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# Characterization of highly concentrated organic aerosols by optical extinction in the mid infrared regime: Application to e-cigarettes

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ABSTRACT

Highly concentrated submicron condensation aerosols are formed in electronic cigarettes. They consist primarily of the carrier substances glycerol, propylene glycol and water. The purpose of this paper is to introduce a three wavelength light extinction method in the near and mid-infrared wavelength regime enabling transient measurements of the mass concentration and the mean particle size of the mainstream, undiluted aerosol. The measuring device uses the strong absorption bands at wavelengths of 3.4 and 2.9 μm caused by the excitation of CH- and OH-vibrations of the dominating aerosol components. The absorption allows for a direct measurement of the mass concentration. Two further light attenuation signals at non-absorbing (or negligibly absorbing) wavelengths of 1.65 and 2.01 μm reveal information on the mean particle size. The data evaluation scheme is based on a set of correlations between light attenuation and size distribution parameters derived from Mie calculations using a lognormal approximation of the mass size distribution. The development of a simple sensor is facilitated due to the availability of light emitting diodes in the mid infrared wavelength range. Extinction path lengths of the order of 0.5 cm are sufficient to measure concentrations larger than several milligrams per liter, typical for the mainstream aerosol of e-cigarettes. The aerosol quantities were measured for a wide range of operating parameters of the e-cigarette. Time integrated signals were compared with results of filter (mass generation) and impactor samples (mean particle size and standard deviation). The sensor's concentration signal is directly proportional to the concentration measured gravimetrically, independent of the relative composition of the condensate in view of glycerol, propylene glycol and water. The mass median droplet diameters determined by the extinction method agree fairly well with cascade impactor measurements. The method, presented here, does not deliver information on the geometric standard deviation of the aerosol mass distribution as it is insensitive to this distribution parameter for values in the range between 1.3 and 2.0, typical for condensation aerosols.



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## 1. Introduction

Electronic cigarettes are devices generating a highly concentrated condensation aerosol composed of organic compounds. The general working principle of this type of aerosol generators is based on evaporation of a liquid by electrically heating a saturated wick. The evaporation is triggered either manually or by the puff drawn through the device. Cooling by the carrier airstream leads to vapor quenching by nucleation and heterogeneous condensation. Additional particle growth takes place by coagulation. The main components of the liquid are propylene glycol, glycerol and water. These three compounds typically make up about 95% of the fluid and, hence, the condensed aerosol. Other components in commercial fluids are nicotine and flavors

The particle size distribution is an important parameter determining the mass transfer processes of the aerosol components within the e-cigarette itself, during inhalation and exhalation. It is an important factor for providing insight into aerosol formation, airway deposition, vapor visibility, and sensory performance. The particle size distribution should differ among different devices, power levels, flow rates, puff duration and fluid composition. Adequate characterization of the aerosol requires the availability of methods for real time intra-puff resolved measurements of the particle size distribution function and the mass concentration of the undiluted aerosol.

Under typical laboratory conditions used to test e-cigarettes, the time scale of puff duration is of the order of seconds (5–8 s), puff volumes are in the range of 50–100 ml and typical quantities of vapors evaporated during a puff are 3–10 mg. This results in aerosol mass concentrations in the range of tens of milligrams per liter of air in the mainstream aerosol leaving the device. The aerosol formation process leads to droplets with diameters primarily in the submicron range as shown among others by Zhang, Sumner, and Chen (2013) and Aldermann, Song, Moldoveanu, and Cole (2014).

Measuring devices serving to characterize the main stream aerosol during a single puff should cope with the high concentration range and provide a time resolution of a few hundred milliseconds. Light extinction is a promising and simple way to achieve this. Multiple wavelength absorption techniques have been used for a long time to reveal size distribution parameters from (visible) light extinction data for highly concentrated aerosols in the industrial environment (Wittig, Feld & Tremmel, 1989) as well as for main stream cigarette smoke (Schneider, Kausch, Wittig & Feld, 1988). In a recent publication Ingebrethsen, Cole, and Aldermann (2012) presented size and concentration data of main stream cigarette and e-cigarette aerosols. They used an experimental approach based on the extinction at 4 different wavelengths in the visible and near infrared regime (550–850 nm). Here, the extinction is primarily controlled by scattering in the Mie-range. The extinction values are used to calculate the parameters of a lognormal approximation of the number distribution function. The fact that the extinction coefficient, $Q_{ext}$, is an oscillating function of the size parameter in that regime makes the inversion a difficult task. The mass concentration is determined from the number mean and the geometric standard deviation using the Hatch–Choate relationship.

In this paper we introduce an alternative approach also based on multi-wavelength extinction, using however wavelengths in the near and mid infrared regime. This technology benefits from the chemical simplicity of the condensation aerosol and makes use of the strong CH and OH absorption bands of the aerosol's main chemical components at a wavelength of 2.9, and 3.42 μm, respectively. This enables a direct measurement of the mass concentration. In the Rayleigh regime it is proportional to the absorption part of the total light extinction. Information about particle size is gained by measuring light extinction at two smaller wavelengths, namely 2.01 and 1.65 μm in the vicinity of the absorption band, where extinction results only from droplet size-dependent light scattering. The development of a simple, cost-effective sensor was possible since narrow-band light-emitting diodes (LED) with emission wavelengths in the MID-IR regime (3–10 μm) became available on the market and are used for analytical purpose (Bui & Hauser, 2015).

The theoretical foundations of this special IR-extinction technique are presented in the next chapter, followed by a detailed description of the sensor in Section 3. Section 4 contains measurement results for condensation aerosols from e-cigarettes obtained by combining the sensor with a smoking machine. Validation and limitations are discussed in the final Chapter of this paper.

## 2. Theory and underlying principle

The attenuation, $A$, of a light beam by an aerosol cloud is given by Lambert–Beer's law. For a polychromatic light source with intensity distribution $I = I_0 \cdot \eta(\lambda)$ the attenuation is related to the mass specific extinction efficiency, $E_m(\lambda)$, the aerosol mass concentration, $C_m$, and the extinction length, $L$; by

$$A = 1 - \int d\lambda \eta(\lambda) \cdot \exp[-C_m \cdot L \cdot E_m(\lambda)] \quad (1)$$

For small values of the attenuation ($A < 0.2$) Eq. (1) can be approximated by its first order Taylor term leading to

$$A = C_m \cdot L \cdot \int d\lambda \eta(\lambda) \cdot E_m(\lambda) = C_m \cdot L \cdot \overline{E}_m. \quad (2)$$

In this case the light attenuation is directly proportional to the aerosol mass concentration, the path length and the mass specific extinction efficiency weighted with the emission spectrum of the light source, $\overline{E}_m = \int d\lambda \eta(\lambda) E(\lambda)$. This average mass