

Evolved Gas Analysis of Ambient and Surrogate Carbonaceous Particles

E. Karg¹, G. Matuschek², O. Schmid¹, A. Schröppel¹ and H. Schulz¹

GSF Research Center for Environment and Health

¹Institute for Inhalation Biology, ²Institute of Ecological Chemistry

Introduction

The content of elemental and organic material of carbonaceous particulates (EC/OC) is an important parameter for characterization, especially the OC content is frequently used for correlation with negative health effects. Most methods detect OC by thermally desorbing OC, oxidizing it to CO₂ and quantify it based on the measured CO₂ concentration (Birch, 1999). Alternatively, one can also use mass spectrometry to chemically characterize the desorbed material for e. g. organic material with higher boiling points, adsorbed gaseous components, low volatile reaction products and disintegrated particulate matter. In this study, the latter approach was employed to analyze the thermally desorbed components from eight types of ambient and laboratory generated particulates for mass as well as organic and inorganic components.

Methods

Ambient samples of Diesel soot and tunnel dust, commercially available furnace soot, diffusion flame soot and spark generated carbon agglomerates were used (see table). Depending on origin and/or generation process these particles were categorized as either high or low OC samples. Aliquots of one milligram from each sample were exposed to progressively increasing temperatures from ambient temperature to 800 °C at a heating rate of 20 K/min. The thermally desorbed mass was quantified by thermogravimetry (TG, model TG209, Netzsch, Germany and Vector 22 FTIR, Bruker, Germany) (Raemaekers, 1997). Another aliquot was pyrolyzed and analyzed by gas chromatography and mass spectrometry (pyr/GC-MS, model "Double Shot Pyrolyzer", Frontier Lab, USA and model 5890/5972 GC-MSD, Agilent, Germany) (Ochsenkuhn-Petropoulou, 2003).

Results and Discussion

With increasing temperature TG indicates for all samples a loss of mass ranging from about 2 % to about 40 % (Fig. 1). Minimum and maximum desorption was found for Printex-G and Palas+OC, respectively. The thermograms of samples with high organic load show several distinct changes in slope which indicate the desorption of specific gas-

Table of particle samples used in this study

	Sample Name	comment	desorbed mass at 800 °C [%]
Low OC	Palas / rt	carbon particles generated by spark discharge (Palas GFG 1000) in pure Argon at room temperature (rt)	27.1
	Printex 90	commercially available gas furnace soot (Degussa), primary particle size 14 nm	9.6
	Printex G	commercially available gas furnace soot (Degussa), primary particle size 50nm	2.1
	CAST low OC	flame soot from Combustion Aerosol Standard (CAST) system operated with 24/76% of oxygen/nitrogen	10.4
High OC	Palas+OC	Palas/rt particles treated with OC at 300 °C	39.3
	CAST high OC	flame soot from Combustion Aerosol Standard system operated with 20/80% of oxygen/nitrogen	7.8
	Diesel	particles from tail pipe of a passenger car	26.4
	CW9	particles from a road tunnel exhaust duct	30.5

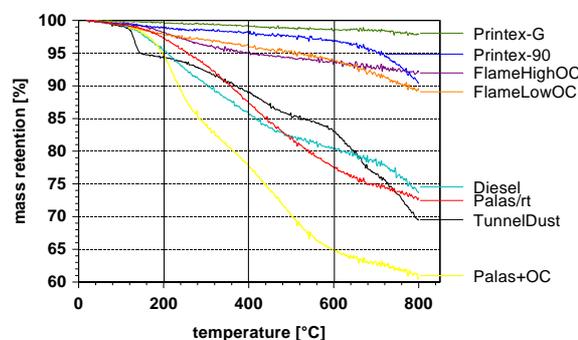


Fig. 1 Thermogravimetry shows the mass decrease during gradual heating in a nitrogen gas flow.

eous compounds. There is no clear correlation between OC category (high/low) and amount of desorbed mass. The pyr/GC-MS system (Fig. 2), however, clearly separates high and low OC samples at temperatures above 200 °C (retention time > 10 min). In search of a single parameter characterizing the OC content we plotted the integrated ion count of this region (200 - 800 °C) normalized with the total ion count versus the thermally desorbed mass (Fig. 3). This shows a clear separation between high OC and low OC samples, where the normalized ion count of high OC samples is around 75 % and the low OC ion counts are below 30 %. While for high OC samples, there are numerous reasons for the observed scatter in thermally desorbed mass (e.g. charring), the situation was expected to be more coherent for low OC samples. Since the latter is contrary to our findings, we have investigated the relationship between desorbed mass and specific surface area of the particles. As seen from Fig. 4 the BET surface area correlates poorly and well for high OC ($r = 0.19$; $p = 0.40$) and low OC samples ($r = 0.94$, $p = 0.031$), respectively. This means that — while particle surface area does not influence the desorption of condensed volatile matter — it affects the desorption of mass from low OC aggregates. This could be an indication for mechanical erosion and/or for EC combustion possibly due to trace impurities of oxygen in the carrier gas.

Conclusion

OC contents measured by mass desorption only, i. e. without evolved gas analysis, may be misleading. Thermally desorbed mass from carbonaceous samples is due not only to volatile OC but also to inorganic gases (such as CO₂, CO and H₂O) and for mechanical erosion. We have also given an indication of inadvertent particle erosion and EC combustion in an oxygen-free atmosphere, which would represent a previously unreported systematic error of the widely used thermodesorption methods.

References

- Birch, M. E., 1999: Elemental Carbon (Diesel Particulate): Method 5040, Issue 3 (interim). 4th edition ed. Vol. DHHS (NIOSH) Publication No. 94-113, NIOSH Manual of Analytical Methods, National Institute of Occupational Safety and Health, US Dept. of Health and Human Services, 1-9 pp.
- Ochsenkuhn-Petropoulou, M., K. Staikos, G. Matuschek, and A. Kettrup, 2003: On-line determination of polycyclic aromatic hydrocarbons in airborne particulate matter by using pyrolysis/GC-MS. *Journal of Analytical and Applied Pyrolysis*, 70, 73-85.
- Raemaekers, K. G. H. and J. C. J. Bart, 1997: Applications of simultaneous thermogravimetry-mass spectrometry in polymer analysis. *Thermochimica Acta*, 295, 1-58.

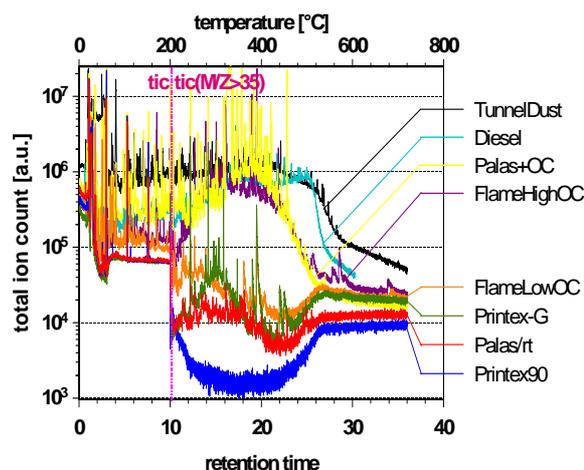


Fig. 2 Ion counts of GC-MS. Temperature rises with 20 K/min. To gain resolution, at 10 minutes retention time, all counts below $M/Z=35$ are neglected.

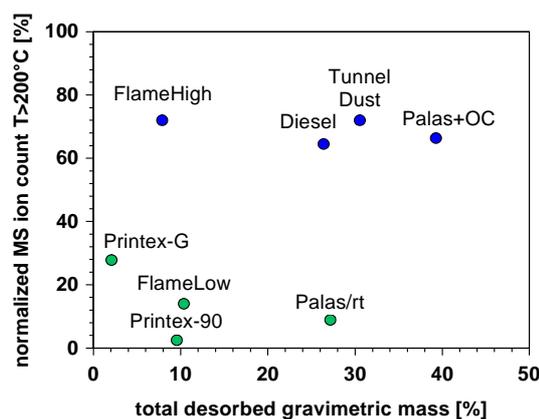


Fig. 3 Desorbed gravimetric mass and integrated normalized total ion count of mass spectrometry for retention time 10 ... 36 min.

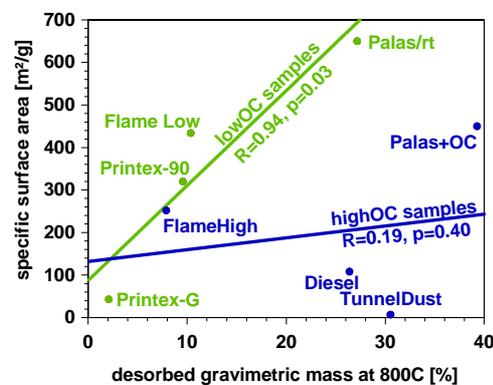


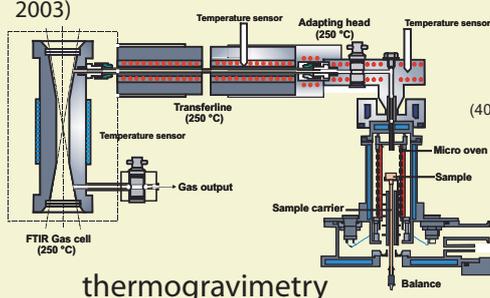
Fig. 4 Desorbed gravimetric mass correlates well with BET specific surface area for the low OC samples (green). No correlation is found for high OC samples (blue).

Introduction

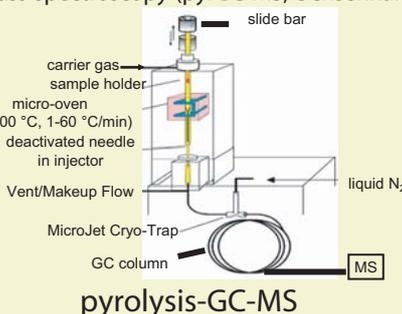
The elemental carbon (EC) and organic carbon (OC) content of carbonaceous particulates is a widely used parameter for particle characterization (Birch, 1999). We tested eight types of ambient and laboratory generated particulates for their temperature dependent gravimetric loss of mass and analyzed additionally for organic and inorganic components by pyrolysis.

Methods

Evolved gas analysis was performed during progressive heating from ambient temperature to 800 °C with 20 K/min in two types of experiments: 1) Loss of mass by thermogravimetry and Fourier transform infrared spectroscopy (TG-FTIR, Raemaekers, 1997), and 2) evolved gases by pyrolysis and gas chromatography / mass spectroscopy (pyrGC-MS, Ochsenkuhn, 2003)



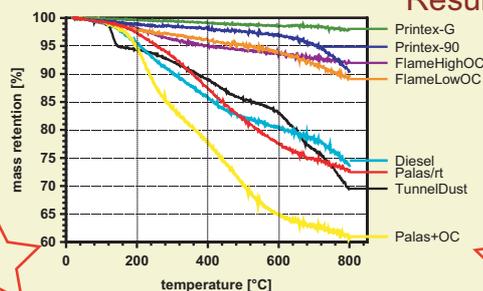
thermogravimetry



pyrolysis-GC-MS

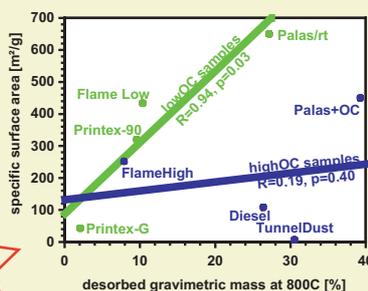
	sample name	comment	desorbed mass at 800 °C [%]
Low OC samples	Palas/rt	carbon particles generated by spark discharge (Palas model GFG1000) in pure Argon at room temperature (rt)	27.1
	Printex-90	commercially available gas furnace soot (Degussa), primary particle size 14 nm	9.6
	Printex-G	commercially available gas furnace soot (Degussa), primary particle size 50nm	2.1
	Flame soot low OC	flame soot from Combustion Aerosol Standard (CAST) system operated with 24/76% of oxygen/nitrogen	10.4
High OC samples	Palas+OC	Palas/rt particles treated with OC at 300 °C	39.3
	Flame soot high OC	flame soot from Combustion Aerosol Standard (CAST) system operated with 20/80% of oxygen/nitrogen	7.8
	Diesel	particles from tail pipe of a passenger car	26.4
	Tunnel dust	particles from a road tunnel exhaust duct; sample CW9	30.5

Results



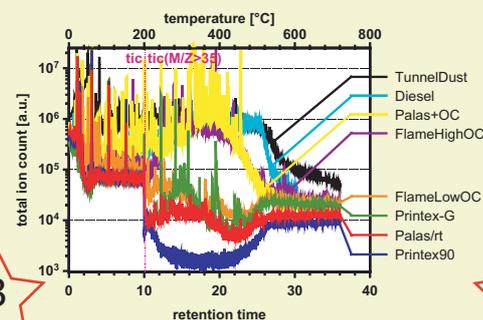
1

Thermogravimetry shows the mass decrease during gradual heating in nitrogen.



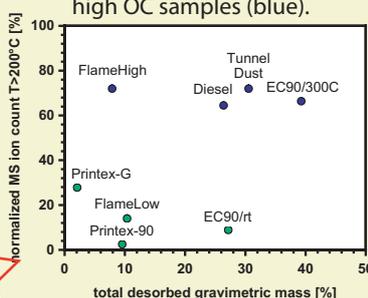
2

Desorbed gravimetric mass correlates well with BET specific surface area for the low OC samples (green). No correlation is found for high OC samples (blue).



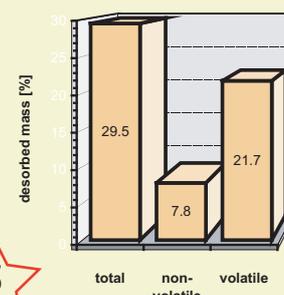
3

PyrGC-MS distinguishes between high and low OC samples at temperatures over 200 °C. For better resolution, components of M/Z < 35 are neglected after 10' retention time



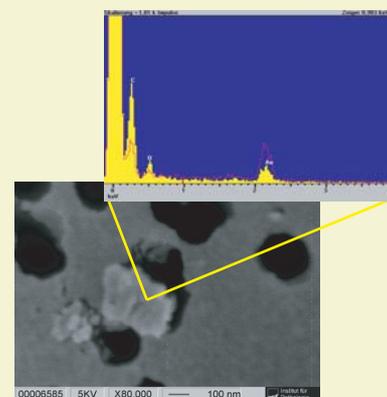
4

Organics are known to volatilize above 200 °C. The ratio of the MS-ion-count for temperatures above 200 °C normalized by the total ion count separates high OC from low OC samples.



5

The desorbed matter does not consist gaseous components only. The gas flow from Palas/rt sample was filtered using a gold sputtered nuclepore filter. We found 7.8 % of the sample mass on it. EDX analysis of the particles on the filter give evidence for carbonaceous particles.



Conclusions

- Pyrolysis distinguishes well between high and low OC samples at temperatures above 200 °C.
- Deriving the OC content from thermal mass desorption only may be misleading.
- Thermally desorbed mass from carbonaceous samples is due not only to volatile OC but also to anorganic gases and particle fragments.

Literature

- Birch, M. E., 1999: Elemental Carbon (Diesel Particulate): Method 5040, Issue 3 (interim). 4th edition ed. Vol. DHHS (NIOSH) Publication No. 94-113, NIOSH Manual of Analytical Methods, National Institute of Occupational Safety and Health, US Dept. of Health and Human Services, 1-9 pp.
- Ochsenkuhn-Petropoulou, M., K. Staikos, G. Matuschek, and A. Kettrup, 2003: On-line determination of polycyclic aromatic hydrocarbons in airborne particulate matter by using pyrolysis/GC-MS. Journal of Analytical and Applied Pyrolysis, 70, 73-85.
- Raemaekers, K. G. H. and J. C. J. Bart, 1997: Applications of simultaneous thermogravimetry-mass spectrometry in polymer analysis. Thermochimica Acta, 295, 1-58.