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Measuring Cell to Follow Structural Changes of Soot *in Situ* with Raman Microspectroscopy during Temperature Programmed Oxidation Experiments

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Chair for Analytical Chemistry

Motivation

- Carbonaceous aerosols like soot are an important fraction of aerosols present in the urban area.
- Diesel particle filters (DPF) are used to minimize soot particle emission.
- Soot reactivity and structure influence oxidation behavior during DPF regeneration.
- Effective soot characterization tools used currently:
  - Temperature-programmed oxidation (TPO)[1]
  - Raman microspectroscopy (RM)[2,3]

Emission of soot
(http://www.windows2universe.org/earth/climate/black_carbon.html)

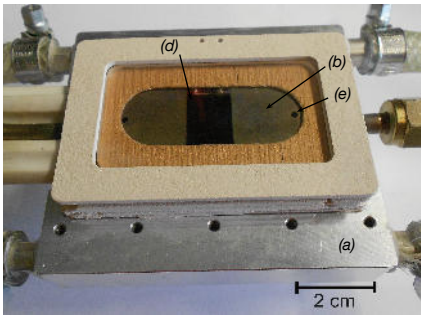
➔Development of a device to combine soot characterization methods.

➔Follow changes of the soot microstructure *in situ* during heating and/ or oxidation.

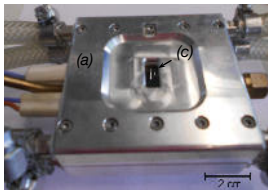
Measuring Cell

Water-cooled aluminum cell frame *(a)*

Heated flow cell for **TPO** measurements up to 1000 °C *(b)*



Opened measuring cell



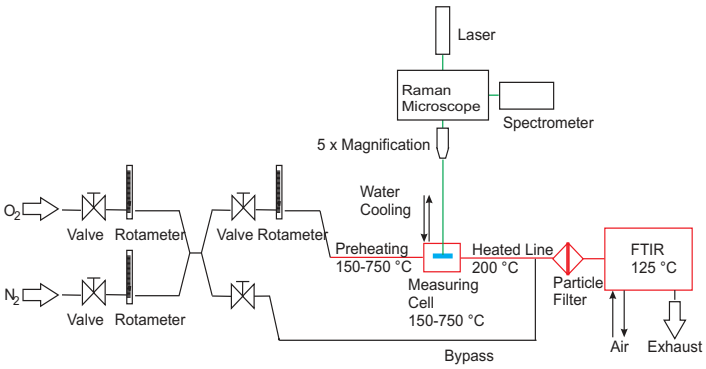
Closed measuring cell

Quartz glass window to enable **RM** measurements *(c)*

Analysis of thermophoretic precipitated soot on sample plate *(d)*

Inlet for different gases for inert or oxidizing atmosphere inside the device *(e)*

Experimental Setup

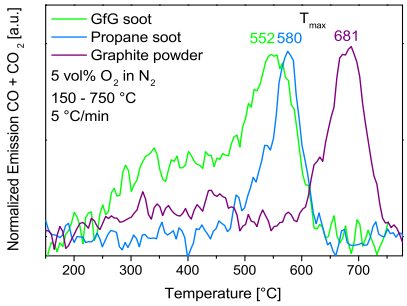


Schematic setup for in situ RM during TPO.

TPO Emission Profiles

- Heating soot sample with 5 °C/min in 5% O_2 in N_2
- FTIR as gas detector for CO and CO_2
- Temperature of maximum emission T_{max} indicates soot reactivity.

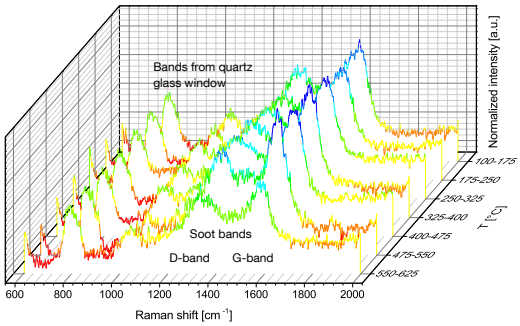
➔Reactivity decreases from spark discharge soot to propane soot to graphite powder.



TPO emission profiles of 0.3 mg soot: graphite powder (T_{max} ≈ 681 °C), propane soot (T_{max} ≈ 580 °C) and spark discharge soot (T_{max} ≈ 552 °C).

Raman Spectra during Soot Oxidation

- Two bands in Raman spectra of soot:
  - G-band, "graphite"- like structure ~1580 cm^{-1}
  - D-band, "defect" structure ~1350 cm^{-1}
- Width and relative intensity depend on microstructure.[2]

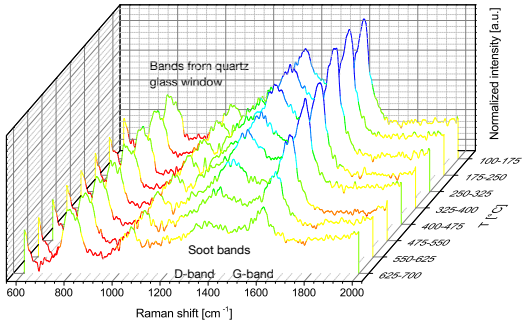


Raman spectra during oxidation of 0.3 mg spark discharge soot, 5 °C/min, 5% O_2.

➔Decrease of amorphous parts (region between peaks) and increase in order (narrowing of peaks) during oxidation.

➔Graphitization of spark discharge soot.

Raman spectra during oxidation of 0.3 mg propane soot, 5 °C/min, 5% O_2.



➔Almost no changes in structural composition (relative peak intensities and region between peaks stay constant).

➔Oxidation without graphitization but with constant structural composition.

Summary and Outlook

- Combination of TPO and RM as different techniques for the study of structure and reactivity in one device is successfully realized.
- Following of graphitization of spark discharge soot and the oxidation of propane soot during TPO possible.
- Analysis of the oxidation of different types of soot at various conditions (temperature ramp, isothermal, different oxygen concentrations) will lead to more detailed information on soot oxidation properties.

Literature:

[1] J. Schmid, B. Grob, R. Niessner, N. P. Ivleva, *Anal. Chem.* **2011**, 83, 1173-1179.

[2] N. P. Ivleva, A. Messerer, X. Yang, R. Niessner, U. Pöschl, *Environ. Sci.Technol.* **2007**, 41, 3702-3707.

[3] B. Grob, J. Schmid, N. P. Ivleva, R. Niessner, *Anal. Chem.* **2012**, 84, 3586-3592.

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