# Detection of tar brown carbon with the single particle soot photometer (SP2)

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## SUMMARY

- In addition to soot black carbon (soot BC), light-absorbing "brown carbon" (brC) plays an important role in the Earth's radiative budget. brC may originate from biomass combustion [1], heavy fuel oil combustion [2], or atmospheric chemistry [1].
- Brown carbon consists either of distinct, generally soluble molecules or the solid amorphous-carbon material known as "tar" [2].
- Tar brC is refractory and absorbs infrared light [2,3], and may therefore be detected as "equivalent BC" by light-absorption-based instruments [2].
- The SP2 employs a continuous-wave 1064 nm laser to heat soot BC to incandescence at about 4000 K. Light scattering is measured simultaneously. The calibrated incandescence signal gives "rBC mass."
- This study explored the possibility that the SP2 is capable of detecting tar particles as well as soot BC. We found that tar particles may evaporate in the SP2, with or without incandescence. Incandescing tar particles scatter more light at the time of incandescence than rBC. We recommend this light scattering signal as the best diagnostic to identify tar with the SP2. This represents the first possibility for a real-time diagnostic of tar brC particles.

## SP2

- A jet nozzle and sheath flow guide particles through the centre of a Gaussian (TEM 00 mode) continuous-wave Nd:YAG laser at 1064 nm.
- If a particle absorbs 1064 nm light efficiently, it may experience a net heat gain and evaporate, with or without incandescence depending on whether it is refractory to 3000 K. For tar, it is important to note that some materials may undergo a change in composition within the laser [4].
- Incandescence (350-880 nm radiation) and scattering (1064 nm) are measured in high enough time resolution that particle trajectories in the laser beam can be followed.
- A four-element scattering detector with 2 positive and 2 negative sectors is used to infer the absolute position of particles within the laser beam.

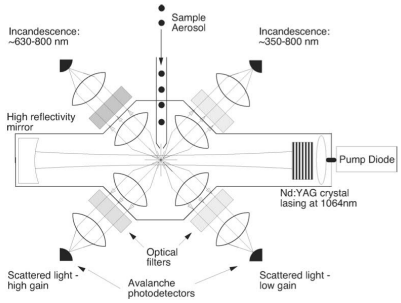


Figure 2. Schematic of the SP2.

## MEASUREMENTS

Two test data sets were used as the basis of this work. Both of these data sets were presented in Ref. [2]. The two test data sets were obtained from a single marine engine operated on the same heavy fuel oil (HFO) at the same engine load, on the same day. The engine tuning parameters were varied such that either a pure-BC or a tar-rich aerosol was produced [2].

We define the relative importance of BC or tar in these samples using the Absorption Ångström exponent (AAE). The AAE is the negative slope of log-log plot of absorption versus wavelength. It is fundamentally related to the degree of graphitization of a carbonaceous material and is 1 for small mature soot BC particles but >1 for less graphitic material such as tar.

The estimated mass ratio of tar to soot BC was 3:1 in the tar-rich case and the AAE was about 2.0. The rBC/EC mass ratio was 0.18, and over half of the total light absorption was due to tar and not soot BC [2]. In the pure-BC case, the rBC/EC ratio was 0.97 and the AAE was close to 1.0. The mass of tar in the soot BC case was negligible.

## RESULTS

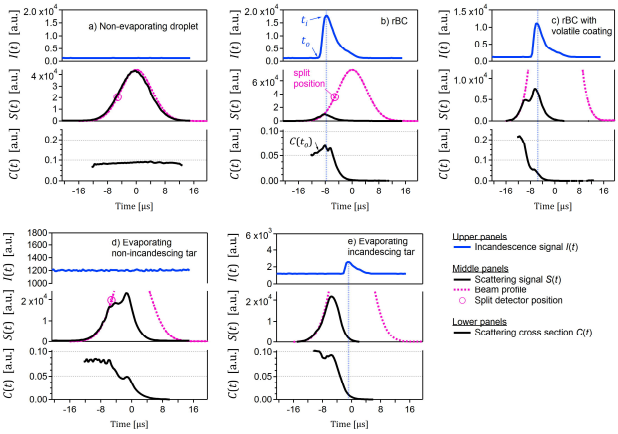


Figure 1. Particle types observed by the SP2 in this work.

These examples were selected to be representative of the trends shown in Figures 2-4, with the exception of c), which was rare in our data set.

a) Typical non-absorbing and therefore non-evaporating particle. (Likely lubricating oil/sulfate mixture.)
b) Typical soot BC particle.
c) Coated soot BC particle.
d) Typical evaporating but non-incandescing particle.
e) Typical evaporating and incandescing particle.

Note the difference between the blue lines showing $t_i$ and the time of stable $C(t)$ in c) and e). Note also the varying ordinate scales.

Symbols are defined in Table 1.

### Evaporating, non-incandescing tar particles

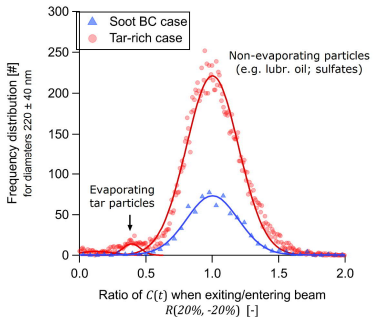


Figure 2. Identification of evaporating but non-incandescing tar particles.
The frequency distributions are highlighted by Gaussian fits, representing random error. Evaporating particles only occurred in the tar-rich case.

- Evaporating but non-incandescing particles were identified for the first time (Figure 2).
- 578 of 2.5 × $10^5$ particles partially evaporated.

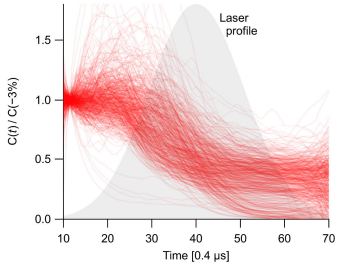


Figure 3. Evaporation trends of tar particles.
Each red line corresponds to the lowest panel of Figure 1d.
Each curve has been normalized to $C(-3\%)$, which is normally used for coating-thickness analysis [2,3].

| Symbol | Meaning |
|---|---|
| $t$ | Time spent by a particle in the SP2 laser beam |
| $S(t)$ | SP2 scattering signal |
| $C(t)$ | Scattering cross-section corresponding to $S(t)$ |
| $C(-3\%)$ | Scattering cross-section at -3% of laser maximum as a particle enters the SP2 laser beam |
| $I(t)$ | SP2 incandescence signal |
| $t_o$ | Time just before onset of incandescence |
| $t_i$ | Time of maximum incandescence |
| $R(-20\%, 20\%)$ | Ratio of $C(t)$ at two different $t$ (Eq. 1) |

Table 1. Definition of symbols.

### Evaporating, incandescing tar particles

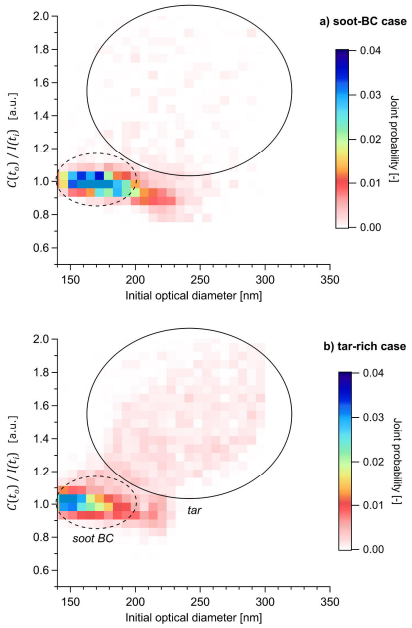


Figure 4. Identification of evaporating and incandescing tar particles.
The abscissa shows particle optical diameter just prior to incandescence (representing the apparent size of non-volatile material within each particle).
The ordinate shows scattering cross-section just prior to incandescence (see Figure 1 for illustration) normalized to the maximum incandescence signal. As the incandescence signal is expected to have a similar calibration factor for soot BC or for tar, an increase in the ordinate reflects an increase in the volume of non-incandescing material present at time of incandescence.
Inspection of the data indicated that the joint probability is not exactly equal to zero in the soot-BC case due to coincidence.

**References**
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