Characterisation of the thermal and kinetic behaviour of various carbon nanoparticles

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Due to the generation of new functionalities and properties of nanoparticles, nanotechnology is a wide growing key technology. The improvement of diesel engine components and their efficiency, the emission of particulate matter is reduced. But nevertheless, the formation of particulate matter is higher than in other engines and furthermore even smaller particles are produced by the combustion engine. These particles are suspected to have an effect on air pollution and are potentially hazardous to human health.
Therefore a characterisation with the help of electron microscopy and thermal analysis, also evolved gas analysis, is best suited [1]. The morphology of the particles can be determined by electron microscopy. Here, agglomerates of primary particles of 10 to 50 nm in size can be observed for carbon black. Whereas the formation of aggregates due to sintering effects during the combustion of diesel soot is noticed, although the particle size is in the nanometer scale, too.
The various forms of carbon such as carbon black or soot produced from diesel engines can't be differentiated optically but they show a completely different thermal behaviour. This can be nicely demonstrated with the help of thermogravimetry. Carbon black is available in sufficient quantity therefore it can be used as a standard material for oxidation processes. Here the combustion is a single step reaction in the thermogravimetry. In contrast, particles produced by diesel engines or during the combustion of liquid or gaseous hydrocarbons show a multi step reaction behaviour (figure 1). The thermogravimetric reaction depends on the origin of the particles and so it is obvious that the released gases are besides carbon dioxide, SO_2 and carbon hydrates, respectively. The evolved gas analysis, for example FT-IR (fourier transform infrared spectroscopy) or MS (mass spectrometry), coupled directly to the thermobalance helps to understand the kinetics and can draw a bow to the combustion behaviour.
By means of kinetic analysis a deeper look into the mechanisms can be examined and proposals for the physicochemical characteristics can be taken into account.
With the help of the NETZSCH Thermokinetics software the calculation of the model-free and model-based kinetic can be done. An ethene soot was measured with three different heating rates to start the kinetic simulation. The model-free method from Friedman and Ozawa-Flynn-Wall is based on isoconversion and calculates the activation energy as a function of conversion.
A multi-step reaction model provides an excellent description of the experimental thermogravimetry results (figure 2). The assumption of n-th order consecutive reaction for all three steps is made and the kinetic triplets for these steps are calculated.

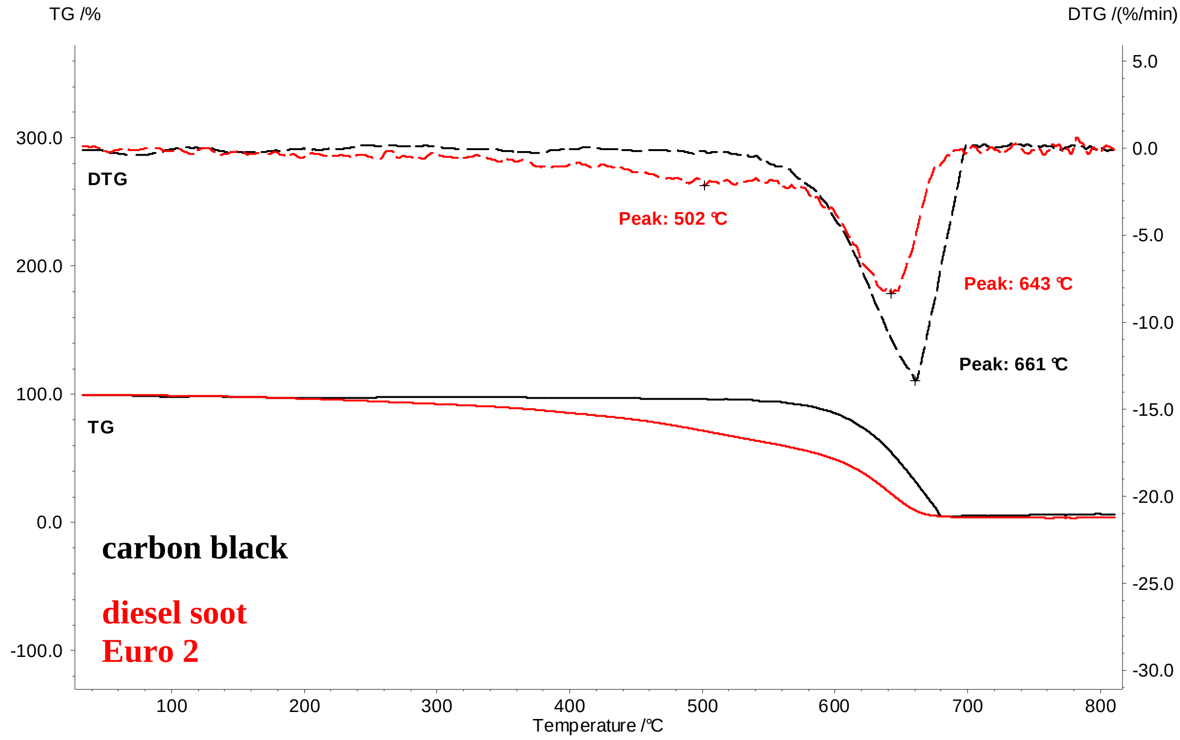

Figure 1: TG-measurement of carbon black and diesel soot

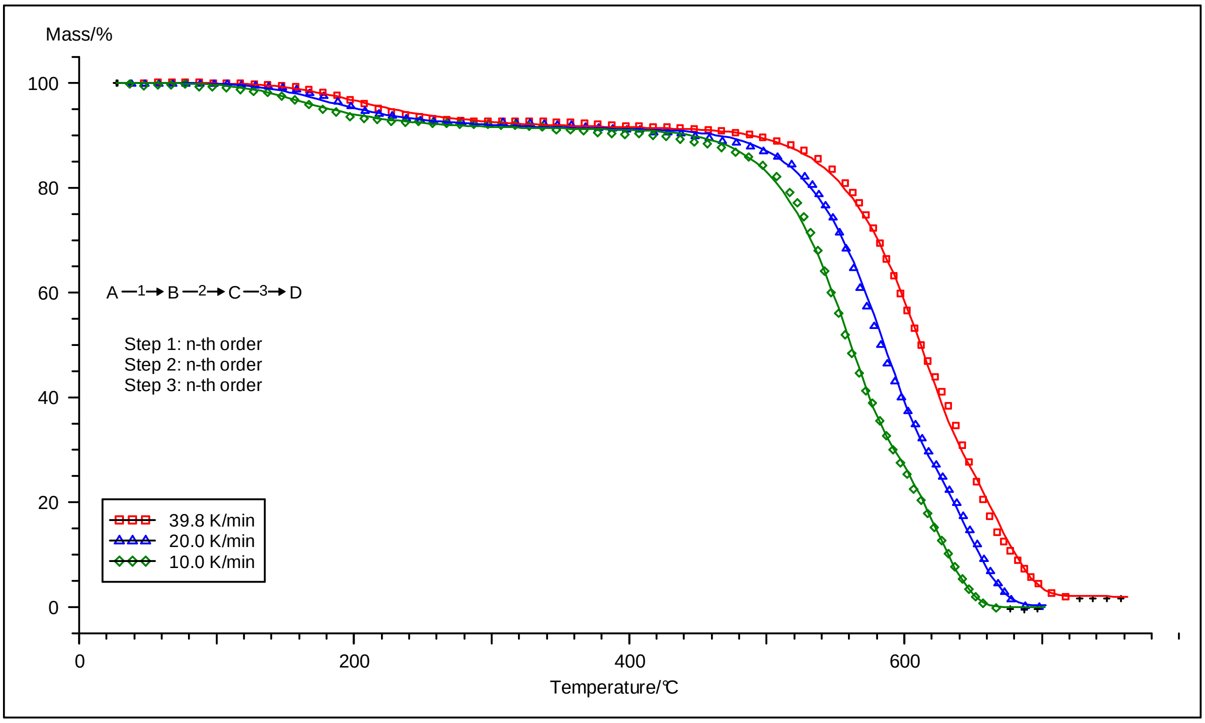

Figure 2: Non-linear regression of TG data of a soot sample

[1] M. Heck, B. Brückel, R. Arhelger, D. Walter, *Arbeitsmed. Sozialmed. Umweltmed.* **2009**, *44*, 187-188.

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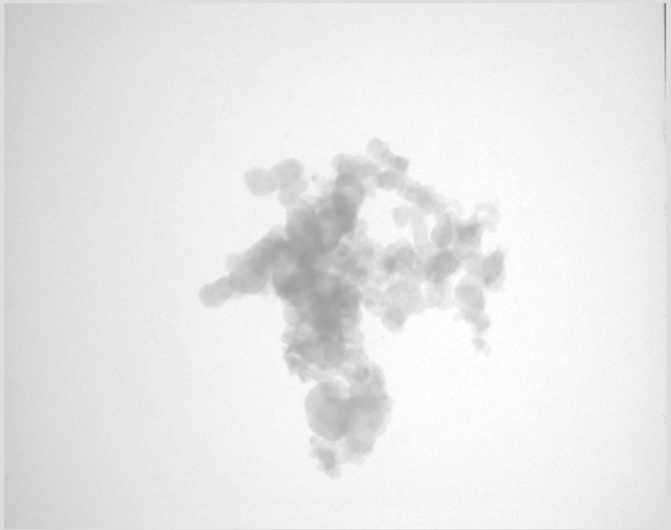
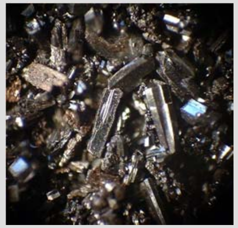
- Introduction
- REM and TEM
- Thermogravimetry (TG)
- TG measurements
- Gas analysis
- Kinetic analysis
- Summary



Carbon

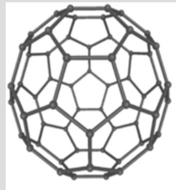
Carbon

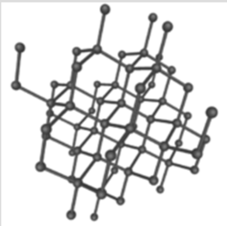


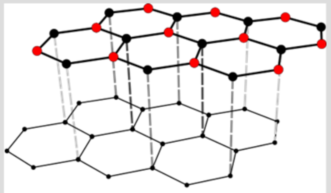
Diamond

Graphite

Fullerenes

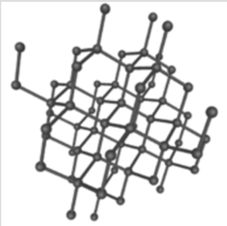






Carbon

Diamond



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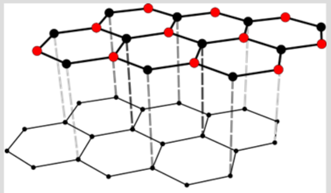
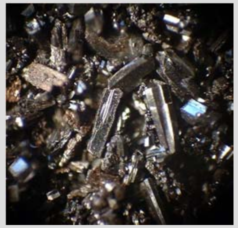
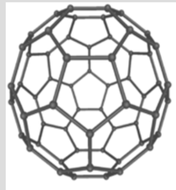


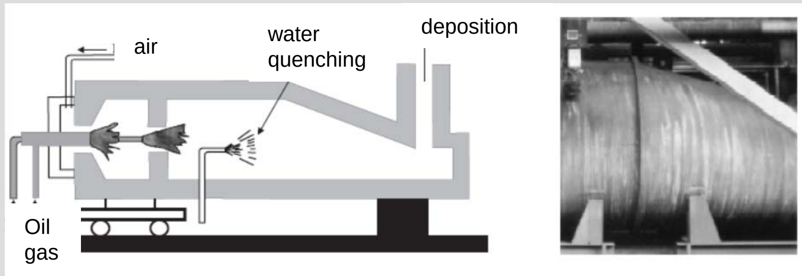
Fullerenes





Soot

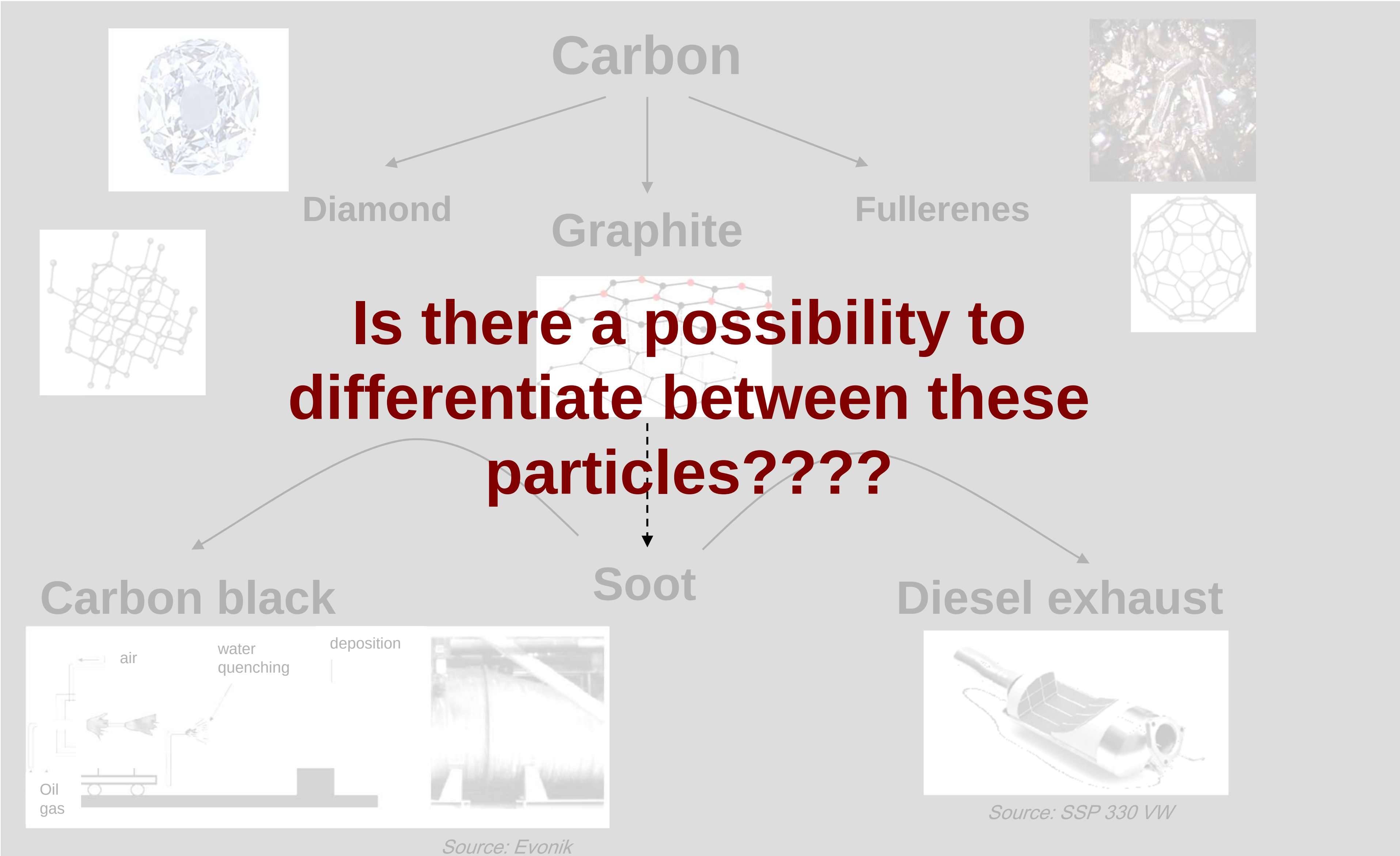
Carbon black



Source: *Evonik*

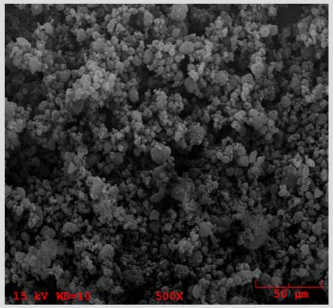
Diesel exhaust

Source: SSP 330 VW

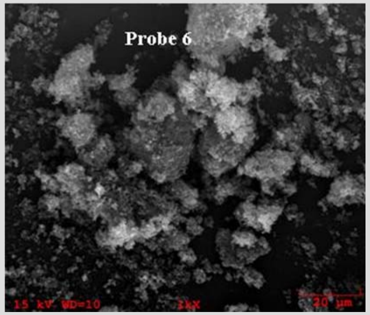


Is there a possibility to differentiate between these particles????

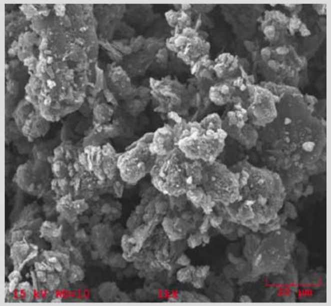
REM measurements



Carbon black



Ethene soot



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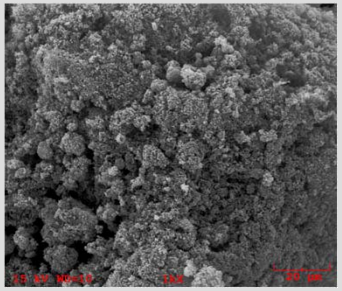
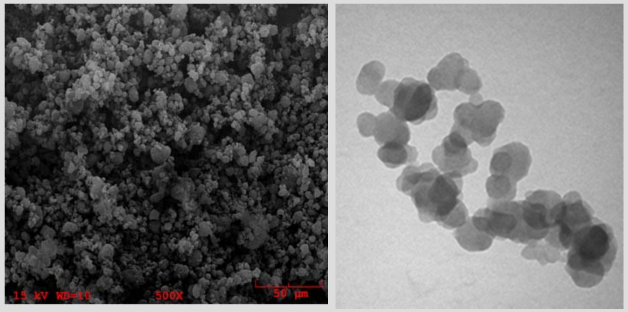
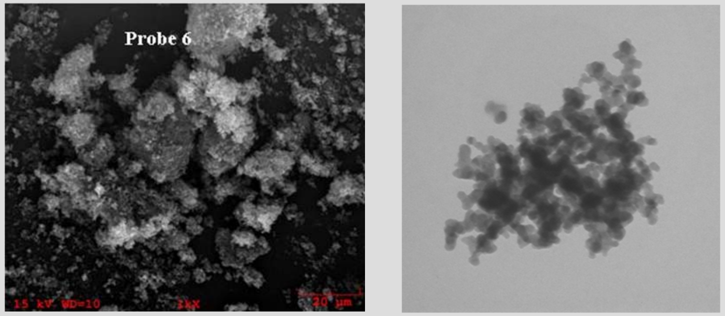


Diesel soot

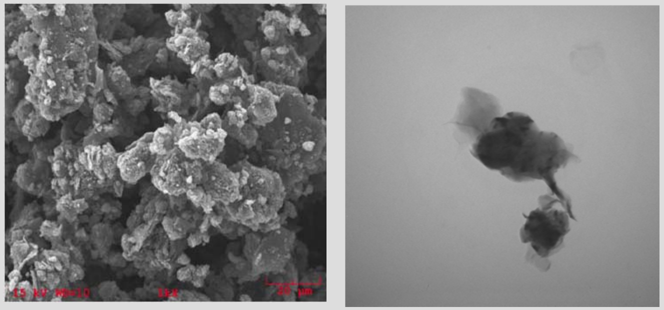
REM and TEM measurements



Carbon black



Ethene soot



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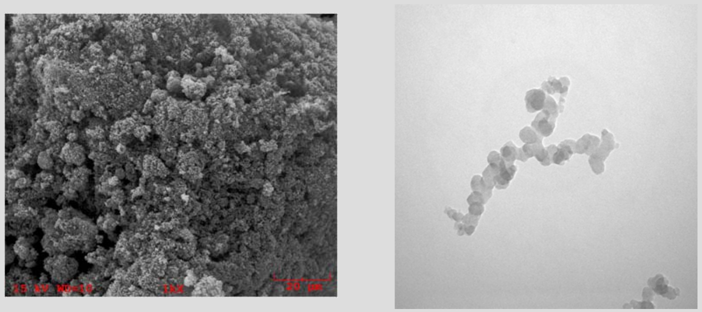
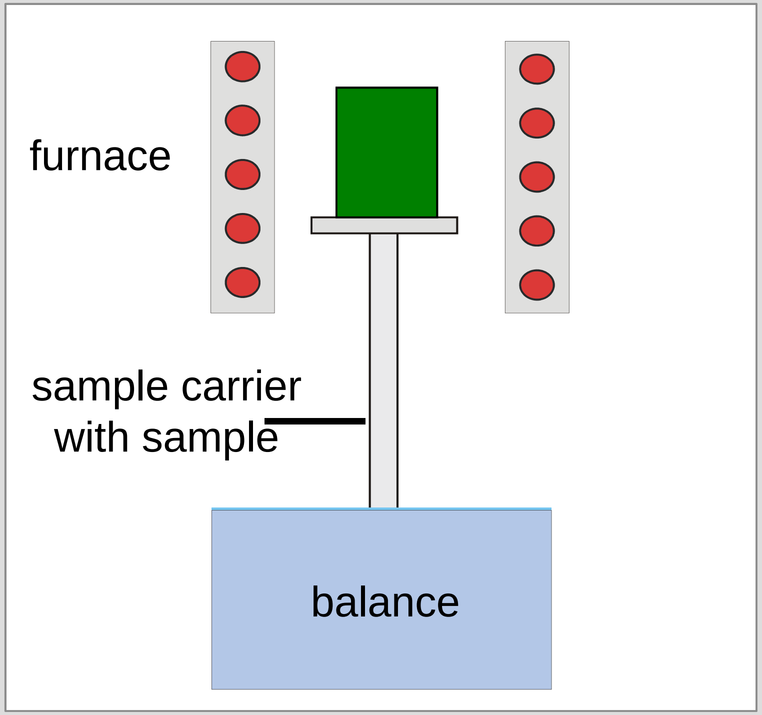
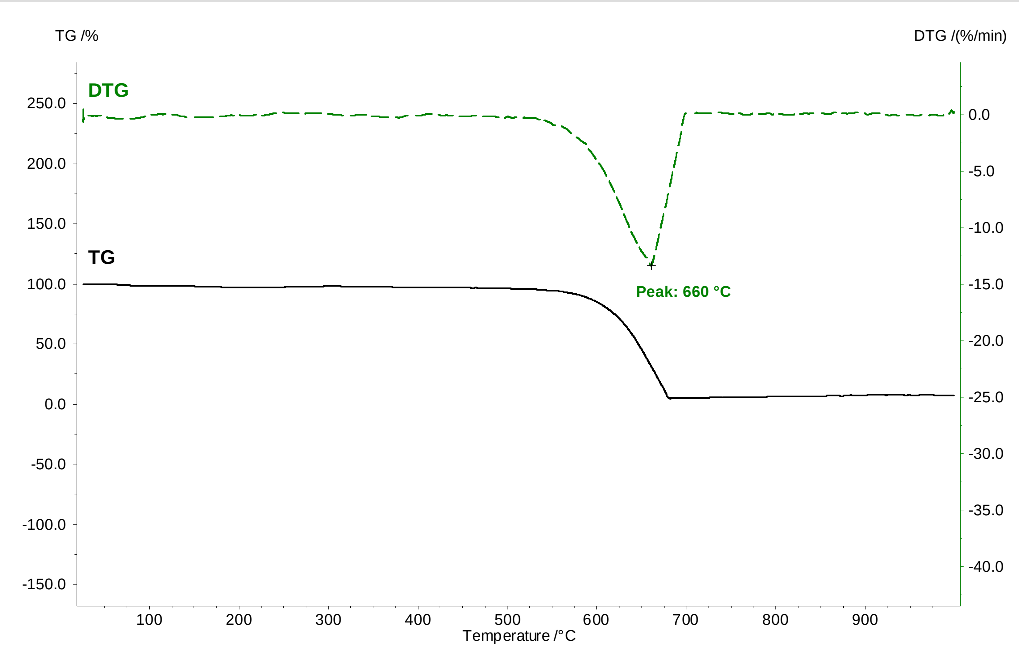


Diesel soot

Thermogravimetry (DIN 51006):

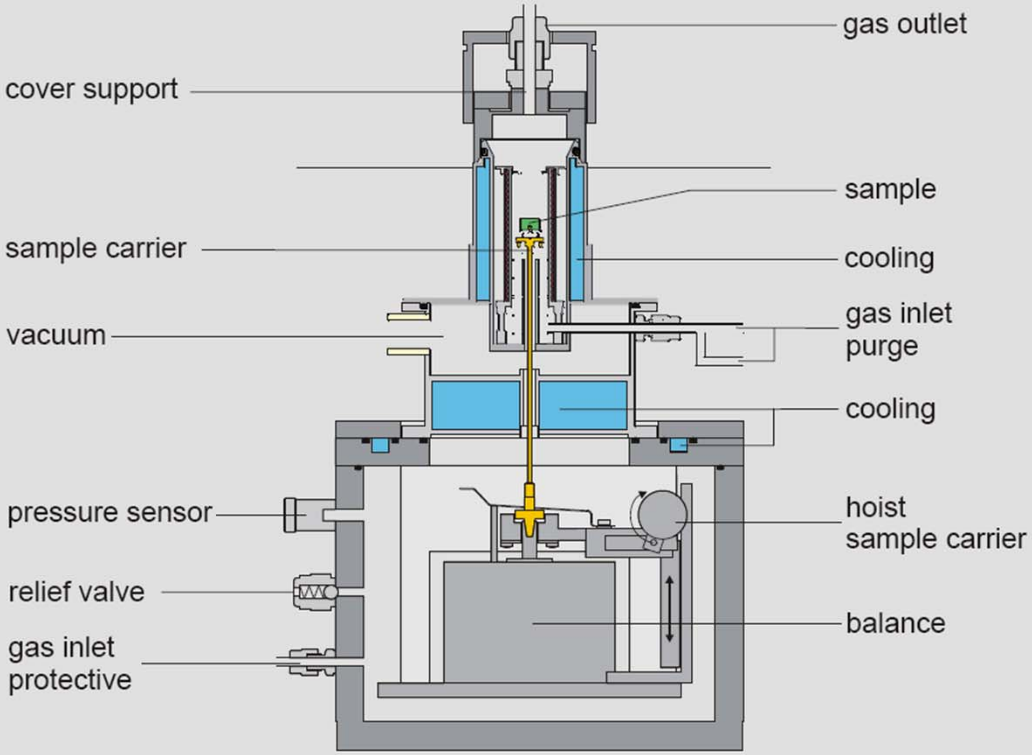
Thermogravimetry is a method where the mass and/ or the mass changes of a sample are measured in dependence of a temperature program.

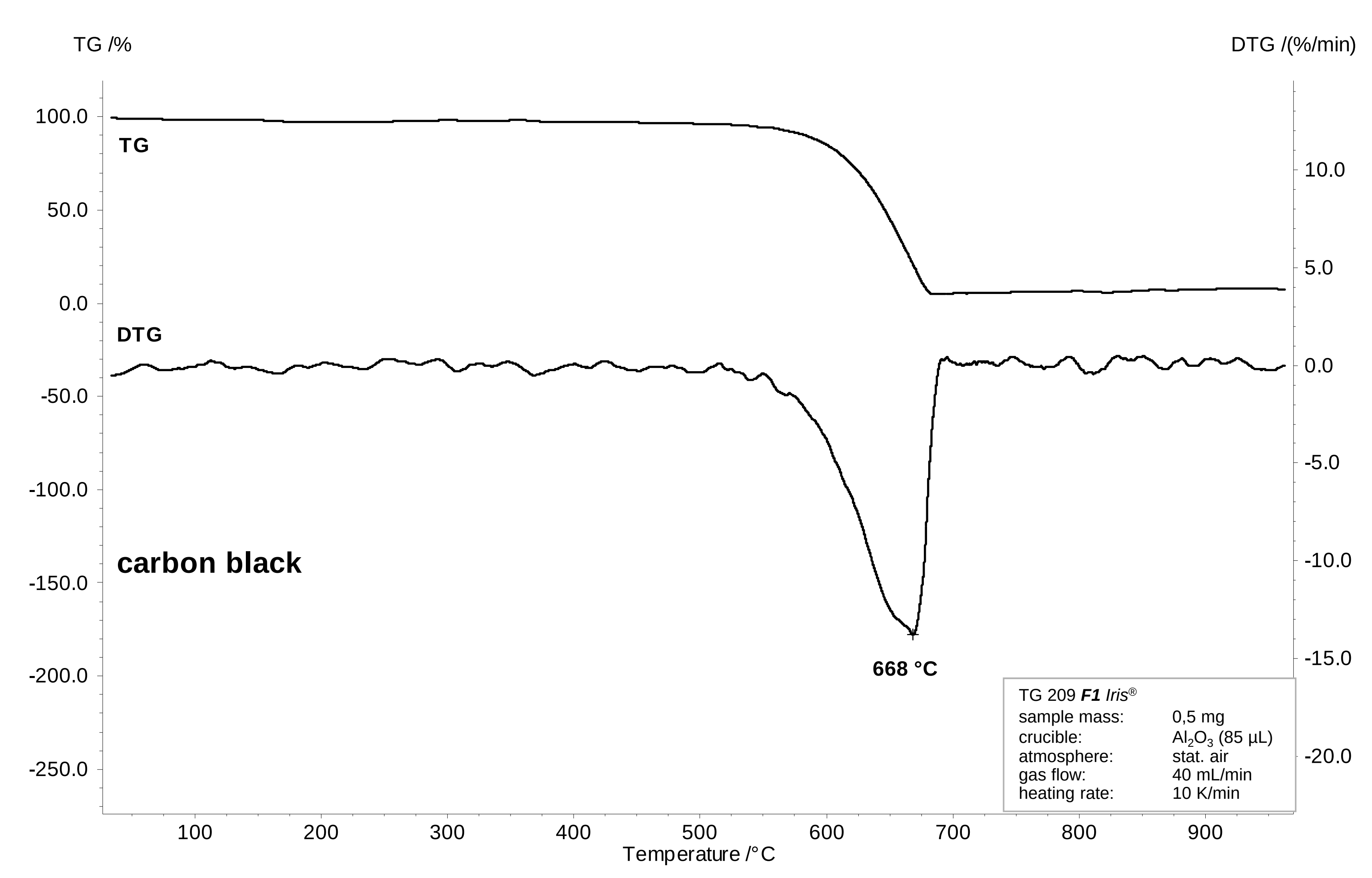




TG 209 ***F1*** *Iris®*

schematic drawing of the TG





TG /%
DTG /(%/min)
100.0
50.0
0.0
-50.0
-100.0
-150.0
-200.0
-250.0
10.0
5.0
0.0
-5.0
-10.0
-15.0
-20.0
TG
DTG
carbon black
668 °C
TG 209 F1 Iris®
sample mass: 0,5 mg
crucible: Al_2O_3 (85 µL)
atmosphere: stat. air
gas flow: 40 mL/min
heating rate: 10 K/min
100
200
300
400
500
600
700
800
900
Temperature /°C

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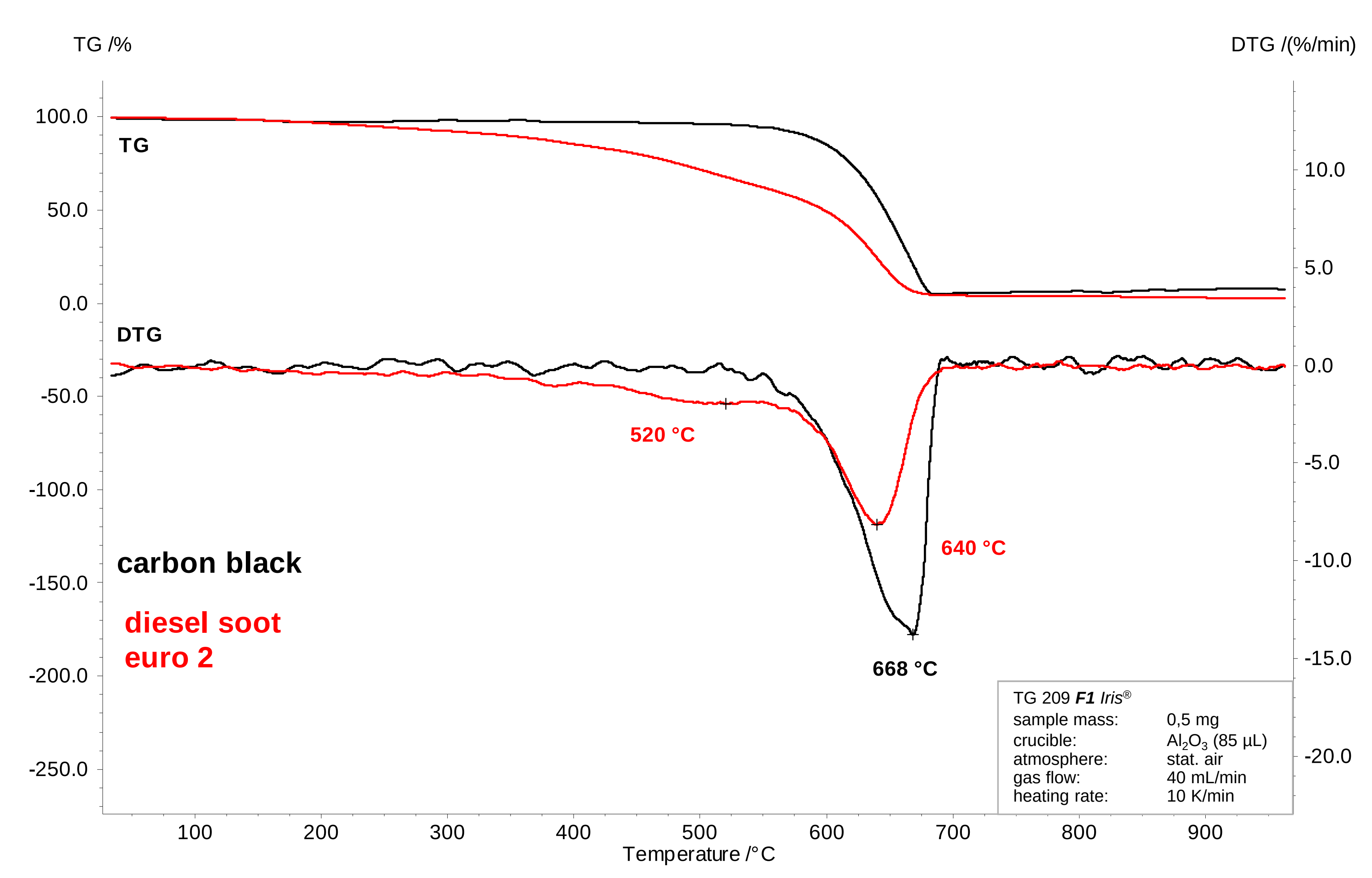

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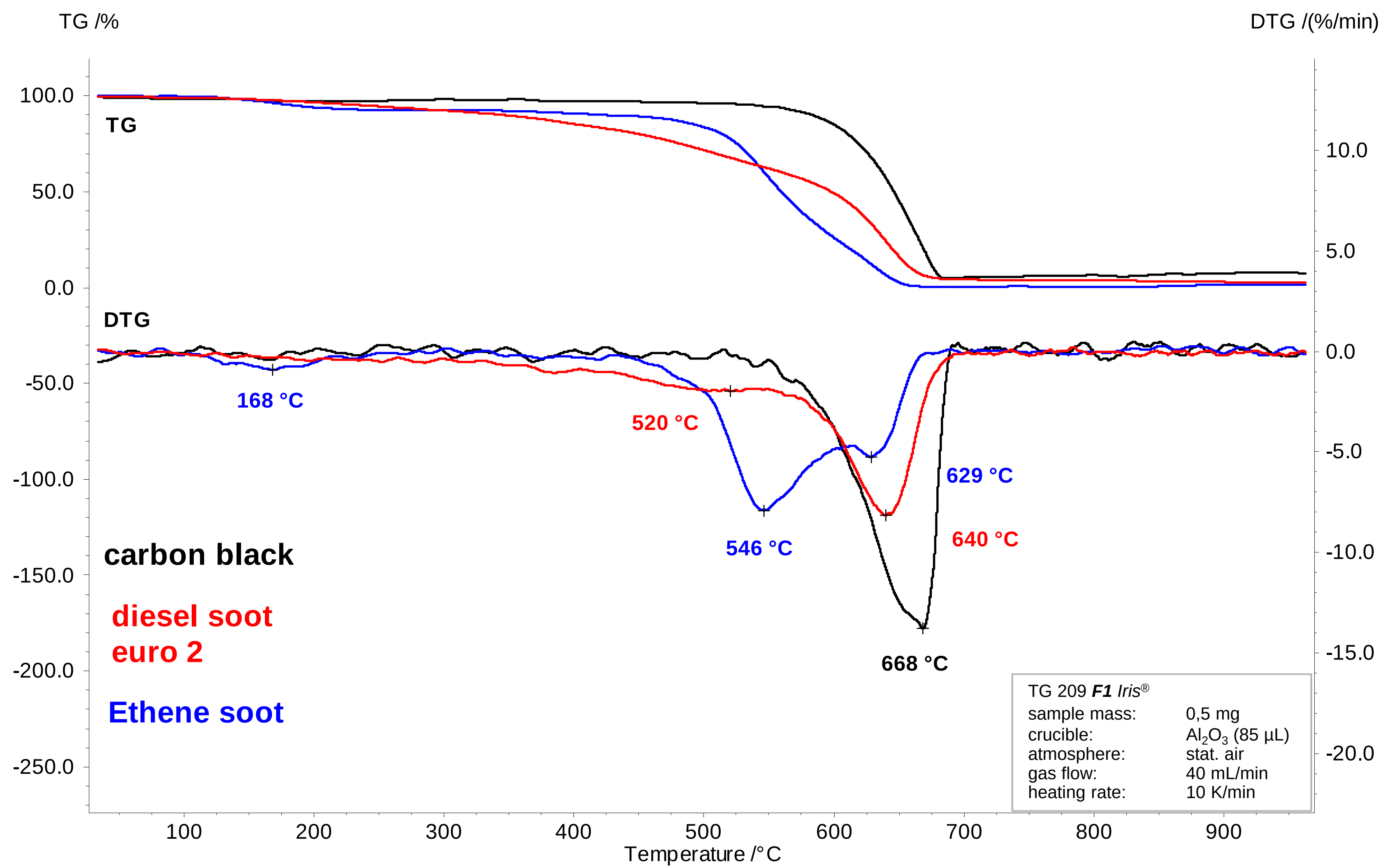
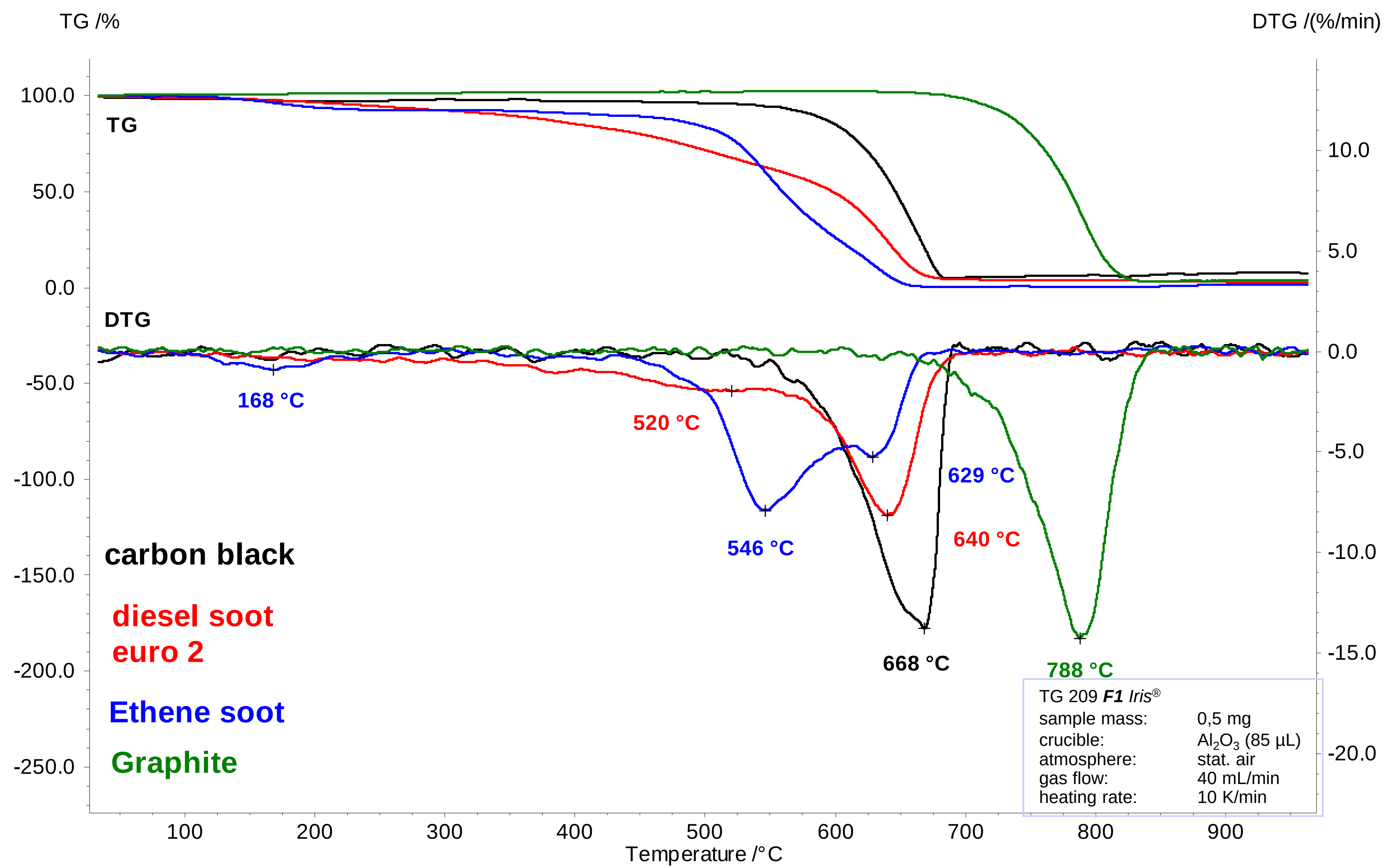
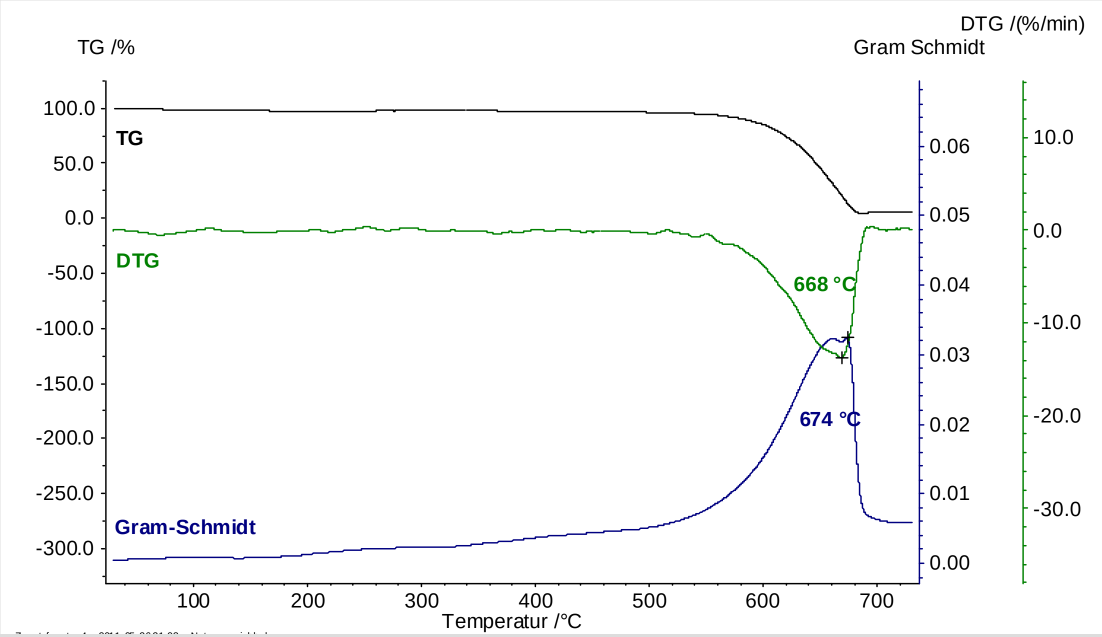
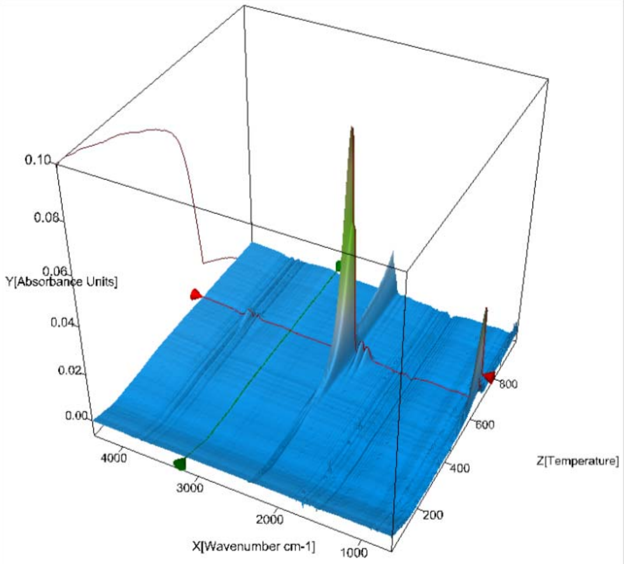
NETZSCH

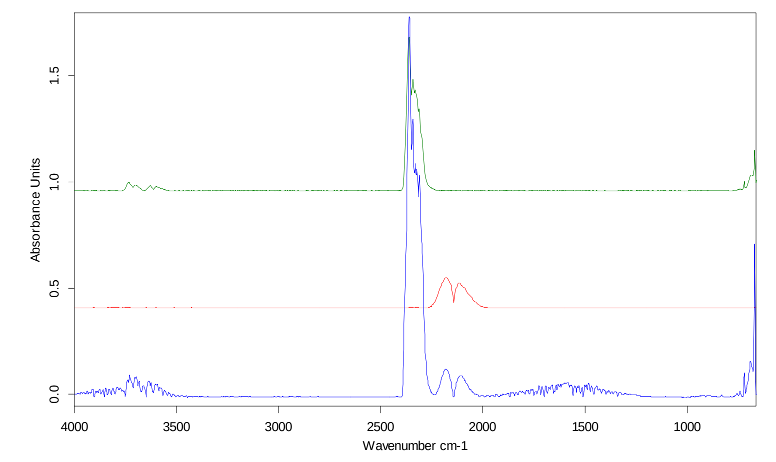



TG /%
DTG /(%/min)
100.0
50.0
0.0
-50.0
-100.0
-150.0
-200.0
-250.0
10.0
5.0
0.0
-5.0
-10.0
-15.0
-20.0
TG
DTG
168 °C
520 °C
546 °C
629 °C
640 °C
668 °C
788 °C
carbon black
diesel soot
euro 2
Ethene soot
Graphite
TG 209 F1 Iris®
sample mass: 0,5 mg
crucible: Al2O3 (85 µL)
atmosphere: stat. air
gas flow: 40 mL/min
heating rate: 10 K/min
100
200
300
400
500
600
700
800
900
Temperature /°C

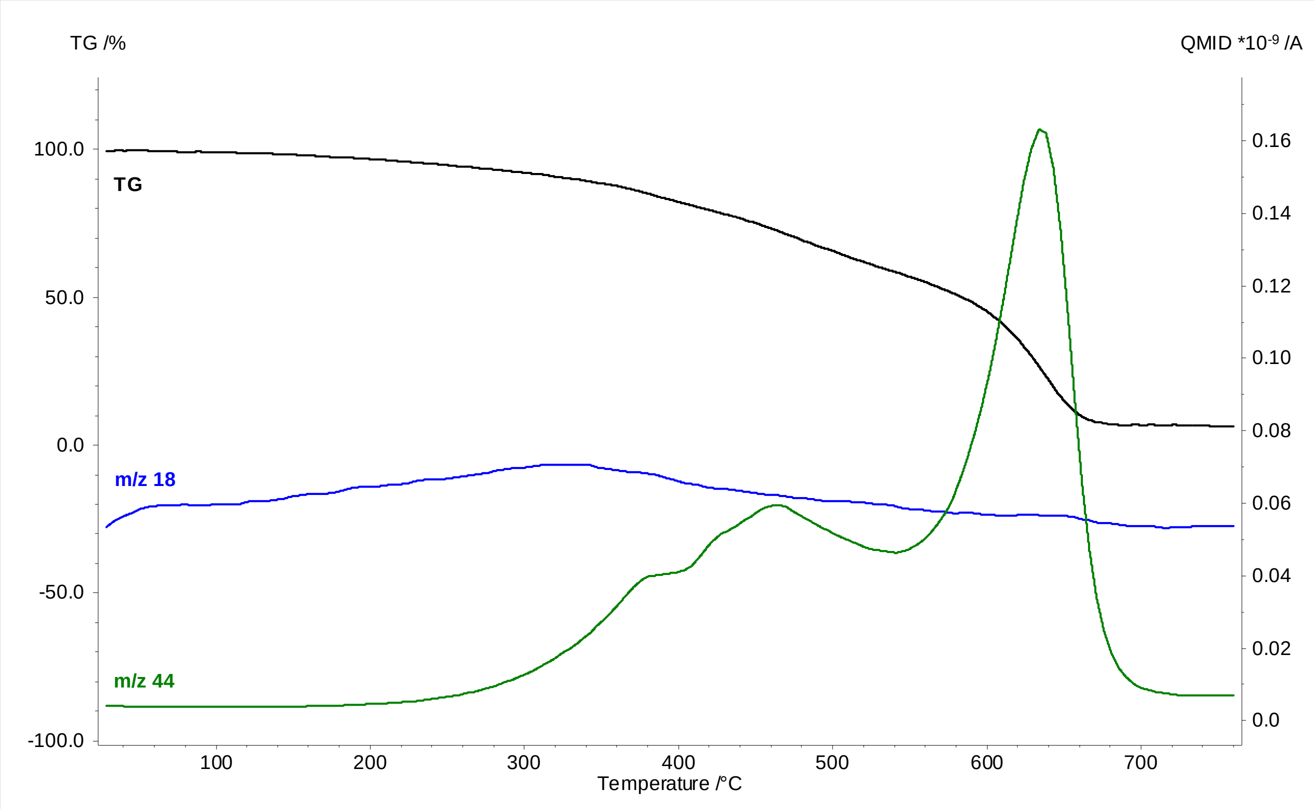
Carbon black





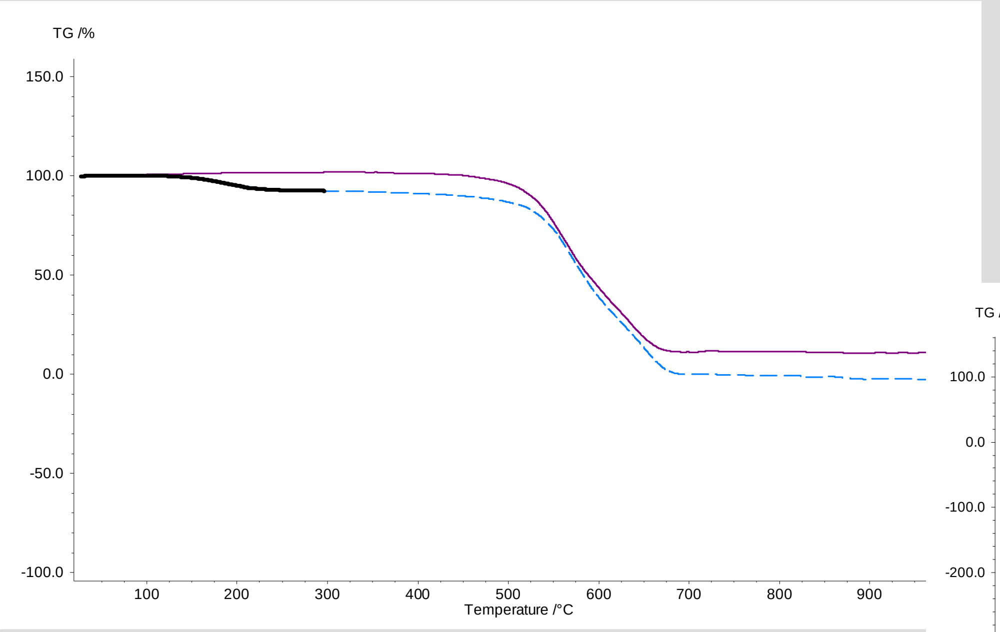


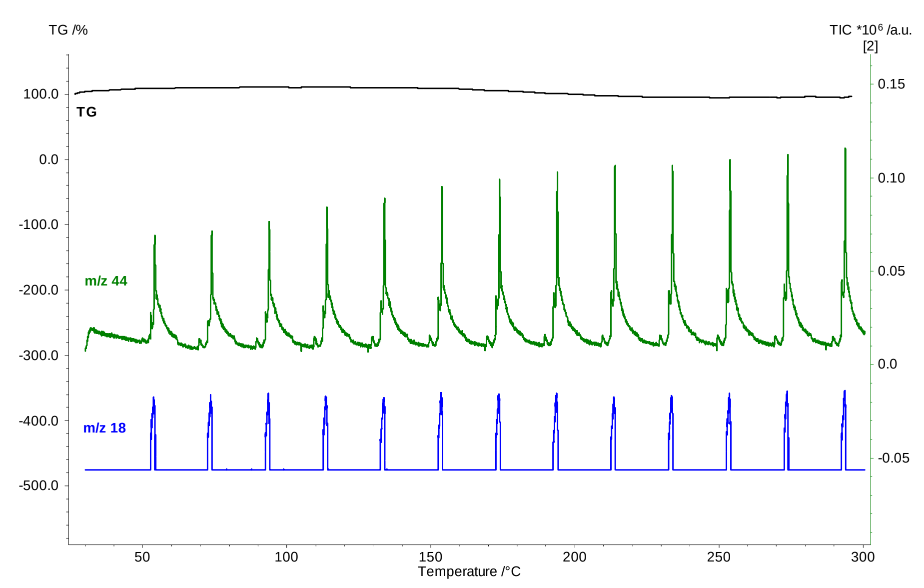
Diesel exhaust
Euro 2



TG-MS capillary coupling

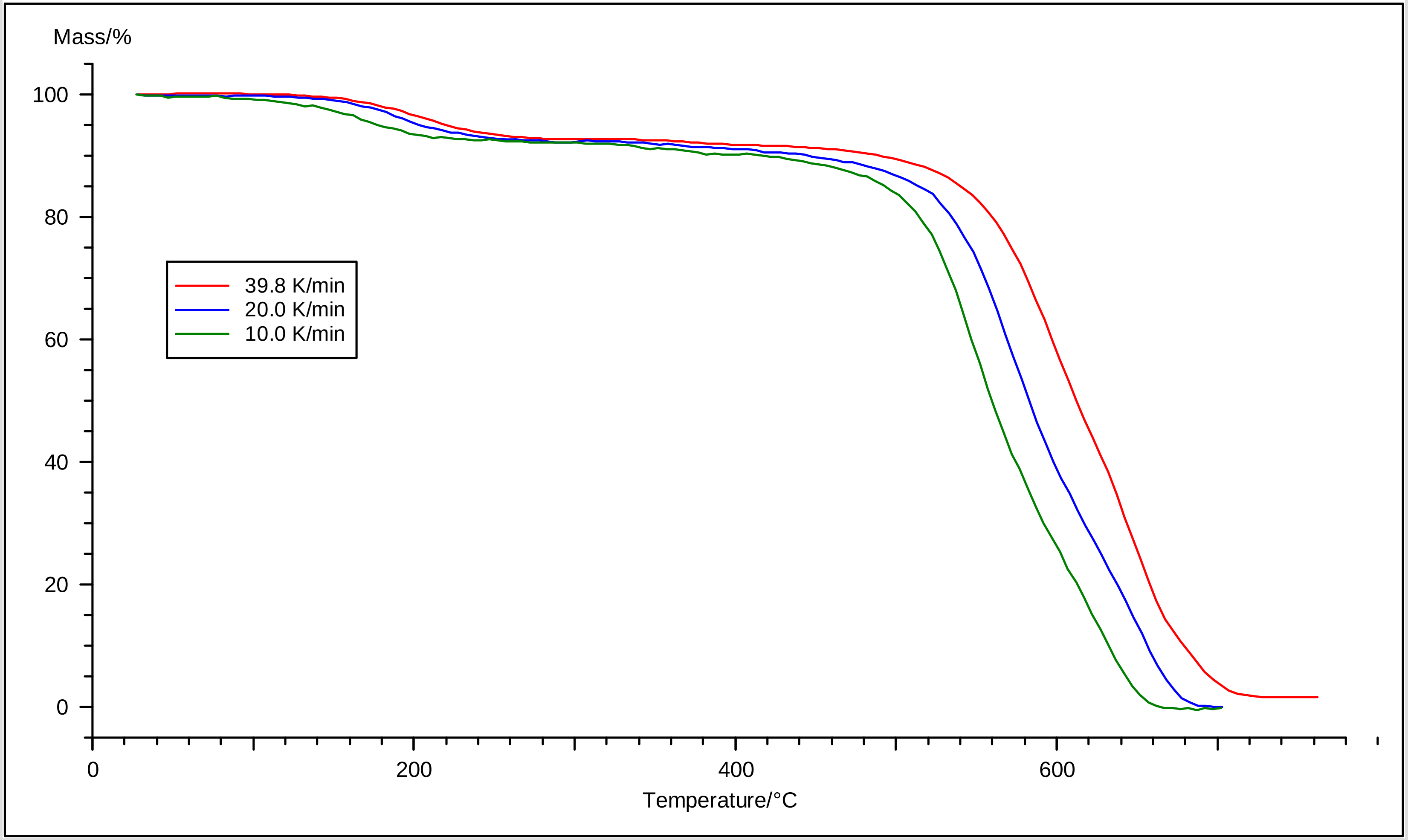
Ethene soot



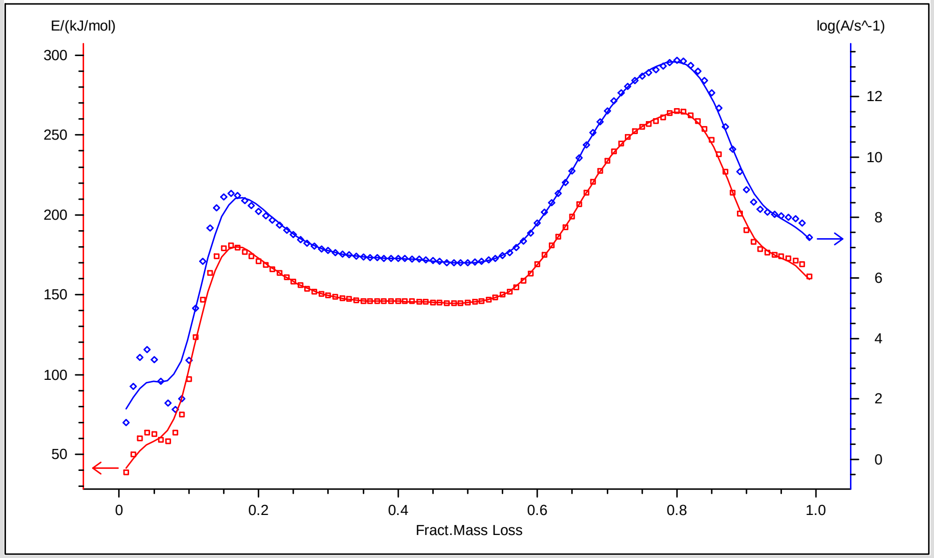


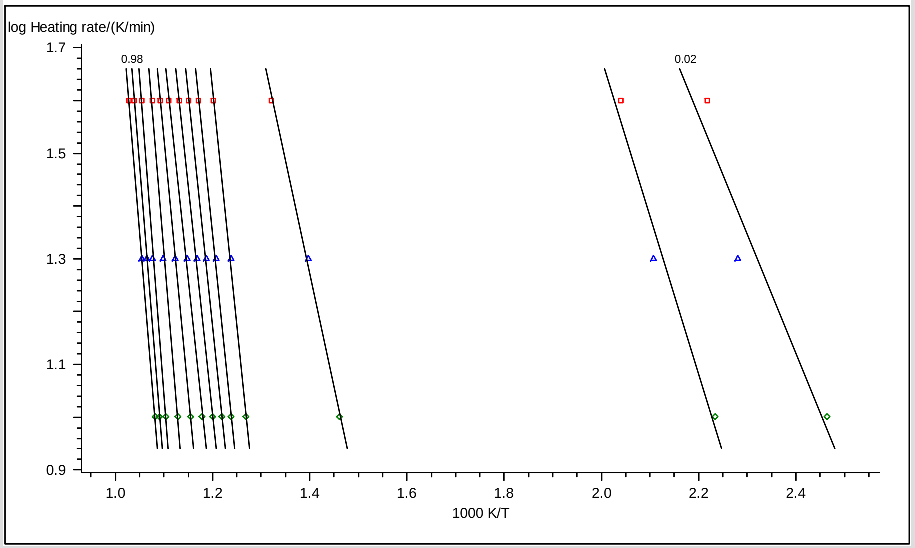
TG-GC-MS coupling

Ethene soot – measurements for kinetics



Model-free evaluation

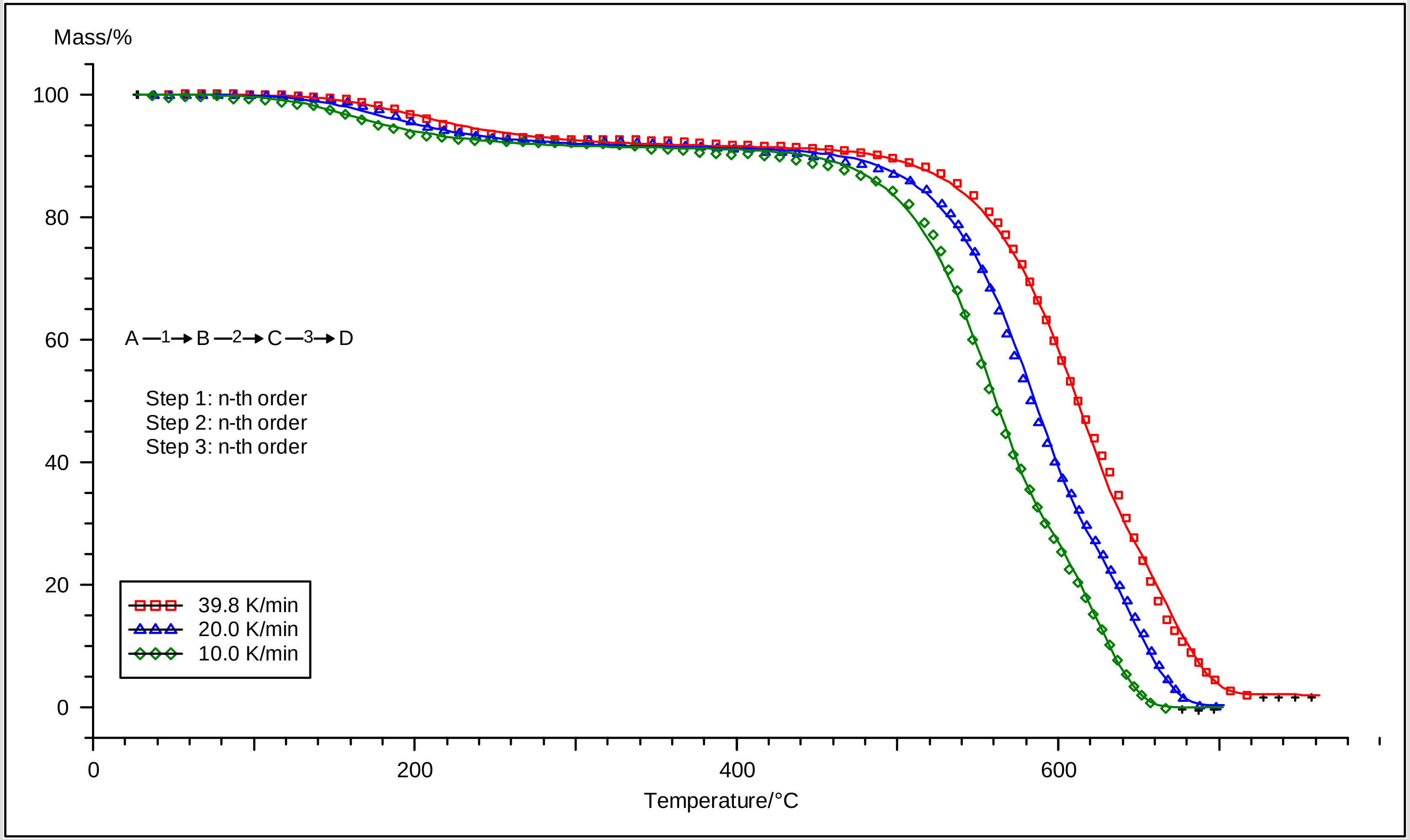




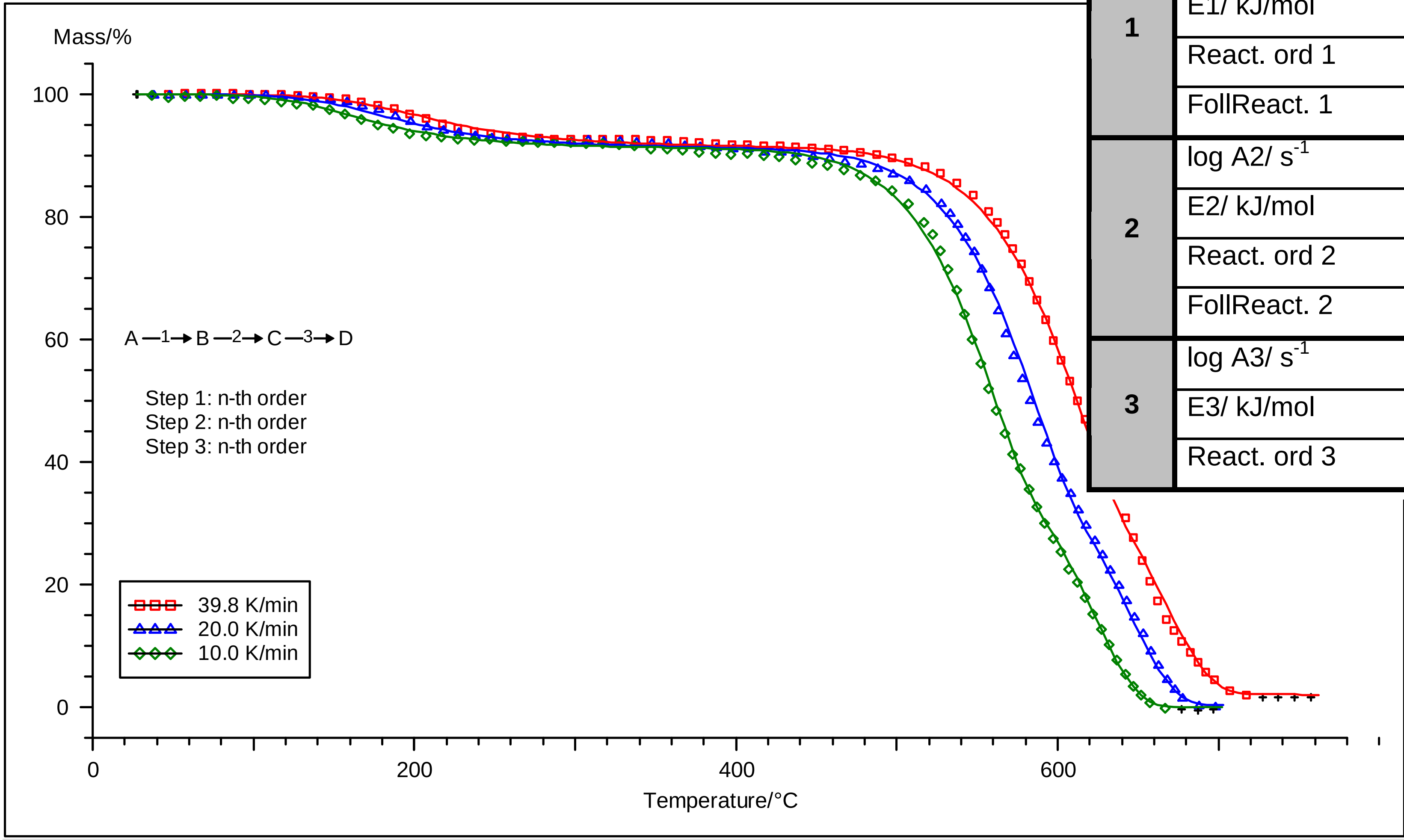
Friedman analysis:
activation energy and pre-exponential factor as a function of conversion degree

Ozawa-Flynn-Wall analysis:
the slope of the isoconversion lines leads to the activation energy

Model-based evaluation

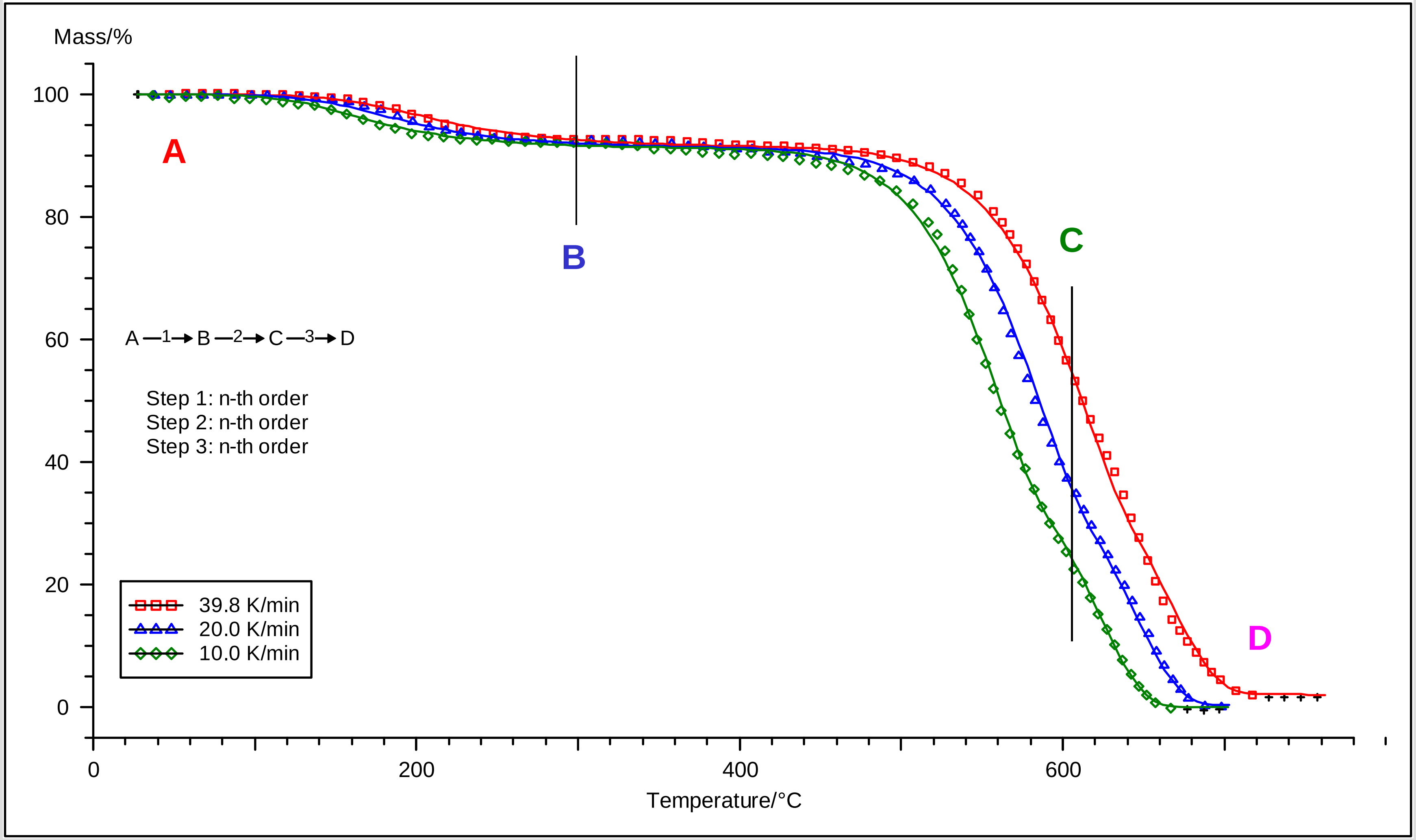


Model-based evaluation

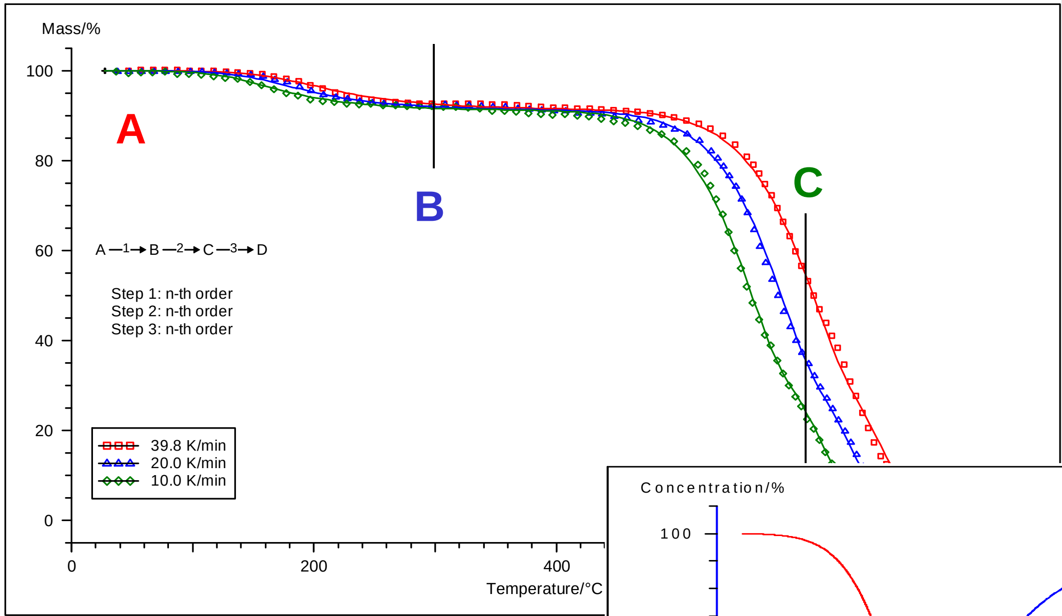


	Parameter	Opt. value
1	log A1/ s^{-1}	4.529
	E1/ kJ/mol	56.587
	React. ord 1	2.762
	FollReact. 1	8.94 E-2
2	log A2/ s^{-1}	7.404
	E2/ kJ/mol	154.439
	React. ord 2	0.670
	FollReact. 2	0.51
3	log A3/ s^{-1}	9.971
	E3/ kJ/mol	209.886
	React. ord 3	0.841

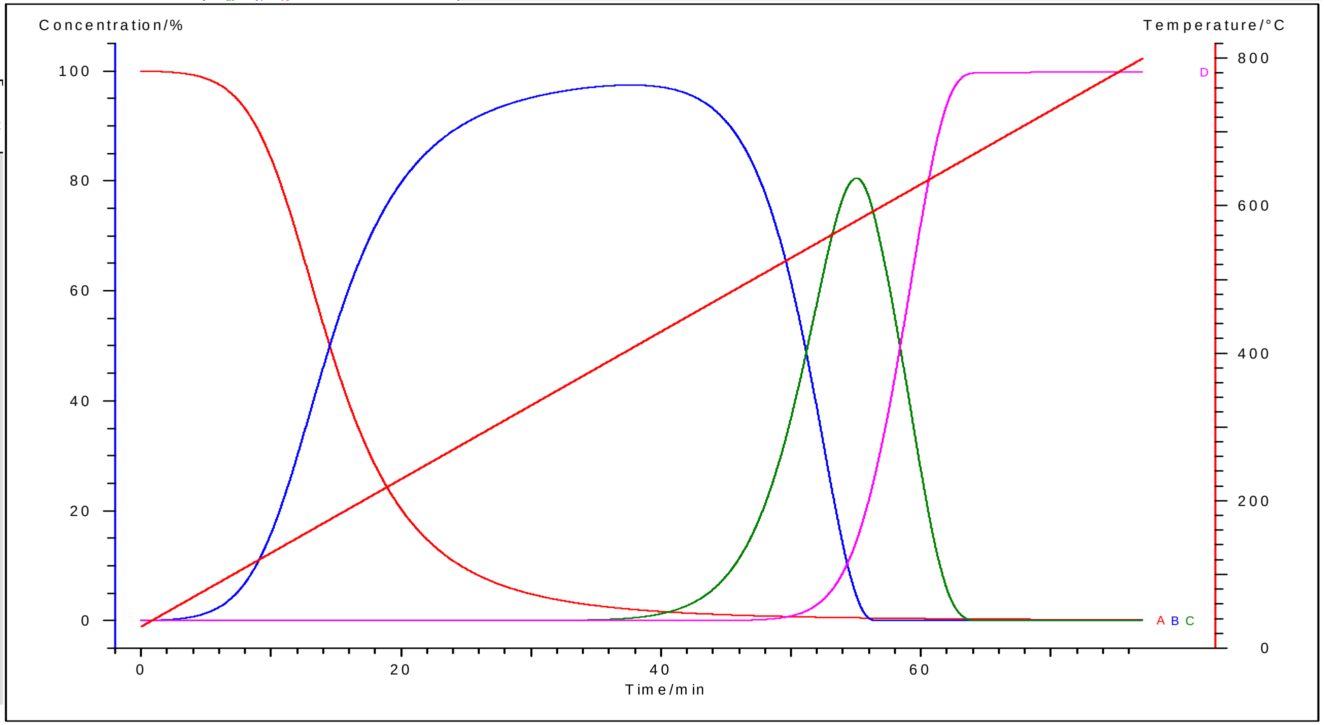
Model-based evaluation



Model-based evaluation



Prediction



Summary

Thermogravimetry is a useful tool to differentiate between the carbon particles

With the help of kinetic analysis the oxidation behaviour and mechanism can be simulated mathematically:

- the reaction order for the last two steps indicates phase boundary processes

- the first step seems to be a more complex process that indicates a starting oxidation, validated by the TG-GC-MS measurements

Thank you for your attention