

**SP2 fails to detect
PALAS soot**

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Technical Note: The single particle soot photometer fails to detect PALAS soot nanoparticles

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Abstract

The single particle soot photometer (SP2) uses laser-induced incandescence (LII) for the measurement of atmospheric black carbon (BC) particles. The BC mass concentration is obtained by combining quantitative detection of BC mass in single particles with a counting efficiency of 100 % above its lower detection limit (LDL). It is commonly accepted that a particle must contain at least several tenths of femtograms BC in order to be detected by the SP2.

Here we show the unexpected result that BC particles from a PALAS spark discharge soot generator remain undetected by the SP2, even if their BC mass, as independently determined with an aerosol particle mass analyser (APM), is clearly above the typical LDL of the SP2. Comparison of counting efficiency and effective density data of PALAS soot with flame generated soot (combustion aerosol standard burner, CAST), fullerene soot and carbon black particles (Cabot Regal 400R) reveals that particle morphology can affect the SP2's LDL. PALAS soot particles are fractal-like agglomerates of very small primary particles with a low fractal dimension, resulting in a very low effective density. Such loosely-packed particles behave like "the sum of individual primary particles" in the SP2's laser. Accordingly, the PALAS soot particles remain undetected as the SP2's laser intensity is insufficient to heat the primary particles to vaporisation because of their small size (primary particle diameter ~5–10 nm). It is not surprising that particle morphology can have an effect on the SP2's LDL, however, such a dramatic effect as reported here for PALAS soot was not expected. In conclusion, the SP2's LDL at a certain laser power depends on total BC mass per particle for compact particles with sufficiently high effective density. However, for fractal-like agglomerates of very small primary particles and low fractal dimension, the BC mass per primary particle determines the limit of detection, independent of the total particle mass. Consequently, care has to be taken when using the SP2 in applications dealing with loosely-packed particles that have very small primary particles as building blocks.

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1 Introduction

Atmospheric black carbon (BC) particles are a concern due to their climate impact and adverse health effects (Shindell et al., 2012). Nevertheless, the measurement of the number and the mass concentration of atmospheric BC particles remains a challenge, as interference from organic carbon and inorganic aerosol components often causes substantial measurement uncertainty (e.g. Schmid et al., 2001; Müller et al., 2011). Few years ago, the single particle soot photometer (SP2; Stephens et al., 2003) was developed. The SP2 uses laser-induced incandescence (LII) to detect BC. The SP2 makes quantitative measurements of BC mass concentrations possible, as it combines quantitative detection of BC mass in single particles with a counting efficiency of 100 % above its lower detection limit (Schwarz et al., 2010; Laborde et al., 2012b). A further key feature is that the BC mass measurement is independent of particle mixing state (Moteki and Kondo, 2007; Slowik et al., 2007; Laborde et al., 2012b).

The lower detection limit (LDL) for successful counting of BC particles by the SP2's incandescence detector, expressed in terms of minimal BC mass in a single particle, depends both on physical limitations of the detection technique as well as instrument parameters chosen by the operator. BC particles fail to heat to their vaporization temperature (~ 4000 K), a requirement for proper detection, if their BC mass is too small or the laser intensity is too low (Schwarz et al., 2010). The assumption currently made among SP2 users is, to our knowledge, that the LDL of the SP2 at a certain laser intensity is given by the total BC mass in a particle, largely independent of coatings with non-refractory matter and the particle's morphology. However, during a recent experiment we stumbled across a counterexample to the assumption that particle morphology is unimportant for successful BC particle detection.

The primary aim of the "BC-act" campaign was comparing and characterising different BC mass and light absorption measurement techniques with different types of BC aerosols. The investigated BC particle sources include, among others, a PALAS GFG 1000 soot generator (Helsper et al., 1993), which applies spark discharge to produce

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pure BC particles. The wholly unexpected result that the SP2's incandescence detector fails to detect the vast majority of PALAS soot particles, even if their BC mass is substantially higher than the normal LDL of the SP2, is presented here. This result is put in the context of effective density measurements, thereby also discussing implications for the measurement of ambient BC particles using the SP2.

2 Methods**2.1 Experimental setup**

The experiments were performed in the framework of the campaign “BC-act” carried out at ETH Zurich in January 2012. The aim of the experiments was to physically and chemically characterise different types of laboratory-generated soot particles, and to intercompare diverse BC measurement techniques.

The experimental setup applied in this study is shown in Fig. 1. The soot aerosol obtained from different sources was diluted and fed into a vessel with a residence time of ~30 min. The sample taken from the vessel was further diluted and neutralized using two ^{210}Po bipolar chargers in series. A differential mobility analyzer (DMA; TSI model 3080L), was used to size-select the soot particles. Particle number size distributions were measured for each soot sample by operating the DMA and a condensation particle counter (CPC; TSI model 3010; labelled as CPC₁ in Fig. 1) as a scanning mobility particle sizer (SMPS). Most of the time the DMA was set to select particles of a fixed size for further experimental characterisation of soot particles with a well-defined electrical mobility diameter ($D_{\text{mob}} = 125, 200, 305$ or 500 nm).

2.2 Single particle soot photometer

The single particle soot photometer (SP2; Stephens et al., 2003) is manufactured by Droplet Measurement Technologies, Boulder USA, and uses a continuous-wave high-intensity intra-cavity laser (Nd : YAG solid state crystal at a wavelength of $\lambda = 1064$ nm)

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to detect refractory black carbon (rBC; henceforth simply referred to as BC) by LII. Key features of the SP2 are quantitative measurement of BC mass in single particles with a counting efficiency of $\sim 100\%$ above its lower detection limit. The SP2 employed in this study uses a H6779 photomultiplier tube (PMT, Hamamatsu Inc.) behind a Schott KG-5 filter to measure broadband incandescence signals and a H6779 PMT behind Schott KG-5 and RG-630 filters to measure narrowband incandescence signals. All BC measurements (counting and BC mass quantification) presented in this study are based on the broadband incandescence signal. The narrowband incandescence signal was only used to check the laser intensity as discussed in Sect. 3. The position sensitive detector (PSD) of the SP2 uses a C30927EH-01 quadrant array avalanche photodiode (Perkin-Elmer) behind a Schott RG-850 filter to determine the particle's position in the laser beam from the elastically scattered light (Gao et al., 2007).

The SP2 was prepared following the instructions given in Laborde et al. (2012b), namely assuring sufficient laser intensity, Gaussian laser beam shape (TEM₀₀ mode) and careful alignment of the particle beam to the centre of the laser beam, as further detailed in Sect. 3. Fullerene soot obtained from Alpha Aesar (lot# FS12S011), the recommended SP2 calibration standard (Moteki and Kondo, 2010; Laborde et al., 2012a; Baumgardner et al., 2012), was used to calibrate the SP2 as described in Laborde et al. (2012a).

2.3 Aerosol particle mass analyser

The mass and effective density of the size-selected soot particles was determined with an aerosol particle mass analyser (APM; Kanomax APM-II model 3601; Ehara et al., 1996), using the approach previously described in the literature (e.g. Park et al., 2003; Olfert et al., 2007; Gysel et al., 2011). Particle mass analysers select particles according to their mass-to-charge ratio by balancing the electrostatic and centrifugal forces which act on particles introduced into a thin annular space formed between rotating cylindrical electrodes. The APM voltage was scanned while holding the APM rotational speed and the DMA voltage constant in order to determine the mass of the

size-selected particles by simultaneous counting of the particle concentration at the APM outlet using a CPC (TSI model 3022; labelled as CPC₂ in Fig. 1). The mass, m , of the particles was determined from the APM voltage, V_{peak} , at which the measured number concentration is at maximum (Ehara et al., 1996):

$$m = \frac{qV_{\text{peak}}}{\omega^2 r_c^2 \ln(r_o/r_i)}, \quad (1)$$

where q is the charge of the particle, r_i and r_o are the inner and the outer radii of the cylinders, ω is the rotational speed of the cylinders (equal for the inner and outer cylinders in the APM), and $r_c = (r_i + r_o)/2$. The DMA and the APM were operated at sufficiently high resolution such that V_{peak} was not biased by the influence of doubly charged particles. The effective density, ρ_{eff} , was calculated from the mass, m , and the mobility diameter, D_{mob} , using the following equation (first variant of effective density definitions described in DeCarlo et al., 2004):

$$\rho_{\text{eff}} = \frac{6m}{\pi D_{\text{mob}}^3}. \quad (2)$$

Certified polystyrene microsphere size standards (PSL spheres; obtained from Duke Scientific Corporation, Palo Alto, USA and from BS-Partikel GmbH, Wiesbaden, Germany) were used to verify accurate operation of the DMA and the APM, resulting in an accuracy of around $\pm 10\%$ for the effective density measurements.

2.4 Soot particle generation

Spark discharge soot was produced using a commercial PALAS GFG 1000 soot generator (Helsper et al., 1993). The PALAS GFG was operated at a spark frequency of 75 Hz between the graphite electrodes, using Argon as carrier gas and without internal dilution flow. The number size distribution of the spark discharge soot, hereafter referred to as PALAS soot, peaked at a mobility diameter of ~ 130 nm.

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Flame generated soot was produced by a co-flow diffusion flame of propane and synthetic air using a combustion aerosol standard burner (CAST; model CAST-00-4; Jing Ltd). The CAST burner was operated with a rich and a lean mixture in order to obtain soot particles with different ratios of organic carbon (OC) to elemental carbon (EC¹). An equivalence ratio of $\phi = 0.85$ (carbon-to-oxygen ratio C/O=0.25) was chosen for the experiment on 25 January 2012, resulting in almost pure EC particles (Schnaiter et al., 2006), henceforth referred to as CAST “black” soot. An equivalence ratio of $\phi = 1.36$ (C/O=0.41) was chosen for the experiment on 27 January 2012, resulting in soot particles containing EC and a substantial fraction of OC (Schnaiter et al., 2006), henceforth referred to as CAST “brown” soot.

Soot particles were also produced from two commercial soot powders, which were dispersed in MilliQ water, nebulised using a Collison type atomizer and dried with a silica gel diffusion dryer.

Cabot Regal 400R powder was obtained from Cabot Corporation. Regal Black, as we name it henceforth, is composed of carbon black, a form of amorphous carbon, and it is the material currently recommended for calibration of Aerodyne Research’s soot particle aerosol mass spectrometer (SP-AMS; Onasch et al., 2012). Our sample originates from the batch (lot# GP-3901), which is centrally stored and distributed by Aerodyne Research to assure consistent SP-AMS calibration.

Fullerene soot “as produced” powder was obtained from Sigma Aldrich (lot# MKBB8240V). Fullerene soot is a form of amorphous carbon containing ~10% fullerenes and it is the material recommended for calibration of Droplet Measurement Technologies’ SP2 (Baumgardner et al., 2012).

¹The terms EC, BC and rBC are operationally defined based on the applied measurement technique (thermal-optical, light absorption and laser-induced incandescence, respectively). However, they synonymously refer to pure carbon (e.g. Kondo et al., 2011), which is the most refractory and light absorbing component of carbonaceous combustion particles.

3 Results and discussion

The counting efficiency of the SP2 for BC particles is compared against CPC₂. The APM was bypassed for this purpose (Fig. 1), such that the SP2 and the CPC measured the same size-selected sample of BC particles. The CPC counts all particles while the SP2's incandescence detector selectively counts BC-containing particles. The counting efficiency calculated from the ratio of the CPC and SP2 number concentrations is only meaningful if every particle of the investigated aerosol contains a BC core. This condition is fulfilled for the CAST soot and PALAS soot aerosols. Nebulisation of aqueous dispersions of fullerene soot and Regal Black samples produces BC-containing particles as well as very small residual particles from those droplets not containing a BC core. However, this mode of residual particles did not extend up to the mobility diameters selected here, such that every particle of the size-selected fullerene soot and Regal Black samples was expected to contain BC.

The results of the counting efficiency measurements as a function of the particle's mobility diameter are shown in Fig. 2a. The SP2 has, within experimental uncertainty, a detection efficiency of 100 % for fullerene soot, Regal Black, CAST "black" soot and CAST "brown" soot in the mobility diameter range of 125–500 nm. This is consistent with previous literature reports on the SP2's detection efficiency (Schwarz et al., 2010; Laborde et al., 2012b). However, the wholly unexpected result is a detection efficiency as low as 0–12 % by the incandescence detector for the PALAS soot at mobility diameters between 200–500 nm (particles with $D_{\text{mob}} = 125$ nm were not investigated).

Figure 2b shows the effective density of the investigated soot types as a function of the particle's mobility diameter. The effective density of all samples decreases with increasing particle size and it is clearly below the void-free material density of BC ($\sim 1800 \text{ kg m}^{-3}$; Mullins and Williams, 1987; Park et al., 2004). This indicates fractal-like or flaky particle structures. The values reported here for the fullerene soot are in the range of previous literature data (Moteki and Kondo, 2010; Gysel et al., 2011), though the fullerene soot sample investigated in this study was obtained from a different

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producer. The size-dependent effective density measured for Regal Black is identical to that previously described in the literature for the same batch (Onasch et al., 2012). This shows that the mass of size-selected Regal Black particles can reliably be calculated from their mobility diameter, at least for the batch which is distributed by Aerodyne Research as calibration standard for the SP-AMS. The effective density of the CAST “black” soot is slightly lower than that of the CAST “brown” soot, consistent with previous reports of the influence of fuel equivalence ratio (Slowik et al., 2004). The PALAS soot’s effective density is ~ 4 – 10 times lower compared to that of all other investigated samples. This gives a first hint that particle morphology might play a role regarding the SP2’s counting efficiency issue for the PALAS soot. However, counting efficiency may have dropped below unity for several other reasons, as follows.

Schwarz et al. (2010) identified sufficiently high laser intensity as a crucial factor for achieving optimal counting efficiency with the SP2. BC particles have to reach their vapourisation temperature for proper detection by the SP2. This is only achieved if the energy uptake rate from absorption of the laser light exceeds the energy loss rate across the whole temperature range passed by the particle until eventually reaching the vapourisation temperature of the BC core. Heat conduction to the surrounding air is the main energy loss term during the phase when the bare BC core approaches vapourisation, while thermal radiation gives a negligible contribution at atmospheric pressure (Kuhlmann et al., 2006). The diameter of the BC core influences the competition between absorption of the laser light and heat conduction, which are proportional to $\sim D^3$ and to $\sim D^2$ (or less), respectively (Bladh et al., 2008). Consequently the ratio of energy loss rate to energy uptake rate increases with decreasing BC mass per particle, thereby imposing the physical limitation for the LDL that can be achieved with the SP2 at a certain laser intensity. Schwarz et al. (2010) also demonstrated two methods to identify the threshold laser intensity for proper BC particle detection by the SP2. Their colour ratio method has been applied to the SP2 employed in this study, in order to ensure sufficient laser intensity for the detection of particles containing at least 1 fg BC. The fact that unit detection efficiency was achieved within uncertainty for all monodisperse

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samples of fullerene soot, Regal Black, CAST “black” soot and CAST “brown” soot, covering the range down to a total particle mass of ~ 1 fg (Fig. 3), confirms that sufficient laser intensity was available for the detection of “normal” BC particles. This holds even for singly charged particles of the smallest sample of the organic-rich CAST “brown” soot ($D_{\text{mob}} = 125$ nm), which contained on average as little as ~ 0.45 fg BC per particle (SP2 measurement) at an average particle mass of ~ 1.2 fg (APM measurement).

The width of the particle beam directed through the SP2’s laser is approximately equal to the width of the range across which the Gaussian laser beam has $\geq 70\%$ of its maximal intensity (Schwarz et al., 2010). Careful alignment of the particle beam to the centre of the laser beam is a critical factor for achieving optimal counting efficiency. Misalignment causes a drop in counting efficiency for small BC particles (Laborde et al., 2012b), as they are exposed to insufficient laser intensity when crossing the laser beam at its edges. At the beginning of the study, the SP2 was carefully aligned following the standard alignment procedures (DMT, 2007). Successful alignment is also confirmed by the fact that unit counting efficiency is achieved for the small particles of all investigated BC samples except for the PALAS soot (Fig. 3). The divergence of the particle beam could possibly be larger for the PALAS soot particles with a very low effective density than for the other BC samples with a higher effective density, thereby causing a similar effect as a misalignment. However, this hypothesis can be discarded, at least for the bigger sizes of the PALAS soot particles ($D_{\text{mob}} = 305$ and 500 nm), as they are properly counted by the SP2’s position sensitive detector (open green symbols in Fig. 2), which detects elastically scattered light. The smallest investigated PALAS soot particles fall below the lower detection limit of the position sensitive detector, such that only the multiply charged particles ($\sim 20\%$) are counted at the nominal size of $D_{\text{mob}} = 200$ nm.

The SP2 records the signals from a particle only if at least one signal crosses the trigger threshold for data storage, which is set in the data acquisition software. Failure of signal triggering or any other issue with the data acquisition software can be excluded as a reason for the incandescence channel’s low counting efficiency for the

PALAS soot. The position sensitive detector's signal triggered storage of the signals from all detectors for all PALAS soot particles with $D_{\text{mob}} = 305$ or 500 nm. However, the recorded broadband incandescence signal contained only baseline noise without appearance of a true incandescence peak for most PALAS soot particles.

The monodisperse samples of PALAS soot particles had a much lower effective density than the other BC samples (Fig. 2b), but the average mass of the singly charged particles still reached up to 2.4 fg per particle at the largest size (Fig. 3). PALAS soot particles contain mainly BC, though up to 25 % organic contamination have previously been identified (Roth et al., 2004; Schneider et al., 2006). The BC mass range covered in this study for the PALAS soot remains above the BC mass limit, below which counting efficiency normally drops for the incandescence detector, even when potential organic contamination is taken into account. The fact that the counting efficiency was as low as 5 % for the PALAS soot particles with a mass of 2.4 fg, while it was ~ 100 % for particles with similar and even clearly lower BC mass content for all other investigated soot types, reveals that BC mass per particle cannot be the only parameter determining the lower detection limit of the SP2 at a certain laser intensity.

The morphology of the particles can obviously have a considerable influence on the SP2's detection efficiency too, as already known from pulsed LII (Bladh et al., 2011). The PALAS soot particles are fractal-like agglomerates with a fractal dimension in the range of ~ 1.7 – 2.1 and with an extremely small primary particle diameter of $D_{\text{pp}} \approx 5$ – 10 nm (e.g. Helsper et al., 1993; Weingartner et al., 1997; Mikhailov et al., 2001; Wentzel et al., 2003; Schneider et al., 2006), which is consistent with very low effective density as reported above (Fig. 2b). Light absorption by fractal-like particles with fractal dimensions of ~ 2 or lower is, for small size parameters of the primary particles ($x_{\text{pp}} = \pi D_{\text{pp}} / \lambda$), approximately equal to the sum of the light absorption by the individual primary particles (Mulholland and Mountain, 1999; Schnaiter et al., 2003). Similarly, heat conduction is approximately equal to the sum of the heat conduction by the individual primary particles (Bladh et al., 2011). Consequently, for particles with a low fractal dimension and very small primary particles, the physical limit for reaching

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incandescence temperatures at a certain laser power depends, for the most part, on the primary particle size, rather than the total mass of the agglomerate.

The fullerene soot and CAST soot particles are also fractal-like agglomerates, but they had higher effective densities (Fig. 2b) and larger primary particle diameters of ~ 50 nm (Moteki et al., 2009) and ~ 15 – 30 nm (e.g. Schnaiter et al., 2006; Bladh et al., 2011), respectively. Although individual primary particles of such sizes remain below the SP2's typical LDL, the fullerene soot and CAST soot agglomerates are sufficiently compact such that their mass specific heat conduction is sufficiently reduced, compared to that of their primary particles, to bring agglomerates with a total mass of ≥ 1 fg above the SP2's incandescence threshold.

The SP2's counting efficiency issue is relevant for applications involving PALAS soot. The key question regarding atmospheric applications of the SP2 is, whether the LDL for unit counting efficiency for diesel soot and biomass burning particles is similar to that for flame generated soot and fullerene soot, which have been used in previous studies addressing counting efficiency. The mass absorption coefficient of diesel soot is a factor of ~ 2 larger than that of PALAS soot (Schnaiter et al., 2003), which can be explained by the larger primary particle size and the higher degree of ordered nanocrystalline graphitic structures of diesel soot compared to PALAS soot (Mulholland and Mountain, 1999; Wentzel et al., 2003; Schnaiter et al., 2003). The specific energy loss rate by heat conduction is expected to be smaller for diesel soot than PALAS soot, as diesel soot has substantially higher effective density (Fig. 2b; Park et al., 2003; Olfert et al., 2007), indicating a lower surface-to-volume ratio. These two factors decrease the threshold laser power for proper detection by the SP2 of diesel soot compared to PALAS soot. Effective density values of diesel soot reported in the literature (Park et al., 2003; Olfert et al., 2007) are similar to those of CAST soot (Fig. 2b). The primary particle diameter of diesel soot agglomerates is in the range of ~ 25 nm (Weingartner et al., 1997; Wentzel et al., 2003), which is also comparable to CAST soot. It can therefore be expected that the SP2 is able to detect diesel soot particles with a similar LDL as for the CAST soot.

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McMeeking et al. (2011) operated an SP2 downstream of a hygroscopicity tandem differential mobility analyzer (HTDMA; see e.g. Swietlicki et al., 2008, for details on the HTDMA technique), in order to determine the number fraction of BC-containing particles as a function of the hygroscopic growth factor (HGF) of size selected particles ($D_{\text{mob}} = 193 \text{ nm}$) in urban air at Manchester, UK. The fact that they detected BC in every particle in the less hygroscopic mode ($\text{HGF} \leq 1.2$) gives direct evidence of unit detection efficiency by the SP2 for freshly emitted diesel soot particles, which are commonly associated with the less hygroscopic mode in urban environments (this applies for a mass of $\sim 1.9 \text{ fg BC}$ per particle, assuming an effective density of $\sim 500 \text{ kg m}^{-3}$ at $D_{\text{mob}} = 193 \text{ nm}$). Nevertheless, it cannot be excluded that a minor subset of atmospheric BC particles, with a morphology at the lower end of effective density and primary particle size, can remain undetected by the SP2 despite containing more BC mass than the commonly accepted LDL of the SP2.

4 Conclusions

This study unexpectedly reveals that the SP2 is essentially unable to detect PALAS soot particles with the incandescence detector, even if they contain substantially more BC mass than the typical LDL of the SP2. This could be attributed to the morphology of the PALAS soot particles, which are fractal-like agglomerates of very small primary particles with a low fractal dimension, resulting in a very low effective density. Such loosely-packed particles behave like “the sum of individual primary particles” in the SP2’s laser. Accordingly, the PALAS soot particles remain undetected as the SP2’s laser intensity is insufficient to heat the primary particles to their vaporisation temperature because of their small size ($D_{\text{pp}} \approx 5\text{--}10 \text{ nm}$). It is not surprising that particle morphology can have an effect on the SP2’s lower detection limit, however, such a dramatic effect as reported here for PALAS soot was not expected. In conclusion, the SP2’s LDL at a certain laser power depends on total BC mass per particle for compact particles with sufficiently high effective density. By contrast, the BC mass per primary particle

determines whether fractal-like particles with low fractal dimension and very small primary particles are detectable, independent of their total BC mass. Consequently, care has to be taken when using the SP2 in applications dealing with loosely-packed particles that have very small primary particles as building blocks.

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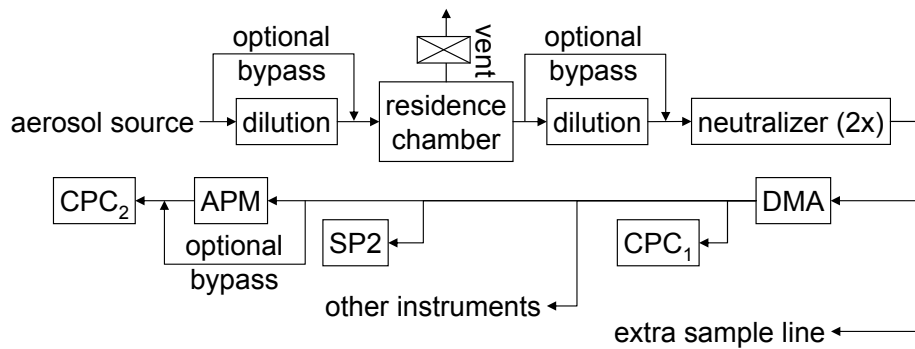


Fig. 1. Experimental setup for the measurement of effective density and SP2 counting efficiency of laboratory-generated soot particles.

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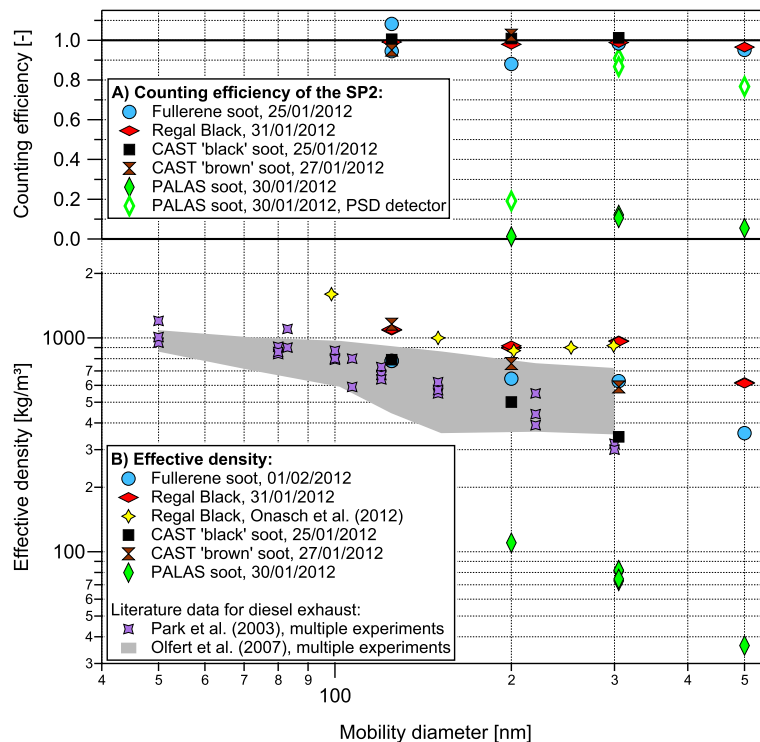


Fig. 2. Different soot samples. **(A)** Counting efficiency of SP2's incandescence detector and position sensitive detector (PALAS soot only) and **(B)** effective density as a function of the particle's mobility diameter. Literature data of Regal Black's effective density are from Onasch et al. (2012). Effective density data of diesel exhaust soot are from Park et al. (2003) and Olfert et al. (2007).

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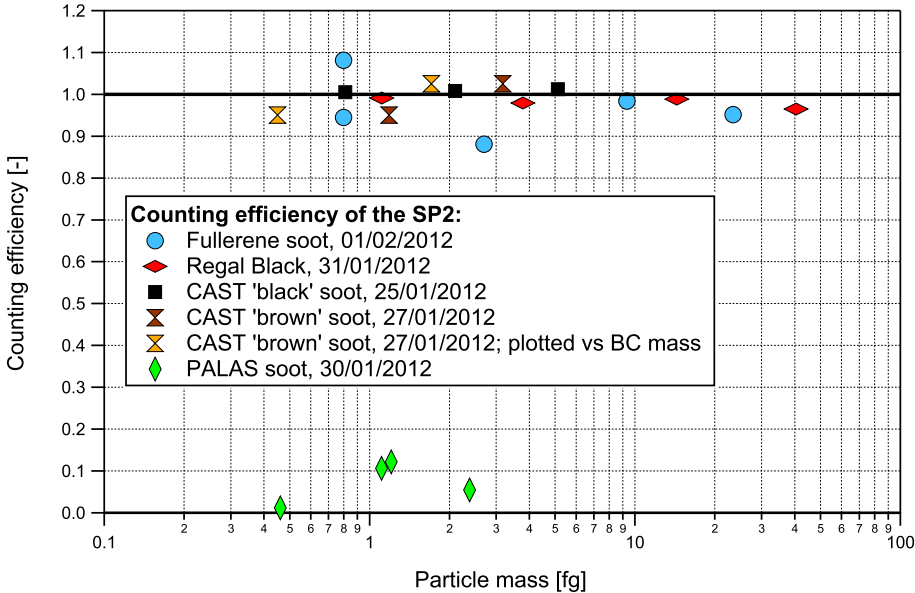


Fig. 3. SP2 counting efficiency relative to CPC for different soot samples as a function of particle mass determined by the APM. The CAST “brown” soot is additionally shown as a function of the mean BC mass per particle determined by the SP2.

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