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APPLICATION NOTE

Single-particle TGA – a new tool to measure the distribution of ash in rCB

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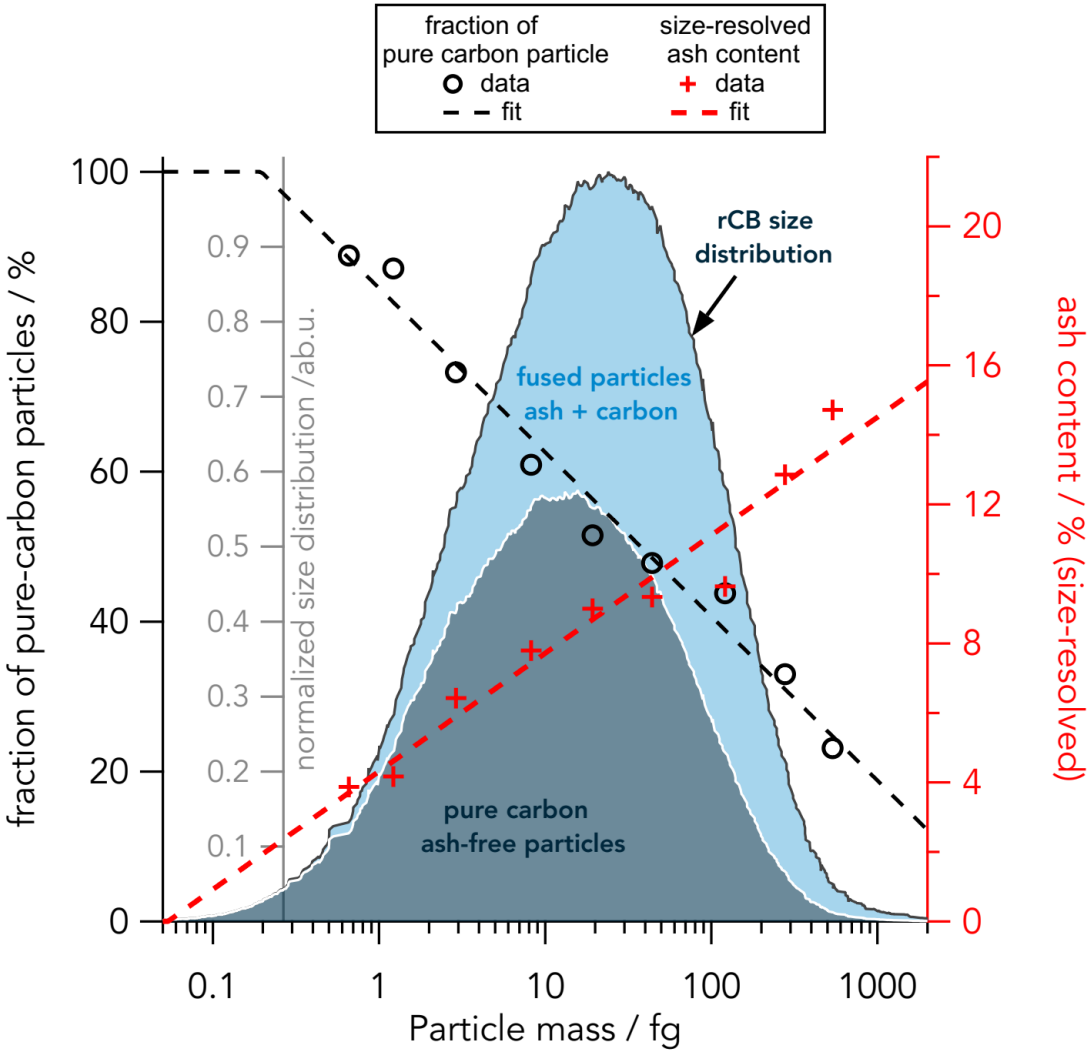
Single-particle TGA – a new tool to measure the distribution of ash in rCB

The *"ash"* (silica, zinc sulfide, …) is a characteristic component of recovered Carbon Black (rCB). The ash content is typically determined by thermogravimetric analysis (TGA), in which rCB is heated up to 550 °C in air for 3h. The carbonaceous components combust, while the refractory ash components remain. From the change in mass, an ash-content can be obtained, typically ranging from 15% to 20%.

The composition of rCB is rather heterogeneous, and there is evidence that suggests that the ash is not uniformly distributed amongst all particles. Conventional TGA can not provide insight to this variation, instead a particle size-resolved ash-content is needed.

The femtoG technology allows to separate particles of different size and to detect their absolute mass. E.g., a typical 420 nm rCB particle weights 19.3 fg (femtogram; 10^{-15} g). By adding a tube furnace to setup, rCB particles can be combusted prior to the mass measurement. This allows to measure an ash-content like a conventional TGA but resolved for every single particle size.

A **single-particle TGA** shows that 1) rCB contains **pure-carbon particles** as well as **mixed-phase particles** in which carbon and ash are fused together, 2) **with increasing particle size (mass), the ash-content increases**, and the percentage of pure-carbon particles declines.

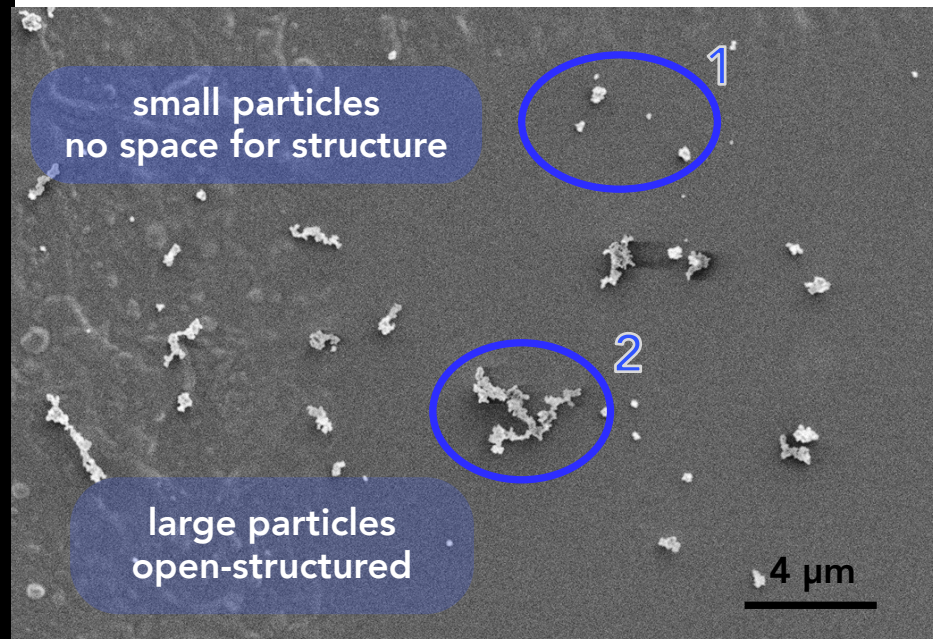


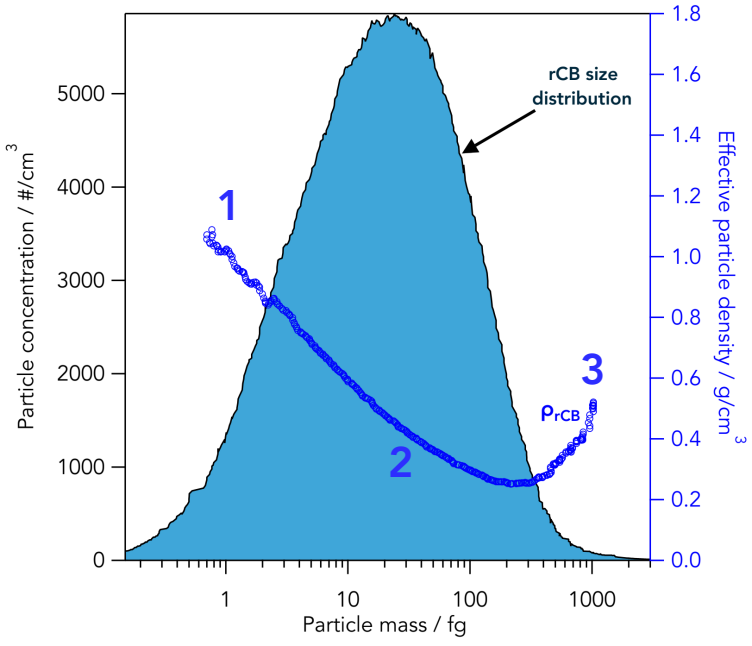
Correlation of mass, diameter and structure

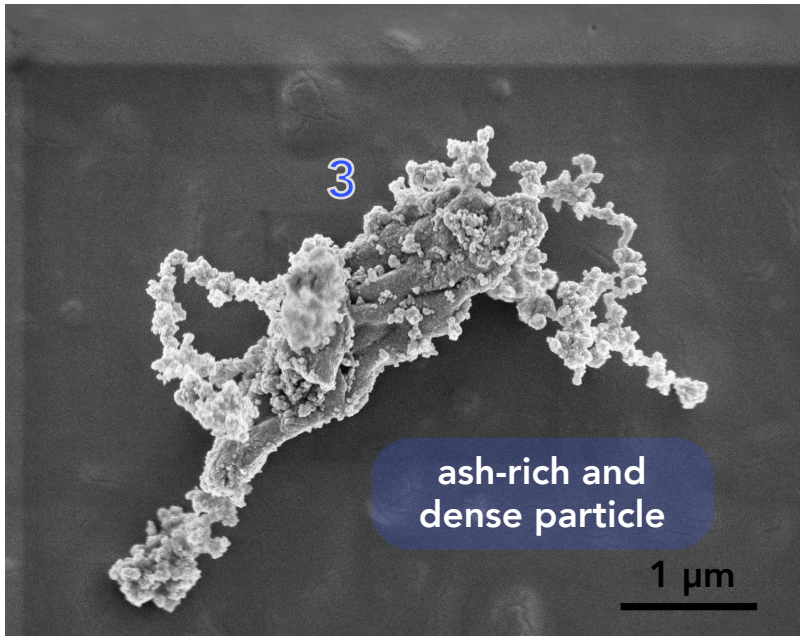
rCB aggregates or fused agglomerates have a complex structure similar to virgin carbon blacks. The femtoG system measures the mass and a diameter of these particle. The mass is independent of the particle shape, its refractive index, the analyze method. The mass is therefore a useful way to quantify the „true" particle size. The unit is femtogram, 10^{-15} g.

The parallel analysis of mass and diameter allows to calculated an effective particle (packing) density, which gives information on the particle structure. Light (small) rCB particles are unstructured and densely packed (1). With increasing particle mass (size), particles are more aggregated and more branched which results in an overall lower packing density (2). Very heavy particles (3) contain an increased amount of ash and therefore have a higher density again.

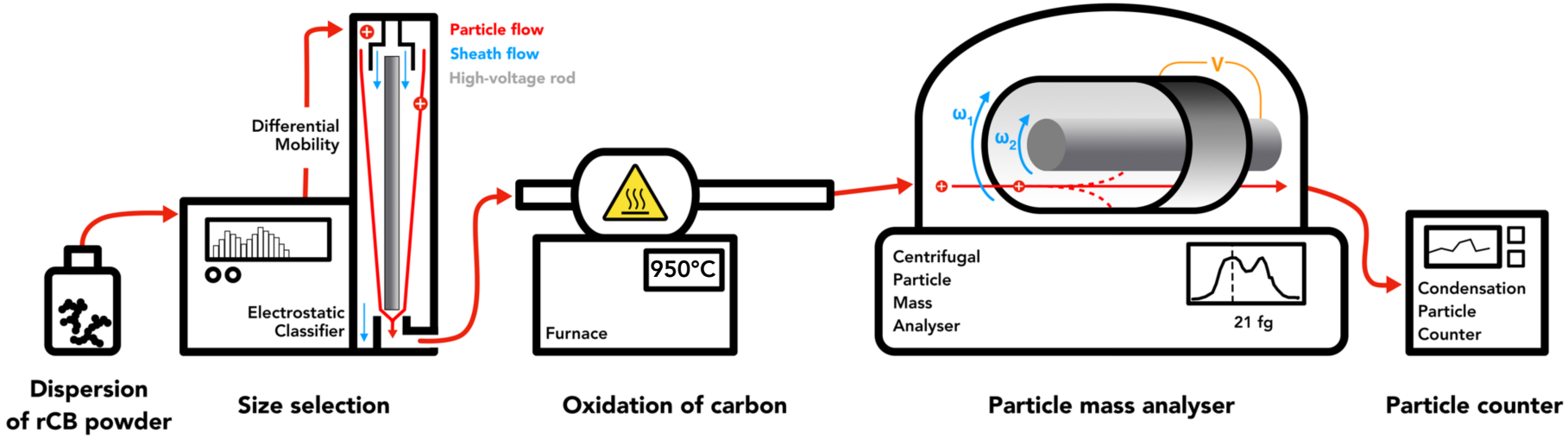
This rCB was milled down to a d_{97} of 5 µm (measured by laser-diffraction). With the femtoG system a median mass and diameter of 19.3 fg and 420 nm (mobility diameter) are obtained.







Single-particle TGA – experimental setup

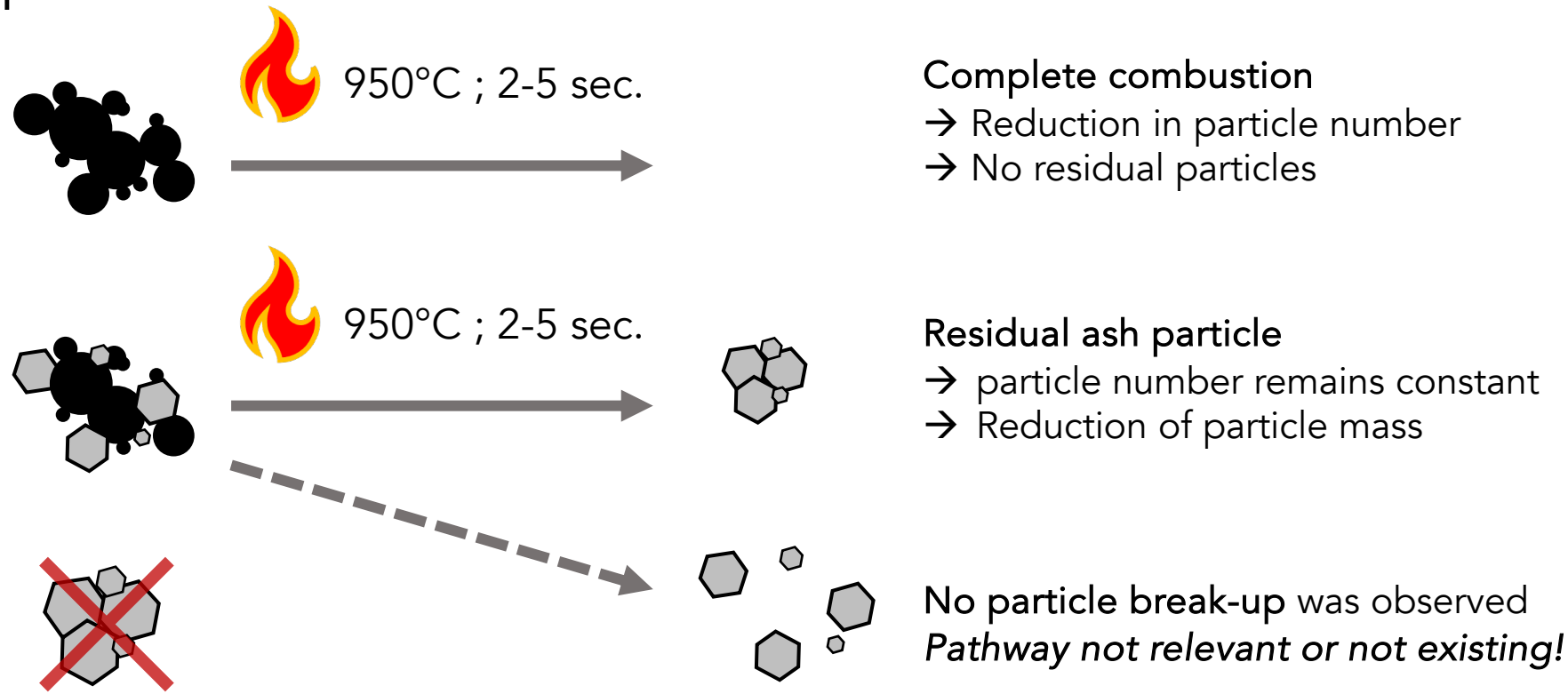


Different experimental setups were explored to test the feasibility of a single-particle TGA. All setups followed the same basic steps:

1. Dry rCB was dispersed in air to generate an aerosol.
2. The aerosolized particles were size-selected based on their **mobility or aerodynamic diameter**.
3. The aerosol was guided through a tubular furnace which was heated up to 950° *(this refers to the temperature of furnace walls, the temperature particles experience is lower).*
4. The particle diameter and mass were detected at different temperatures.

The fate of an rCB particle during combustion

Our experiments have shown that even same sized particles have different compositions. Some particles consist of **pure-carbon**, others are **mixed-phase particles** which contain both carbon and ash. Both fractions show different behavior during the combustion and lead to changes in total particle number and mass. No evidence was found for the presence of **pure-ash particles**.

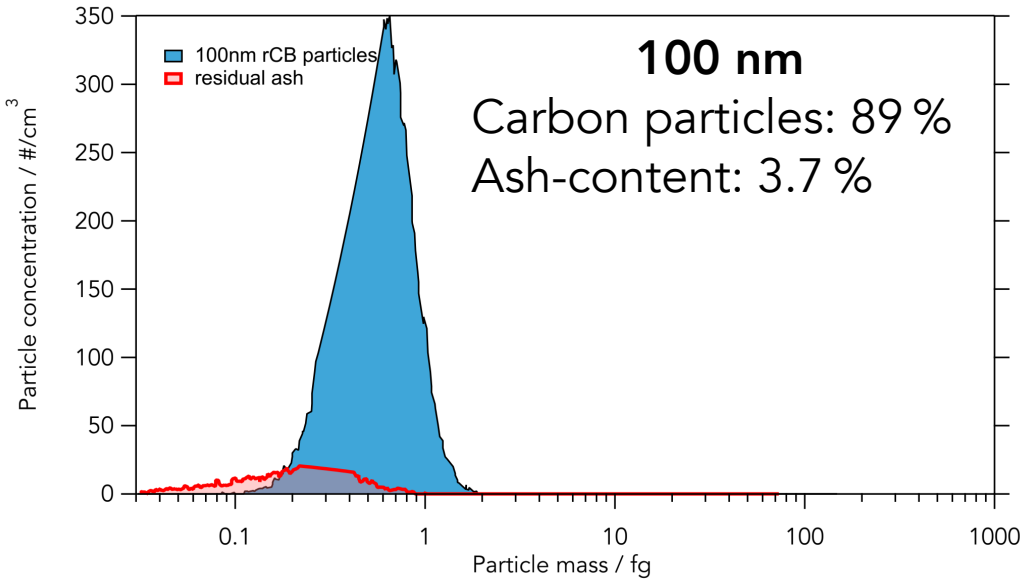


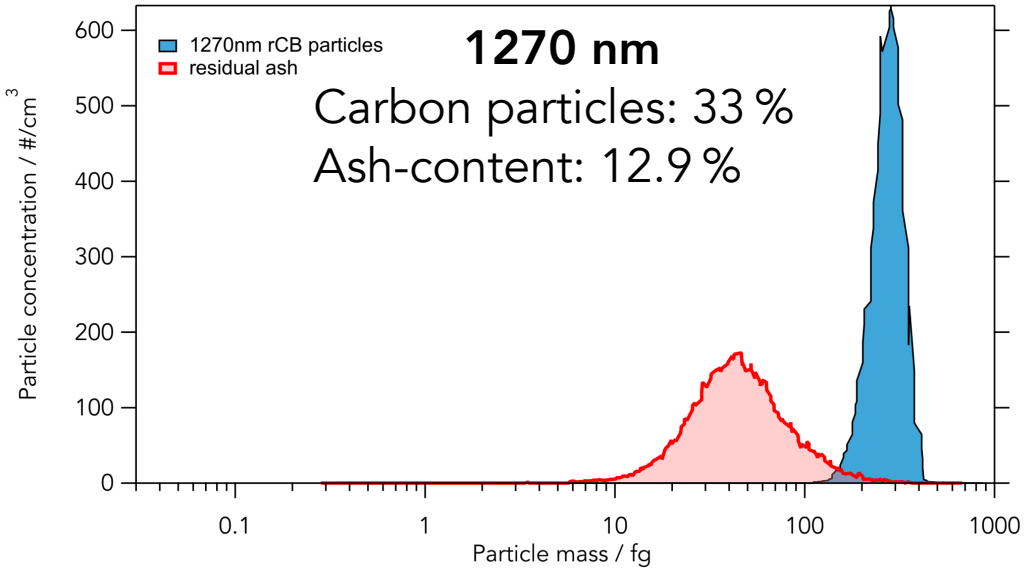
Composition analysis of small and large particles

The diagram shows a mass distribution of 100 nm size-selected particles. The mass and the particle concentration is recorded before (blue) and after the combustion in the furnace (red). By integrating the area under the curve, the total particle mass and number is obtained. During the combustion more 89% of all 100 nm particles are lost, since they consist only of carbon and burn off completely. The other 11% are mixed ash-carbon particles and leave a small residue after the combustion. From that, a total ash content of 3.7% is calculated.

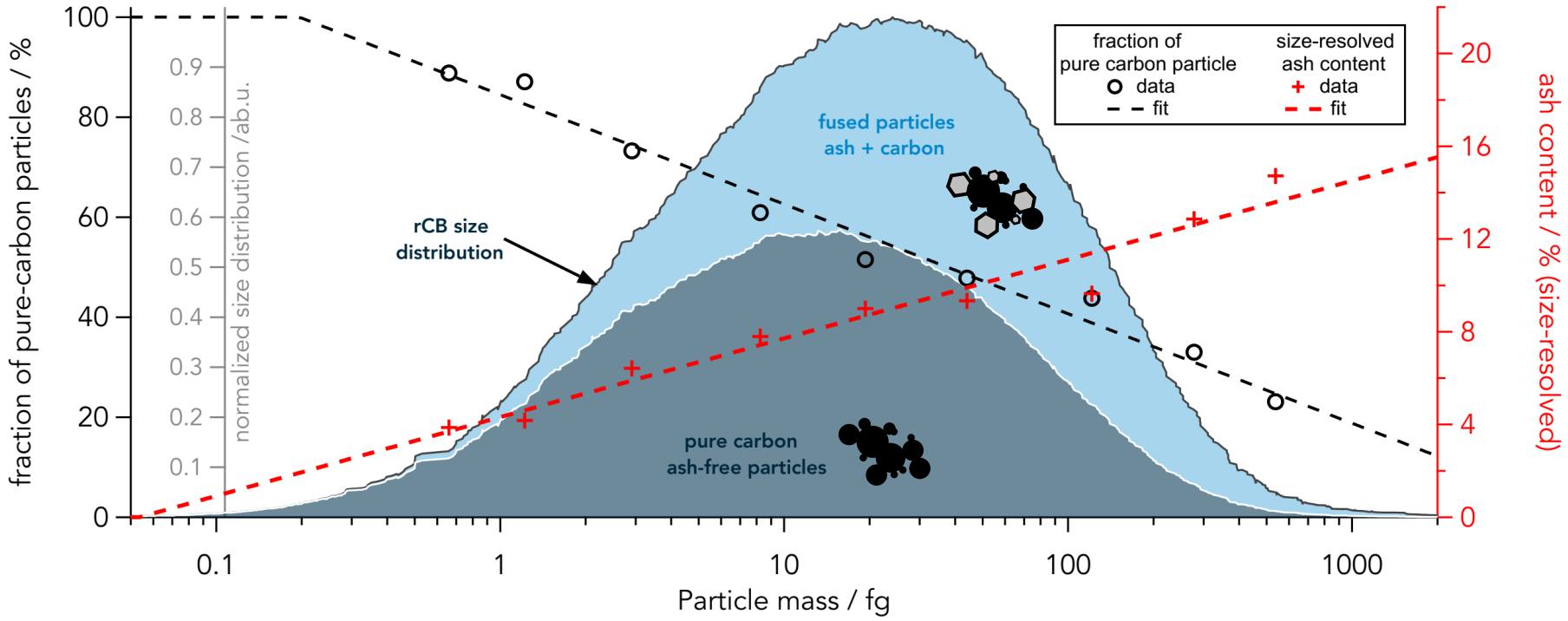
In a similar way, particles with a diameter of 1270 nm are selected and analyzed. Prior to the combustion they have a mass of 280 fg. During the combustion only 33% of all particles are lost. The residual ash particles have a mass of only 53 fg, which results in a total ash content of 12.9%.

Such analysis is repeated for multiple different particle sizes to cover the whole size distribution.





Overview and outlook



What is the effect of milling on the ash distribution?

Grinding down fused particles vs separating ash and carbon?

Does rCB upgrading remove ash uniformly?

Scanning with our single particle TGA setup through the whole particle size range revealed that small particles consist of **pure carbon** and are practically ash-free. With increasing size, the fraction of mixed-phase particles as well as the absolute ash-content increases.

Disclaimer

The analysis and results presented in this application paper pertain specifically to the recovered Carbon Black sample evaluated during this study. While the described technology offers a novel approach to determining ash-content size-resolved across the size distribution and is generally applicable to any recovered Carbon Black, the specific results may vary depending on the batch of the sample analyzed, as well as the feedstock and processing conditions used. Therefore, the findings and conclusions should not be generalized to all recovered Carbon Blacks without further validation on different batches, feedstocks, and processing conditions. The data and conclusions presented herein are provided for informational purposes only and should not be interpreted as guarantees or warranties of performance for other samples or under different conditions. In no event shall femtoG be responsible or liable for any direct, indirect, punitive, incidental, special, or consequential damages whatsoever arising out of or connected with the use of, misuse of, or reliance upon such results or analysis.