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Calibration system with an indirect photoelectric charger for legislated vehicle number emission measurement counters in the single counting mode

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ABSTRACT

A calibration setup has been established to calibrate or validate UN-ECE Regulation 83 compliant CPCs. A spark discharge generator (GFG 1000) is used to produce carbon particles. For charge conditioning an indirect photoelectric charger is combined with an electrostatic precipitator instead of the very common radioactive bipolar charger. The particle number concentration is determined with a Faraday cup electrometer. Detailed studies have been conducted to validate the calibration setup. The particle size classification was checked by a screen-type diffusion battery. Moreover the effect of multiple charged particles was investigated. Three independent measurements of the counting efficiency as well as the linearity of a typical regulation compliant counter were performed. The calibration setup was also compared with a similar system using a radioactive bipolar charger. The obtained results demonstrate that the counting efficiency can be measured in a particle size range from 13 nm to 60 nm with a high repeatability. A linearity check at a particle size of 55 nm is possible in a concentration range of 1000–10 000 cm^3. The effect of multiple charged particles produced by the indirect photoelectric charger was found to be negligible. Additionally, the difference between a CAST aerosol and a GFG aerosol as a calibration material is discussed.

1. Introduction

The measurement of non-volatile particle number concentration emitted by light or heavy duty vehicles has received much attention in the last years due to the introduction of UN-ECE Regulations 83 and 49, respectively (Giechaskiel & Bergmann, 2011; Giechaskiel et al., 2008a, 2008b). On account of the legislation, the commercially available systems consist of a heated diluter and an evaporation tube combined with a dilution at ambient temperature for removal of the volatiles and semi-volatile components in the aerosol (Giechaskiel et al., 2010; Wei et al., 2006). The remaining non-volatile particles larger than 23 nm are counted by a condensation particle counter (CPC). Therefore the legislation dictates counting efficiencies for the CPCs at 23 nm and 41 nm of $50 \pm 12\%$ and $>90\%$, respectively. The efficiency can be determined either by comparing the counter with an electrometer or another CPC (calibrated with an electrometer). In addition, the linear response of the counter in the concentration range from 1 cm^{-3} to the upper threshold of the single particle count mode

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has to be checked. The slope has to be 1 ± 0.1. In the case of an electrometer as reference the linearity is checked above $1000\ \text{cm}^{-3}$ due to the high signal-to-noise ratio of the amplifier for very low concentrations.

Due to the fact that a decrease in counting efficiency up to 20% within 1.5 years of measuring exhaust has been observed for CPCs (Giechaskiel & Bergmann, 2011), a periodical check of the calibration is absolutely necessary. So far, the most common method to calibrate a CPC is to use a diluted test aerosol, which gets neutralized by a bipolar charger containing a radioactive source. A monodisperse aerosol is produced by a differential mobility analyzer (DMA) followed by a second diluter. As long as the fraction of multiple charged particles is low the charge number concentration of the monodisperse aerosol can be measured and the counting efficiency of a parallel connected CPC obtained (Giechaskiel et al., 2009; Wang et al., 2010; Wiedensohler et al., 1997).

However, in the legislation there is no calibration material specified, even though it is known that the counting efficiency of a CPC depends strongly on the chemical composition and morphology of the particles (Giechaskiel et al., 2011; Helsper & Niessner, 1985; Mamakos et al., 2013; Sem, 2002; Wang et al., 2010). So far it is only recommended in the legislation to use emery oil (undefined mixture of poly-α-olefins) or flame soot particles produced by a Combustion Aerosol Standard (CAST). Nevertheless the counting efficiency of emery oil seems to be significantly higher than for particles generated by the CAST within the relevant size range (23–41 nm) as shown by Wang et al. (2010) and Giechaskiel & Bergmann (2011). For diesel engine exhaust particles a difference between about 7% and 9% in the total number concentration was observed for two CPCs calibrated with emery oil and a CAST, respectively (Wang et al., 2010). Moreover, a combustion flame generated aerosol always contains an amount of volatile polycyclic aromatic hydrocarbons which are also present on the particle surface due to condensation. The composition is affected by the physical properties (vapor pressure) as well as by the chemical composition of the fuel and the mixing gases and therefore it is very difficult to guarantee a repeatable production of particles with the same composition and morphology.

Because of all these obvious problems a calibration standard is necessary which is standardized and has a repeatable composition, surface property, and morphology of the produced aerosol particles. An alternative to the CAST can be a spark discharge generator to produce a carbon aerosol. With such a generator it is possible to generate an aerosol of predictable characteristics as it contains pure carbon particles and an inert gas as the carrier gas (mostly argon) (Evans et al., 2003; Helsper et al., 1993). Furthermore a calibration system containing no radioactive source for charge conditioning would be an extreme advantage due to legislation issues.

In this study we present a calibration setup for legislation compliant CPCs, containing a spark discharge generator equipped with analytically ultrapure graphite electrodes. For charge conditioning a newly developed indirect photoelectric unipolar charger (Grob et al., 2013) is used instead of a radioactive bipolar charger. The charger allows very soft ion production without any ozone formation. This is important, as ozone would immediately produce easily wettable particle surfaces, which are prone to lower needed supersaturation within a CPC (Kotzick et al., 1997). To avoid a high fraction of multiple charged particles coming from the spark discharge generator an electrostatic precipitator is placed in front of the indirect photoelectric charger. Analogous to the described method above, the aerosol is separated by an electrostatic classifier, and a Faraday cup electrometer is used as the reference counter. The system is validated by a reference CPC (for particle concentration) and a diffusion battery (for particle size). The purpose of this study is to demonstrate that the effect of multiple charged particles produced by the unipolar charger is negligible and it is possible to calibrate a legislation compliant counter. Moreover the results are compared with measurements done with a CAST-generated aerosol.

2. Material and methods

2.1. Aerosol generator

As an aerosol generator a spark discharge generator (GFG 1000, Palas GmbH, Germany) was used. The aerosol is produced by spark discharge between two graphite electrodes with a high purity (99.9995%). The gap between the electrodes is kept constant automatically to compensate for the electrode consumption. To avoid the oxidation of carbon in the created plasma an argon (purity 99.998%) stream is focused between the gaps for shielding and is also used as the carrier gas for the particles. For all experiments the argon stream was adjusted to 3.8 l/min. Directly after the electrodes the aerosol is diluted with dried particle-free air (5.5 l/min) to avoid further coagulation of the particles. The particle concentration as well as the median of the particle size distribution can be changed by the discharge frequency (Evans et al., 2003; Helsper et al., 1993). For our setup it was varied between 7 Hz and 22 Hz. The composition and nanostructure of such produced carbon aerosol has been comprehensively studied by (Knauer et al., 2009; Schuster et al., 2011). Additionally, this procedure is a standardized aerosol generator (VDI 3491, Part 16).

2.2. Indirect photoelectric charger (IPC)

Figure 1 shows the indirect photoelectric charger (IPC) used as a unipolar charger in front of a differential mobility analyzer. A Pen-Ray low pressure mercury lamp, emitting solely at 254 nm, is applied in the focus (F_1) of an elliptical mirror. As an electron emitter a glassy carbon rod is fixed in the second focus (F_2). Glassy carbon is used on account of its photoelectron emission threshold in the range of the incident photon energy and the very inert surface with respect to degradation. This is essential to achieve a constant electron emission. The rod is covered with a quartz tube where the