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Titel der Diplomarbeit

**Untersuchungen von verschiedenen Kohlenstoff-hältigen Aerosolen und
ihrer Temperaturstabilität**

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**Investigation of various carbonaceous aerosols and their temperature
stability**

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Abstract:

Aerosol black carbon (BC, measured by optical techniques) or elemental carbon (EC, measured by thermal or thermal optical techniques), is produced by incomplete combustion of carbonaceous fuels. Brown carbon (BrC), which is part of the organic carbon (OC), is mainly produced by biomass combustion. The importance of BC, EC and BrC is based on their light absorbing characteristics (Bond and Bergstrom 2006) and possible health effects (Kim et al. 2003; Giechaskiel et al. 2009). Despite various method intercomparisons were performed over the last three decades (Watson et al. 2005) no generally accepted standard method exists. In this study the results of a thermal optical method (Sunset Analyzer, Birch and Cary 1996) and optical method (Integrating Sphere, Hitzenberger et al. 1996, Wonaschütz et al. 2009) are compared.

The first experiment consisted of a two months wintertime campaign in Vienna where space heating (also with biomass fuels) increases and therefore also the importance of BrC. The ratio of BC and EC was found to be rather constant except when the contribution of BrC (measured with the modified Integrating Sphere technique) was largest. Since EC was underestimated when BrC increased, it can be deduced that the quantification of EC by the Sunset Analyzer is influenced by the presence of BrC. These results coincide very well with the intercomparison performed by Reisinger et al (2008).

In a second experiment, the effect of inorganic substances (NaCl, ammonium sulfate) and three different BrC proxies (humic acid sodium salt, Leonardite, Pahokee Peat) on the OC/EC split in the Sunset Analyzer were analyzed on laboratory generated samples. Industrial carbon black (Elftex 125, Cabot Corp.) was used as proxy for EC and BC. With regard to the only Elftex analysis, using the automatic setting of the split point is inadvisable. The reason is that the laser signal remains constant till EC combusts and therefore the setting of the split point is performed randomly by the instrument. Measurements of Elftex and NaCl mixtures revealed that Na lowers the combustion temperature of EC from 870 °C to approximately 800 °C. The presence of oxygen in ammonium sulfate falsifies the OC and EC concentrations by releasing O in the pure He cycle and therefore allowing some of the EC to evolve in this first cycle. All three BrC proxies presented massive charring which can increase

the pyrolytically generated EC (PEC). This can further falsely be classified as EC and therefore lead to an overestimation of EC and underestimation of OC. Comparisons between “EC Trans” (corrected by the laser transmittance signal), “EC Refl” (corrected by the laser reflectance signal) and BC yielded lower BC masses at all times. Moreover the comparison of “EC Trans” and “EC Refl” illustrated a linear regression ($R^2=0.92$) with always higher “EC Refl” concentrations.

Zusammenfassung:

Schwarzer Kohlenstoff (BC, mittels optischen Methoden gemessen) beziehungsweise elementarer Kohlenstoff (EC, mittels thermischen oder thermo-optischen Methoden gemessen), entsteht bei der unvollständigen Verbrennung kohlenstoffhaltiger Brennstoffe. Brauner Kohlenstoff (BrC), der ein Teil des organischen Kohlenstoffs (OC) ist, entsteht vor allem bei der Biomasseverbrennung. Auf Grund ihrer Licht absorbierenden Eigenschaften (Bond and Bergstrom 2006) und möglichen Gesundheitsauswirkungen sind BC, EC und BrC von großer Bedeutung (Kim et al. 2003; Giechaskiel et al. 2009). Trotz vieler Vergleichstudien (Watson et al. 2005) konnte bis jetzt noch keine Standardmessmethode gefunden werden.

In der vorliegenden Diplomarbeit werden die Ergebnisse einer thermo-optischen (Sunset Analyzer, Birch and Cary 1996) und optischen Methode (Integrierende Kugel, Hitzenberger et al. 1996, Wonaschütz et al. 2009) verglichen. Im ersten Experiment wurde eine zweimonatige Winter – Messkampagne in Wien durchgeführt. Die Messdaten ergaben konstante BC/EC Verhältnisse an Tagen mit geringer BrC Konzentration, stieg diese aber an, so wurde der EC unterschätzt. Damit kann man davon ausgehen, dass die Anwesenheit von BrC die Quantifizierung von EC beeinflusst. Diese Ergebnisse stimmen mit den Resultaten von Reisinger et al (2008) überein. Um den Einfluss anorganischer Substanzen (NaCl, Ammonsulfat) und dreier BrC Standards (Huminsäure Natriumsalz, Leonardit, Pahokee Peat) auf den OC/EC „split“ im Sunset Analyzer zu prüfen, wurden Laboraerosole generiert. Industrieruß (Elftex 125, Cabot Corp.) wurde als BC beziehungsweise EC Standard verwendet. Bei der Analyse dieser Substanz ist es nicht empfehlenswert den automatisch gesetzten „split point“ zu verwenden. Messungen mit Elftex – NaCl Mischungen ergaben eine niedrigere Verbrennungstemperatur von EC (circa 800°C statt 870°C) auf Grund des Na Einflusses. Die Anwesenheit von zusätzlichem Sauerstoff im Ammonsulfat falsifiziert die OC und EC Konzentration. Alle drei BrC Standards führten zu starker Verkohlung und damit einen höheren PEC (pyrolytisch generierten elementaren Kohlenstoff) - Gehalt. Dies kann wiederum zu einer Überschätzung der EC Konzentration beziehungsweise Unterschätzung des OC führen. Weiters wurden zwei Wege, die Verkohlung zu korrigieren, verglichen. Wird die Korrektur mit einem transmittierten Laserstrahl („trans“) durchgeführt, erhält man in allen Fällen niedrigere EC Massen als bei einer Korrektur mit einem reflektierten Laserstrahl

(„refl“). Die lineare Regression ergab einen Korrelationskoeffizienten von $R^2=0.92$, wobei die “EC Refl” Werte immer über den “EC Trans” Werten lagen.

ACKNOWLEDGEMENTS.....	I
ABSTRACT:.....	II
ZUSAMMENFASSUNG:	IV
1. INTRODUCTION:.....	1
2. CARBON IN ATMOSPHERIC AEROSOLS:.....	2
2.1. TERMINOLOGY	2
2.2. BLACK CARBON – ELEMENTAL CARBON – SOOT	3
2.3. ORGANIC CARBON	5
2.4. BROWN CARBON	6
2.5. ATMOSPHERIC CONCENTRATIONS OF BC (EC) AND OC	7
2.6. SIZE DISTRIBUTIONS	10
2.7. OPTICAL PROPERTIES	11
2.7.1. Extinction:	11
2.7.1.1. Extinction Efficiency:	12
2.7.1.2. Extinction Coefficient:	13
2.7.2. Scattering:	14
2.7.2.1. Rayleigh Theory:.....	14
2.7.2.2. Mie Theory:.....	16
2.7.3. Absorption:.....	18
2.7.3.1. Index of Refraction:	19
2.7.3.2. Absorption Efficiency:	20
2.7.3.3. Absorption Coefficient:.....	21
2.8. OPTICAL PROPERTIES OF BRC	22
2.9. THERMAL PROPERTIES	23
2.10. IMPACT OF BC (EC), OC AND BRC ON CLIMATE AND HEALTH.....	23
2.10.1. Climate:	23
2.10.2. Health:.....	25
3. MEASUREMENT TECHNIQUES:.....	29
3.1. OVERVIEW	29
3.2. THERMAL OPTICAL MEASURING METHOD	29
3.2.1. Instrument Setup:	30
3.2.2. Measurement Procedure:	32
3.2.3. Calibration:	35
3.2.4. Temperature Protocol:	37
3.3. OPTICAL MEASURING METHOD	38
3.3.1. Instrument Setup:	38
3.3.2. Measurement Procedure:	40
3.3.3. Sample Preparation:	41
3.3.4. Calibration and Conversion to $\mu\text{g BC}$:	41
3.3.5. Separation of BC and BrC:	44
3.3.6. Advantages and Disadvantages of the IS:.....	44
4. EXPERIMENTAL SETUP:	47
4.1. ATMOSPHERIC AEROSOLS	47
4.1.1. Sampling site and period:	47

4.1.2. Sampling method:.....	48
4.2. LABORATORY GENERATED AEROSOLS	49
4.2.1. Production:.....	51
4.2.2. Sampling methods:	51
4.2.2.1. Nebulizing a suspension:.....	52
4.2.2.2. Spiking the filter punches directly with the analytes:	53
5. RESULTS.....	55
5.1. ATMOSPHERIC AEROSOLS:.....	55
5.1.1. Winter aerosols analyzed in the IS:.....	55
5.1.2. Winter aerosols analyzed in the Sunset Analyzer:	56
5.1.3. Comparison of the measurement techniques:	57
5.1.3.1. Influence of the BrC in the BC/EC measurement:	58
5.1.3.2. Comparison of EC and BC:.....	60
5.2. LABORATORY GENERATED AEROSOLS:.....	63
5.2.1. Analysis in Sunset Analyzer and Integrating Sphere:	63
5.2.1.1. Influence of BrC proxies on OC/EC split:	63
5.2.1.2. Influence of inorganic substances on EC:	69
5.2.1.2.1. Influence of oxygen containing compounds on EC:	71
5.2.1.2.2. Influence of Na on EC:.....	72
5.2.1.3. Influence of inorganics on mixtures:.....	73
5.2.1.4. Contribution of EC to BrC measurements:	75
5.2.2. Comparison of “EC Reflectance” to “EC Transmittance”:.....	77
6. CONCLUSIONS.....	79
REFERENCES	81
LIST OF FIGURES:	87
CURRICULUM VITAE:.....	89

1. Introduction:

Aerosols are defined as suspended solid particles in a gas or a liquid. Atmospheric aerosols consist of more than one constituent and in the majority of cases an anthropogenic ambient aerosol is a mixture of sulphate, nitrate, ammonium, trace metals and carbonaceous compounds (Seinfeld and Pandis 1998). Though carbonaceous matter is just a fraction of the atmospheric aerosol, it plays an important part in both climate and health effects. Therefore this study will mainly focus on black, elemental, organic and brown carbon which are the most important carbonaceous fractions.

To determine the different fractions of carbonaceous material is a real challenge since no standard method exists. Nevertheless there is a great number of measurement techniques either based on an optical, thermal or thermal optical method. Numerous intercomparisons (e.g. Watson et al. 2005; ten Brink et al. 2004) between the techniques showed little differences with regard to total carbon (TC) concentrations. Considering the elemental carbon (EC) or black carbon (BC) fraction differences up to a factor of 3 or 4 depending on aerosol characteristics, age and size distribution occur. A very difficult task is to perform the split between EC and organic carbon (OC). Moreover in recent years the influence of brown carbon (BrC) both in optical and thermal analysis is being studied.

The results of the methods depend on aerosol type. Hitzenberger et al. (2006) performed a summer study in the urban area of Vienna comparing most methods for EC and BC determination. The results obtained with different methods agreed within their standard deviation. As opposed to this, the study by Reisinger et al. (2008) conducted under wintertime conditions displayed large discrepancies between the EC and BC concentrations. During summer months diesel traffic is the major source for EC and BC in Vienna, whereas in wintertime an additional source exists, namely space heating. In this latter process significant amounts of BrC are released which interfere with the EC/BC measurements.

The goal of this study is on the one hand to determine the influence BrC has on the EC/BC measurement during wintertime and on the other to better understand how specific substances alter the measurements in the thermal optical method (Sunset Analyzer).

2. Carbon in atmospheric aerosols:

2.1. Terminology

Carbon is a very important component of the atmospheric aerosol. The elemental carbon (EC) mass fraction is not really significant (ca. 5-15% Schaap et al. 2004), whereas the sum of the elemental and organic carbon mass fractions can represent up to about 50% of the aerosol mass concentration (Gelencsér 2006). This fractional amount plays an important part considering climatic and health effects but it always differs with regard to time, place and meteorological situation. Depending on which measurement procedure and carbonaceous fraction we are dealing with, we can define several types of carbonaceous aerosols:

- Black Carbon (BC) is the result of incomplete combustion of carbonaceous fuels. As the word “black” suggests, BC absorbs light and can therefore be measured by optical instruments.
- Elemental Carbon (EC) should be equivalent to BC but is measured with thermal or thermal optical techniques.
- Brown Carbon (BrC, C_{brown}) is part of the organic carbon but shows light absorption especially in the shorter wavelength range (blue light). It is consequently measured by optical techniques.
- Organic Carbon (OC) denotes the carbon amount present in organic compounds. It is measured by thermal or thermal optical techniques because it can be distinguished from BC or EC due to its small temperature resistance.
- Carbonate Carbon (CC) is part of inorganic carbon.
- Total Carbon (TC) is the sum of OC, EC and CC and can be measured by e.g. a thermal or thermal optical technique.

2.2. Black Carbon – Elemental Carbon – Soot

Mostly the terms BC, EC or soot are used interchangeably. The amount of BC, gained by an optical technique and EC, obtained by a thermal method, should be comparable. Nonetheless several intercomparison studies showed that analyzing the amount of BC and EC by different methods, the results deviate up to a factor of 2 or more (Schmid et al. 2001; ten Brink et al. 2004). The term soot is more common in everyday language but it actually consists for the most part of BC or EC and several organic compounds (Seinfeld and Pandis 1998). Here I will use the term EC when I am referring to the amount obtained by the thermal optical technique (Sunset Analyzer), and BC for the amount measured with the optical method (Integrating Sphere).

As mentioned before, BC originates mostly from incomplete combustion of fossil fuels but also from wood combustion, though in a much lower quantity. Besides, there is another anthropogenic source, namely the abrasion of car tires, which emits a small amount of industrially generated “carbon black”. This type of carbon ranges from 10 to 50 μm and occurs mainly in the vicinity of traffic sites (Schultz 1993).

Considering biomass burning, black carbon as well as organic carbon is emitted. K and Na, which are commonly present in biomass smoke, lower the combustion temperature of EC in a way that the split between OC and EC gets a lot trickier. They undertake the role as catalyst which finally leads to an underestimation of OC and overestimation of EC (Novakov and Corrigan 1995).

The specific conditions under which the combustion takes place determine the composition of the resulting particles. Soot particles comprise agglomerates of small spherical graphitic particles of several nanometers in size (see figure1). Besides, carbon can also be found in its purest forms as diamond or mineral graphite (Watson et al. 2005).

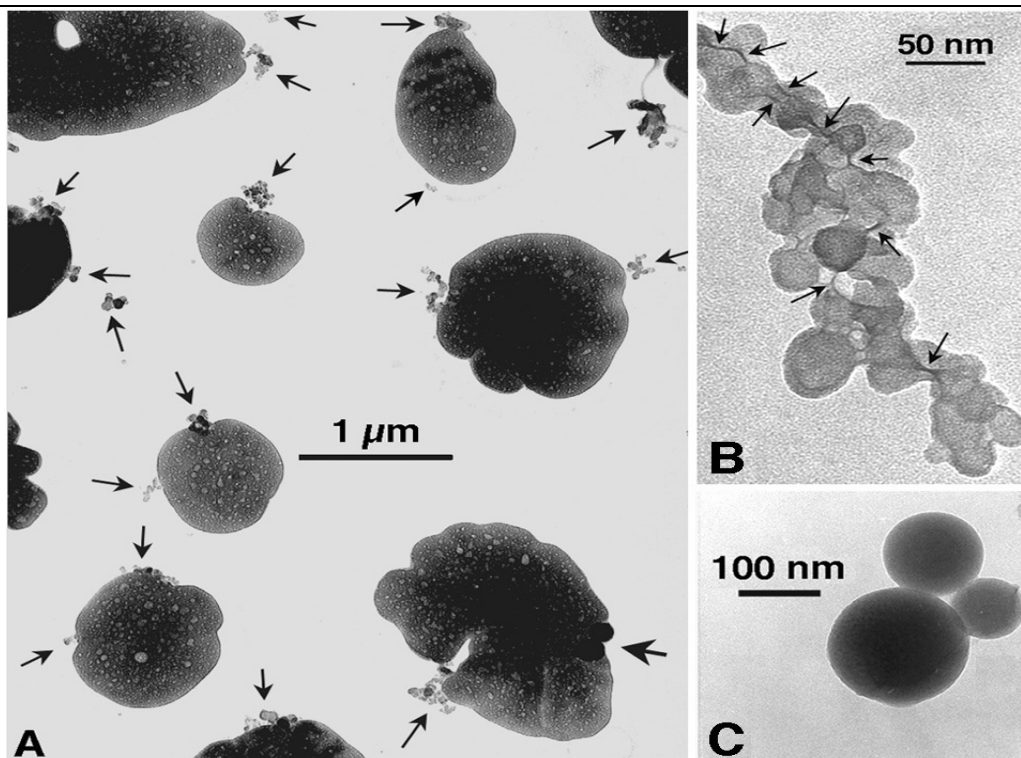


Figure 1: A shows how soot particles (arrows) are annexed on air droplets, B illustrates the detailed composition of soot and C shows flue ash which is a byproduct of combustion.
(Source: <http://www.raumfahrer.net/news/astronomie/11042009163016.shtml>)

As mentioned before combustion is the main source of carbonaceous aerosols. Therefore a more accurate explanation of the combustion process is necessary (Burtcher 1992) to understand the development of these aerosols.

Firstly pyrolysis of combustible molecules yields many different chemicals, particularly acetylene, hydrocarbon radicals and different unsaturated aliphatic and aromatic compounds. These substances further become macromolecules as a consequence of polymerization. In this step, aromatic compounds play a decisive role because they are supposed to stabilize radicals, which is important for the growth processes. Besides also ionic reactions seem to influence the soot formation. Primary soot particles are formed in the so called “nucleation zone”. Afterwards these particles start to grow due to condensation of products from the vapor phase and coagulation and finally become spherical (see figure 2). When all condensable material is exhausted agglomeration prevails and primary particles reach diameters between 20 and 50nm. While the size distribution in the “nucleation zone” is roughly Gaussian, it changes to a log-normal distribution when agglomeration predominates. The structure of the particles is similar to

graphite which is very probably caused by polyaromatic hydrocarbons (PAH). Finally particles pass to the “oxidation zone” where they will either undergo a total or partial combustion depending on temperature and oxygen conditions. If, for example, temperature and oxygen concentration are fairly low, particles do not combust completely. Ultimately, the crucial factor to determine how many particles are emitted is the coagulation and not the initial amount of particles generated.

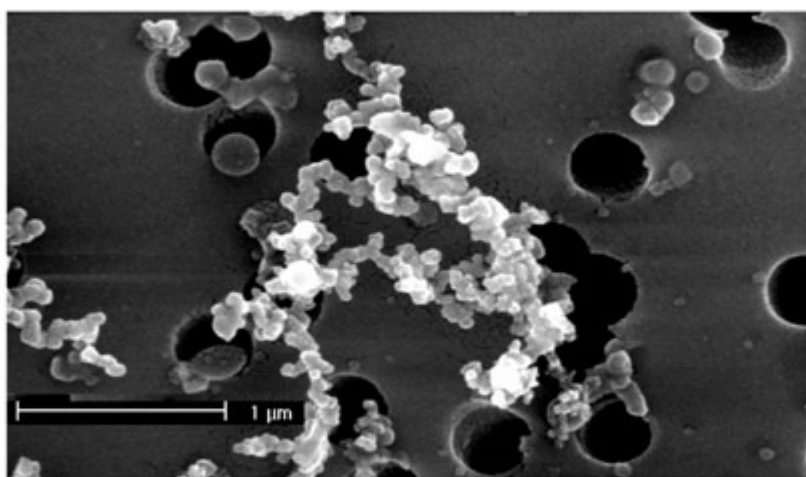


Figure 2: soot particles on a nucleopore filter seen under an electron microscope;
(Source:
<http://www.mpg.de/bilderBerichteDokumente/dokumentation/jahrbuch/2003/chemie/forschungsschwerpunkt/abbildung2.jpg>)

2.3. Organic Carbon

Organic Carbon (OC) is the carbon fraction present in organic compounds. Usually OC constitutes 10 to 50% of the atmospheric organic mass concentration, depending on the source (Seinfeld and Pandis 1998). The composition of the organic carbon part of an aerosol is rather complex since it is a mixture of hundreds of different organic compounds. Organic Carbon is either emitted directly into the atmosphere (primary OC), e.g. by combustion or from natural sources, or formed by condensation of products of the photo-oxidation of hydrocarbons (secondary OC). Common sources include combustion of fossil fuels or biomass, bubble bursting processes which release organic matter into the

atmosphere from the ocean surface and the *gas-to-particle conversion* of volatile organic compounds (VOC) mostly emitted by motor vehicles.

Another interesting fact is that OC shows very little temperature stability. With regard to thermal measurement techniques, the charring of OC has to be considered. Some OC constituents of atmospheric aerosols have a propensity to char during the heating process forming pyrolytically generated EC (PEC) (Yu et al. 2002). This newly produced type of EC can bias the amount of OC and EC when using the wrong charring correction, by overestimating the amount of EC and underestimating the OC or vice versa. According to Yu et al. (2002) the amount of PEC is influenced by the amount of OC present on the filter, as well as the temperature steps used in the thermal treatment and the residence time at each step. Furthermore also inorganic components and the carrier gas have an influence on the charring process. If, for example, the filter contains starch or cellulose and ammonium bisulfate (inorganic component) the amount of PEC increases, whereas if laevoglucosan and ammonium bisulfate are present the PEC amount is reduced. A quantification of this portion of PEC is very difficult. Nevertheless Yu et al. (2002) found out that 13 to 66% of PEC is due to the water soluble organic carbon fraction (WSOC). Besides they noticed a linear increase of charring with the WSOC loading up to a certain point that differs from sample to sample and afterwards the percentage of charring stays relatively constant.

With regard to optical properties, OC can be divided in two main parts: the fraction which doesn't show any absorption of visible light is referred to as organic carbon (OC) whereas the absorbing part is called brown carbon (C_{brown} , BrC).

2.4. Brown Carbon

According to Havers et al. (Havers et al. 1998) BrC accounts for about 10% of the total organic carbon present in the atmospheric aerosol. It comprises all humic- like substances (HULIS) as well as bio - aerosols and soil humics (Andreae and Gelencsér 2006). Mostly these humic like particles contain a large water soluble fraction and have light absorbing properties. The main sources of BrC are biomass fires, atmospheric reactions (Graber and Rudich 2006; Gelencsér et al. 2007) and plant degradation products (Likens et al. 1983). Humic Acid Sodium Salt (HASS) is commonly used as a proxy for

BrC because it shows very similar characteristics as the extracts from biomass burning smoke particles.

As noted before the most important aspect of BrC is its light absorption ability. Especially the BrCs' characteristic to absorb better at shorter wavelengths facilitates the separation of BrC and BC. Besides, as the name already suggests BrC is a brownish substance mix.

2.5. Atmospheric Concentrations of BC (EC) and OC

Determining the concentrations of carbonaceous chemical compounds in the atmosphere is quite difficult because they change with weather conditions and characteristic site. In addition every combustion process emits a different amount of carbon. Nowadays the global annually emitted black carbon (BC) and OC are estimated to be around 8.0 tera grams (Tg) and 33.9 Tg, respectively (Bond et al. 2004). In these estimates, emissions from fossil fuels, biofuels, open biomass burning and burning of urban waste were included. Compared to earlier estimates, these values are lower by 25 to 35 %. With regard to BC, 42 % derive from open burning, 38 % from fossil fuels and 20 % from biofuels. However 74 % of the OC constituents are produced from open burning, 19 % from biofuels and 7 % from fossil fuels.

Comparing urban to rural areas one will find that urban areas have a much higher concentration of BC originating from diesel engines whereas rural areas show higher BC concentrations deriving from biomass fires. This trend can also be found globally: in the northern hemisphere the main source of BC consists of fossil fuel combustion and in the southern hemisphere wood burning prevails (Seinfeld and Pandis 1998).

The studies performed by Putaud et al. (2010) investigate the particulate matter (PM) 2.5 and PM10 mass concentrations, particle number and aerosol composition data for several sites across Europe. PM2.5 and PM10 include all particles with an aerodynamic diameter (see section 2.6 for definition) smaller than 2.5 μm and 10 μm , respectively. The EC and OC contribution differs depending on the sampling site. However for Central Europe, which includes Austria, EC contributions to PM10 are around 6 % in rural surroundings, 10 % at urban and 17 % at kerbside sites. With regard to OC, the contribution of organic matter (OM), which is calculated from the OC, is given

as 23 % in rural regions, 21 % at urban sites and 21 % in kerbside areas. PM_{2.5} contains 5 % of EC and 15% of OM in rural areas, 14 % EC and 22 % OM in urban regions and 21 % EC and 26 % OM at kerbside sites. PM₁₀ mass concentrations in Central Europe range from 10 µg/m³ at rural sites, to 54 µg/m³ in kerbside areas and for PM_{2.5} concentrations range from 5 µg/m³ in rural surroundings, to 25 µg/m³ in urban regions.

Figure 3 and 4 illustrate the percentage of the most important constituents (mineral dust, sea salt, sulfates, nitrates, organic matter, elemental carbon and total carbon) in the urban central European atmospheric aerosol (PM_{2.5} and PM₁₀).

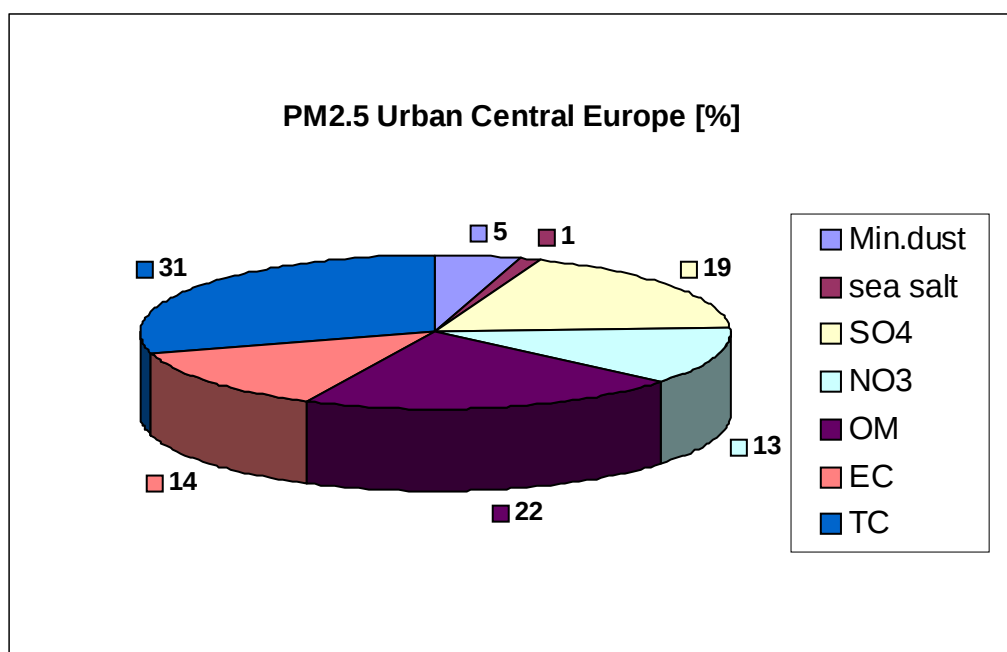


Figure 3: The composition of the PM_{2.5} urban atmospheric aerosol in central Europe according to the study performed by Putaud et al.
(Source: Putaud et al. 2010)

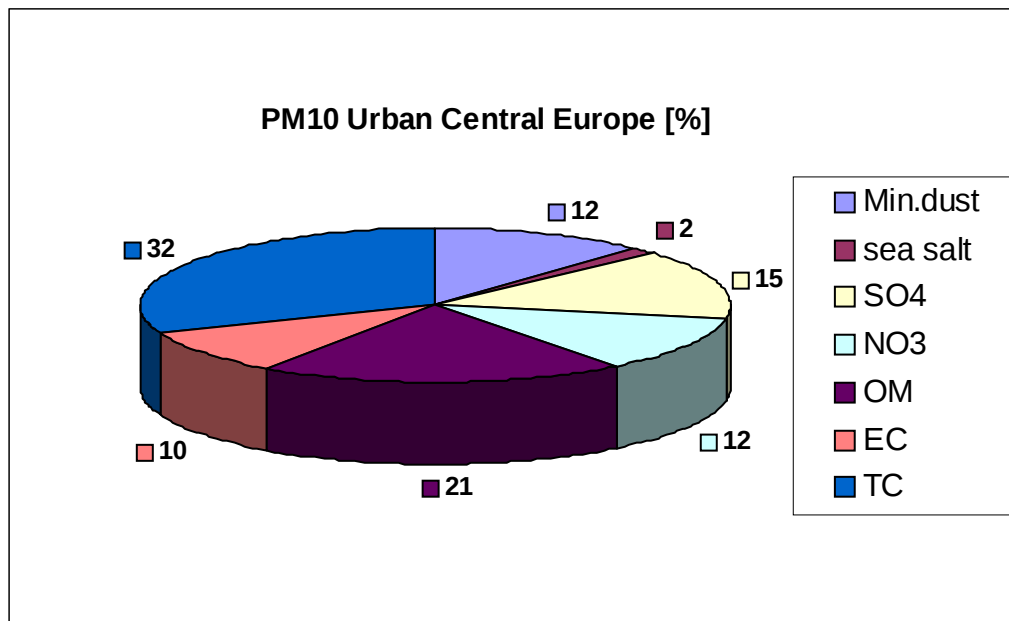


Figure 4: The composition of the PM10 urban atmospheric aerosol in central Europe according to the study performed by Putaud et al.
(Source: Putaud et al. 2010)

Another investigation which took place in Vienna in the years 1998/1999 showed a total mass concentration of approximately $60 \mu\text{g}/\text{m}^3$ in wintertime and around $34 \mu\text{g}/\text{m}^3$ in summertime, with a BC contribution of 11 % during the winter months and 9 % in summer (Hitzenberger and Tohno 2001). These seasonal patterns originate in the different activities of soot sources.

The concentration of carbonaceous aerosols also depends on the precipitation rate which is the predominant way to remove them from the atmosphere. This sink, where rain droplets carry the carbonaceous aerosols to the ground is referred to as wet deposition. While a freshly emitted carbon containing aerosol is actually hydrophobic, in consequence of the aging process most aerosols become hygroscopic (Smith et al. 1989; Chughtai et al. 1996; Weingartner et al. 1997). Moreover small particles can easily become cloud condensation nuclei and thus have a substantial effect on cloud properties and the initiation of precipitation (Hallett et al. 1989; Lammel and Novakov 1995). This depends on the chemical composition and size of the aerosol. A small quantity of particles is removed by dry deposition through sedimentation, if the particles are big enough, or diffusion processes. Usually soot particles have tropospheric residence times of about a week before they are finally washed out (Seinfeld and Pandis 1998).

2.6. Size Distributions

The atmosphere contains 10^3 to 10^8 particles per cubic centimeter, depending on the sampling sites. Their sizes range from some nanometers up to $100\text{ }\mu\text{m}$. Carbonaceous aerosols produced in combustion with sizes varying from a few nanometers to $1\text{ }\mu\text{m}$ (Seinfeld and Pandis, 1998) are of our special interest here. The most important parameter to characterize the size of a particle is its diameter. In this regard the definition of the equivalent aerodynamic diameter should be introduced, which is defined as the diameter of a completely spherical particle with the density of 1000 kg/m^3 and the same settling velocity as the aerosol particle in question.

There are different parameters, dependent on the particle diameter, which are necessary to obtain a distribution: One option is to take a certain air – volume with a certain number of particles having diameters in the range of D_p (particle diameter) to D_p+d D_p and calculating the concentration. By plotting it as a function of D_p a number size distribution n_N follows. Other common distributions are surface area and volume size distributions, meaning the total surface area (or volume) of particles per cm^3 of air having diameters in the range of D_p to D_p+d D_p plotted as a function of D_p . Besides if all particles have a known density, a mass size distribution can be obtained as well.

The most convenient types of size distributions for aerosols are the lognormal size distributions because they can handle the wide range of aerosol diameters (Hinds 1999). Other distributions, which were used in past years, are the power – law and the modified gamma distribution (Seinfeld and Pandis 1998). The characteristic parameters of the log normal mass size distribution functions are the mass median diameter (MMD), the geometric standard deviation (σ_g) and the total modal mass concentration (c_m).

As an example for a typical size distribution the results of Hitzenberger et al.'s (2006) study are presented here. The mass log normal size distributions of two campaigns performed in winter 2004, one in Vienna and one in Ljubljana (Slovenia) are compared. To quantify the differences, the log normal distributions were fitted to the impactor histograms by an iterative procedure originally described by Lürzer (1980). All samples were analyzed for TC, BC, major inorganic ions and short chain organic acids. To give an

idea of an average size distribution for central Europe, in the table below the MMD, σ_g and total modal concentration c_m for the most important fractions are listed.

Campaign average mass median diameter d , geometric standard deviation σ_g and total modal concentration c_m for major species

Component	Vienna			Ljubljana		
	d (μm)	σ_g	c_m ($\mu\text{g m}^{-3}$)	d (μm)	σ_g	c_m ($\mu\text{g m}^{-3}$)
Total mass	0.43	2.08	29.02	0.55	1.93	29.20
TC	0.41	2.18	5.51	0.44	2.07	6.68
Sulfate	0.48	2.01	4.32	0.60	1.79	4.53
BC	0.38	2.23	1.52	0.42	2.34	1.77

(Source: R. Hittenberger et al. 2006)

2.7. Optical Properties

In this section an overview of the most important optical features of soot particles will be given (Hinds 1999). These characteristics are used in most optical measurement techniques. Furthermore these optical properties are necessary to understand the interactions between carbonaceous aerosols and climate. Considering the light spectrum, it is just the visible range with wavelengths between 400 nm (violet) and approximately 700 nm (red) that will be referred to.

2.7.1. Extinction:

Extinction describes the attenuation of a light beam as a consequence of scattering and absorption by the particles. Both processes affect the atmospheric visibility and explain phenomena such as a red sky. The decrease of intensity can be calculated by the Lambert – Beer law:

$$\frac{I}{I_0} = e^{-\sigma_E L} \quad 2.1$$

I_0 expresses the intensity of the incident light beam and I is the intensity of the beam that passed through the aerosol. σ_E is called the *extinction coefficient* [m^{-1}] (see section 2.7.1.2) of the aerosol and L the path length of the light beam through the aerosol. As mentioned above the two reasons for extinction are the absorption of light by the particle and the scattering of the incident light beam by the particle. The former implies a conversion of the beam's energy into heat but only aerosols made of absorbing material can absorb light while all aerosol particles can scatter light.

2.7.1.1. *Extinction Efficiency:*

To describe the meaning of extinction, the particle extinction efficiency Q_e should be introduced:

$$Q_E = \frac{\text{radiant power scattered and absorbed by a particle}}{\text{radiant power geometrically incident on the particle}} \quad 2.2$$

The denominator describes the energy per second intercepted by the geometric cross section of the particle A_p and the numerator the amount of energy removed from the beam by scattering and absorption. This efficiency is a dimensionless number and strongly dependent on the particle size, wavelength of the incident light and complex refractive index of the particle.

The extinction efficiency is the sum of the scattering efficiency Q_s and absorption efficiency Q_A :

$$Q_E = Q_s + Q_A \quad 2.3$$

Non – absorbing particles in the size range between 0.3 and 1 μm have a peak value of Q_E of about 4 with oscillations. In contrast, absorbing particles and particles with diameters (d) larger than 4 μm have a maximum of $Q_E = 2$ without oscillations. This convergence to a value of 2 is referred to as *extinction paradox*. It means that very large particles, if observed at distances large compared to 10 times d^2/λ , where λ is the wavelength of the incident light, remove an area twice their projected area.

These values depend on the incident wavelength and the refractive index of the particles. The stated values are valid for $\lambda=0.52 \mu\text{m}$.

2.7.1.2. *Extinction Coefficient:*

The extinction coefficient of a monodisperse (particles are all of the same size) aerosol with diameter d of N particles per unit volume can be obtained by:

$$\sigma_E = N \cdot A_p \cdot Q_E = \frac{\pi N d^2 Q_E}{4} \quad 2.4$$

A_p is again the cross – sectional area of the particle. The extinction coefficient consists of the sum of the scattering (σ_S) and the absorption coefficient (σ_A):

$$\sigma_E = \sigma_S + \sigma_A \quad 2.5$$

This can be derived from equation 2.1: Firstly 2.1 has to be expressed once for the scattering and once for the absorption coefficient. To obtain the decrease of intensity due to extinction, both exponential functions have to be considered which finally leads to:

$$I = I_0 \cdot e^{-L(\sigma_S + \sigma_A)} \quad 2.6$$

Both σ_S and σ_A are defined equivalently to equation 2.4 substituting Q_E by Q_S and Q_A , respectively. In the case of a polydisperse aerosol, the size distribution of the aerosol and the dependence of the extinction efficiency on the different particles require integrating the results for equation 2.4 over the entire size range.

2.7.2. Scattering:

Scattering describes the interaction between an aerosol particle and a light beam as an electromagnetic wave. To analyze this process the particle diameter (d) and the wavelength of the incident light (λ) play a very important role. The size parameter α is proportional to the ratio of these two quantities:

$$\alpha = \frac{\pi d}{\lambda} \quad 2.7$$

The general theory to describe scattering is the Mie – theory but depending on the size parameter also limiting cases can be used to facilitate the calculation of the resulting equations to determine the angular distribution of scattered light. In the case of a large α , which means that the diameter is rather large (more than 100 μm) and the wavelength short, the theory of geometric optics can be applied (reflectance, refraction). In the visible light range and if diameter and wavelength are both between 0.05 μm and 100 μm , Mie – theory is applicable. The last theory, namely Rayleigh – theory, deals with much larger wavelengths compared to the particle diameter which will be smaller than 0.05 μm .

For large soot particles and visible light, mainly Mie - theory applies.

2.7.2.1. *Rayleigh Theory:*

The interaction between the incident light beam (electromagnetic wave) and the particle creates a dipole which oscillates in synchronization to the surrounding electromagnetic field initialized by the light wave. In addition to this, the newly created dipole now emits electromagnetic energy in all directions. The intensity, which is a function of the scattering angle Θ , can be described as follows:

$$I(\Theta) = \frac{I_0 \pi^4 d^6}{8R^2 \lambda^4} \left(\frac{m^2 - 1}{m^2 + 2} \right)^2 \cdot (1 + \cos^2 \Theta) \quad 2.8$$

for $d < 0.05 \mu\text{m}$ and visible light

$I(\Theta)$ is the total intensity at of the light scattered in the direction Θ a specific distance R from the particle with a diameter d . m denotes the complex refractive index of the particle and λ the wavelength of the light beam.

As we can see clearly in this equation (2.8), the intensity of the scattered light is proportional to d^6/λ^4 which describes very well the much stronger scattering of short wavelengths (blue) as opposed to long wavelengths (red). This is the reason why the sky appears blue. Rayleigh scattering further depends on the particle volume squared. The scattering angle dependence of the intensity is represented in the latter term of the equation. The scattered light is composed by two intensity components: one is polarized perpendicularly (I_1) and the other one parallel (I_2) to the scattering plane. The first is in fact independent of the scattering angle while the parallel one is proportional to $\cos^2 \Theta$. Therefore this latter part becomes zero in case of $\Theta = 90^\circ$ or $\Theta = 270^\circ$ and reaches its maximum at 0° and 180° .

In the figure below (figure 5) one can see a polar diagram of Rayleigh scattered light. The most important attribute is the symmetrical scattering in both the forward and rear hemispheres, which implies that the same amount of light is distributed in both directions.

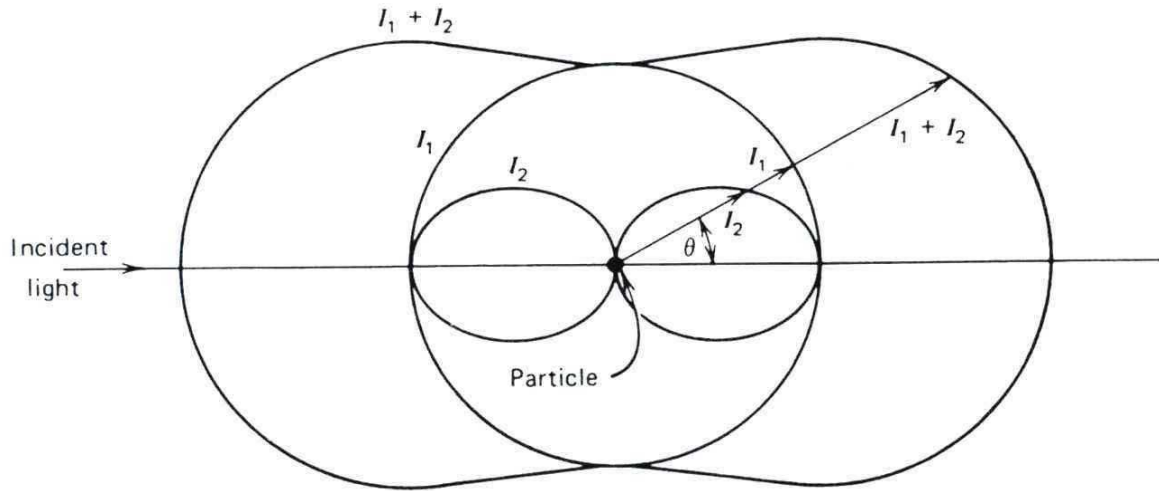


Figure 5: Polar diagram of Rayleigh scattered light. Scattering plane is parallel to the paper.
(Source: Hinds 1999: figure 16.7)

2.7.2.2. *Mie Theory:*

This theory is named after Gustav Mie, a German physicist who provided a theoretical description to understand the interaction between electromagnetic waves with spherical, isotropic particles. Since aerosol particles are ideally seen as such, this theory offers the best description. Rayleigh theory and geometric optics represent mainly the extremes of Mie theory, one for very small particles and the other for very large ones. The Mie equations are the exact solutions of Maxwell's electromagnetic equations in the far field of the particle.

The interaction can be described very similarly to Rayleigh theory (2.7.2.1.): when the particle is illuminated by the incident light (electromagnetic wave) it behaves like an oscillator. Mie theory is needed for larger particles ($\alpha > 0.3$), consequently the oscillating object is further seen as a multipole which radiates so called secondary partial waves in all directions. For non – polarized light with an initial intensity equivalent to I_0 [W/m²], the intensity which is dependent on the scattering angle is given by:

$$I(\Theta) = \frac{I_0 \lambda^2 (i_1 + i_2)}{8\pi^2 R^2} \quad 2.9$$

Where R is the distance from a spherical particle, λ the wavelength of the incident light and i_1 and i_2 are the Mie intensity functions for scattered light with perpendicular (i_1) and parallel (i_2) polarization. These intensity functions depend on the complex index of refraction m , the size parameter α and the scattering angle Θ . The most significant parameter in scattering processes is the scattering efficiency Q_s (see section 2.7.1.1) together with the scattering cross section which is necessary to calculate Q_s . This scattering cross section is defined as scattered light intensity ($I(\Theta)$) in Watts per square meters and steradian divided by incident light intensity (I_0) in Watts per square meters, and can therefore be calculated as follows:

$$\sigma(\Theta) = \frac{I(\Theta)}{I_0} \cdot R^2 = \frac{\lambda^2 \cdot (i_1 + i_2)}{8\pi^2} \quad 2.10$$

By integrating over the whole solid angle, the total scattering cross section can be determined and finally also the total scattering efficiency Q_s :

$$Q_s = \frac{\sigma_s}{\frac{\pi d^2}{4}} = \frac{1}{\alpha^2} \int_0^\pi (i_1 + i_2) \sin \Theta d\Theta \quad 2.11$$

In the following figure (figure 6) the strong angular dependence of the Mie scattering and the very strong forward scattering is observable.

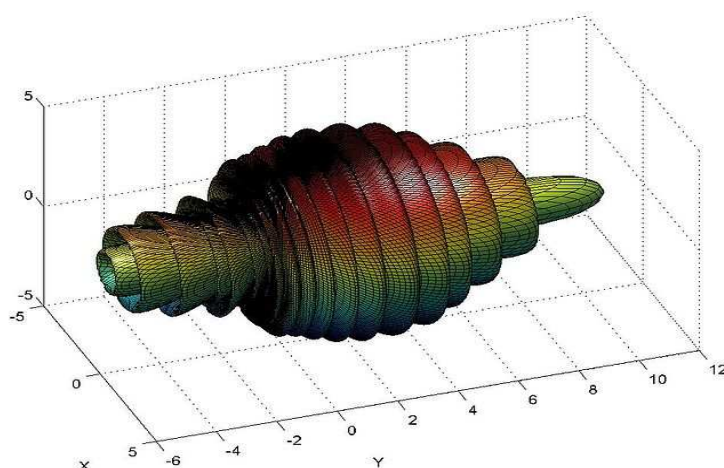


Figure 6: Mie scattering of light ($\lambda=633\text{nm}$) by a spherical particle ($d=2\mu\text{m}$); $\alpha=9.92$; one can clearly see the intensities at different scattering angles (note the logarithmic axes).

(Source:

http://de.wikipedia.org/w/index.php?title=Datei:3D_Miestreuung_an_2um_Kugel.jpg&filetimestamp=20060712110500)

2.7.3. Absorption:

During absorption of a light beam, a particle absorbs the incident photons and converts them into thermal energy. As conveyed in the term photon, quantum theory and changes in energy states are required to describe this phenomenon. There are three main internal energies present in the molecules namely the rotational, the vibrational and the electronic energy (McCartney 1976). Besides also the kinetic energy of the molecular translation has to be considered. All these energies have to be quantized to discrete, permitted levels. Conversely to the explanation of the scattering process, also the incident light must be quantized. The absorption event can now be explained as a transition from a lower level to a higher state of one of the three inner energies. The process is discontinuous due to the quantization and spectrally seen it is selective because only quanta whose energies are the same as the differences between permitted levels can be absorbed. Resulting from molecular motion and collisions, the internal

energies can be exchanged for translational energy and vice versa. Or more specifically, molecules at higher levels are deexcited to lower levels and molecules at lower levels are excited to upper levels by collisions. The upper levels are principally instable; hence quanta of radiant energy are emitted. This process can either be spontaneous, as it usually is for atmospheric aerosols, or stimulated. The energy emitted by the quanta equals the difference between the initial and the final energy level.

Taking a closer look at ambient aerosols, we find that soot particles are the most significant absorbers of visible light. This fraction is referred to as black carbon (BC). Given that the magnitude of absorption is practically the same for all wavelengths in the visible light spectrum, BC can be measured by optical techniques.

2.7.3.1. Index of Refraction:

The refractive index explains to which extent the phase velocity of a wave is reduced passing from one medium to another. The real part of the *refractive index* n is defined as the ratio of the phase velocity of light in vacuum c to the phase velocity of the light in another medium v_p :

$$n(\lambda) = \frac{c}{v_p(\lambda)} \quad 2.12$$

where λ is the wavelength of the incident radiation. If, however, the observed particle shows absorbing properties, and has appreciable electrical conductivity, the *complex refractive index* m is needed where absorption is taken into account by the imaginary part k :

$$m(\lambda) = n(\lambda) - i \cdot k(\lambda) \quad 2.13$$

Again λ is the wavelength of the light and all constituents of this equation are functions of λ . k expresses the diminishing of the amplitude of the electromagnetic

wave due to absorption. The real part of the refractive index for air is for example 1.00028 at a wavelength of 589 nm (Hinds 1999). Hence when a beam passes from air to another medium equation 2.12 can be used. Water has a negligibly small value of k in the visible range of the spectrum, whereas the real part for $\lambda = 589$ nm is 1.333 (Hinds 1999). Typical values of n for atmospheric aerosol particles are between 1.33 and 1.60. For a black carbon particle (soot) a typical complex refractive index is: $m = 1.96 - i 0.66$ at a wavelength of 589 nm but as Kattawar and Hood (1976) found this value can vary depending on different soot types.

The imaginary part k , also called absorption index of the material, is related to the absorption coefficient of the bulk material (σ_A) (see 2.7.3.3)

$$\sigma_A = \frac{4\pi k}{\lambda} \quad 2.14$$

When particles are situated in a two-phase system, a relative index of refraction is used. This index can then be calculated as the ratio of the phase velocity of light in the suspending medium v_m and the phase velocity in a particle v_p .

$$n_r = \frac{v_m}{v_p} \quad 2.15$$

Aerosols are a two-phase system mostly composed of a gas (air) and a solid particle. Since the refractive indices of air and vacuum are practically the same, either of the two equations 2.12 or 2.15 can be used. However some aerosol particles are suspended in liquids and therefore equation 2.15 has to be applied.

2.7.3.2. **Absorption Efficiency:**

In chapter 2.7.1 and 2.7.1.1 the term *absorption efficiency* Q_A was already introduced as one part of the light extinction efficiency Q_E . The other one was the scattering efficiency Q_S . To calculate Q_A we just need to transform equation 2.3 to:

$$Q_A = Q_E - Q_S \quad 2.16$$

where Q_E can be calculated in analogy to Q_S in 2.11.

2.7.3.3. *Absorption Coefficient:*

The absorption coefficient σ_A depends on the wavelength of the incident radiation, and the optical density and the morphology of the absorbing material. It is defined like equation 2.4, exchanging σ_E by σ_A and Q_E by Q_A :

$$\sigma_A = \frac{\pi N d^2 Q_A}{4} \quad 2.17$$

Where N describes the number concentration of particles, d is the diameter and Q_A the absorption efficiency. This formula applies again just for a monodisperse aerosol, whereas for a polydisperse particle the size distribution $n(d)$ and the diameter dependence of the absorption efficiency have to be considered:

$$\sigma_A(\lambda) = \int_0^\infty \frac{d^2 \pi}{4} Q_A(\lambda, d, m) n(d) dd \quad 2.18$$

Another very frequently used parameter is the absorption coefficient per unit mass, which is defined as *specific absorption coefficient* B_A [m²/g]:

$$B_A = \frac{\sigma_A}{c_m} \quad 2.19$$

c_m is the mass concentration [μg/m³] of the aerosol. For a BC aerosol of known size distribution and refractive index, B_A can be calculated from Mie theory (see section 2.7.2.4). Common values for BC aerosols are between 3 and 17 m²/g depending on

size distribution and index of refraction (Wolff et al. 1982; Truex and Anderson 1979).

2.8. Optical Properties of BrC

In section 2.4 the term brown carbon (BrC) is introduced. As mentioned there its main sources are smoldering combustion (e.g. biomass burning) and chemical reactions in the atmosphere. Besides, its sharply increasing absorption towards UV (ultraviolet) radiation was pointed out. Therefore BrC is part of the light – absorbing carbonaceous matter (LAC) in the atmosphere (Andreae and Gelencsér 2006; Hoffer et al. 2006).

To determine the spectral properties of absorbing particles, very frequently the Ångström power – law relationship is used. After calculating the absorption efficiency at a certain wavelength, the following equation is used to extrapolate to other wavelengths:

$$B_A = K \cdot \lambda^{-\alpha_{abs}} \quad 2.20$$

B_A is the mass absorption efficiency of the particle [m^2/g], K is a constant that includes the aerosol mass concentration, λ [nm] is the wavelength of the light and α_{abs} is the Ångström exponent for absorption. The Ångström exponent is an empirical measure to determine the sensitivity of the particle extinction efficiency to wavelength (in this case only absorption is considered). Aerosols with dominant soot fractions typically show α_{abs} close to 1 (e.g. Bond and Bergstrom 2006) whereas for wavelength dependent BrC the α_{abs} is considerably larger. Water – soluble HULIS from biomass burning, which make up a significant fraction of the BrC, show the highest values for α_{abs} of about 6 – 7 (Hofmann et al. 2009). Hence due to the spectral dependence of light absorption by BrC, when the BrC amount predominates, the extrapolation of absorption of a value measured at a single wavelength to the solar spectrum is likely to be wrong if only BC is considered.

Furthermore the large fraction of BrC which is soluble in water, leads to another important fact with regard to atmospheric light absorption: Due to this property some of the BrC can dissolve into growing cloud droplets during cloud formation and finally

produce homogeneously absorbing droplets. These can further alter the cloud absorption, especially in the UV (Andreae and A. Gelencsér 2006).

2.9. Thermal Properties

As stated before, thermal properties of carbonaceous aerosols differ depending on the specific type (EC, BrC, and OC). Here we will take a closer look at how EC and OC behave under different thermal conditions.

In section 2.2 a general introduction for EC was given and it was noted that EC is always measured by thermal or thermal optical measurement techniques making use of its very strong temperature stability. Given that EC doesn't evolve without oxidants up to about 700°C (J.C. Chow et al. 2004) and with oxidants not before 340°C it can be separated from organic compounds.

With regard to organic carbon (OC), it is not easy determining a specific temperature behavior since it is strongly dependent on the specific constituents that form the OC particle. Nevertheless it is known that OC doesn't have such high temperature stability and therefore it should oxidize or evolve in an inert atmosphere, before the EC.

Considering BrC, which is part of the OC, it is known that it also shows certain temperature stability but no specific evolving temperature can be given.

2.10. Impact of BC (EC), OC and BrC on climate and health

Carbonaceous matter, like BC (EC), OC and BrC, is a very important component of the atmospheric aerosol. Therefore its impact on climate and health will be discussed in the following section.

2.10.1. Climate:

The main influence carbonaceous aerosols have on climate is the alteration of the earth's energy budget. This global variation is described by the radiative forcing [W/m²]. The impact of BC (EC), OC and BrC can either be warming or cooling of the

atmosphere, which is referred to as positive and negative forcing, respectively. Which kind of radiative forcing occurs depends on the size and composition of the aerosols, on their quantity and the solar angle (Seinfeld and Pandis 1998).

In this respect one has to differentiate between two possible effects: the direct and the indirect one. The *direct effect* is caused by scattering or absorption of the incident light or the infrared radiation emitted by the earth (terrestrial radiation) by the carbonaceous and in general, aerosol particles. The so called *indirect effect* is caused by changes of cloud formation and cloud properties such as the life time and albedo.

Mostly non absorbing particles are supposed to have a cooling effect on the atmosphere while absorbing particles show a positive forcing. The large number of parameters which are involved in the determination of the radiative forcing caused by a specific aerosol, make it impossible to quantify the effect of each one accurately. According to the Intergovernmental Panel of Climate Change's (IPCC) report from 2007 (Internet Ref.: http://www.ipcc.ch/publications_and_data/ar4/wg1/en/ch2s2-es.html; last page view: 12.08.2010) the combined anthropogenic radiative forcing is estimated to be +1.6 [-1.0, +0.8] W/m². Furthermore radiative forcing due to the direct effect of BC produced in fossil fuel combustion is given as +0.2 [±0.15] W/m², of fossil fuel OC as -0.05 [±0.05] W/m² and for aerosols produced in biomass burning as +0.03 [±0.12] W/m². On the other hand radiative forcing caused by the cloud albedo effect (indirect effect) is -0.7 [-1.1, +0.4] W/m².

The importance of aerosols increased drastically since the industrial revolution, when anthropogenic sources of carbonaceous particles were multiplied. Figure 7 shows the atmospheric radiative forcing for gases and aerosols, including BC.

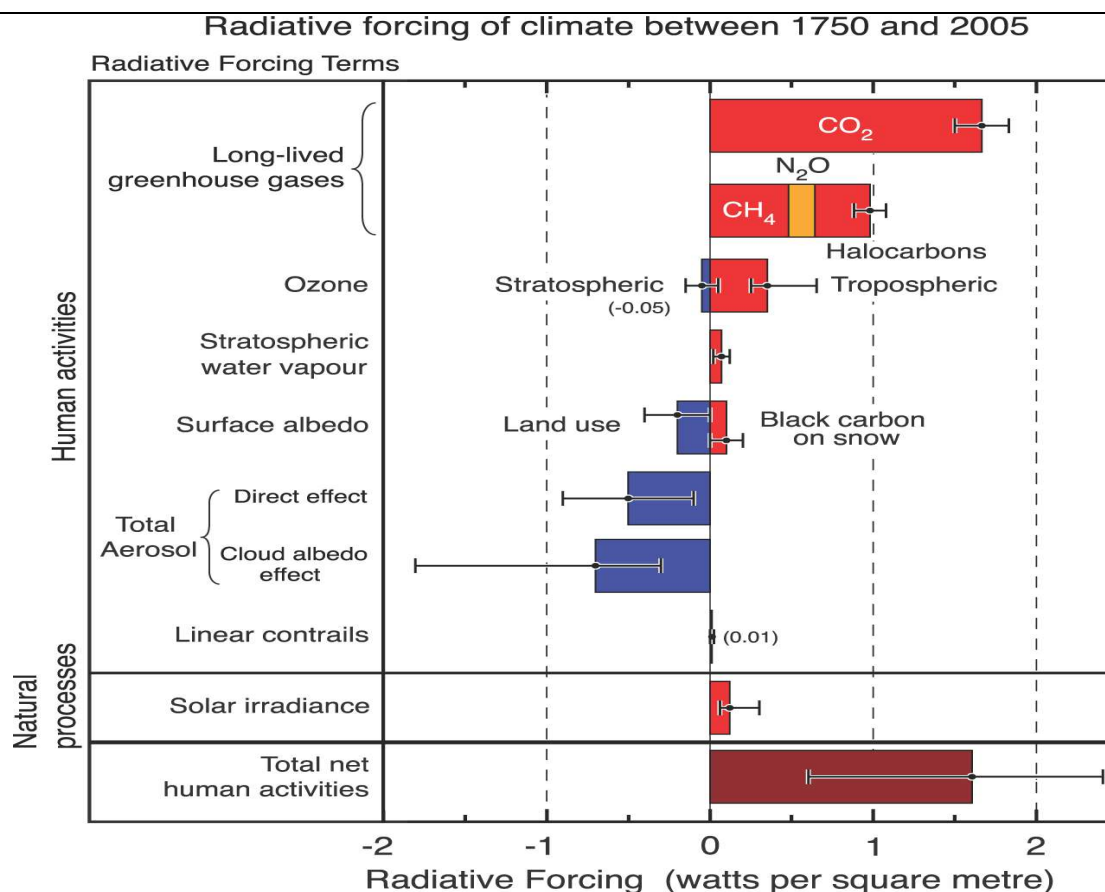


Figure 7: Radiative Forcing between 1750 and 2005.

(Source: IPCC, Working Group I Contribution to the Fourth Assessment Report, *Climate change 2007—the physical science basis*, http://www.ipcc.ch/publications_and_data/ar4/wg1/en/faq-2-1.html; last page view: 11.08.2010)

The figure above shows both the negative (blue) and positive (red) forcing by aerosols. While the total amount of radiative forcing is definitely positive, the direct and indirect effect by aerosols results in negative radiative forcing, which means cooling of the atmosphere. Besides the thin lines represent the uncertainties for each value which appear to be relatively large especially for the total aerosol's direct and cloud albedo (indirect) effect.

2.10.2. Health:

The impact aerosol particles have on the human body is another important topic which has to be considered. How aerosols influence the respiratory system of the

human body has already been studied for many years. Especially after events like the “London smog” in 1952, where several thousands of people died due to the consequences of smog mostly generated by coal burning, research in this area augmented considerably. The most common diseases related to high aerosol concentrations are asthma, bronchitis, all kinds of pulmonary diseases, cancer and cardiovascular diseases

(<http://www.portfolio.mvm.ed.ac.uk/studentwebs/session4/27/greatsmog52.htm>; last page view: 11.08.2010). Nevertheless, inhaling therapeutic aerosols is also a common treatment for many diseases associated with the respiratory system.

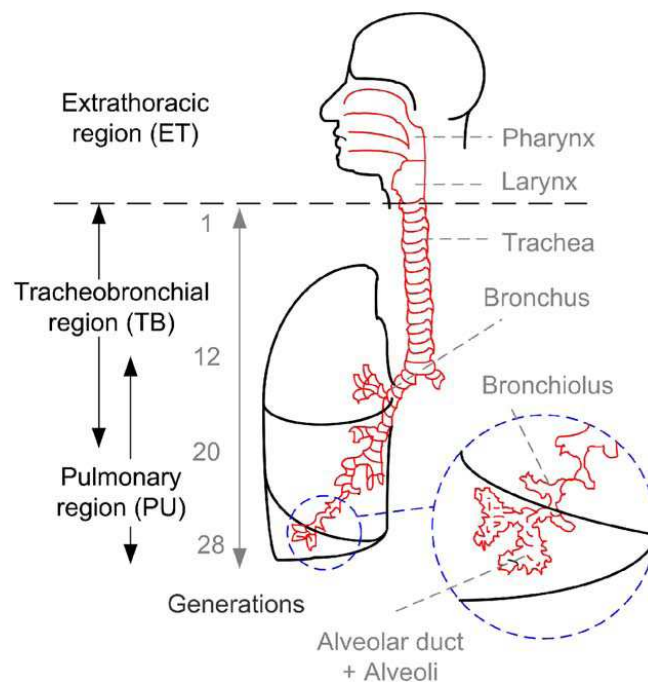


Figure 8: A schematic representation of the human respiratory tract.
(Source: Alföldy et al. 2009)

Figure 8 shows the human respiratory tract, denoting the three main regions: the extrathoracic region (ET), the tracheobronchial region (TB) and the pulmonary region (PU) (Alföldy et al. 2009). The generations range indicates the number of bifurcations in this region and it can easily be seen that the TB consists of generations 1-20 and the PU of generations 12-25 or higher depending on lung morphology. While

inhaling, a certain amount of particles, determined by the tidal volume, breathing frequency and flow rate, enters the respiratory tract. Depending on the size, particles are deposited in different regions of the human respiratory system. The three possible deposition mechanisms are sedimentation, impaction and diffusion. The first two occur for larger particles of an aerodynamic diameter (AD) around 10 μm , whereas small particles (aerodynamic diameter < 0.5 μm) are usually deposited by diffusion. Parameters like breathing velocity and morphology of the cylindrical airways can influence the amount of impaction. Figure 9 gives the deposition fraction for various particle diameters for the ET, TB and alveolar region.

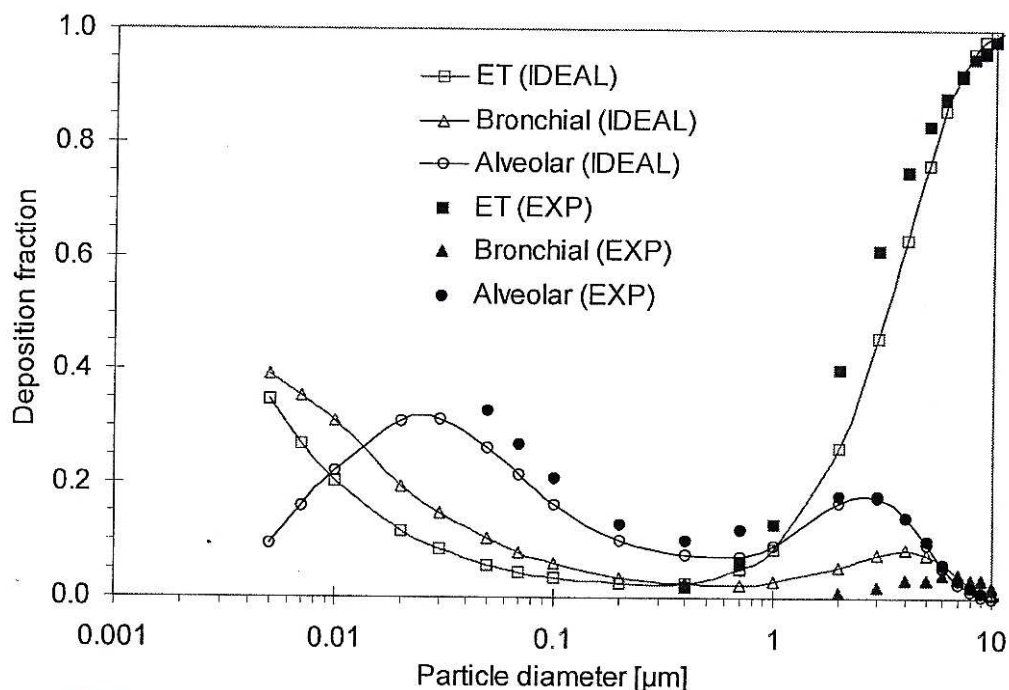


Figure 9: Deposition in extrathoracic, tracheobronchial and alveolar regions versus particle diameter. The filled signs represent measured values whereas the empty ones are theoretical, ideal values.

(Source: Heyder et al. 1986)

According to Hinds (1999) 20% of the 5 μm (AD) particles and 70% of the 10 μm aerosols (AD) reach just the oral and nasal part (extrathoracic region, ET) without passing into the tracheo-bronchial region (TB). These numbers are only valid for nose breathing, whereas mouth breathing and exercise increase these rates to 80% and 95%

respectively. In addition to these aerosols also those with an AD of 0.01 μm mostly stay in the entrance area because of diffusion processes. Still small particles can also enter the TB region but only particles with diameters around 3 μm are finally sedimented there. Particles with diameters smaller than 0.1 μm are also of special interest because of their possibility to penetrate the membranes and further reach the cell interstitial volume or even the brain (Kim et al. 2003).

Fumes which are produced by diesel engines are known to cause adverse health effects. Due to their size distribution their primary deposition mechanism is diffusion (Giechaskiel et al. 2009). Commonly particulate matter emissions from diesel engines are divided into volatile and non – volatile mass fractions. The former is mainly composed of organic compounds (e.g., unburned hydrocarbons), nitrates and sulfates and emitted as liquid droplets in the nanometer range and/or as condensed coating on the surface of soot particles. This fraction forms the nucleation mode with particle diameters less than approximately 50 nm. Furthermore it is assumed that the cores are non – volatile and contain mainly carbon and possibly metal oxides from engine lubricants. Both these substances are soluble in the lung fluid, generating reactive oxygen species, such as superoxide, hydrogen peroxide and hydroxyl radicals that cause oxidative stress on epithelial cells. The non – volatile mass fraction includes the non – volatile components of particles in the accumulation mode, meaning diameters in the range between 50 and 500 nm. The interactions of the lung fluid particles take place on the surface of these particles; therefore it can be assumed that the quantity of produced oxidants is proportional to the exposed lung fluid surface area of deposited particles (Giechaskiel et al. 2009).

3. Measurement Techniques:

To analyze the filter samples two different instruments will be used: Firstly the Sunset Analyzer and secondly the Integrating Sphere (IS). The first one uses a so called thermal optical- whereas the second one is a purely optical measurement method. By using the Sunset Analyzer the OC, EC and TC concentrations [$\mu\text{g}/\text{cm}^2$] of deposited aerosol samples can be determined. This instrument is based on the thermal stability of the two soot fractions (EC, OC). On the other hand the IS is able to measure BC and BrC concentrations by using the spectral light absorption ability of these components.

3.1. Overview

The number of existing measurement techniques for EC, BC and OC is vast. Mostly the carbonaceous fraction can be analyzed by collecting particulate matter (PM) on filters. Commonly used optical techniques include the integrating plate method (Lin et al. 1973), the integrating sphere method (Hitzenberger et al. 1996), the aethalometer (Hansen et al. 1984), the multiangle absorption photometer (MAAP) (Petzold and Schönlinner 2004) and the coefficient of haze (COH) (Hemeon et al. 1953). With regard to thermal and thermo optical methods the modified Cachier method (Cachier et al. 1989), TOT (thermal/optical transmission; Huntzicker et al. 1982; Birch and Cary 1996) and TOR (thermal/optical reflectance; Chow et al. 1993) methods, the thermal optical method developed by Malissa et al. (1976) and the VDI method (VDI 2465 Part I 1996) are frequently used. Besides there are further procedures to determine the TC amount e.g. the combustion method by Puxbaum and Rendl (1983) and many others (see overview by Watson et al. 2005).

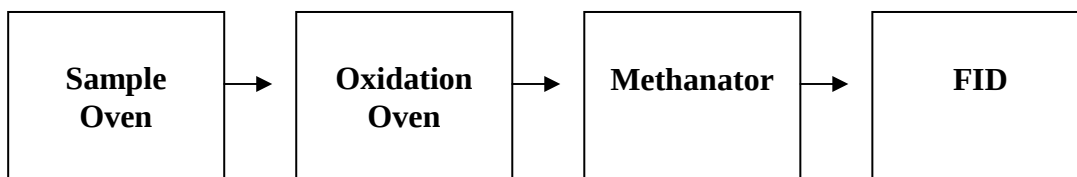
3.2. Thermal Optical Measuring Method

The Sunset Analyzer (OCEC Dual Optics Lab Instrument, Version 6.4, Sunset Laboratory Inc.) is based on two physical properties of carbonaceous aerosols: their optical properties and thermal stability (Sunset Laboratory Inc.- Instrument Manual). Thereby it separates the organic carbon from the elemental carbon present on a quartz fiber filter.

In all measurements presented in this thesis the already mentioned tissue – quartz filters were used. This special type of filters is advantageous for OC measurements because it can withstand the pressure drop during sampling without any organic binder to increase rigidity (Gelencsér 2006). The density of the here used **Tissuquartz™** filters 2500 QAT-UP 47 mm (diameter) (Pall Life Sciences) is 5.8 mg/cm², the thickness 432 µm and their particle collection efficiency is 99.94 %. Nonetheless due to the reactivity of the surface, sampling artifacts occur. These can be understood as errors with regard to the particulate phase concentration. While a positive artifact includes adsorption of gaseous components (semi – volatile organic species), the negative artifact is caused by desorption of these substances. Quartz filters are good adsorbents, which can further lead to an overestimation of the particulate phase concentration. Besides, the negative artifacts (volatilization artifacts) are particularly dependent on temperature even if their overall influence is usually of less significance. These errors make sampling with this type of filters much more complicated. Another issue is whether it is advisable to pre – bake the filters before sampling or not. In all experiments which took place in the laboratory I chose to bake out the filters to minimize the organic carbon blanks (for procedure see section 3.3.3). On the contrary for the atmospheric aerosol measurements most of the filters were not pretreated. In this way they had the chance to acclimatize and therefore find equilibrium with the ambient air and the semi – volatile organic species. Consequently the blank values for the organic carbon are larger but the positive artifacts are not relevant. Starting from the 20th of November pre – baked filters were used.

3.2.1. Instrument Setup:

More precisely the instrument contains a 6 mW laser with a wavelength of 658 nm coupled to two photodiodes, to measure the transmission or reflectance through the filter sample, which is necessary to determine the amount of EC and the respective uncertainty. The two photodiodes are positioned beneath (for transmission) and above (for reflectance) the filter punches. Moreover the instrument includes two ovens: the main oven with adjustable temperatures for the back and front side and the methanator oven. The front side of the main oven is also called sample oven and the back side oxidation oven. Beneath a schematic diagram of the gas flow's path is shown:



In the first step the front oven is purged with helium and the organic matter is supposed to be released from the filter. In the following step the OC reaches the oxidation oven where it is transformed to carbon dioxide (CO_2) gas. Finally the flow of helium, containing carbon dioxide, goes to the manganese dioxide (MnO_2 - Methanator) oven where the CO_2 - gas is mixed with some hydrogen and finally passed through a heated nickel catalyst which transforms it into CH_4 (methane). Then a flame ionization detector (FID) can measure the CH_4 amount. This detector is very sensitive and best for easily flammable matter like hydrocarbons. Besides it has two electronic circuits, one for high sensitivity (FID1 signal) and the other one for low sensitivity (FID2 signal). The data received by FID2 is only used when the FID1 signal over ranges the analog-to-digital circuitry (denoted as “off scale” by the OCEC calculation program). Therefore low level samples will be analyzed using the more sensitive FID1 signal and high level samples the less sensitive FID2 signal. For the helium, hydrogen and oxygen gases there are 6 external valves and an additional one for the calibration gas. The second step implies lowering the heat to a certain temperature, then adding some oxygen (final mixture: 2% oxygen/helium) and finally restarting a certain temperature ramp. Now the EC is oxidized and evolves equivalently to the OC until it is measured as CH_4 by a FID. By using the signals measured by the FID, the Sunset Analyzer identifies the total amount of carbon (TC) which was present on the filter punch. To obtain the OC amount, EC must be subtracted from TC.

In chapter 2.3 the problem which occurs when OC is heated in helium, namely the charring of OC was already mentioned. While this phenomenon occurs, the laser signal decreases due to the absorption by this charred organic carbon (PEC). In the He/Ox (Helium/Oxygen) atmosphere, this charred OC is burnt and the laser signal

increases again. The so called *split point* is defined as the moment when the laser signal reaches its initial value again and from where on all oxidized carbon is attributed to EC. The main assumption to allow this differentiation is that the absorption coefficients at a certain wavelength are the same for EC and PEC. The uncertainties for this charring correction are really large especially since Yang and Yu (2002) proved this theory wrong. Therefore the correct measurement by the Sunset Analyzer is dependent on the PEC amount present on the filter.

In the final phase, when all carbon has been removed from the filter, the sample oven is filled with a known volume and concentration of methane. Consequently each sample is calibrated to a known quantity of carbon. This phase is also referred to as Cal-gas (calibration – gas) phase.

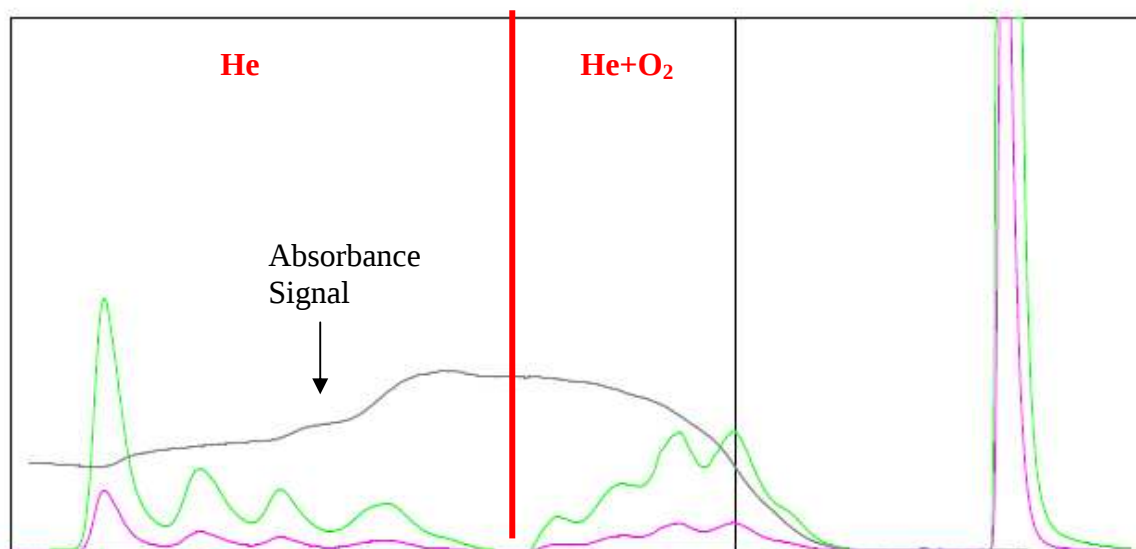
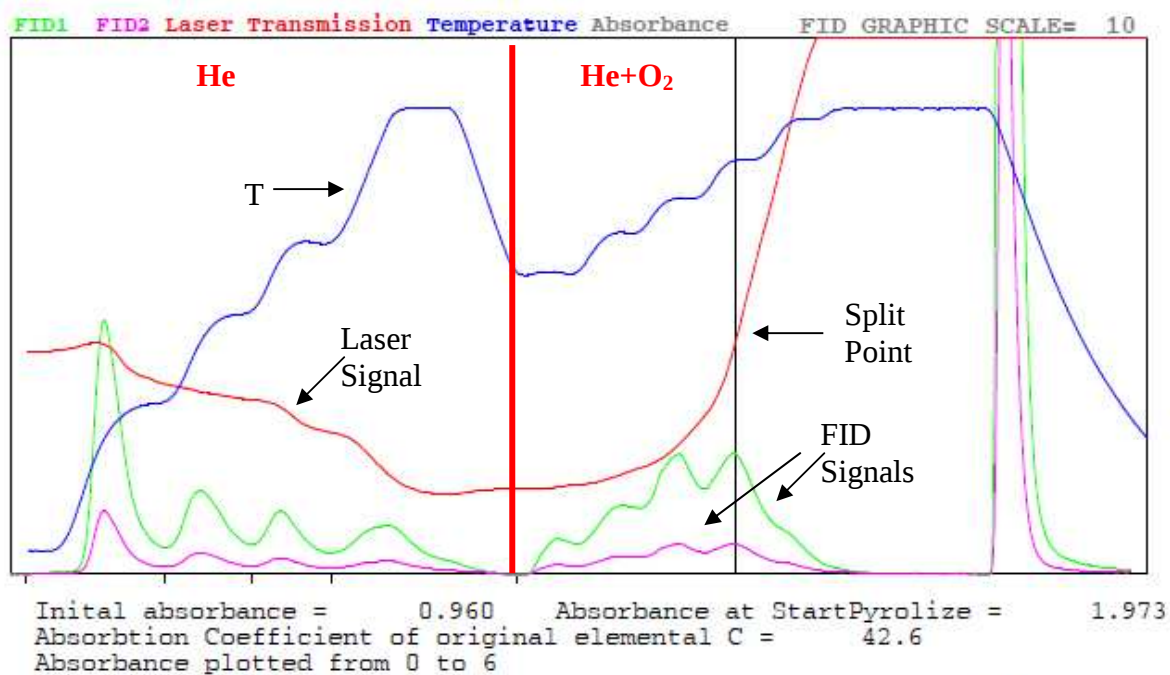
3.2.2. Measurement Procedure:

Firstly the OCEC software is started and the flow rates for Air, H₂, He1 (helium), He2, He3, He/O_x and CalGas (calibration gas) are set according to the flow table. To start the FID (flame ionizing detector) first the H₂ flow has to be increased up to 80 –100 ml/min and then the red button on the FID box can be pushed to ignite the flame for the detector. To analyze a loaded filter, a punch with an area of maximum 1.5 cm² is taken out of the filter and put on a quartz spoon. To make sure that both a transmittance and reflectance measurement are possible, the loaded side of the filter punch should not face the spoon. The analysis is started after entering a sample ID, analyst name, choosing a punch area and an output raw data file. During the measurement, which takes about 15 minutes, the thermogram shows the temperature steps performed according to the chosen protocol at one second intervals. Furthermore the progress of the laser and the FID signals can be seen (figure 10). After analysis the calculating software calculates the mass concentrations (µg/cm²) determined for BC, OC and TC of the analyzed filter punch. It is possible to see both results: one obtained by transmittance and one by reflectance.

Figure 10 shows a typical thermogram (data from winter campaign 2009) given by the Sunset Analyzer. The first diagram shows the temperature (blue line), laser signal (red line), FID 1 and FID 2 processes (green and pink lines, respectively)

and the perpendicular, black line which indicates the split time. After this split point all oxidized carbon is EC. The second diagram displays the absorbance (grey line). At the top date, time and mode of analysis plus the organic carbon, elemental carbon and total carbon masses with respective errors are noted. Besides the chosen punch area, calibration constant, laser correction factor and used split time are listed. With regard to the blue temperature line, in the initial part till the first decrease (red perpendicular line) the sample is in a helium atmosphere and afterwards in a helium oxygen mixture. Looking at the laser behavior, at the beginning a clear decrease is visible which is due to charring of the organic carbon fraction. During the charring process the OC on the filter blackens and can therefore absorb some of the laser light. When the laser signal returns to the initial intensity, the split point is set. After the split point the laser signal increases sharply which can be related to the combustion of EC. Besides, the FID signals give information on when and at which temperature carbonaceous matter was combusted.

Analysis Date/Time 27.11.2009 12:42:55
 Instrument: Inst.#223-34 Univ. of Wien Mode: Transmittance
 Organic C = 15.49 +-0.97 ug/sq cm
 Carbonate C = 0.00 +- ug/sq cm
 Elemental C = 2.25 +-0.31 ug/sq cm
 Total C = 17.75 +-1.19 ug/sq cm
 EC/TC ratio = 0.127
 FID: FID1: OK FID2: OK DL = 10
 Punch Area, sq cm = 0.785
 Calibration Constant = 20.12
 Calibration area Used = 330910.0
 Laser correction factor = 0.98
 Split time Used = 520 seconds Split time Calculated = 520 seconds
 Pk1 = 4.04 Pk2 = 2.04 Pk3 = 1.42 PK4 = 1.81
 EC1 = 0.55 EC2 = 1.54 EC3 = 2.75 PyC = 6.19



OC/EC Analysis Program (c) Sunset Laboratory, Inc.

Analyst - br

Figure 10: Thermogram gained by the Sunset Analyzer.

According to the paper published by Sunset Corporation (see: <http://www.sunlab.com/uploads/assets/file/Sunlab-Analysis-Method.pdf>; last page view: 11.08.2010) best ranges for OC are between 5 and 400 $\mu\text{g}/\text{cm}^2$ and between 1 to 15 $\mu\text{g}/\text{cm}^2$ for EC. The lower detection limit is 0.2 $\mu\text{g}/\text{cm}^2$ for both EC and OC. If the measured amounts are in these ranges, the relative standard deviations are given as 4-6 %. This error accounts for variations due to the instrument and variations of the filters, like the density on the surface for instance but does not include uncertainties due to the OC/EC split, inhomogeneous filter loading and filter blank values for OC.

3.2.3. Calibration:

To assure the reliability of the measurements a calibration curve is necessary. For this purpose sucrose standards have to be prepared. To begin with, a sucrose suspension must be mixed. To receive a concentration of $c = 1 \text{ mg/ml}$ a certain amount of sucrose (Merck KgaA 1.07687.1000) is weighed on the Mettler M3 balance, filled into a glass bottle and finally the same amount of ultrapure water is added with a volumetric or graduated pipette. To keep the contamination low, it is best to firstly run an instrument blank in the Sunset Analyzer and use the same filter punch to create a sucrose standard. A certain amount of the suspension is then dripped on the punch either with a 10 μl or an adjustable 100 μl Eppendorf Reference pipette. Before analyzing, each punch has to be dried either in a desiccator for about 4 hours or directly in the instrument. When choosing the second option the “clean oven” button has to be actuated and after about 5 seconds the run has to be canceled. In this way the oven heats up very quickly to about 100 $^{\circ}\text{C}$, which is enough to evaporate the water and finally cools down again. To get a conclusive curve, a 9 point calibration was performed. Besides it has to be noted that sucrose ($\text{C}_{12} \text{H}_{22} \text{O}_{11}$) is composed of 3 different elements and the carbon percentage is only 42.1 %. The table below shows the sucrose concentrations that were chosen and the finally measured values.

	calculated	measured
Sample ID	c [$\mu\text{g}/\text{cm}^2$]	c [$\mu\text{g}/\text{cm}^2$]
k1	2.81	2.91
k2	5.62	6.01
k3	8.42	8.48
k4	11.23	11.39
k5	16.84	17.27
k6	19.65	19.56
k7	22.45	24.35
k8	28.07	28.67
k9	42.10	43.09

Figure 11 shows the diagram to the values listed above.

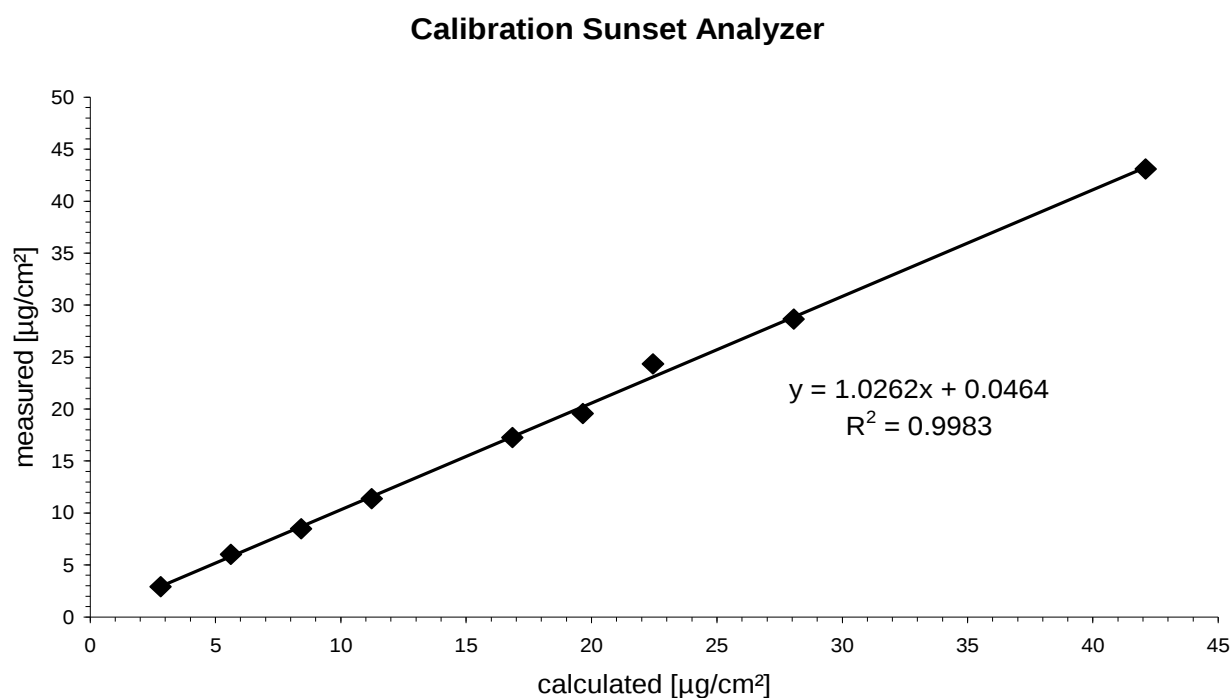


Figure 11: Calibration curve for sucrose.

As one can see in figure 11, the measured values coincide pretty well with the calculated ones. The correlation coefficient of the regression line is 0.9983 which also underlines the good match. The discrepancy between the measured and calculated values is on average only 3 %.

3.2.4. Temperature Protocol:

The Sunset Analyzer offers 10 different temperature protocols to choose from. For the measurements in this study the “quartz.par” – protocol was selected. This protocol is based upon the standard method NIOSH (National Institute for Occupational Safety and Health) 5040, which is especially designed to determine the OC – EC mass concentrations from a filter sample while using the Sunset Analyzer (Ng et al. 2007). The following table lists all theoretical temperature and time steps at each gas phase:

	Time [s]	Temperature [°C]	Time const. [s]
Minimum Step Time	45		
Maximum Step Time	300		
Helium	10	1	100
' start ramping the temperature			
Helium	80	310	95
Helium	60	475	70
Helium	60	615	45
Helium	90	870	27
' let the oven cool before starting elemental			
Helium	40	0	100
' elemental			
Oxygen	15	550	60
Oxygen	30	550	60
Oxygen	45	625	45
Oxygen	45	700	40
Oxygen	45	775	35
Oxygen	45	850	30
Oxygen	120	870	25
CalibrationOx	120	1	100
Offline	1	0	100

The time constant expressed in seconds should be between +1 and +200, generally it is going to be larger than 10 s and smaller than 120 s. While the temperatures are low the time constant is rather long, whereas at high temperatures the time constant is short.

3.3. Optical Measuring Method

As an optical method an Integrating Sphere (IS) is used. This kind of instrument was firstly used by Ulbricht in 1900 and afterwards by Heintzenberg (Heintzenberg 1982). The latest developments were described by Hitzenger et al. (1996) and Wonaschütz et al. (2009). With this expanded technique the BC and BrC fraction can be determined.

3.3.1. Instrument Setup:

The instrument used comprises a 6 inch Integrating Sphere manufactured by Labsphere Inc. The interior wall is covered with Spectralect, which reflects practically all incident light (i.e., > 99 %) diffusely. Furthermore a 75 W halogen lamp with a stable current source, functions as a light source (see figure 9). Before the incident light enters the sphere, it passes through a diffusor, then an iris stop, an interference filter (filters with wavelengths of 450, 550 or 650 nanometers can be chosen) and finally another diffusor (Wonaschütz et al. 2009). The purpose of the diffusors is to scatter all light even before it enters the IS. To capture the signal a silicon photodiode is placed at the bottom of the sphere and protected by a baffle from directly entering light. This detector registers the light intensity given at a certain moment in the sphere. On the top of the instrument is a removable lid with a sample holder to place the sample vial in the center of the sphere. To maintain a perfectly diffuse environment the holder is painted a matte white. Across from the light source a laser diode (wavelength: 405 nm) and a diffusor is mounted after another. This second light source can be used instead of the halogen lamp which means that if one is in use the other one is switched off and vice versa. To avoid further errors only ratios of signals, one gained with a reference (empty) vial and one with a full one, are used.

Thus the final signal is dimensionless. The radiometer display offers 5 different sensibility levels, which can be chosen depending on which interference filter is currently used. As the last digit tends to fluctuate, the iris stop is always positioned in a way that a value close to the maximum signal, which is 1.999, is reached with the empty vial and therefore the error remains small.

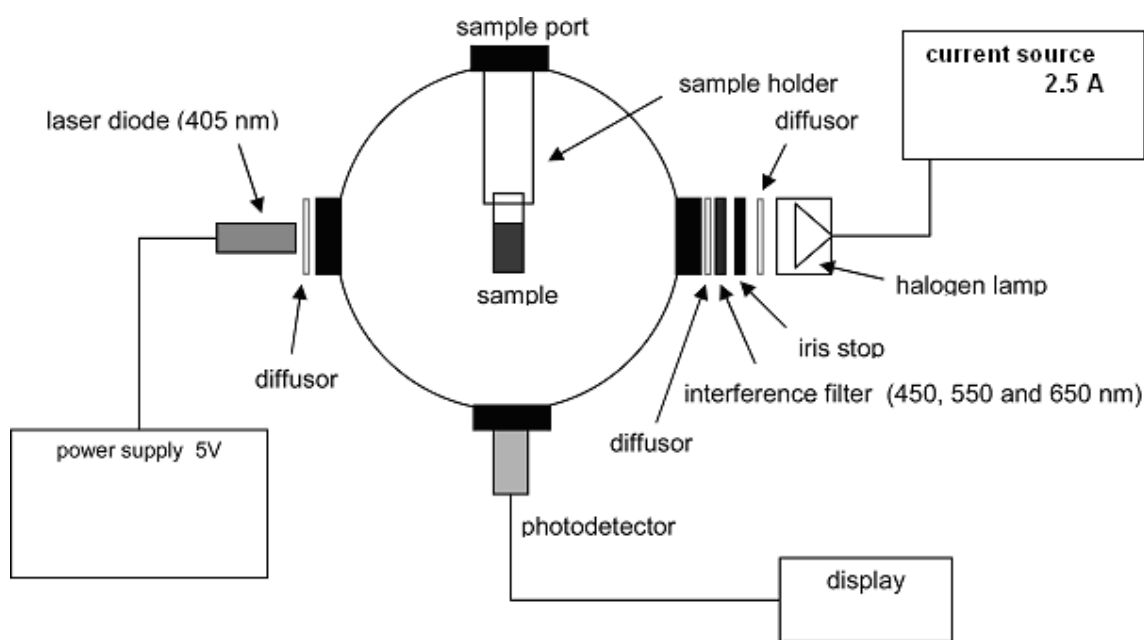


Figure 12: Setup of an integrating sphere;
(Source: Wonaschütz et al. 2009)

To analyze a filter sample using the IS a punch is taken from the filter and placed in a transparent vial which can be mounted in the sample holder (see figure 12). The arrangement necessitates homogeneously loaded filters, punches from a filter or liquid suspensions or, in the case of insoluble filters, samples enclosed by a liquid. Hence, using the sphere as an integrating detector a signal which depends on the light absorption of the liquid sample can be measured directly.

3.3.2. Measurement Procedure:

To analyze the punches each one is placed in a vial and then 2 ml of acetone and 2 ml of a 2-propanol – ultra pure water (ratio 20:80) mixture are added (for the detailed procedure see 3.3.3). For each vial 2 signals are finally obtained, one reference signal (empty vial) and a sample signal. Due to the absorption caused by the loaded filter punch, the transmission decreases. This reduction can be seen as a measure of light attenuation which is symbolized as L in equation 3.1:

$$L = -\ln \frac{T}{T_0} = -\ln \left(\frac{S}{S_R} \cdot \frac{B_R}{B} \right) \quad 3.1$$

S denotes the signal recorded with a vial containing a loaded filter punch, S_R is the signal of an empty vial measured just before or after the full vial to compensate for eventual intensity fluctuations on account of the halogen lamp or long-term variations of the signal indicator. B describes the signal received with a vial comprising a punch of an unloaded filter (blank) and B_R is once more the signal of a reference (empty) vial gained just before or after the vial containing the unloaded punch. Concerning the blank value, it is actually gained by forming a mean value out of the signals of 3 vials containing an unloaded filter punch each.

To get an even more accurate signal it is best to measure all empty vials at all three wavelengths (red, green, and blue) before filling them. Subsequently the obtained signals have to be combined in equation 3.1:

$$L = -\ln \left(\frac{\frac{S}{S_R}}{\frac{S_{before}}{S_{Rbefore}}} \cdot \frac{\frac{B_{before}}{B_{Rbefore}}}{\frac{B}{B_R}} \right) \quad 3.2$$

Where S_{before} is the signal of the empty vials before the filter punches and liquids are filled in, $S_{Rbefore}$ is the reference vial measured just before or after the S_{before} , B_{before}

denotes the empty vial where afterwards the blank punch will be put in and $B_{Rbefore}$ is again the reference vial to it. By performing this extra step any absorption due to the transparent bottles can be taken into account in the measurements.

In my experiments, as you can see in figure 12, the current for the halogen lamp was set to 2.5 A, which allows measuring at all 3 wavelengths with the same range setting of the radiometer by proper adjustment of the iris stop.

3.3.3. Sample Preparation:

Each tissue – quartz filter was pre-baked in a muffle furnace before being loaded. Firstly an aluminum dish was put in the oven for 1 hour at 450 °C to remove OC from the aluminum surface and then the filters were put inside the dishes in the oven and baked for another 4 hours. Finally the filters together with the aluminum dishes were put in a desiccator with a water vapor atmosphere for 24 hours to prevent an adsorption of organic vapors present in the laboratory air. In the last step, when the filters were taken out, the Petri dishes were immediately sealed with parafilm.

For each measurement circular filter punches with a diameter of 8 mm were put into the vials. 2 ml of acetone and 2 ml of a mixture (80 % ultra pure water and 20 % 2-propanol) were added with a 20 ml graduated pipette. As a result the organic matter on the filter should be extracted. To guarantee a homogeneous suspension, all filled vials were put for 5 minutes in an ultrasonic bath. Since quartz fiber filters were used, the punches didn't dissolve. Therefore the vials finally contain a filter punch surrounded by the suspension. Finally all vials were put in a numbered holder.

3.3.4. Calibration and Conversion to $\mu\text{g BC}$:

As mentioned before the resulting signal is a dimensionless value. To convert this signal into BC or BrC a calibration curve is necessary. For the black carbon (BC) amount the industrially generated carbon black (Elftex 125, Cabot Corporation) was used as a proxy, whereas for the brown carbon (BrC) the commercially available

humic acid sodium salt (Acros Organics, no. 68131-04-4) was selected. The substances are supposed to show absorption properties of ambient black carbon and brown carbon, respectively. By using calibration curves obtained with these two substances, it is clear that the resulting values for BC and BrC actually correlate with the Elftex 125 and humic acid sodium salt masses which would give the same absorption signal.

Before preparing the calibration curve for BC with different concentrations, it is advisable to bake out the powder of the proxy, to assure that no other adsorbed material is present.

For all measurements in the Integrating Sphere the calibration curves generated by Wonaschütz et al. (2009) for the wavelengths 450 nm (blue), 550 nm (green) and 650 nm (red) for both the BC and BrC standard were used (see figure 13). To create the calibration curves, a certain quantity of each powder was firstly weighed and then a mixture of 20 % 2-propanol and 80 % ultra pure water was added. The amount of the liquid is selected in a way to finally get a suspension with the concentration of 1 mg per ml. Thus the vials can be filled with certain amounts of the suspension which are then diluted with the mixture of alcohol and water, to achieve different concentrations of the suspension. Before analyzing the small bottles in the IS, they are homogenized in an ultrasonic bath.

Figure 13 shows $L (-\ln T)$ as function of carbon black (squares) and humic acid sodium salt (triangles) masses. The red lines are measured at a wavelength of 650 nm and the blue ones at 404 nm. It can clearly be seen that BC (carbon black) absorbs equally well at both wavelengths whereas BrC (humic acid sodium salt) shows a stronger absorption at a wavelength of 404 nm. Nonetheless the absorption of BC is still a lot stronger than the one of BrC at 404 nm.

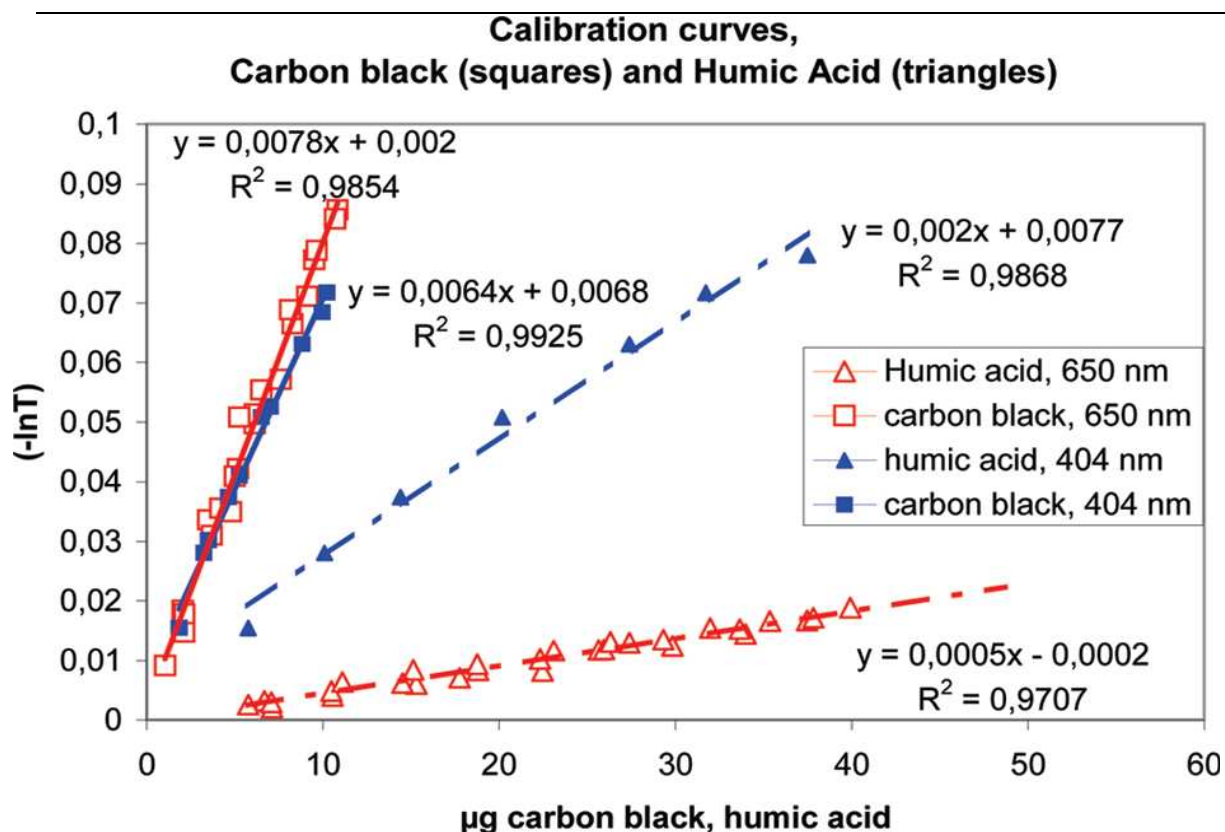


Figure 13: Calibration curves for carbon black (squares, full lines) and humic acid sodium salt (triangles, broken lines) at 404 (blue symbols) and 650 nm (red symbols).
(Source: Wonaschütz et al. 2009)

Beneath the calibration equations for red (650 nm), green (550 nm) and blue (450 nm) for both standards are listed:

	Humic acid sodium salt	Elftex 125
RED	$y=0,0005x-0,0001$	$y=0,0076x+0,0027$
GREEN	$y=0,0006x+0,0003$	$y=0,0071x+0,0024$
BLUE	$y=0,0013x+0,0038$	$y=0,0073x+0,0034$

3.3.5. Separation of BC and BrC:

In chapter 2.4 and 2.8 the wavelength dependence of light absorption by brown carbon (Kirchstetter et al. 2004) has already been discussed. To separate the amounts of BrC and BC their different spectral dependence of absorption is used. Previously tests were made with suspensions of known carbon black and humic acid sodium salt concentrations by Wonaschütz et al. (2009), to assure the validity of the results gained by the IS. Following their iterative technique the amounts of both substances were calculated as follows:

First of all the BC amount at 650 nm was determined by using the respective calibration curve (see 3.2.4). The result can be interpreted as the maximum existing BC amount for this sample, as BC absorbs equally well at all wavelengths while BrC absorbs distinctively better at smaller wavelengths. The next step is to calculate the signal this BC amount would give at 450 nm. Now this signal is subtracted from the actually measured signal at 450 nm. The remaining signal is assigned to the absorption by humic acid sodium salt and used to calculate a first guess BrC amount from the calibration equation for humic acid sodium salt at 450 nm. With this first guess BrC the signal at 650 nm is calculated, subtracted from the measured signal at 650 nm and the remaining signal used to calculate a new BC value which is the starting point for the second iteration. In my measurements the final mass amounts for BC and humic acid sodium salt, are obtained after 3 iteration steps. If negative amounts of BrC or BC occur, no iteration is performed and if BC is present, the BC value obtained from the “standard” IS method (at 550 nm) is given.

3.3.6. Advantages and Disadvantages of the IS:

The main advantage of this method is the fact that no scattering light is lost. This is possible due to the surface coating which allows multiple scattering of all rays in the sphere. Another negligible problem using the IS, is the one concerning whether the particles are covered by a transparent shell which could increase the absorption or not (Bond et al. 2006). When aerosols consist of more than one substance it is

important to differentiate two types of mixing: the internal and the external one (Martins et al. 1998). Furthermore the mixture can include absorbing as well as non-absorbing materials. An internal mixture is defined as an aerosol with at least two components, a BC core and a surrounding, mostly non-absorbing shell. On the contrary an external mixture consists of particles of just one compound (see figure 14 below). For coated BC particles, absorption is greatly enhanced by the focusing effect of the non – absorbing shell, which depends on the relative refraction index of the coating material in the surrounding medium (air).

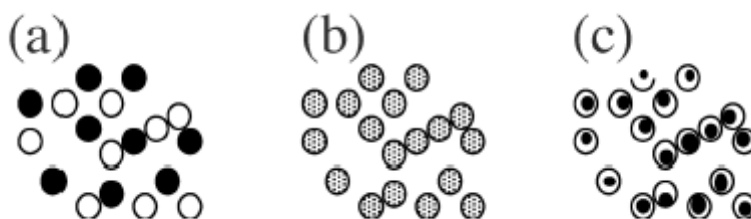


Figure 14: Mixing state: a) External mixture: a heterogeneous population of internally homogeneous particles; b) Internal mixture: homogeneous population of internally homogeneous particles; c) Internal mixture: heterogeneous particle composition and population;

(Source: Bond and Bergstrom 2006)

For the IS an internal mixture is not a problem because the coating substances dissolved from the filters mostly disappear. Even if this is not the case, the influence is rather small because the suspension liquid and the material of the transparent covering have a very similar refractive index. Most inorganic and organic aerosol substances have an index of refraction around 1.4 in air (d'Almeida, Koepke, and Hess 1989). Here a liquid of 2 ml acetone ($n = 1.359$) and 2 ml of a mixture of 20 % 2-propanol ($n = 1.374$) and 80 % ultra pure water ($n = 1.333$) are used (<http://www.hbcnetbase.com/>; last page view: 11.08.2010). These values apply for a wavelength of 589 nm and 20 °C. Hence the total mixture has a refractive index of $n = 1.35$. When the filter punch with organic matter is put into the solution the relative index of refraction of the non – absorbing aerosol material is 1.037 which is so close to 1 that absorption enhancement can be excluded (Hitzenberger and Tohno 2001).

As a consequence of the diffusely scattering, inner sphere covering, it is not possible to measure the absorption of the material on the filter punch. While the light is scattered several times, also the absorption will take place more than once in the filter. Therefore a calibration standard and further a calibration curve are necessary to translate the given signals to actual mass values of absorbed BC or BrC by the filter.

One last important fact is that the IS is not able to measure infinitely high concentrations of carbon. At a certain point saturation occurs so measurements are limited. This effect was already mentioned by Hitzenberger et al. (1999) and Wonaschütz (2006) and it occurs when the suspensions or solutions contain too high concentrations of absorbing material. In other words when the filters are overloaded there is no log – linear relation between the absorbing matter and the attenuated signal anymore. The light attenuation by the absorbing matter becomes so large that no additional absorbing matter can be detected. According to Wonaschütz (2006) the lower and upper detection limits for Elftex (BC proxy) in the IS are of 0.5 µg and 11 µg, respectively. For humic acid sodium salt (BrC proxy) masses between 2 µg and 40 µg are needed for detection.

4. Experimental Setup:

For my thesis two different experiments were performed. The first one involves collecting atmospheric aerosols and analyzing them with the Integrating Sphere and the Sunset Analyzer. Hence the amount of BC, BrC, OC, EC and TC can be determined. Furthermore the BC and EC, which can additionally be measured for the transmittance and reflectance laser signal, are compared and the effect of BrC on the measurements is examined. The second experiment was performed on laboratory generated aerosols and investigated their influence on the measurements in the Sunset Analyzer.

4.1. Atmospheric aerosols

4.1.1. Sampling site and period:

The sampling took place in Vienna (elevation 210 m a.s.l.), a densely populated city (population 1.8 million) surrounded from N to SW by hills with elevations around 600 m above sea level (a.s.l.). Since the sampling occurred in wintertime it is important to consider the meteorological situation in this period: Very commonly weak easterly winds blow and the surrounding hills and low inversion layers impede the mixing of the air masses. As a result pollution is higher. According to Hitzenberger et al. (2006) highest concentrations of total mass were reported for weak winds from S and SE.

The main sources for air pollution in Vienna are traffic emissions, space heating, which is very important to consider for winter campaigns and domestic oil and biomass combustion, whereby the first mentioned prevails in Vienna.

All measurements took place at the department of physics, at the roof laboratory. The building is situated in downtown Vienna. Though a major road passes within 100 m, fresh traffic emissions are shielded by the geometry of interconnecting buildings and courtyards. The only direct emissions which can reach the sampling site are from the street passing in front of the physics building. However, this street is mainly used for parking. At the roof, which is approximately 35 m above ground,

winds can pass unhindered from all sides except from the west, where the Vienna General Hospital buildings create turbulences.

4.1.2. Sampling method:

Sampling was started on the 8th October 2009 and stopped on the 2nd December 2009. Each day a tissue – quartz filter was placed in the open face filter holder with protection cap (see figure 13) situated on the roof of the physics department. Sampling lasted 24 hours, starting from between 12 and 13 o'clock and including short intervals for sample change. At the week-ends a time switch was used to collect only 15 minutes per hour. To measure the air volume which traversed the filter a Balgen – gas meter ($\pm 3 \%$) was used. In this way the tissue – quartz filter collects all suspended particles present in the Viennese ambient air. Then the BC, EC, OC and BrC mass can be determined by analyzing filter punches in the Sunset Analyzer and the Integrating Sphere. Besides before analyzing, the filters had to acclimatize for at least 12 hours in the laboratory. Knowing the air volume through the filter and the time of collection the BC, EC, OC and BrC mass concentrations can be determined for each filter sample.



Figure 15: To the left: Filter holder with protection cap and plastic bag to prevent water from getting into the holder and directly onto the filter; to the right above: Balgen-gas meter to measure the flow rate; to the right bottom: pump;

4.2. Laboratory generated aerosols

Since soot (BC, EC), ammonium sulfate (AS – $(\text{NH}_4)_2\text{SO}_4$) and sodium chloride (NaCl) play an important role in the atmospheric aerosol (see figure 3 and 4) some filter punches were spiked with different suspensions containing these substances and finally analyzed in the Sunset Analyzer and the Integrating Sphere to determine EC, OC, BC and BrC. Furthermore also the BrC amount is very significant considering the ambient aerosol. Therefore three different proxies were chosen to determine its quantity: humic acid sodium salt (HASS), Pahokee Peat and Leonardite. One or two spiked punches were analyzed in the Integrating Sphere to gain the BrC and BC amount and another one in the Sunset Analyzer to obtain the EC and OC masses. Thus EC can be compared to BC and the influence BrC has on the OC/EC split can be investigated.

To determine which masses are necessary in order to detect the BrC amount with the IS the exact composition of the proxies is needed:

	Pahokee Peat	Leonardite	HASS
C [%]	56.84	63.81	47.80
H [%]	3.60	3.70	3.57
O [%]	36.62	31.27	28.30
N [%]	3.74	1.23	
S [%]	0.70	0.76	
P [%]	0.03	< 0.01	
H₂O [%]	10.40	7.20	
ash [%]	1.72	2.58	
Na [%]			20.33

The composition of Pahokee Peat and Leonardite are taken from the International Humic Substance Society (IHSS) (<http://www.ihss.gatech.edu/elements.html>; last page view: 10.08.2010) and the HASS composition was calculated from the formula given by www.chemicalbook.com/ChemicalProductProperty_EN_CB2368636.htm (last page view: 05.08.2010) which is: $C_6H_8Na_2O_4$.

The suspensions which were mixed are:

- Soot
- HASS
- Pahokee Peat (PP)
- Leonardite (L)
- Soot and NaCl in a ratio of 1:1
- Soot and NaCl in a ratio of 1:2
- Soot and HASS in a ratio of 1:10
- Soot and PP in a ratio of 1:5
- Soot and PP in a ratio of 1:10
- Soot and L in a ratio of 1:5
- Soot and L in a ratio of 1:10
- Soot and AS in a ratio of 1:9

-
- Soot, HASS and AS in a ratio of 1:6:9
 - Soot, HASS and AS in a ratio of 1:8.3:9
 - Soot, HASS and AS in a ratio of 1:12:9
 - Soot, PP and AS in a ratio of 1:5:9
 - Soot, PP and AS in a ratio of 1:8.3:9
 - Soot, PP and AS in a ratio of 1:10:9
 - Soot, L and AS in a ratio of 1:5:9
 - Soot, L and AS in a ratio of 1:10:9

4.2.1. Production:

First of all certain amounts of soot (Elftex 125, Cabot Corp.), HASS (HASS tech., 50-60% as humic acid – Acros Organics), Leonardite (HA Standard – 1S104 H-5), Pahokee Peat (HA Reference – 1R103 H-2), NaCl (Merck – Sodium Chloride GR for analysis) and AS (Fluka Chemie AG – Assay >99.5% (T)) are weighed on a Mettler ME3 microbalance (balance $\pm 1 \mu\text{g}$, handling $\pm 3 \mu\text{g}$). Each substance is then filled in a glass bottle. Now some of the mixture of 2-propanol (20 %) and ultrapure water (80 %) is added to gain a certain concentration for each substance. Finally the solutions and suspensions are ultrasonicated for 5 minutes. Then suspensions are mixed together according to the list above and put again in the ultrasonic bath for at least 5 minutes.

4.2.2. Sampling methods:

Two different sampling methods were chosen to load the filters. The first one consists of the collection of nebulized suspensions on a filter. In this case all suspension concentrations are chosen to be 1 mg/ml. In the second method suspensions are spiked directly on a filter punch. Here the suspension concentrations vary from 1 to 10 mg/ml.

4.2.2.1. *Nebulizing a suspension:*

In this first method the quartz filter is placed in an open face filter holder which is positioned in the middle of a Plexiglass cylinder (see figure 16 below). This cylinder is open on one end and on the other one a nebulizer (commercially available nebulizer for medical purposes) is mounted. The filter holder is connected to a pump and a gas meter to monitor sample volumes. For each suspension three filters are loaded with different concentrations. This can be done by either changing the sampling time or the distance between nebulizer and filter holder, or both. Before sampling the cylinder is purged with very clean air for at least 15 minutes. After the filters are loaded they are put in a desiccator for 24 hours to make sure all liquids are removed. Afterwards the filters are put in Petri dishes which are then sealed with parafilm to prevent adsorption of any other organic vapors present in the laboratory air.

To obtain this “very clean air” a special setup had to be arranged. The air coming from the compressor contained a non negligible amount of organic matter so the compressed air was cleaned by an active carbon filter (see figure 15) followed by an absolute filter (Pall Hepa – high efficiency particulate free air – Capsule). The former adsorbs the organic vapors in the air and the latter ensures particle free air to 99.97 %.

After these two filters a T – piece separates the flows. One is directed straight to the cylinder to provide clean sheath air. The other one is connected to the nebulizer and can be controlled by a pressure regulator which is mounted in-between.

The nebulizer (see figure 16) is then filled with 800 µl of a suspension. The air pressure is regulated to ca. 0.75 bar.

This method provides more or less homogeneous filter deposits but the actual concentrations on the filters remain unknown. Nevertheless punches taken for both analyses originate from the same filter and one can assume that they have comparable but unknown concentrations.

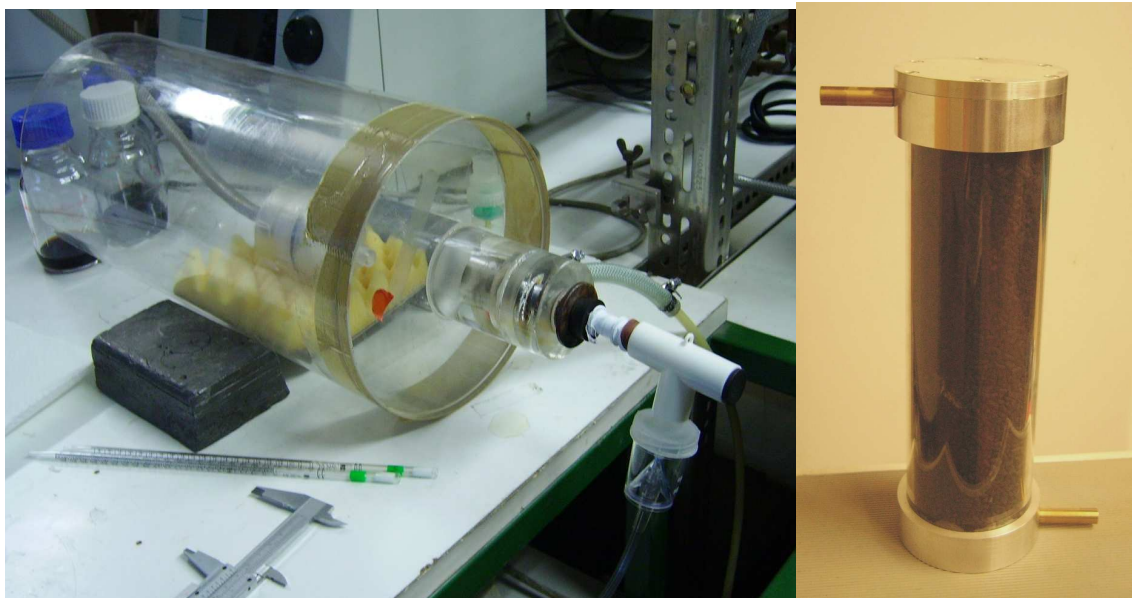


Figure 16: To the left: The cylindrical tube with at one end the nebulizer and inside the filter holder; to the right: the active carbon filter constructed in the workshop of the faculty of physics (construction plans by Gerhard Steiner).

4.2.2.2. *Spiking the filter punches directly with the analytes:*

Conversely to the method described in 4.2.2.1 this second approach implies taking a punch from a baked, unloaded filter and directly spiking this punch with a known concentration of one or more suspensions. For this purpose an Eppendorf Reference pipette is used. For each concentration two punches have to be loaded, one to be analyzed in the Sunset Analyzer and the other one in the Integrating Sphere.

The chosen mixtures and concentrations are:

		µg	µg	µg	µg	µg	µg
sample ID	suspensions	HASS	Soot	AS	PP	L	NaCl
lga1	HASS	30					
lga2	HASS	60					
lga3	HASS	100					
lag4	Soot:10HASS	100	10				
lag5	Soot:10HASS	150	15				
lag6	Soot:10HASS	200	20				

lag7	PP				50		
lag8	PP				60		
lag9	PP				75		
lga10	5PP:Soot		10		50		
lga11	5PP:Soot		15		75		
lga12	10PP:Soot		10		100		
lga13	L					50	
lga14	L					60	
lga15	L					75	
lga16	5L:Soot		10			50	
lga17	5L:Soot		15			75	
lga18	10L:Soot		10			100	
lga19	Soot:6HASS:9AS	60	10	90			
lga20	Soot:8.3HASS:9AS	100	12	108			
lga21	Soot:12HASS:9AS	120	10	90			
lga22	Soot:5PP:9AS		10	90	50		
lga23	Soot:8.3PP:9AS		12	108	100		
lga24	Soot:10PP:9AS		10	90	100		
lga25	Soot:5L:9AS		10	90		50	
lga26	Soot:10L:9AS		12	108		120	
lga27	Soot:10L:9AS		10	90		100	
lga28	Soot		10				
lga29	Soot		15				
lga30	Soot: NaCl		10				10
lga31	Soot: NaCl		15				15
lga32	Soot:2NaCl		10				20
lga33	Soot:9AS		10	90			
lga34	Soot:9AS		12	108			

After spiking the filter punches with the respective suspensions, they were put in a desiccator for about 24 hours to dry before they could be analyzed.

5. Results

5.1. Atmospheric aerosols:

The goal of these measurements is to determine the influence of BrC in the atmospheric aerosol in the winter months (October till December 2009). Its concentration mainly increases due to space heating in the cold period. Finally the results obtained by the two different measurement techniques are compared.

5.1.1. Winter aerosols analyzed in the IS:

By analyzing the filters in the Integrating Sphere the BC and BrC mass concentrations for each day can be determined if the air volume, measured by the gas flow meter, is also taken into account. Figure 17 illustrates that starting from mid October BrC concentrations increase which coincides with the beginning of the heating season. Highest values for BrC are found in November. The BC concentration on the first sampling day in October is 3 times as high as on the following days, which matches the temperature trend of those days, namely an average temperature of 22 °C on October the 8th and the two preceding days but only 13 °C on the 9th and on the 10th (climate data received from ZAMG). The concentrations depend on the amount of emissions and the meteorological stability. Higher temperatures imply fewer aerosols emitted by space heating but considering that the conditions were stable, wind velocities decreased and eventually the aerosol concentrations increased. The warm, stable period was then ended by a cold front with peak winds on the 14th (velocities up to 100 km/h) which then lowered the aerosol concentration. On the 3rd and 10th November precipitation occurred (up to 18 mm of rain and snow), and BC concentrations decreased. Finally starting from the 1st of December the lower concentration of BC goes again hand in hand with rainfall and cooler windy weather (< 6 °C).

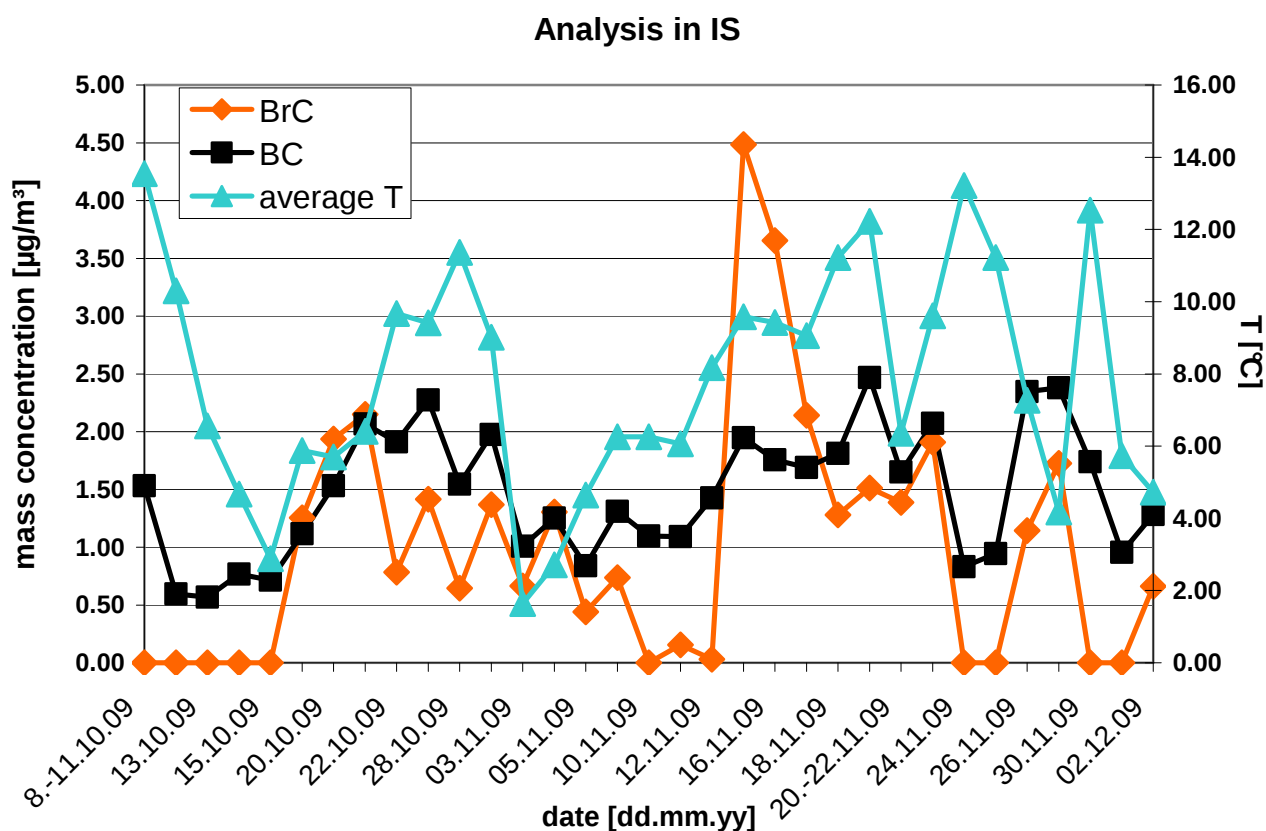


Figure 17: BC and BrC mass concentrations obtained by the Integrating Sphere; the secondary y – axis illustrates the average temperature of those days.

5.1.2. Winter aerosols analyzed in the Sunset Analyzer:

The Sunset Analyzer enables to measure the EC, OC and TC masses deposited on a filter. Dividing the masses by the air volume that passed the filter, the mass concentrations can be found. Figure 18 displays the EC and OC concentrations for each measurement day and their ratio. The weather conditions stated in 5.1.1 influence the EC and OC values in the same way as explained in that section. The peaks in EC concentration at the end of November occur on the days with the highest BC concentrations.

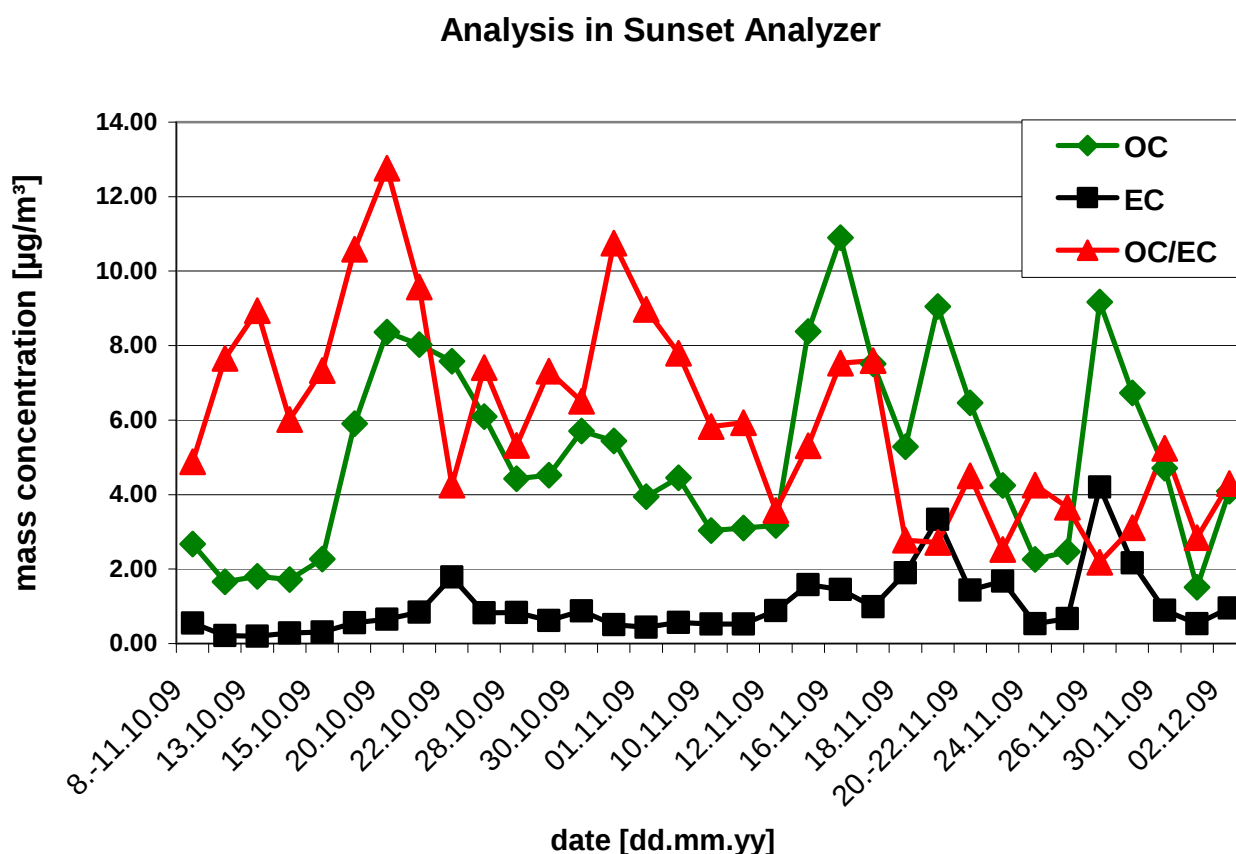


Figure 18: OC and EC mass concentrations obtained by the Sunset Analyzer and ratio of OC/EC.

5.1.3. Comparison of the measurement techniques:

The BC and EC concentrations are compared. Several studies performed in earlier days showed that the two concentrations differed due to the different measurement techniques (ten Brink et al. 2004; Hitzengerger et al. 2006; Reisinger et al. 2008). The results for this measurement campaign and possible reasons for discrepancies are discussed.

5.1.3.1. Influence of the BrC in the BC/EC measurement:

All samples were analyzed in both instruments and plotted as a time series (figure 19). On the abscissa the dates are denoted whereas on the ordinate the mass concentrations in $\mu\text{g}/\text{m}^3$ are given.

Compared to the BC values, obtained by the optical instrument (IS), figure 19 illustrates that the “EC Trans” (the transmittance laser signal is used for the charring correction) underestimates these quantities. One of the reasons could be that the presence of BrC influences the quantification of EC. When little BrC is present in the air, the ratio of EC and BC is rather constant, around a value of 2, which indicates an underestimation of EC by approximately 50 % compared to BC. However, when the BrC concentration increases the discrepancy between EC and BC increases except for 3 BrC data points.

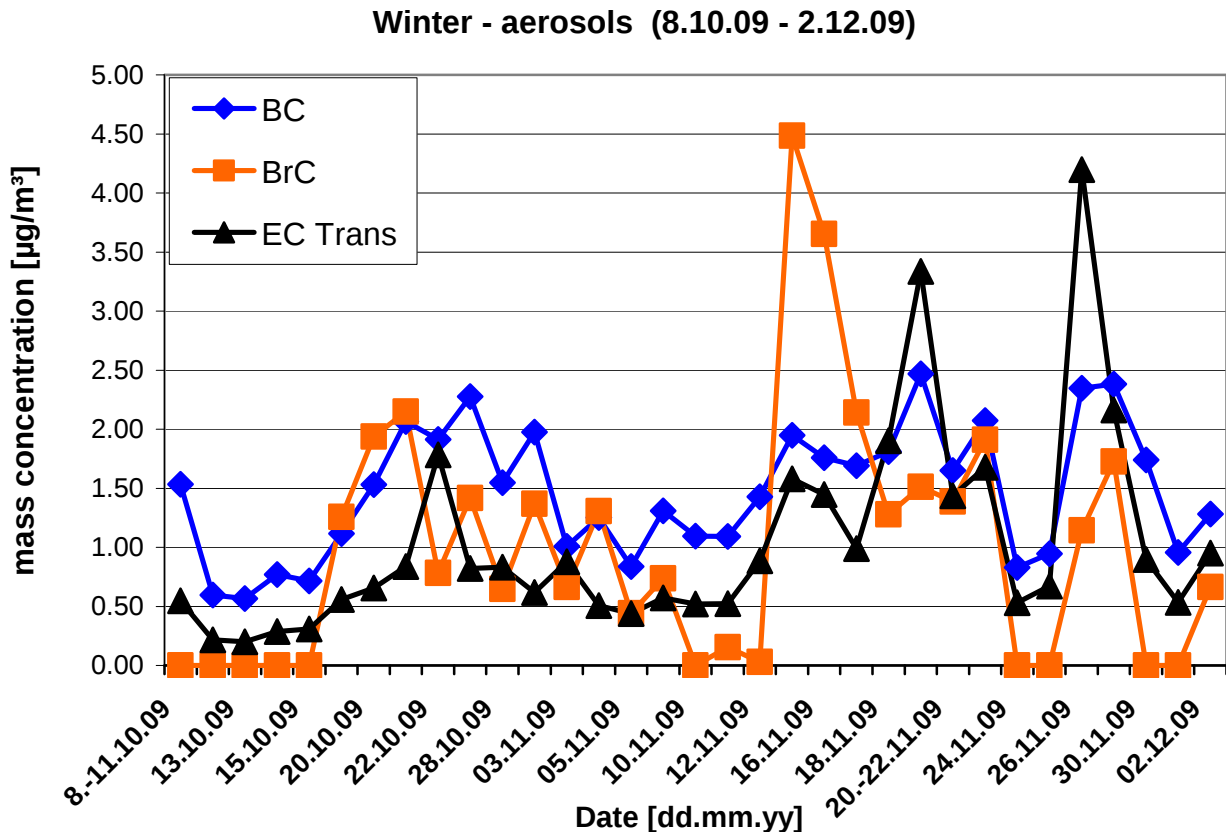


Figure 19: Time series of winter aerosols mass concentrations.

In the study performed by Reisinger et al. (2008) different measurement techniques for black and elemental carbon in wintertime were compared. Since the investigation took also place in Vienna their findings can be compared to the results of this study. While the general trend of EC and BC was similar, on particularly cold days when space heating increased the discrepancies were largest. This can be traced back to the higher BrC concentration present in those days. Besides their results illustrated that the TOT (thermo – optical transmittance) – NIOSH method underestimated the EC concentrations at all times by approximately 33 %. Considering that in our investigation a similar NIOSH method was used, their results coincide very well with the ones obtained in this study.

Though the Sunset Analyzer is not able to determine BrC, contrary to the Integrating Sphere, OC can be detected. Figure 20 displays OC versus BrC obtained for the measurement period.

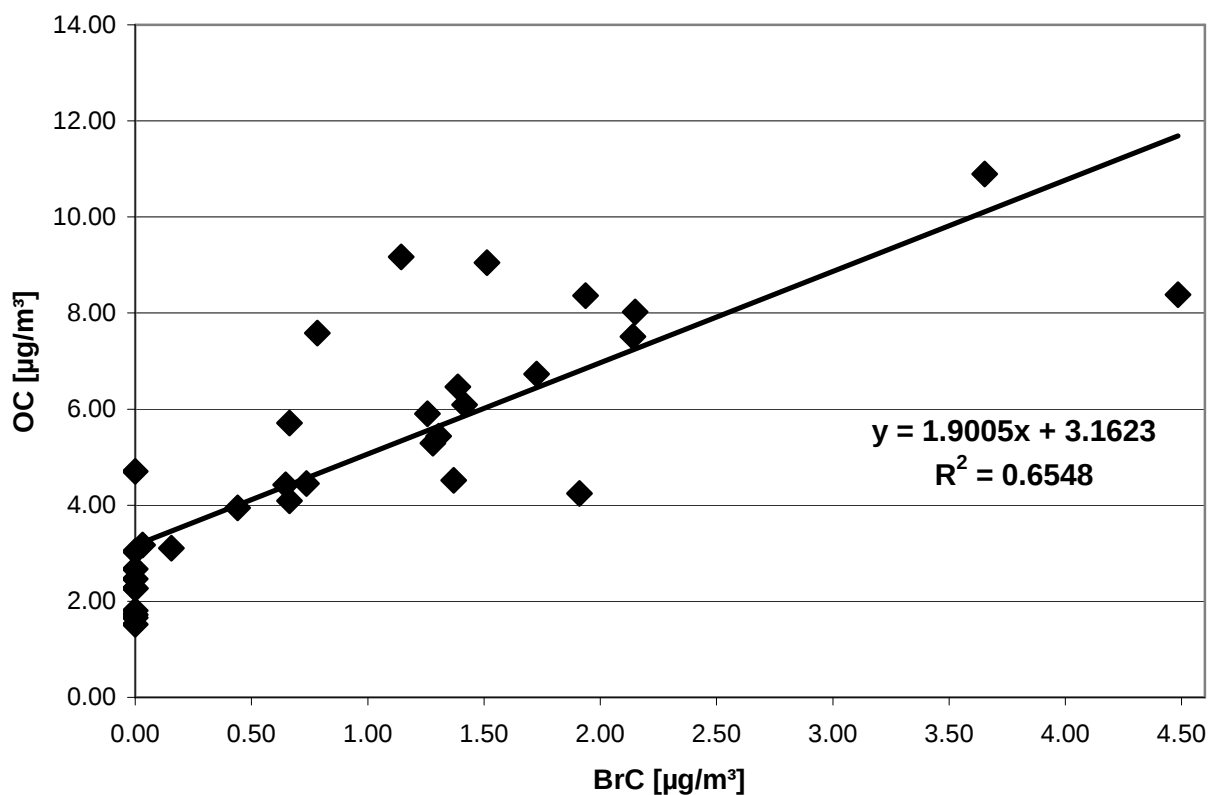


Figure 20: OC versus BrC.

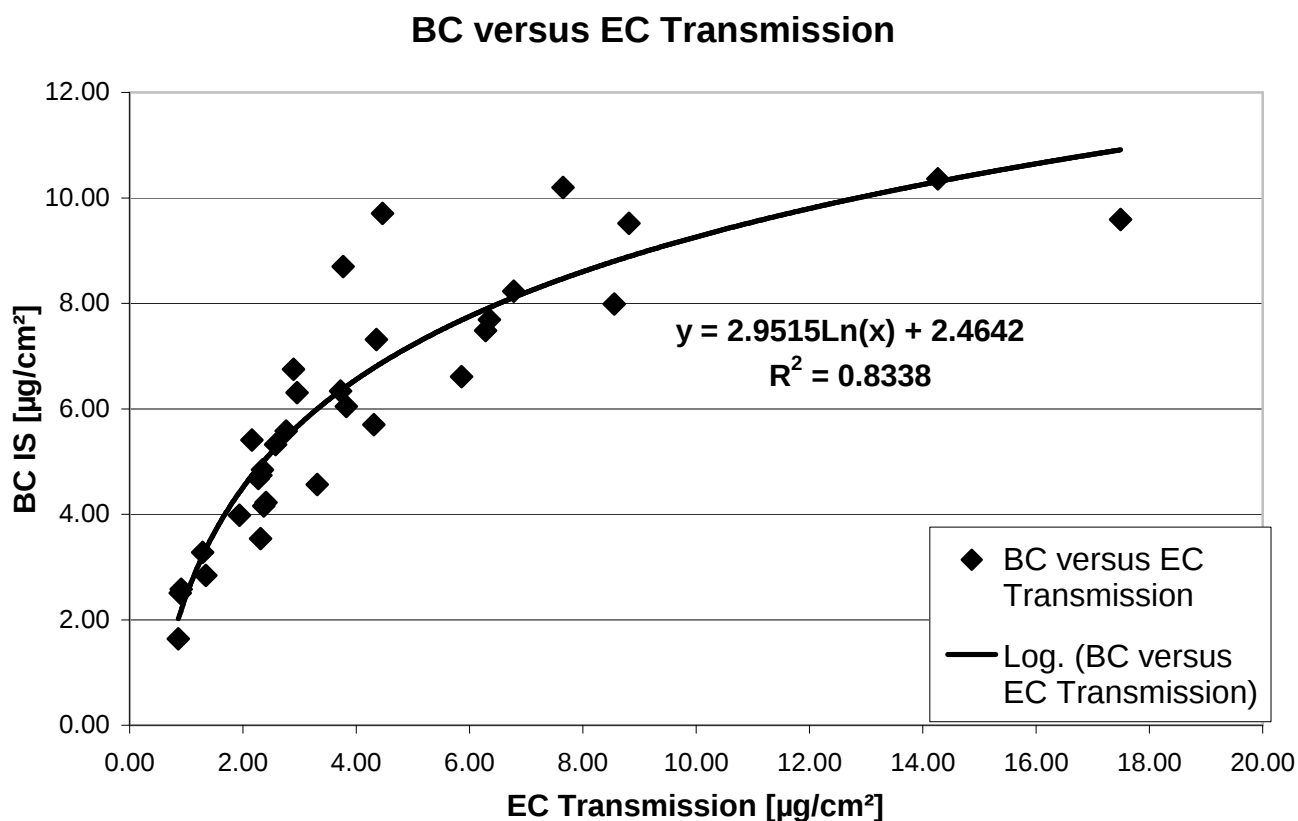
The figure above (figure 20) shows a poor correlation coefficient of only 0.66. The great difference in concentrations derives from the fact that BrC is just a highly variable part of the organic matter present in the atmosphere.

Moreover, the last data points in figure 19 merit closer examination. One can clearly see that at the end of November “EC Trans” exceeds BC values twice. The cause will further be explained in 5.1.3.2.

5.1.3.2. Comparison of EC and BC:

EC and BC should have comparable values even if they are obtained by two different measurement techniques. Section 5.1.3.2 demonstrated that with regard to this short time series, concentration ratios vary by a constant value except if another substance, like BrC, influences the analysis. Then the discrepancy can be much higher.

In this section EC is plotted against BC concentrations. The first figure (figure 21) illustrates all EC and BC data gained in this campaign given as mass loading per filter area.



As one can note very easily, the trend in figure 21 is not linear but much rather logarithmic suggesting a saturation effect in the BC IS data in the concentration range above $10 \mu\text{g}/\text{cm}^2$. In the range below a linear trend is visible. Hence, for closer investigation only values smaller than $10 \mu\text{g}/\text{cm}^2$ are chosen and plotted in figure 22.

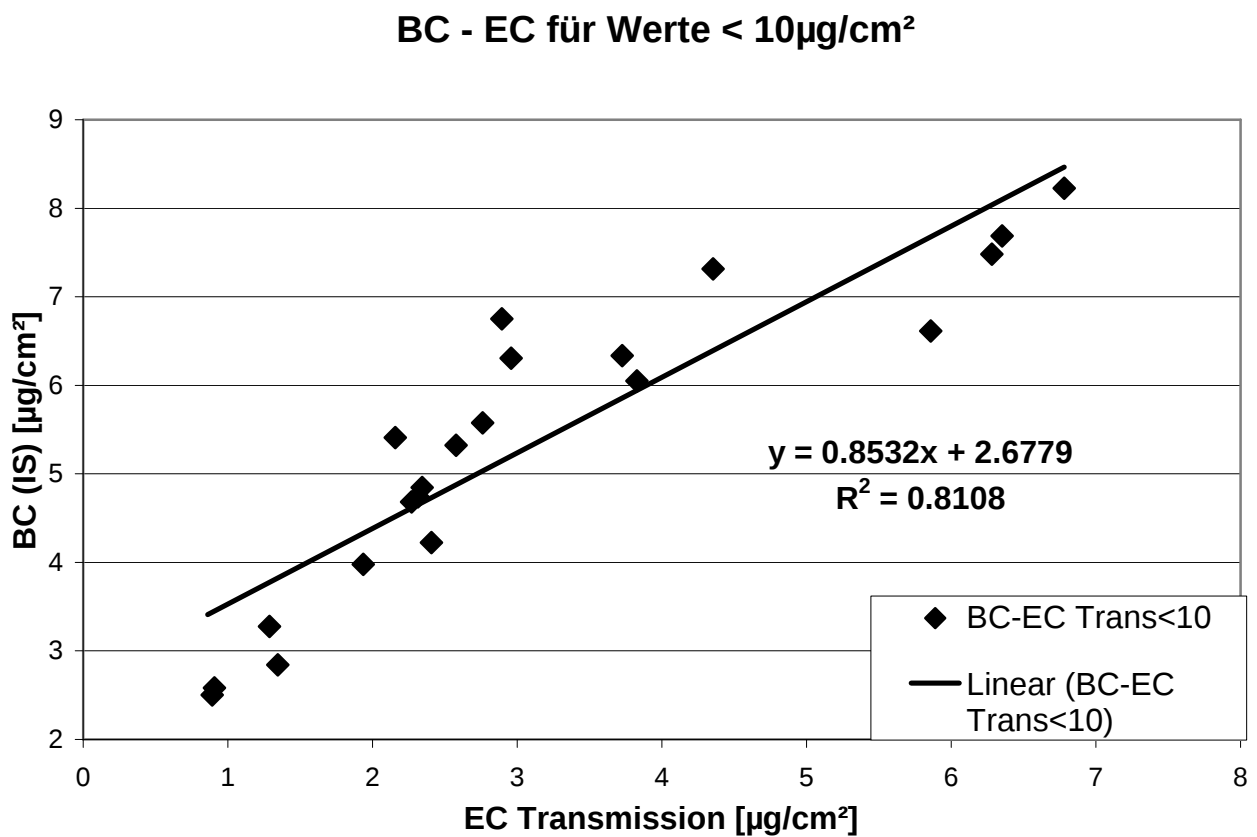


Figure 22: BC and EC values smaller than 10 µg/cm²;

The figure above shows the linear trend and the correlation coefficient of 0.8108 which underlines the relatively good match. Besides also the underestimation of “EC Trans” compared to BC can be seen.

Resulting from this last figure one can infer that the Integrating Sphere is only able to measure BC masses up to a value of 10 µg/cm² correctly, afterwards it reaches the point of saturation. Consequently those EC values, that exceeded the BC values in figure 19, occurred under conditions when the BC concentrations are biased low because of the saturation effect (see 3.3.6 for details).

5.2. Laboratory generated aerosols:

Though measurements were performed for both filter samples and spiked filters (4.2.2.1 and 4.2.2.2) only the results obtained with the second setup will be presented here. The reason is that using the nebulizing method it was practically impossible to prevent adsorption of organic vapors on the quartz fiber filters. Furthermore due to the not entirely homogeneous loading, two punches even from the same filter varied too much in concentration. Unlike the first, the second method was easier to handle because the handling time is very short and therefore the filter punches can be put in the desiccator immediately to dry after spiking. In this way the organic matter adsorbed by the filters is negligible (OC concentration approximately $0.3 \mu\text{g}/\text{cm}^2$).

5.2.1. Analysis in Sunset Analyzer and Integrating Sphere:

5.2.1.1. *Influence of BrC proxies on OC/EC split:*

Firstly all single suspensions (soot, Pahokee peat, Leonardite, HASS) were measured in the optical and thermal optical instrument and compared to the theoretical concentrations on the spiked filter punches (figure 23 below). In this respect it has to be mentioned that the theoretical values in figure 23 always denote the theoretical masses of the suspended substances and not the carbon mass.

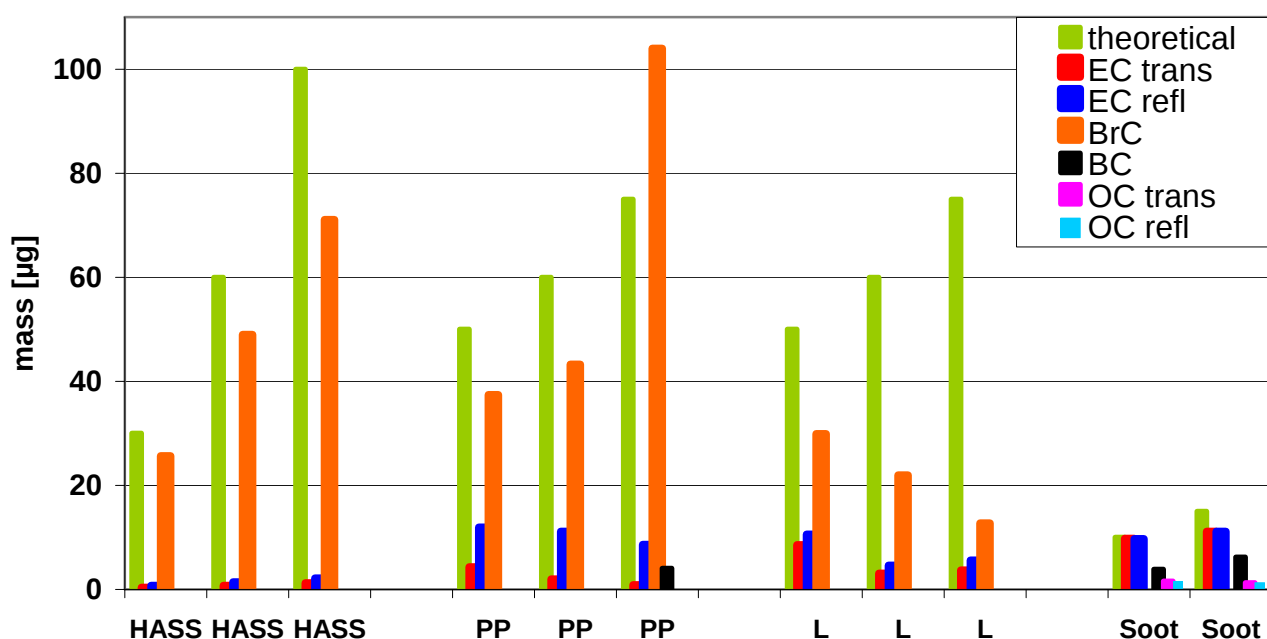


Figure 23: Theoretical masses compared to BrC, BC measured in the IS and EC/OC transmittance and EC/OC reflectance in the Sunset Analyzer.

Even though the first three substances do not contain any soot, the Sunset Analyzer detects considerable amounts of “EC Trans” and “EC Refl”. In all cases the “EC Refl” exceeds the “EC Trans”, where discrepancies are biggest for PP. The measurements of HASS reveal “EC Refl” and “EC Trans” masses of the order of 2 % and 1% of the total HASS masses put on the filter punches, respectively. For PP the “EC Refl” masses make up to 24 % of the total mass, whereas the “EC Trans” masses reach maximally 9 %. With regard to L in the most extreme case “EC Refl” is 21 % and “EC Trans” 17 % of the total Leonardite masses on the spiked punches.

Considering the BrC determined by the IS, for HASS it can be seen that it is always lower than the actual masses applied on the filter punch. However, the masses increase with increasing HASS concentrations and underestimate the theoretical values by about 15 to 29 %. In the case of PP the underestimation is around 25 % in the first two examples but in the third the measured BrC mass overshoots the theoretical concentration. There is reason to believe that this overestimation originates from additional matter present on the filter punch, since

it is also the only case where the IS detects a BC mass even if there should not be any. For the Leonardite the BrC masses decrease with increasing theoretical concentrations. It should be stressed here that the IS measures the BrC mass according to the HASS calibration. Therefore the HASS samples are the only ones with reliable results. To gain reliable PP and L masses respective calibrations are needed. Consequently discrepancies between theoretical PP and L masses and measured masses can be traced back to using an inadequate calibration.

Looking at the two soot concentrations, the results obtained by the IS indicate that no BrC is present and that the BC masses underestimate the theoretical ones by approximately 60 %! Conversely the “EC Refl” and “EC Trans” masses are rather close to the theoretical concentrations especially in the first case. They underestimate the soot masses by about 3 % in the first example and 25 % in the second one. Besides the soot samples are the only ones where the “EC Trans” masses are higher than the “EC Refl” ones. Furthermore the Sunset Analyzer detects some OC in the soot measurements equivalent to about 1.45 µg for both concentrations and this mass is considerably higher than the common blank mass of 0.3 µg for pre – baked filters.

For a closer examination the thermograms for each single substance are presented here:

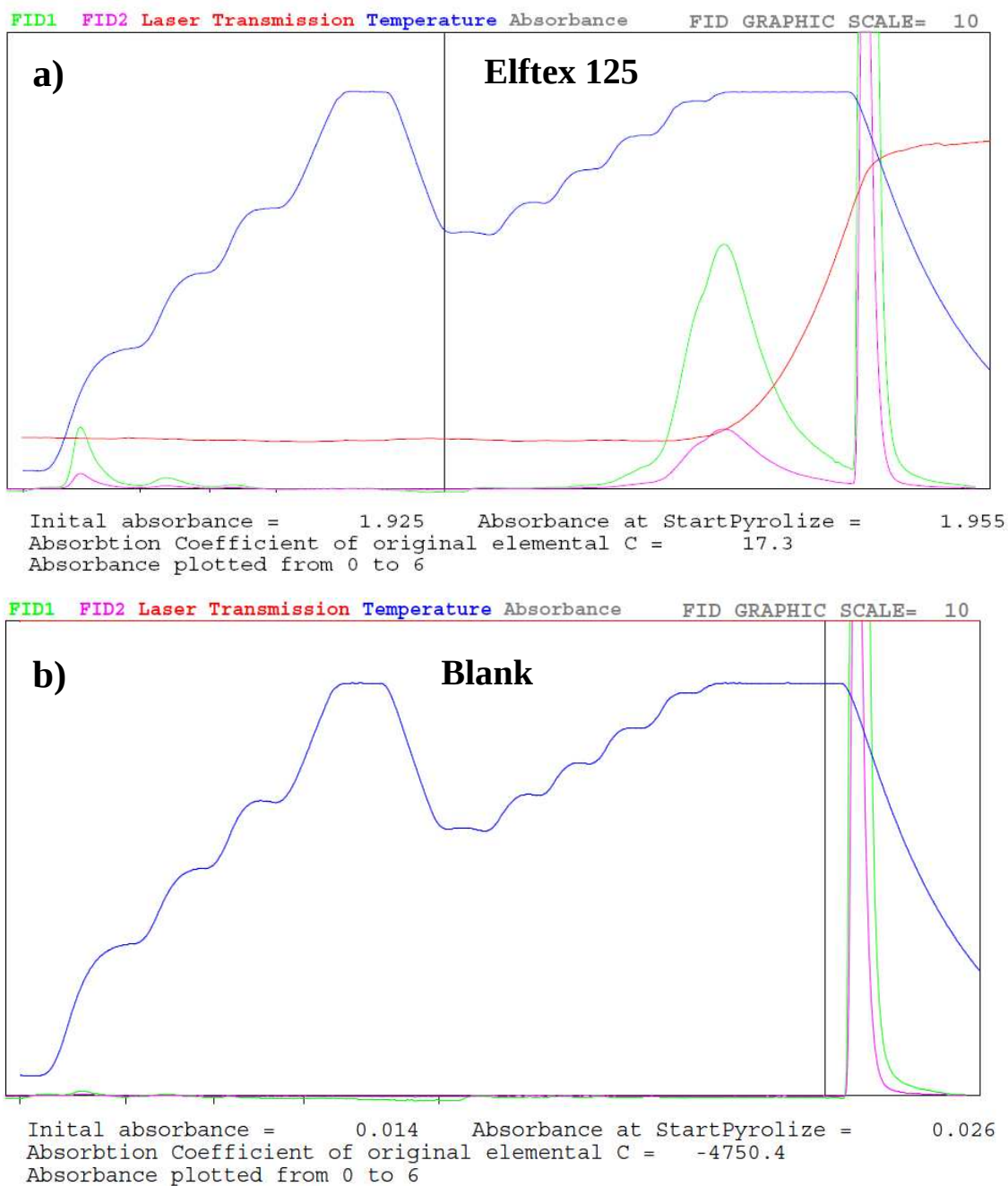


Figure 24: a) typical thermogram for soot (Elftex 125);
b) Thermogram for a pre baked blank filter;

Figure 24 a) illustrates a typical thermogram for a pure soot suspension. In this case the split point indicates at the same time the introduction of the filter punch in a He/O₂ atmosphere. Following the FID signals one can see that some carbon evolved off the filter mainly at the beginning (He atmosphere – at ~ 310

°C) and combustion occurred mainly at the last temperature step (870°C) in the He/O₂ atmosphere. This latter peak is the characteristic one for soot. The resulting concentrations for this analysis are:

Organic C = 1.29 +-0.26 µg/cm²
Carbonate C = 0.00 +- µg/cm²
Elemental C = 11.15 +-0.76 µg/cm²
Total C = 12.45 +-0.92 µg/cm²
EC/TC ratio = 0.896

An important problem that occurs for soot samples concerns the setting of the split point. Since no charring occurs the laser signal is constant, except for some small fluctuations, till the main combustion takes place. Therefore the Sunset Analyzer chooses the split point rather randomly misinterpreting the highest fluctuation peak. In order to compare soot samples in this study the split point was set manually at the point where O₂ is injected in the He – atmosphere.

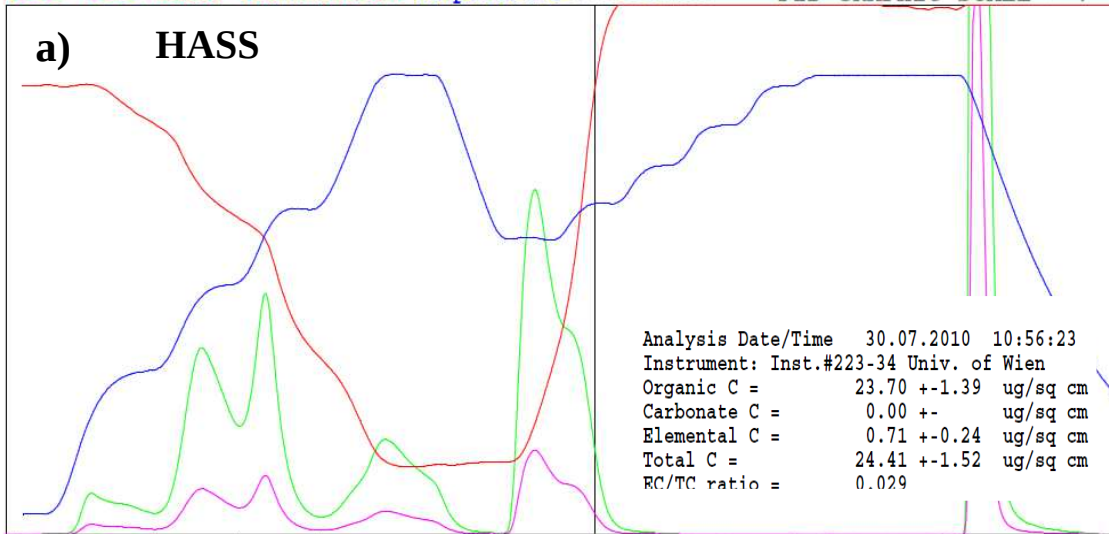
Figure 24 b) shows the thermogram of a pre – baked blank. Hardly any FID signals are visible and no split time is indicated. The results for this sample are:

Organic C = 0.07 +-0.20 µg/cm²
Carbonate C = 0.00 +- µg/cm²
Elemental C = 0.00 +-0.20 µg/cm²
Total C = 0.07 +-0.30 µg/cm²
EC/TC ratio = -0.005

For filters that were exposed to laboratory air for at least 15 minutes the OC blank values were of approximately 2 µg/cm² in contrast to the approximately 0.3 µg/cm² of freshly pre – baked blanks.

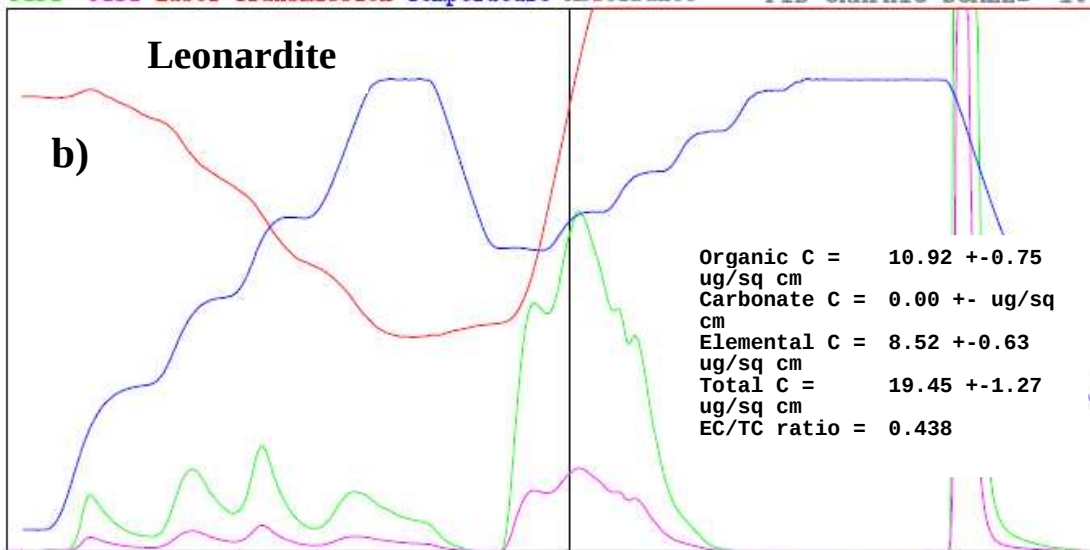
The next figures illustrate the thermograms for the BrC proxies HASS, L and PP:

FID1 FID2 Laser Transmission Temperature Absorbance FID GRAPHIC SCALE= 7



Initial absorbance = 0.231 Absorbance at StartPyrolyze = 2.022
 Absorbation Coefficient of original elemental C = 32.7
 Absorbance plotted from 0 to 6

FID1 FID2 Laser Transmission Temperature Absorbance FID GRAPHIC SCALE= 10



Initial absorbance = 0.490 Absorbance at StartPyrolyze = 1.185
 Absorbation Coefficient of original elemental C = 5.7
 Absorbance plotted from 0 to 6

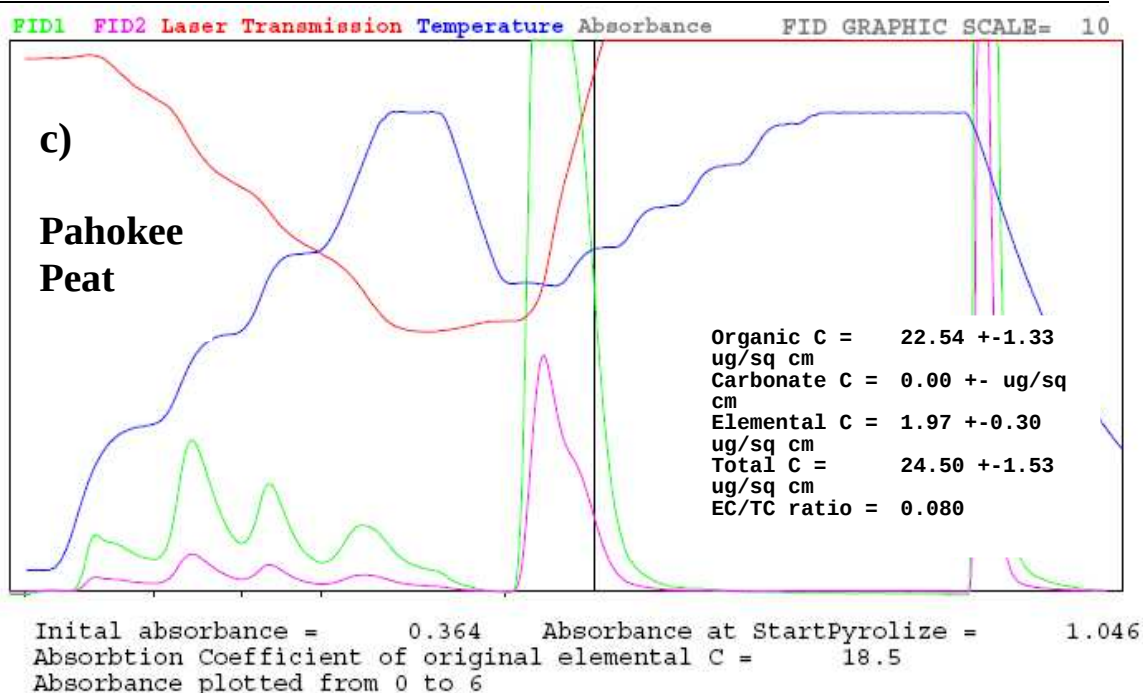


Figure 25: a) Thermogram of humic acid sodium salt (HASS);
b) Thermogram of Leonardite (L);
c) Thermogram of Pahokee Peat (PP);

The three figures above all clearly illustrate the decreasing laser signal due to the charring process. Besides looking at the main combustion peaks differences between the substances are visible. For instance HASS shows the main peak at 550°C in the He/O₂ atmosphere and a small one in the step afterwards at 625°C. Contrarily Leonardite has its characteristic peak at 625°C in the He/O₂ atmosphere. The Pahokee Peat thermogram is more similar to the HASS one, having the main peak at 550°C and a small one at 625°C.

5.2.1.2. Influence of inorganic substances on EC:

To determine the influence inorganic substances have on the EC analysis in the Sunset Analyzer, two different chemicals were chosen: sodium chloride and ammonium sulfate. Mixtures of soot and these substances were prepared and

finally filter punches were spiked with known concentrations. The graph below shows the results of these measurements.

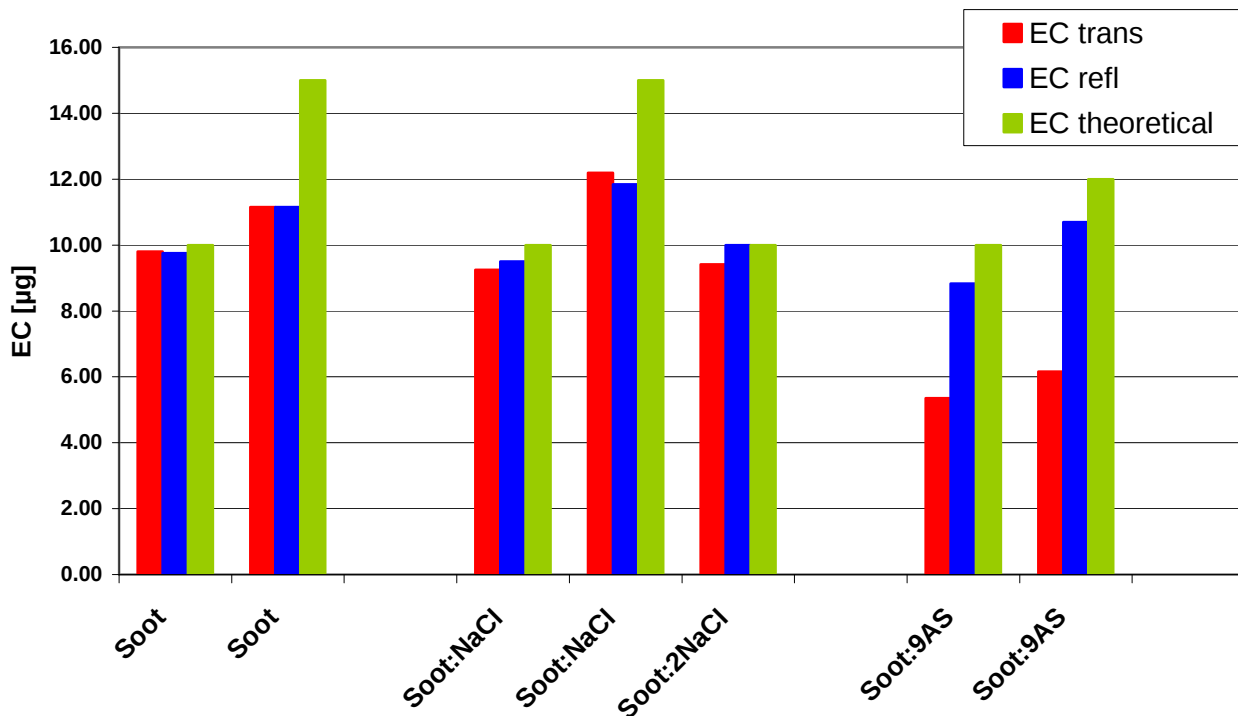


Figure 26: Analysis of soot, soot and NaCl and soot and AS in the Sunset Analyzer compared to theoretical values.

The overall picture shows that in every case the “EC Trans” and “EC Refl” underestimate the theoretical EC (Elftex) mass. The “EC Trans” signal of the soot/NaCl mixture differs on average 11 % from the theoretical values, the “EC Refl” 9 %. With regard to the soot/ammonium sulfate mixtures, the discrepancy between these two EC masses is significant. While the “EC Trans” underestimates the theoretical masses by approximately 48 %, the “EC Refl” is much closer to the theoretical values only differing by 11 %.

5.2.1.2.1. Influence of oxygen containing compounds on EC:

The operating principle of the Sunset Analyzer requires a pure helium atmosphere during the first cycle of the analysis. Since ammonium sulfate contains oxygen it influences this step by releasing its oxygen. Consequently some of the elemental carbon can be oxidized earlier, influencing the split point in a way that the EC mass is underestimated because some of it is interpreted as OC.

Figure 27 illustrates the thermogram for the soot/9AS mixture.

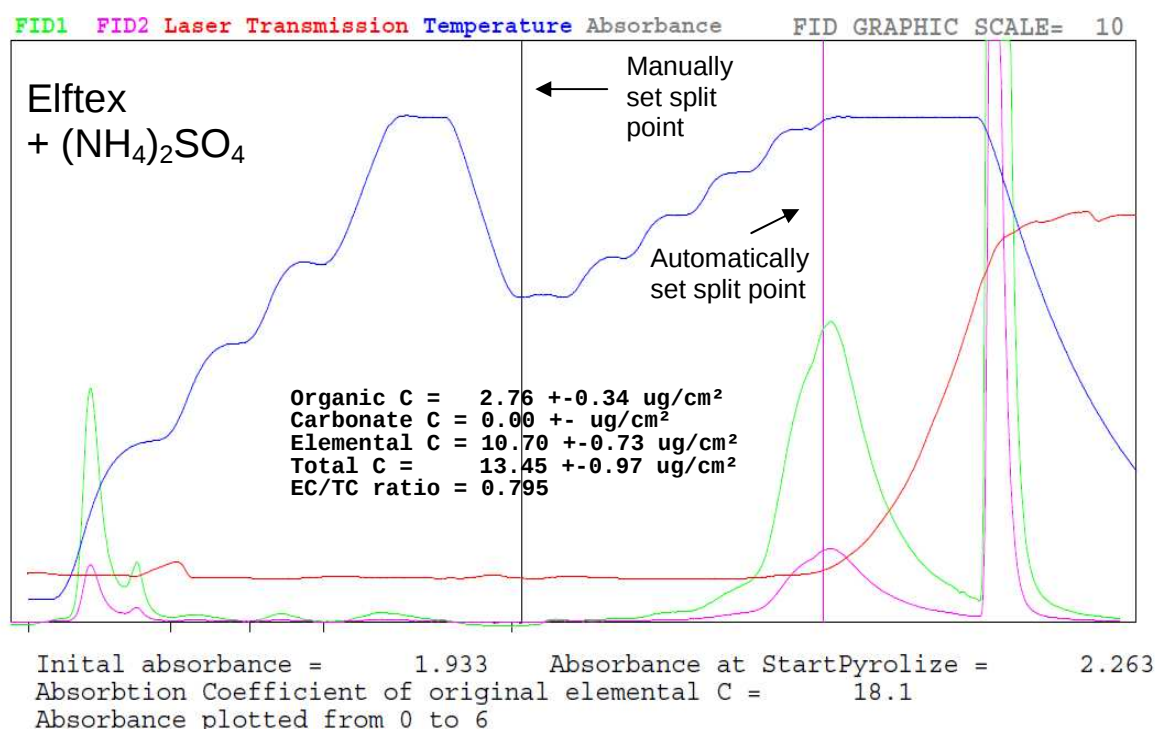


Figure 27: Thermogram of the mixture soot: 9AS.

First of all we can see that the automatically set split point is very late, therefore it had to be set manually. Actually the automatic split point is set at the exact temperature step where the soot peak is. One can clearly see that in this analysis just half of the soot peak is interpreted as EC whereas the other half is seen as OC. Even if the split point is manually set where the He atmosphere is changed to He/O₂, a considerable OC mass is detected. Therefore the role of the

oxygen that is released in the He cycle becomes clear namely that it falsifies the OC signal, leading to an underestimation of EC.

5.2.1.2.2. *Influence of Na on EC:*

In section 2.2 the problematic nature of Na is shown which can influence the combustion temperature of the EC. This will be further illustrated by reference to the corresponding thermogram (figure 28 below).

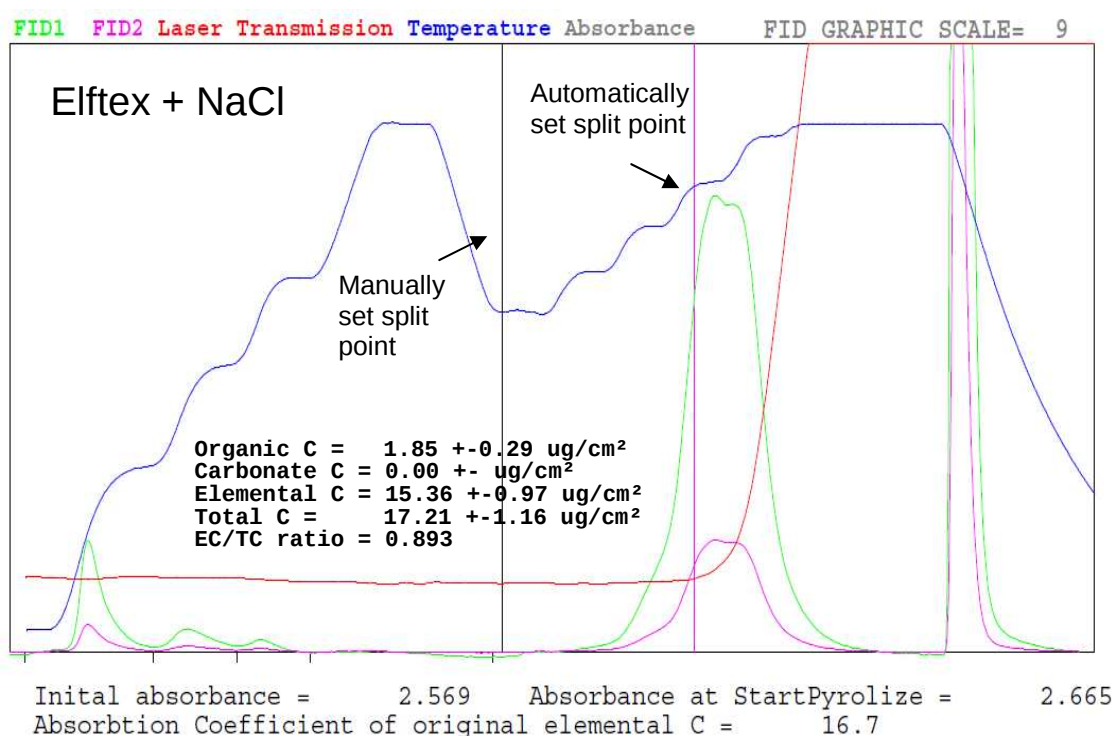


Figure 28: Thermogram of the mixture soot: NaCl.

When comparing this thermogram to the one shown in figure 24 a) for soot a significant change is noticeable with regard to the main peak. While the soot peak was placed at the maximum temperature step of 870°C, the thermogram above shows the peak between the third step in He/O₂ (775°C) and the forth (850°C). Therefore we can conclude that the Na acted like a catalyst and lowered

the combustion temperature of EC as suggested by Novakov and Corrigan (1995). Besides also in this case the split point was set manually.

5.2.1.3. Influence of inorganics on mixtures:

Several suspensions were mixed containing soot, one BrC proxy and one inorganic compound, being either AS or NaCl. The influences these two inorganics have on the soot analysis were discussed in 5.1.2.2. Now mixtures are considered and the figure below illustrates the measured masses.

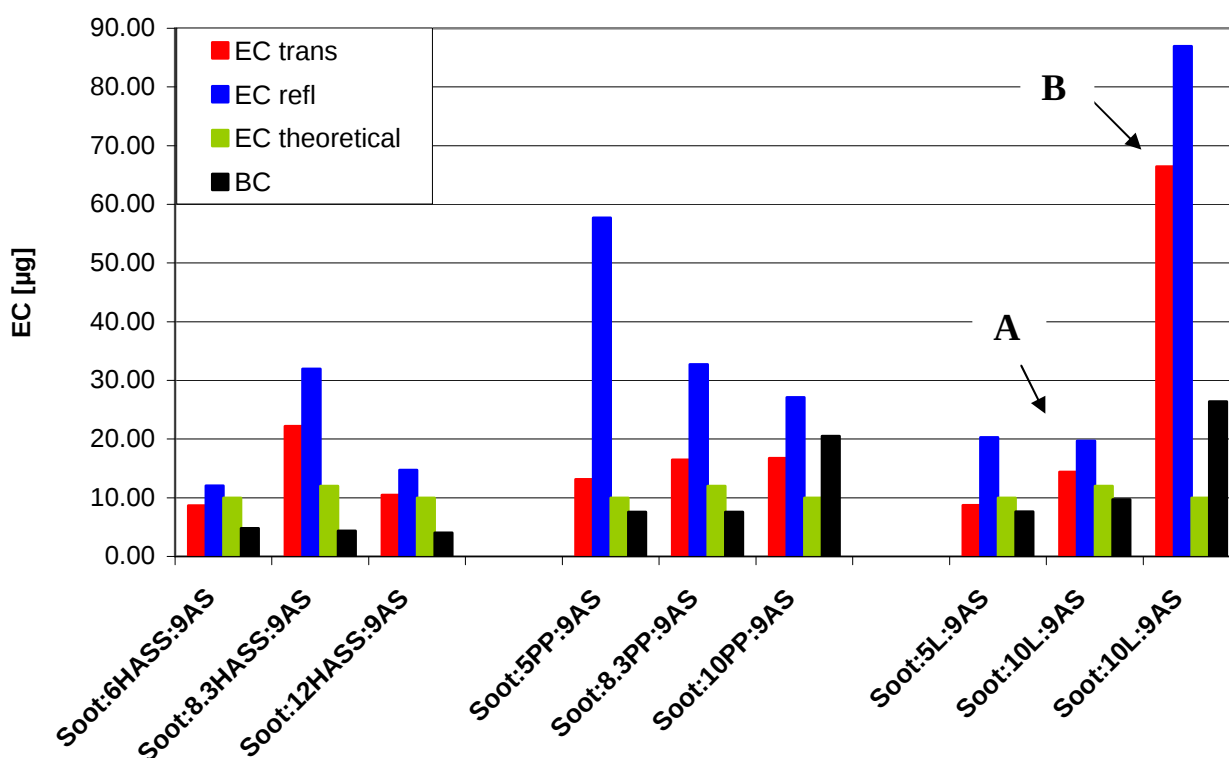
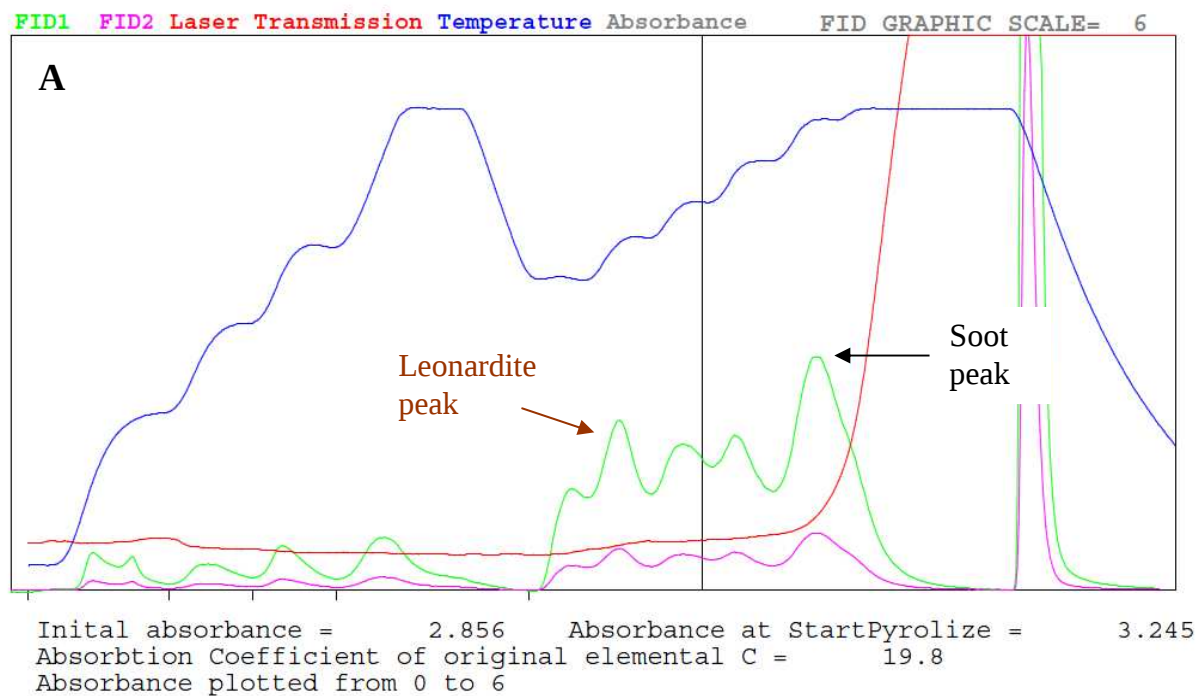


Figure 29: Theoretical EC mass in mixtures compared to “EC Trans”, “EC Refl” and BC.

It can clearly be seen that the “EC Refl” always strongly overestimates the theoretical EC mass. The “EC Trans” overestimates the theoretical EC mass in the majority of cases but it is always smaller than the “EC Refl” signal. With regard to BC, it underestimates the theoretical EC mass except for two mixtures which present higher BC masses than the theoretical ones. Especially the Soot: 10L: 9AS

mixture shows unique results. To take a closer look the thermograms are shown in figure 30.



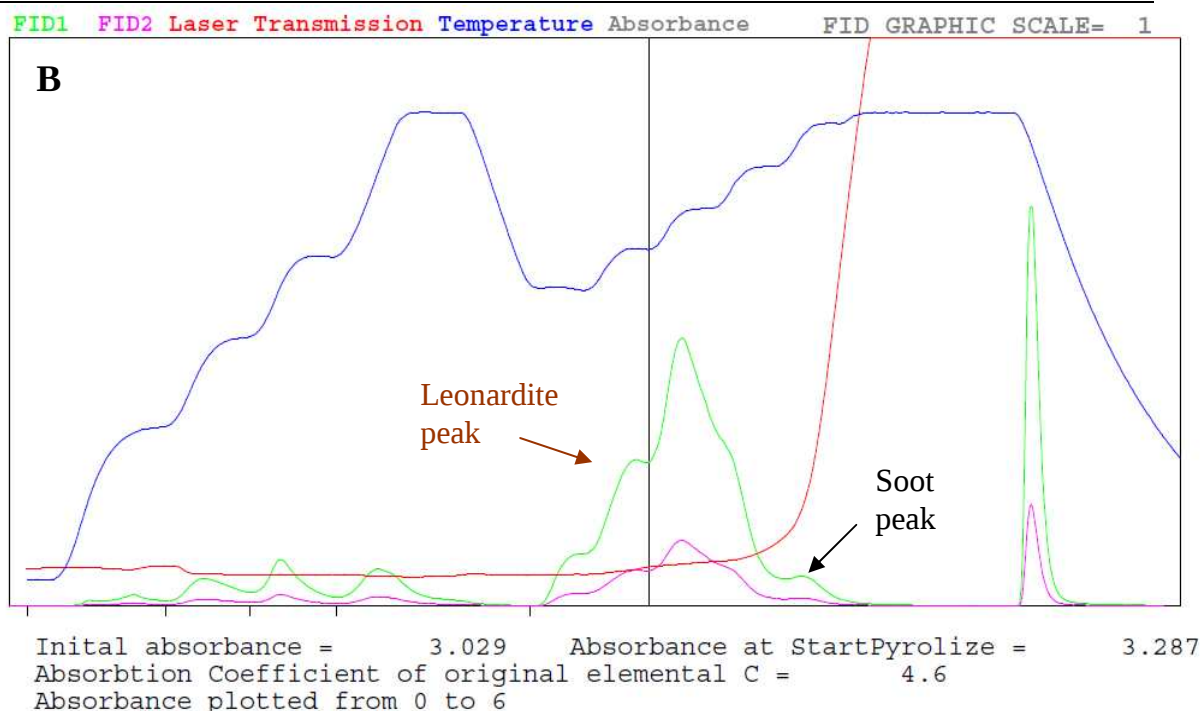


Figure 30: Thermograms of the mixtures A and B soot: 10L: 9AS;

One can see that both thermograms show five peaks in the He/O₂ atmosphere but while the peaks of thermogram A are more or less equally strong with a more distinct peak for soot, the thermogram for B has a more pronounced peak at 700 °C (third step), then a relatively high peak at 625 °C (Leonardite peak) and 775 °C and two small peaks at 550 °C and 850 °C (soot peak). The biggest difference between the two thermograms is concerning the soot peaks. The reasons for this discrepancy remain unknown.

5.2.1.4. Contribution of EC to BrC measurements:

As we could see in figure 23 a certain EC concentration can be found on filter punches that were only spiked with BrC proxies and therefore should not contain any EC. Here we will examine this fact more closely. Figure 31 illustrates all single substance and soot/BrC mixtures and the EC mass that was found in the filter punches by the Sunset Analyzer. Figures 23 and 31 show that the Integrating

Sphere did not find any BC in the BrC proxies' single substances except in one PP analysis but this exception was discussed earlier.

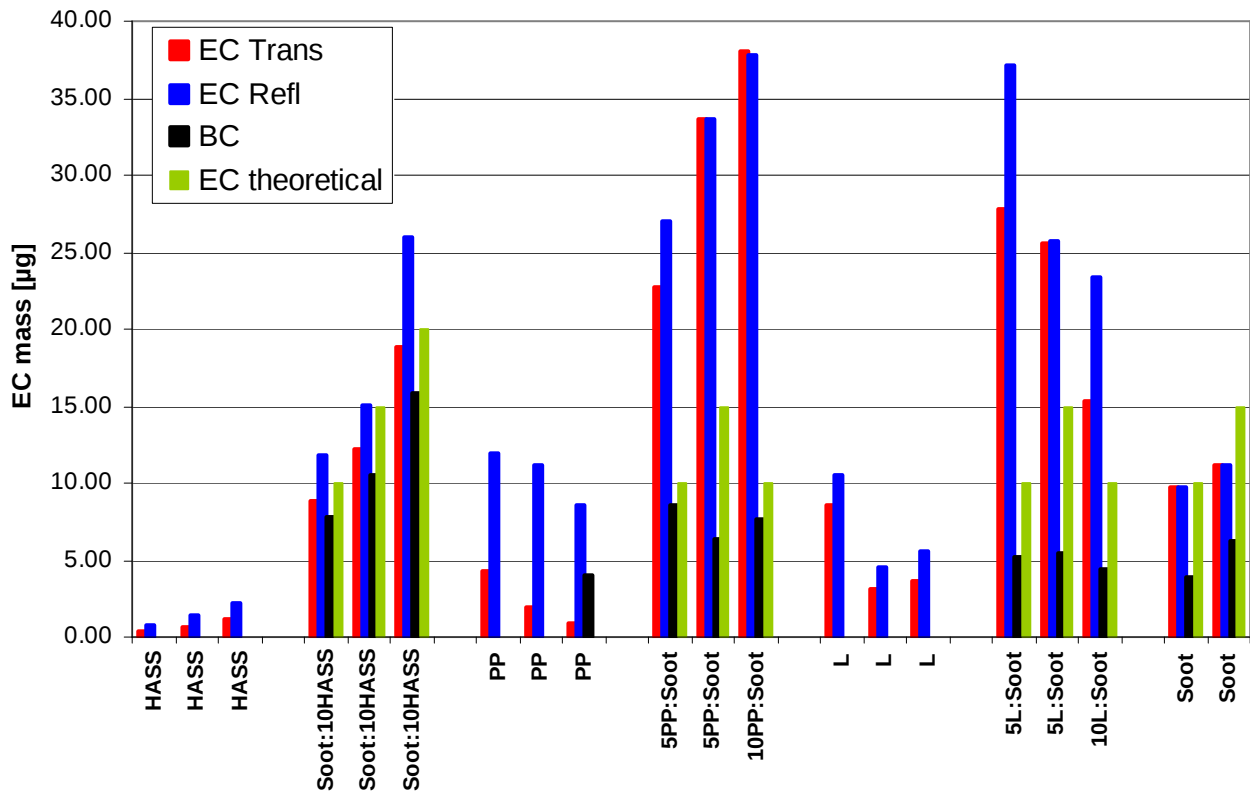


Figure 31: Contribution of EC in BrC measurements.

The figure above displays again the wrongly measured EC in BrC proxy samples. With regard to the mixtures, it can be seen that for the soot/HASS mixture the “EC Refl” and “EC Trans” are more or less in the range of the theoretical EC masses. However, the BC always underestimates the theoretical EC mass. For the soot/PP and soot/L mixtures the “EC Refl” and “EC trans” largely overestimate the theoretical masses, while the BC is again lower than the EC theoretical. These EC findings indicate that the Sunset Analyzer wrongly attributes some of the BrC mass to EC. How much EC is found, depends on the specific BrC proxy and its composition (see section 4.2). Comparing these three proxies the HASS seems to be the easiest one to handle for the Sunset Analyzer since the EC

mass in the single suspension is the smallest. Therefore also in soot/BrC mixtures some of the BrC will be attributed to the EC mass, falsifying the total EC mass.

5.2.2. Comparison of “EC Reflectance” to “EC Transmittance”:

The Sunset Analyzer offers two different optical monitoring methods namely the laser’s transmittance and reflectance signals through the filter punch. The figure below illustrates the EC and OC corrected for charring by reflectance versus the EC and OC corrected by transmittance:

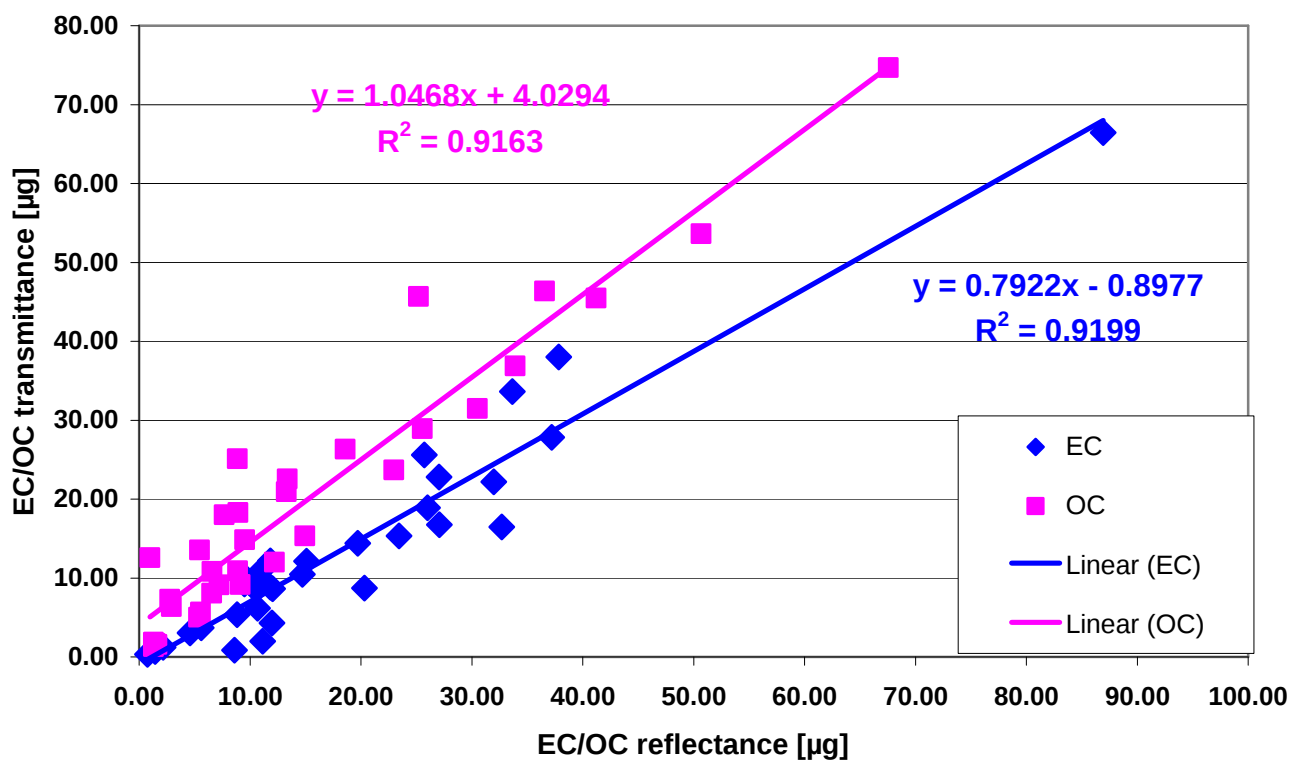


Figure 32: “EC reflectance” versus “EC transmittance”.

Comparing these EC/OC masses one can clearly see that the linear regression fits very well. The squared correlation coefficients are of 0.9199 for the EC regression and 0.9163 for the OC regression. As one could notice also in the former figures the “EC

reflectance” values are always higher than the “EC transmittance”. Conversely the OC transmittance exceeds the OC reflectance at all times.

The question which correction is best has not yet been solved but we know that the transmittance monitoring depends on absorption and forward scattering through the filter while the reflectance is dominated by backscattering of the filter surface with particle deposit (Chen et al. 2004). Besides it was found that during the He cycle, pyrolysis leads to totally black filters on both sides (Huntzicker et al. 1982; Chow et al. 2004).

Chow et al. (2005) performed many comparisons between thermal/optical reflectance (TOR) and transmittance (TOT) methods. For the EC, plotting the reflectance signal on the x-axis and the transmittance on the y-axis, regression slopes of 0.90, 0.68 and 0.83 for different temperature protocols were found. Figure 32 shows a regression slope of 0.79 for the EC comparison.

6. Conclusions

The following conclusions can be deduced from the measurements performed in the course of the presented thesis:

The wintertime campaign illustrated that the ratio of BC, obtained by the Integrating Sphere, and EC, given by the Sunset Analyzer, depends on the BrC concentration present in the atmosphere. If no BrC is present, the ratio is rather constant while increasing BrC is followed by decreasing EC concentrations. Therefore it can be concluded that the Sunset Analyzer is unable to measure EC correctly in the presence of BrC. Besides the BC concentration always exceeds the EC concentration. In two cases the saturation effect occurred in the Integrating Sphere, implying that the BC concentrations exceeded the detection limit determined by this optical technique.

The measurements performed in the laboratory revealed that for filters loaded with solely soot, soot/ammonium sulfate and soot/NaCl an automatic setting of the split point in the Sunset Analyzer is inadvisable because in this case the instrument chooses it rather randomly.

Analysis of soot and inorganic salt (NaCl , $(\text{NH}_4)_2\text{SO}_4$) mixtures illustrated that the presence of Na lowers the EC combustion temperature while ammonium sulfate provides oxygen which falsifies the OC and EC results. Besides traces of OC were found in all measurements even if none should have been present.

Several BrC proxies were analyzed in the Sunset Analyzer and all of them showed massive charring. Due to the unknown optical properties of pyrolytically generated elemental carbon (PEC) this could lead to an overestimation of EC and therefore underestimation of OC as a consequence of a wrong split point setting.

The comparison of “EC Trans” and “EC Refl” illustrated a higher “EC Refl” concentration at all times. Comparing “EC Trans” and “EC Refl” to BC, the former showed values closer to the measured BC masses but BC concentrations were always lowest. Besides the BC masses underestimated the theoretical Elftex masses at all times except in two cases namely in the mixtures soot: 10PP: 9AS and soot: 10L: 9AS (figure 29). This could be explained by the high concentration of BrC proxy present in the sample which could be misinterpreted as BC by the IS.

The overall picture shows that the Sunset Analyzer is not capable of measuring the EC and OC concentrations in these soot mixtures and BrC proxies correctly. One of the reasons why BC and EC are always lower than the theoretical Elftex concentrations is due to the process of spiking the filter punches, where wall losses occur (loss of approximately 10 %; Clarke et al. 1967).

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List of Figures:

FIGURE 1: A SHOWS HOW SOOT PARTICLES (ARROWS) ARE ANNEXED ON AIR DROPLETS, B ILLUSTRATES THE DETAILED COMPOSITION OF SOOT AND C SHOWS FLUE ASH WHICH IS A BYPRODUCT OF COMBUSTION.	4
FIGURE 2: SOOT PARTICLES ON A NUCLEOPORE FILTER SEEN UNDER AN ELECTRON MICROSCOPE;	5
FIGURE 3: THE COMPOSITION OF THE PM _{2.5} URBAN ATMOSPHERIC AEROSOL IN CENTRAL EUROPE ACCORDING TO THE STUDY PERFORMED BY PUTAUD ET AL.	8
FIGURE 4: THE COMPOSITION OF THE PM ₁₀ URBAN ATMOSPHERIC AEROSOL IN CENTRAL EUROPE ACCORDING TO THE STUDY PERFORMED BY PUTAUD ET AL.	9
FIGURE 5: POLAR DIAGRAM OF RAYLEIGH SCATTERED LIGHT. SCATTERING PLANE IS PARALLEL TO THE PAPER.	16
FIGURE 6: MIE SCATTERING OF LIGHT ($\lambda=633\text{nm}$) BY A SPHERICAL PARTICLE ($D=2\mu\text{m}$); $A=9.92$; ONE CAN CLEARLY SEE THE INTENSITIES AT DIFFERENT SCATTERING ANGLES (NOTE THE LOGARITHMIC AXES).	18
FIGURE 7: RADIATIVE FORCING BETWEEN 1750 AND 2005.	25
FIGURE 8: A SCHEMATIC REPRESENTATION OF THE HUMAN RESPIRATORY TRACT.....	26
FIGURE 9: DEPOSITION IN EXTRATHORACIC, TRACHEOBRONCHIAL AND ALVEOLAR REGIONS VERSUS PARTICLE DIAMETER. THE FILLED SIGNS REPRESENT MEASURED VALUES WHEREAS THE EMPTY ONES ARE THEORETICAL, IDEAL VALUES.	27
FIGURE 10: THERMOGRAM GAINED BY THE SUNSET ANALYZER.	34
FIGURE 11: CALIBRATION CURVE FOR SUCROSE.....	36
FIGURE 12: SETUP OF AN INTEGRATING SPHERE;	39
FIGURE 13: CALIBRATION CURVES FOR CARBON BLACK (SQUARES, FULL LINES) AND HUMIC ACID SODIUM SALT (TRIANGLES, BROKEN LINES) AT 404 (BLUE SYMBOLS) AND 650 NM (RED SYMBOLS).	43
FIGURE 14: MIXING STATE: A) EXTERNAL MIXTURE: A HETEROGENEOUS POPULATION OF INTERNALLY HOMOGENEOUS PARTICLES; B) INTERNAL MIXTURE: HOMOGENEOUS POPULATION OF INTERNALLY HOMOGENEOUS PARTICLES; C) INTERNAL MIXTURE: HETEROGENEOUS PARTICLE COMPOSITION AND POPULATION;	45
FIGURE 15: TO THE LEFT: FILTER HOLDER WITH PROTECTION CAP AND PLASTIC BAG TO PREVENT WATER FROM GETTING IN THE HOLDER AND DIRECTLY ONTO THE FILTER; TO THE RIGHT ABOVE: BALGEN-GAS METER TO MEASURE THE FLOW RATE; TO THE RIGHT BOTTOM: PUMP;	49
FIGURE 16: TO THE LEFT: THE CYLINDRICAL TUBE WITH AT ONE END THE NEBULIZER AND INSIDE THE FILTER HOLDER; TO THE RIGHT: THE ACTIVE CARBON FILTER CONSTRUCTED IN THE WORKSHOP OF THE FACULTY OF PHYSICS (CONSTRUCTION PLANS BY GERHARD STEINER).	53
FIGURE 17: BC AND BrC MASS CONCENTRATIONS OBTAINED BY THE INTEGRATING SPHERE; THE SECONDARY Y – AXIS ILLUSTRATES THE AVERAGE TEMPERATURE OF THOSE DAYS. ...	56
FIGURE 18: OC AND EC MASS CONCENTRATIONS OBTAINED BY THE SUNSET ANALYZER AND RATIO OF OC/EC.....	57
FIGURE 19: TIME SERIES OF WINTER AEROSOLS MASS CONCENTRATIONS.....	58
FIGURE 20: BrC VERSUS OC.....	59
FIGURE 21: BC VERSUS EC TRANS.	61

FIGURE 22: BC AND EC VALUES SMALLER THAN 10 $\mu\text{G}/\text{CM}^2$;	62
FIGURE 23: THEORETICAL MASSES COMPARED TO BrC, BC MEASURED IN THE IS AND EC/OC TRANSMITTANCE AND EC/OC REFLECTANCE IN THE SUNSET ANALYZER.	64
FIGURE 24: A) TYPICAL THERMOGRAM FOR SOOT (ELFTEX 125);	66
FIGURE 25: A) THERMOGRAM OF HUMIC ACID SODIUM SALT (HASS);	69
FIGURE 26: ANALYSIS OF SOOT, SOOT AND NaCl AND SOOT AND AS IN THE SUNSET ANALYZER COMPARED TO THEORETICAL VALUES.	70
FIGURE 27: THERMOGRAM OF THE MIXTURE SOOT: 9AS.	71
FIGURE 28: THERMOGRAM OF THE MIXTURE SOOT: NaCl.	72
FIGURE 29: THEORETICAL EC MASS IN MIXTURES COMPARED TO EC TRANS, EC REFL AND BC.	73
FIGURE 30: THERMOGRAMS OF THE MIXTURES A AND B SOOT: 10L: 9AS;	75
FIGURE 31: CONTRIBUTION OF EC IN BrC MEASUREMENTS.	76
FIGURE 32: EC REFLECTANCE VERSUS EC TRANSMITTANCE.....	77

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