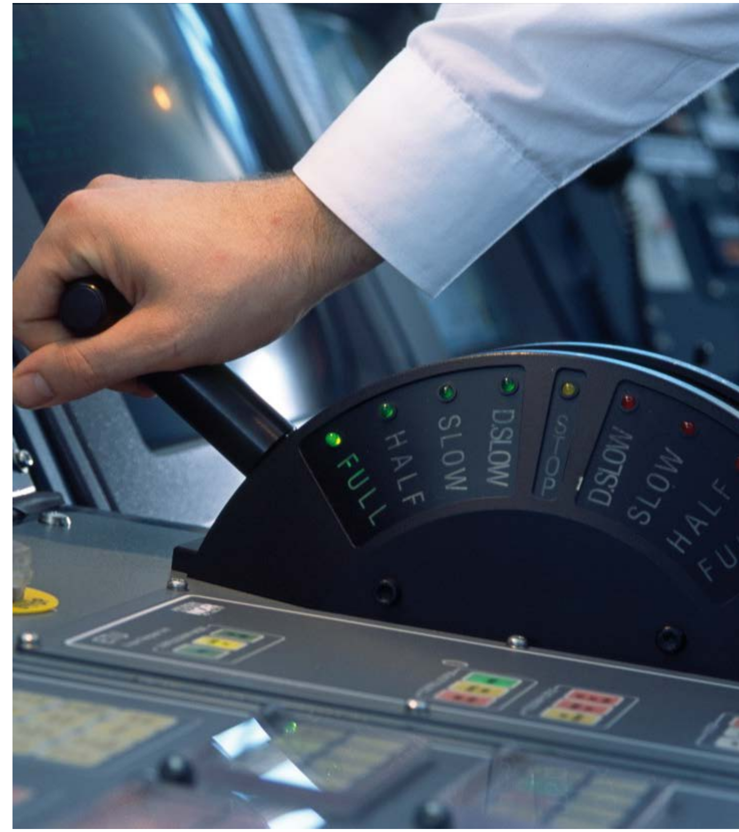


Synopsis

Synopsis

The first analysis of measurement techniques has shown:

- There are many techniques available
- Every technique has it's **bias**
- The measurement result depends on the measurement technique, measurement protocol and calibration method used
- The measurement system has to be chosen according to the **intended use** and measurement place
- correlation from one measurement technique to others is hardly or even not possible.
- High sensitivity on sulphur exists!



- For any intended regulatory purpose, **a standard measurement technique, a test protocol and (a) calibration material has to be defined**

Thank you for your attention!

Torsten Mundt
Torsten.Mundt@dnvgl.com

www.dnvgl.com

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