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Investigation of diesel soot reactivities with condensable and corrosive gases in a new TG-FTIR system

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A new TG-FTIR (T_hermogravimetry coupled with F_ourier-T_ransform I_nfra-R_ed spectroscopy) system was developed at Paul Scherrer Institute (PSI) in the last two years, which allows to investigate particulate matter and exhaust catalysts with condensable, reactive and corrosive gases. TG is an established method for the quantification of adsorption and desorption processes during the thermal treatment of catalysts or soot samples. The desorbed gas phase components as well as new products from reactions with reactive feed gases can be precisely and stably analyzed by FTIR spectroscopy, when combined with a multi-component method for the parallel quantification of several gas components.

As an example for the potential of the system in the area of particulate matter analysis the reactivities of diesel soot in form of powders and collected on filters were investigated with different reactive gases (Figure 1). The different gas compositions were 10% O₂ in N₂, 10% O₂ + 5% H₂O in N₂, 10% O₂ + 0.1% NO₂ in N₂ and 10% O₂ + 5% H₂O + 0.1% NO₂ in N₂, respectively. The influence of NO₂ and H₂O could be clearly observed. The C oxidation rates of the experiments are plotted in relation to the part of carbon still existing at the point of measurement.

In the presence of NO₂, an increased oxidation rate is already observed below 200°C due to the reaction of soot with NO₂ [1], but the humidity of the reactive gas does not influence the oxidation in this temperature range. Above 350°C, the oxidation rates with NO₂ flatten out, which is probably related to a diffusion limitation.

At higher temperatures, O₂ oxidation becomes the determinant reaction. In NO₂-free experiments, the C oxidation rate up to 350°C is mainly increased by the desorption of CO_x from the thermal decomposition of surface groups, is thereafter almost constant up to 400°C, and then continues rising with the start of O₂ oxidation. Above 500°C, the oxidation rates rise for all reactive gas compositions. At this point the influence of water on the oxidation behaviour of the soot sample becomes visible. As a consequence, the oxidation rates of the samples

treated with humid reactive gas reach their maxima at lower temperatures, which can be observed from the crossing of the curves between 610°C and 650°C in Figure 1.

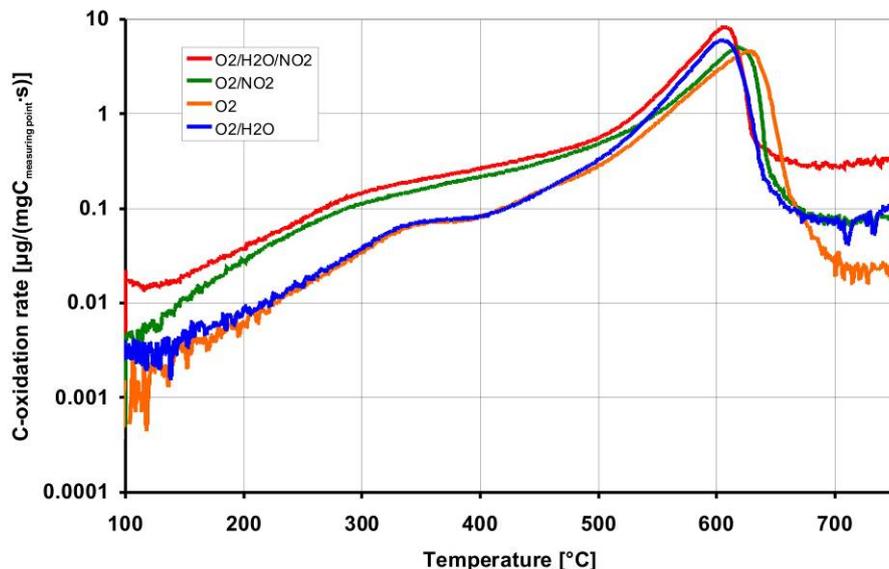


Figure 1: C oxidation rates during TPO experiments of a real diesel soot sample with four different reactive gas mixtures. The oxidation rates refer to the amount of carbon still present at the point of measurement.

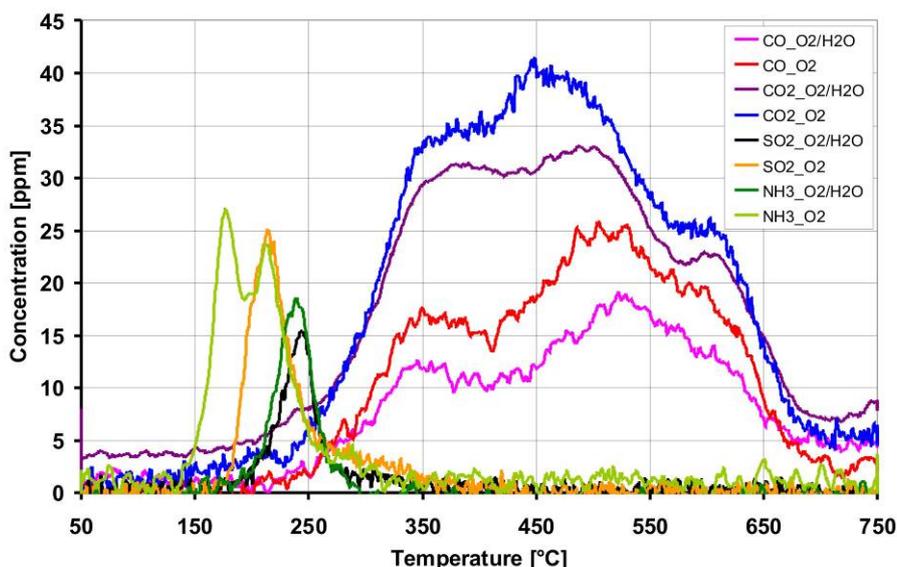


Figure 2: Influence of water on the evolution of NH_3 and SO_2 from soot samples.

Furthermore, the influence of water on the evolution of SO_2 and NH_3 from some soot samples during the TPO experiments was remarkable. In Figure 2 the TPO of a soot sample from a ship diesel engine operated with a fuel, which contains 2.14% sulphur, is shown. In the presence of water, the SO_2 and NH_3 evolution is shifted to higher temperatures and the detectable amount decreases. Additionally the NH_3 double peak, resulting most likely from the decomposition of ammonium sulphate in the experiment with dry reactive gas, disappears. So far no definitive explanation can be given for these phenomena and additional experiments are

needed to clarify the mechanism, but it can be speculated that sulphuric acid and ammonium hydroxide are formed, which cannot be detected with the spectrometer.

Beside the TPO experiments, the new system gives the opportunity to investigate soot samples with so-called TPD/O analysis, which is a combination of temperature-programmed desorption (TPD) under inert conditions and temperature-programmed oxidation (TPO) experiments under oxidizing conditions. In these TPD/O experiments the EC (Elemental Carbon) and OC (Organic Carbon) content can be quantified, whereby the contributions of thermally unstable surface functional groups and adsorbed hydrocarbons (HC) to the OC could be discriminated. The water content of the samples can be measured and from the CO and CO₂ evolved during the OC measurement the oxygen concentration could be calculated. Hydrogen is estimated from the water, which is formed during the oxidation part of the TPD/O experiments. Sulfur can be quantified as long as it is not strongly bound as sulfate in the ash. From the thermogravimetric mass signal the ash content of powder samples and the formation of surface functional groups by reaction with of reactive gas components can be observed and quantified.

The observed influence of the gas composition shows that for the investigation of the reactivities of real soot samples, water and NO₂ should be used to simulate real conditions.

References

[1] B.R. Stanmore, V. Tschamber, and J.F. Brilhac, Fuel 87 (2008) 131-146.

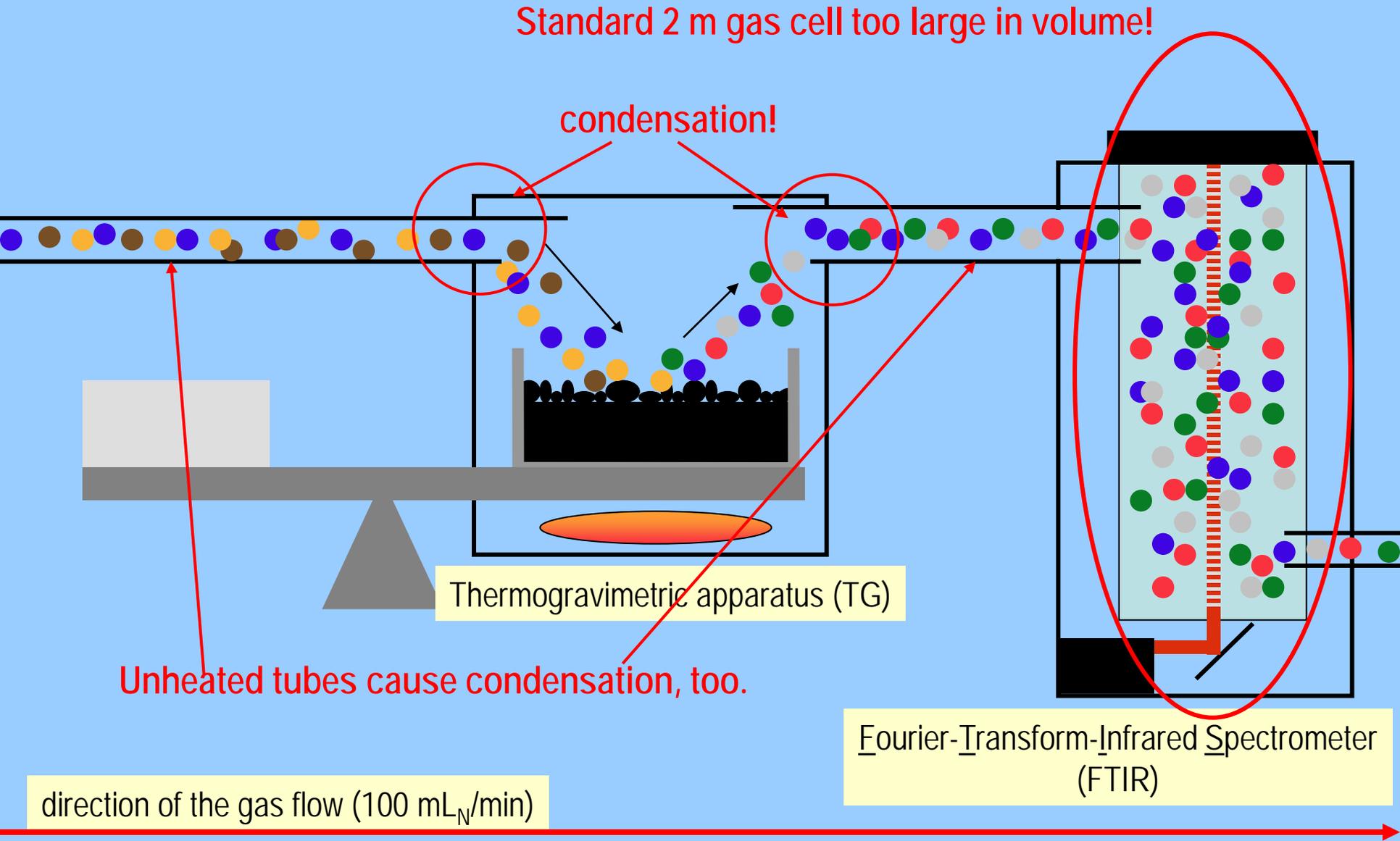


Wir schaffen Wissen – heute für morgen

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Standard 2 m gas cell too large in volume!

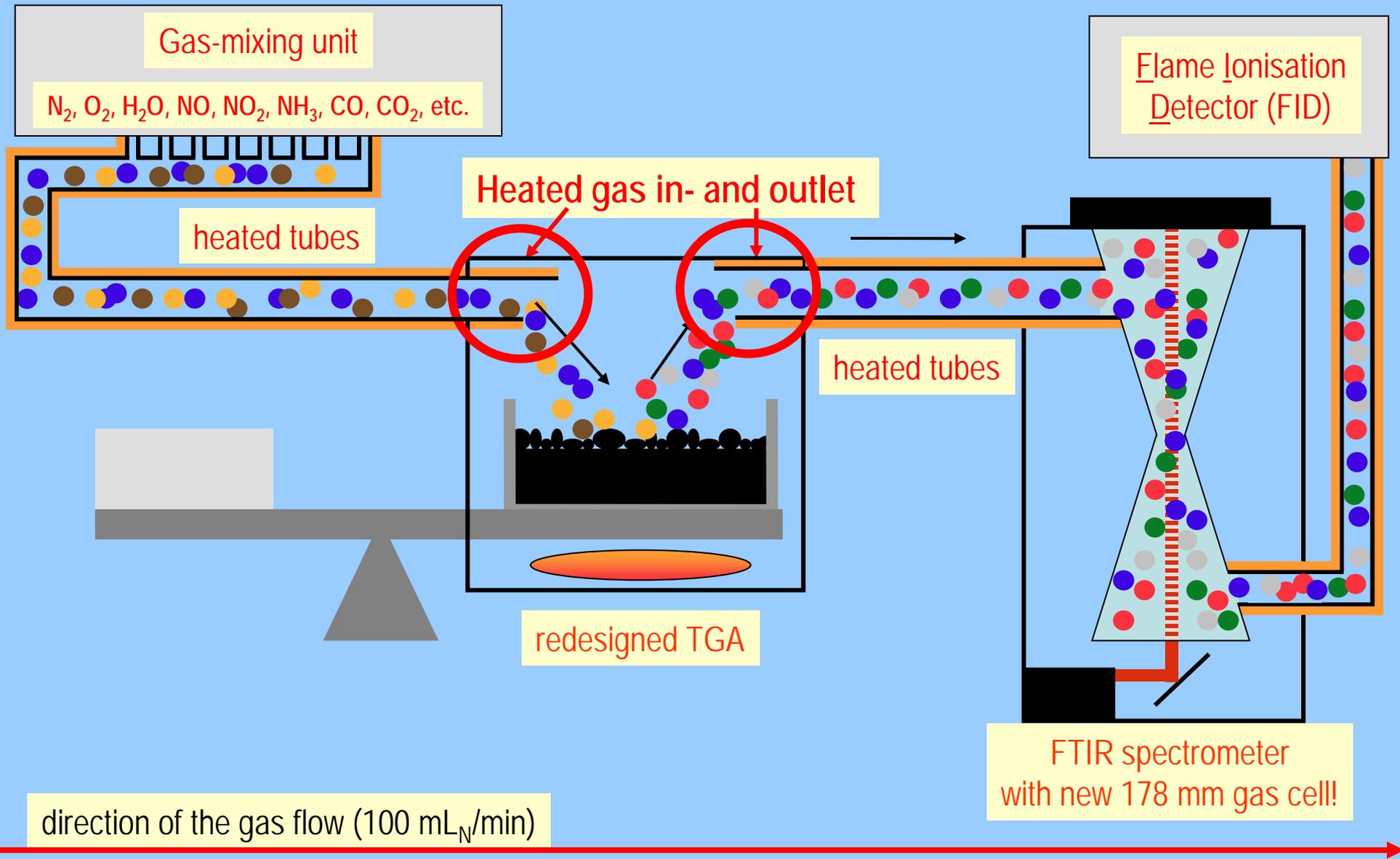
condensation!

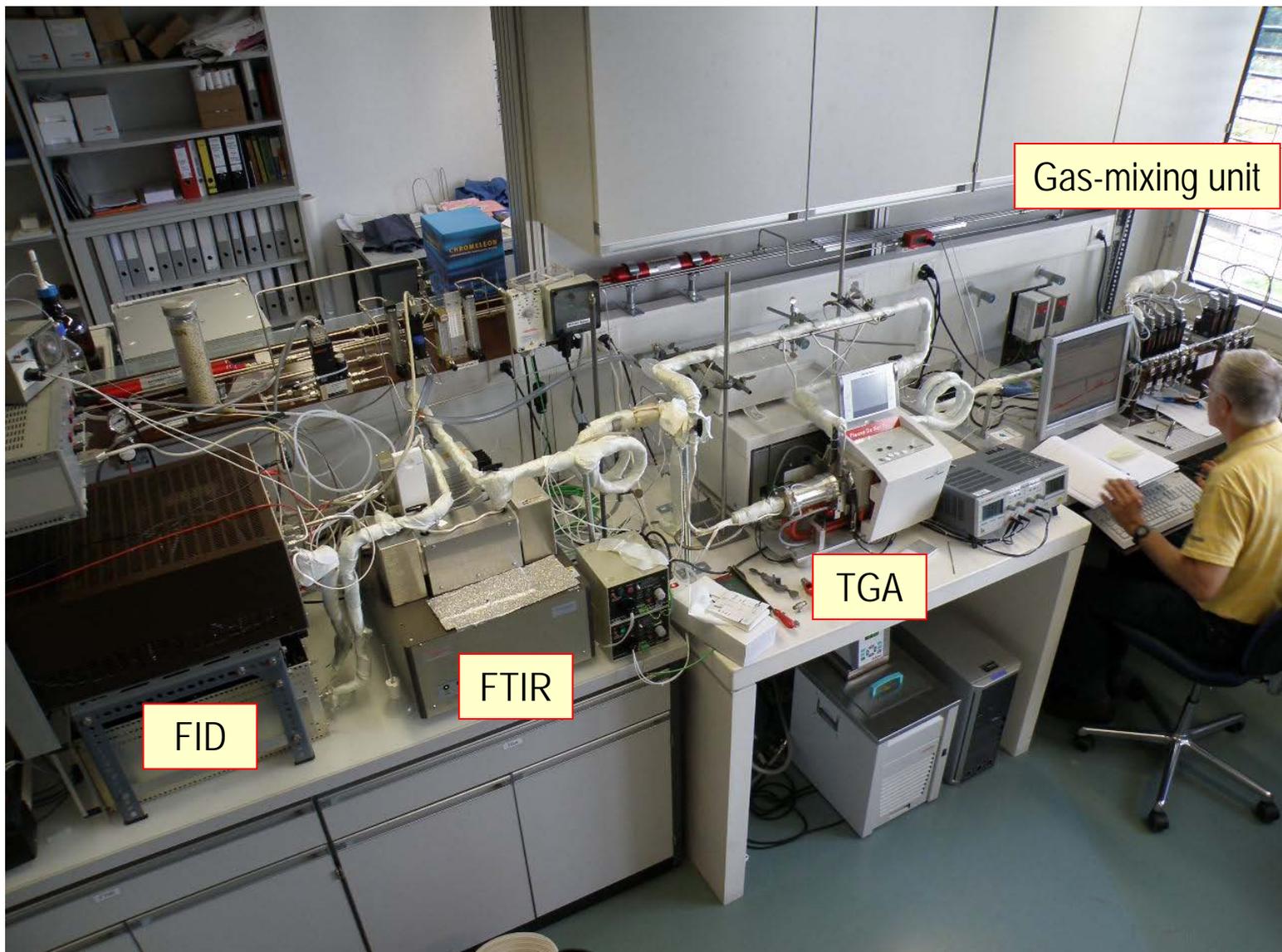
Unheated tubes cause condensation, too.

Thermogravimetric apparatus (TG)

Fourier-Transform-Infrared Spectrometer (FTIR)

direction of the gas flow (100 mL_N/min)

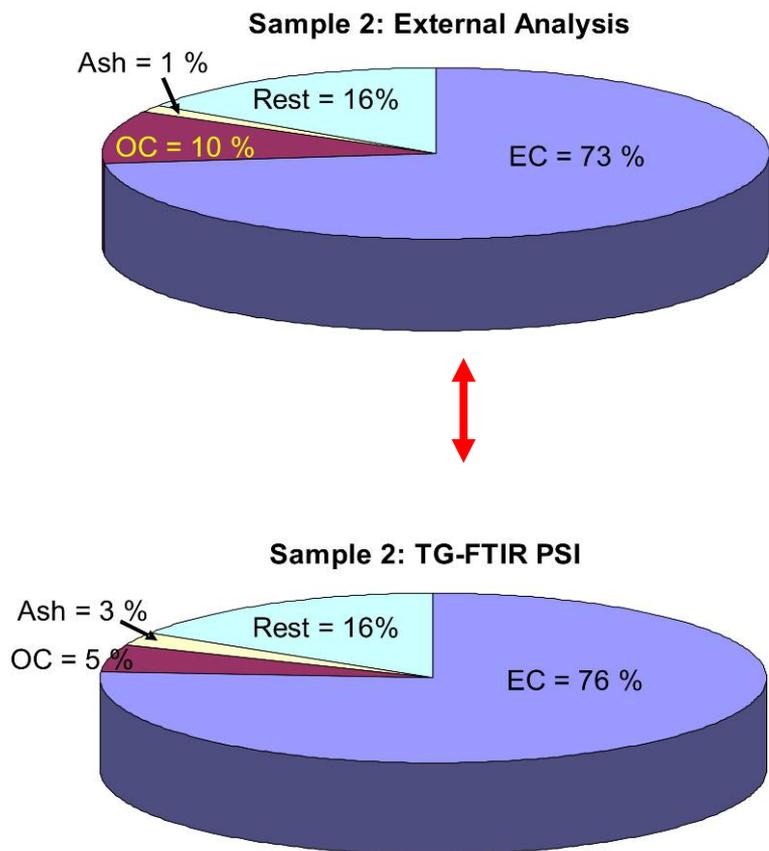




- **TPD/O¹ analysis** of soot samples down to **300 µg**:
separation of EC and OC (discrimination of contributions of HC & thermally unstable surface groups to OC), water, sulphur, oxygen and hydrogen content of soot samples
- **TPO² analysis** of soot samples down to **300 µg** with **condensable, reactive and corrosive** gas mixtures:
Estimation of the **CO₂/CO ratios**, investigation of **oxidation kinetics**
- Tested reactive gases: **O₂, H₂O, NH₃, NO₂, NO** (separately or in mixtures)
- **Total carbon analysis** of soot samples down to **10 µg** (only FTIR signal used)
- Investigation of **adsorption and desorption processes** on other **catalysts** and observation of the **gaseous chemical reaction products** in parallel

¹TPD/O: Temperature-programmed desorption followed by oxidation

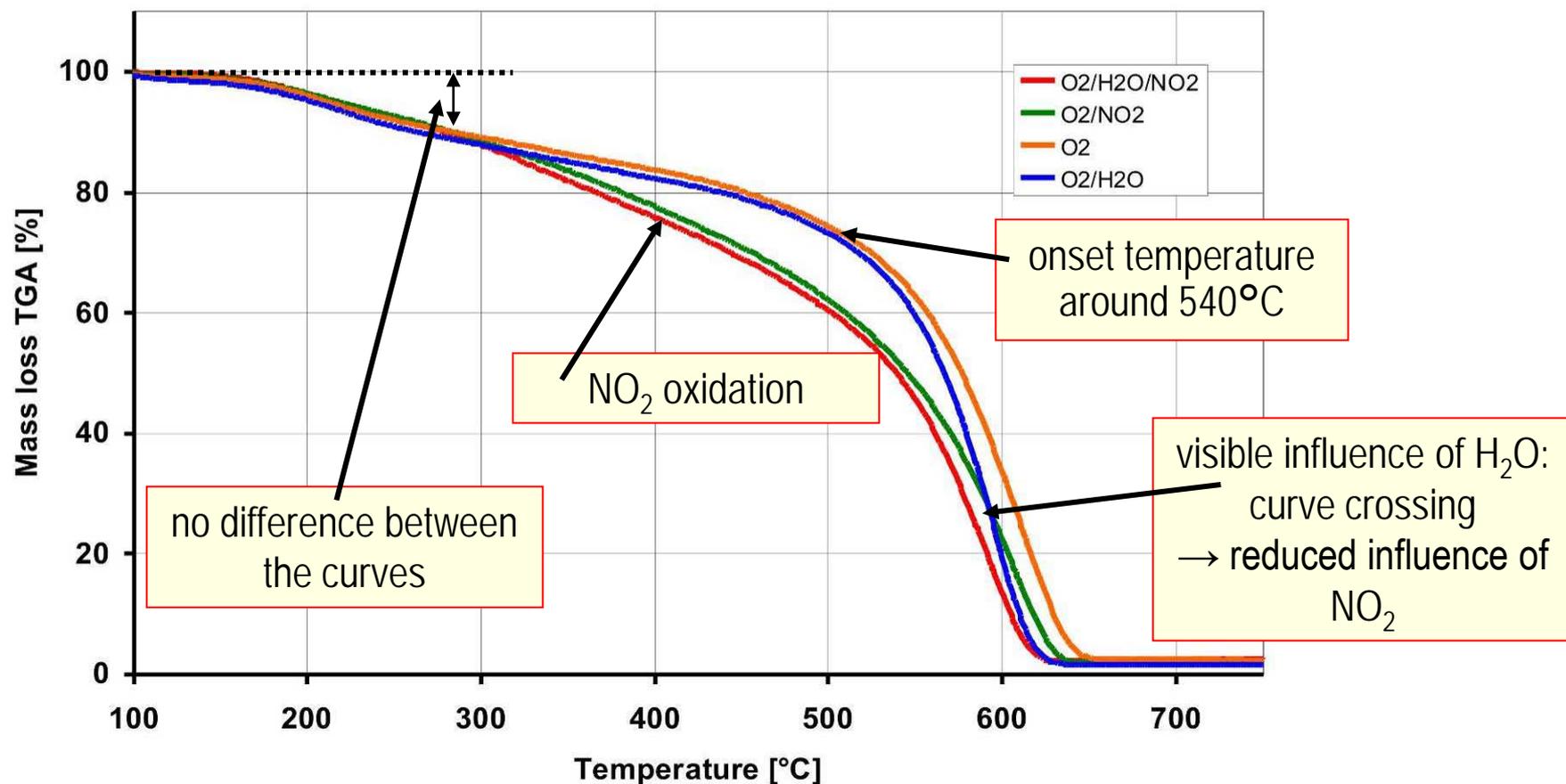
²TPD/O: Temperature-programmed oxidation



	Sample 2
Initial weight [mg]	1.492
EC [%]	76.0
OC [%]	5.4
S [%]	0.1
N [%]	0.2
O [%]	8.0
H [%]	0.2
Water [%]	8.0
Ash [%]	3.0
Sum [%]	100.9

45% of OC consists of adsorbed hydrocarbons and 55% of thermally unstable surface groups.

Good agreement of external analysis with TG-FTIR method at PSI.
Discrepancy between the EC and OC content due to positioning of the OC/EC cut.



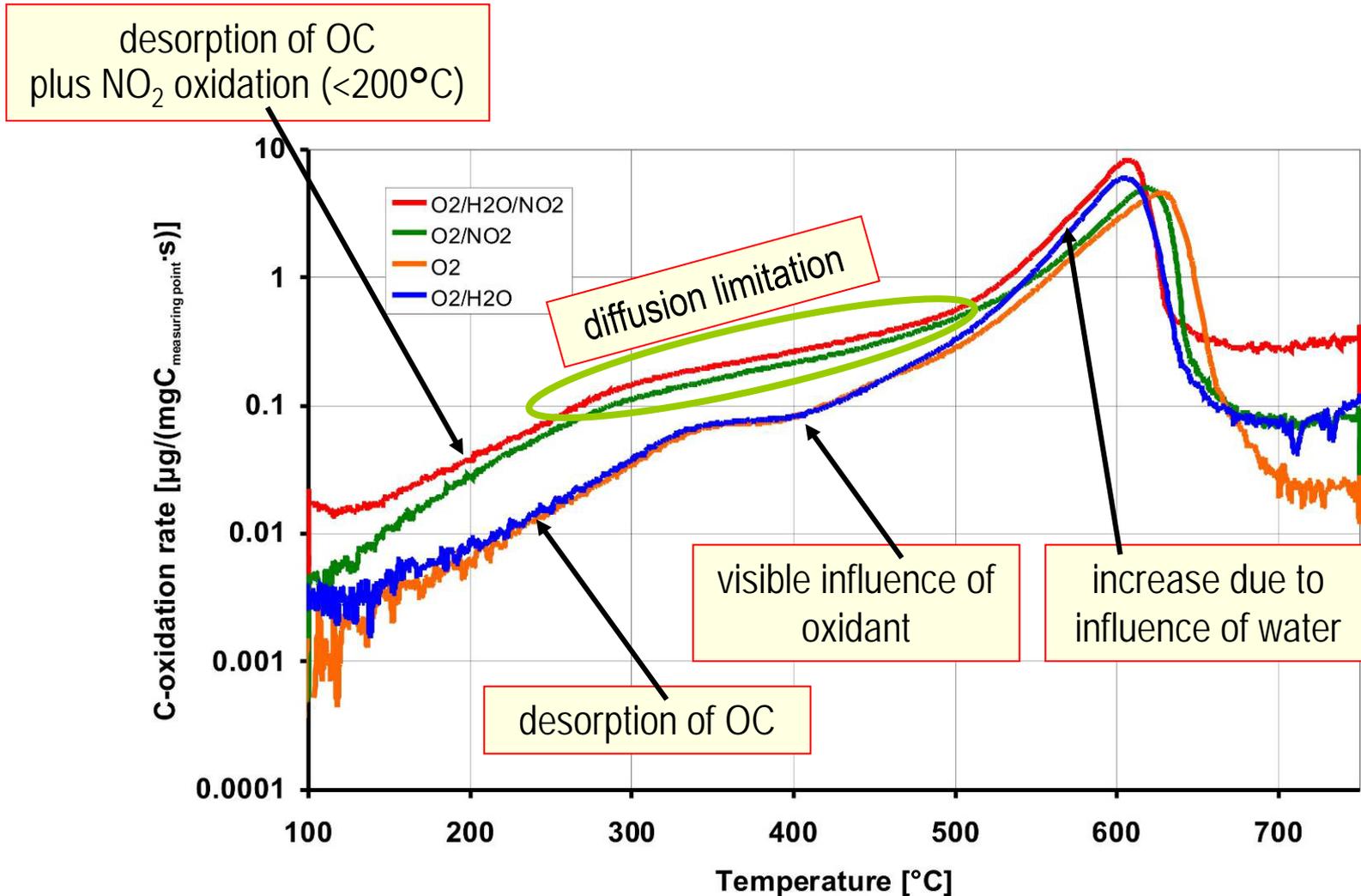
heating rate: 10 K/min (N₂ as carrier gas)

1: 10% O₂, 5% H₂O, 1000 ppm NO₂

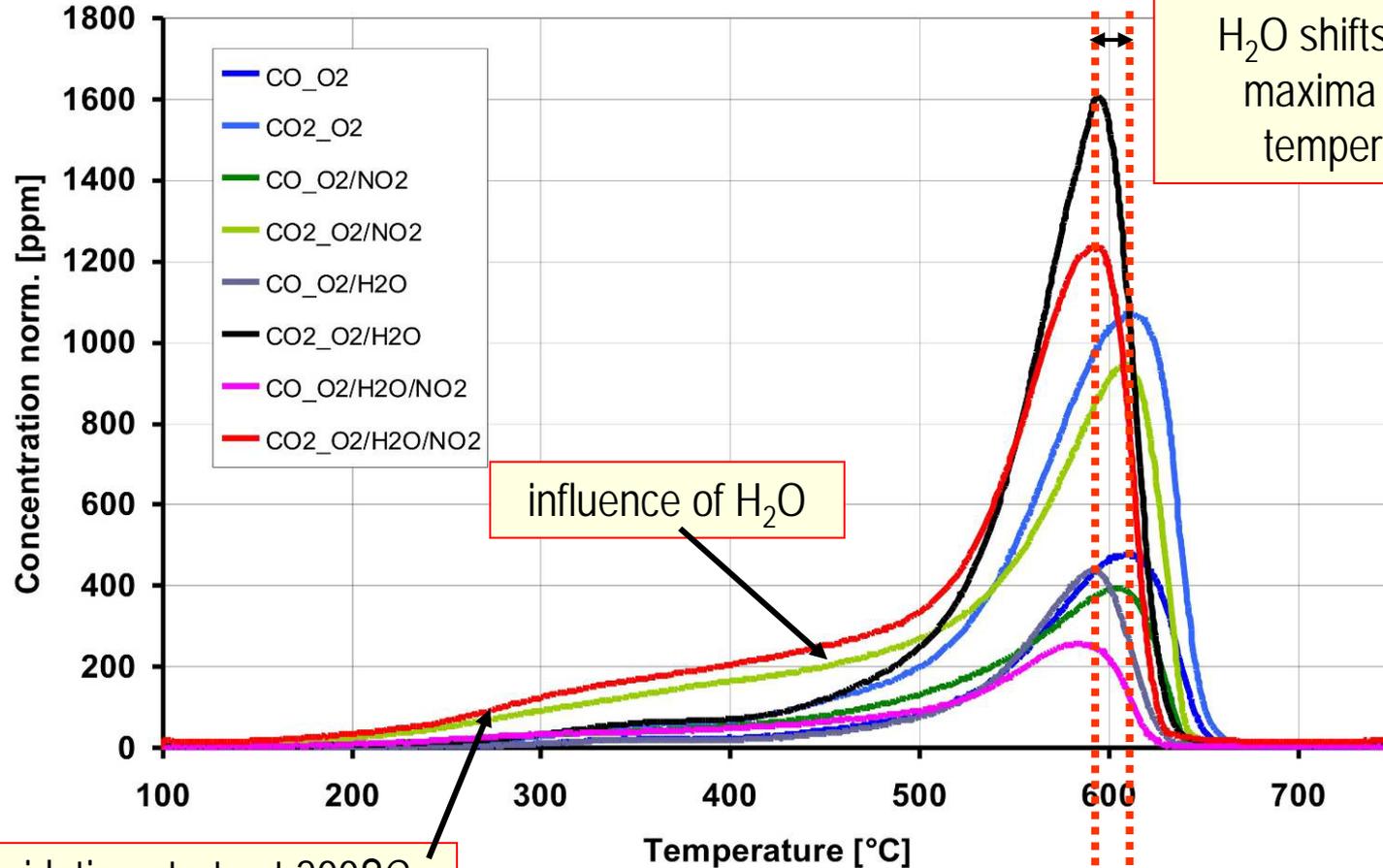
2: 10% O₂, 1000 ppm NO₂

3: 10% O₂

4: 10% O₂, 5% H₂O



TPO of sample 2 – CO₂ and CO measured by FTIR

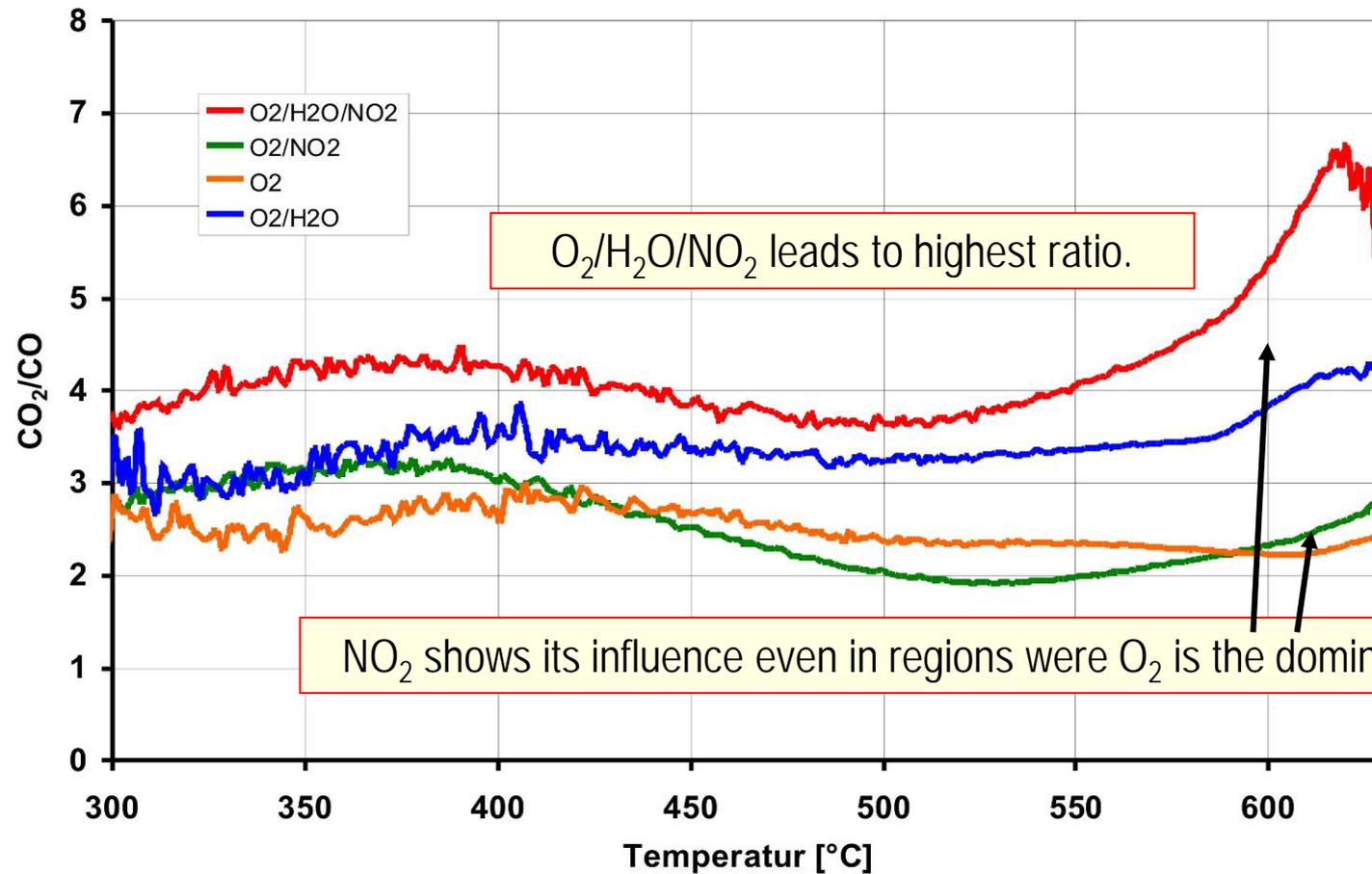


NO₂ oxidation starts at 200°C.

Addition of water leads to an increase of the CO₂/CO ratio
→ changes in the reaction mechanism

H₂O shifts the peak maxima to lower temperatures.

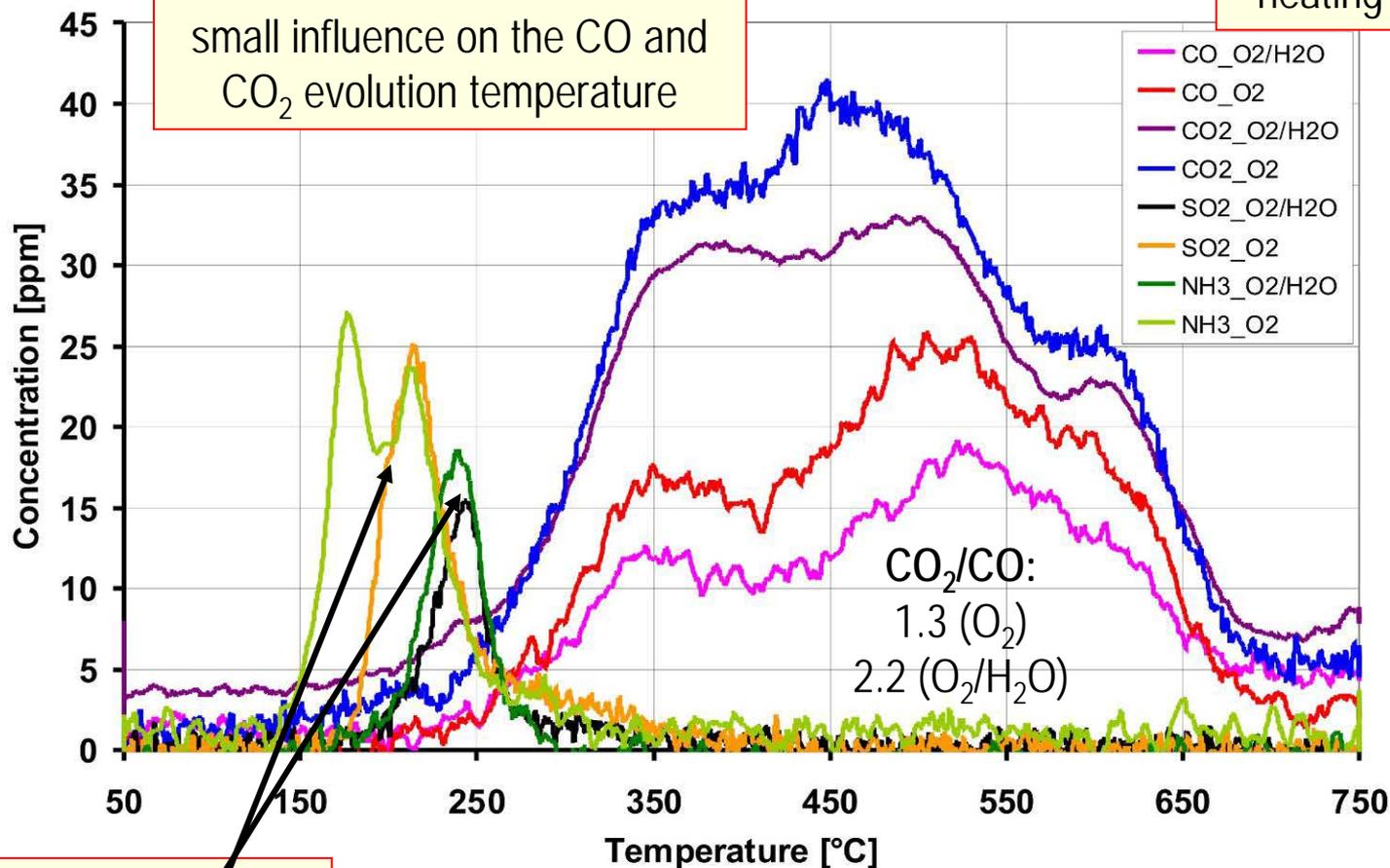
CO₂/CO at peak maxima:
 O₂: 2.2
 O₂ / NO₂: 2.4
 O₂ / H₂O: 3.6
 O₂ / H₂O / NO₂: 4.8



Trends are similar for experiments with NO₂ in the feed gas as well as for experiments without NO₂.

TPO of soot sample from ship engine

heating rate: 10 K/min



loss of NH₃ and SO₂
with humid reactive gas

- reactive gases: 10% O₂ and 10% O₂ + 5% H₂O
- fuel: ship diesel with a sulphur content of 2.14%
- OC content: >80%
- collected on quartz filter

Thanks to

- L. Bächli
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...and you for your attention!