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Development of a portable reference aerosol generator (PRAG) for calibration of particle mass concentration measurements

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ABSTRACT

The tapered element oscillating microbalance with filter dynamics measurement system (TEOM-FDMS) is an instrument commonly employed by the French air quality monitoring network. This instrument is currently calibrated with calibration weights traceable to SI but having value and mass differences between each of them that are not representative of real atmospheric particle mass measurements. Moreover, these calibration weights do not allow detection of any technical problems associated with either the TEOM-FDMS sampling system upstream of the mass measurement or the intrinsic TEOM-FDMS filtration system. Therefore, a calibration method was developed using a portable reference aerosol generator (PRAG) that produces known and stable particle mass concentrations over time. Here, we present the characterization of the PRAG system in terms of a reference range of particle masses between 30 ± 10 and 3456 ± 83 μg at three sampling times. Its coupling with the TEOM-FDMS and a global comparison between the defined reference range of particle masses and the measured masses obtained with each TEOM-FDMS implicated in this study are also presented.

Introduction

Atmospheric aerosols are known to have considerable impact on human health (Vedal & Dutton, 2006; Lawrence, Butler, Steinkamp, Gurjar, & Lelieveld, 2007; Forster et al., 2007), atmospheric chemistry and climate (Forster et al., 2007). Concerning human exposure in workplace and in outdoor environments, aerosol inhalation can cause adverse health effects due to their deposition in respiratory tract regions (Tranfield & Walker, 2012; ICRP, 1994). To control atmospheric particulate matter (PM) levels, European legislation (European Parliament, 2008) has established limits and target values for annual and daily mean mass concentrations of atmospheric PM_{10} and $PM_{2.5}$. To investigate PM pollution in Europe, and more specifically in France, a dedicated air quality monitoring network has been deployed under the responsibility of 26 regional air quality survey networks (AQSNs) whose management team is shared between national and local authorities, industry representatives, and public environmental associations. By the transposition of European Directives into French law, the annual mean limit values for mass concentrations of atmospheric PM_{10} and $PM_{2.5}$ have been fixed at 40 and 25 μg/m^3 since 2005 and 2015, respectively. The daily average PM_{10} concentration of 50 μg/m^3 should not be exceeded more than 35 days per year. Thus, particle mass concentrations must be measured routinely by monitoring stations in various locations. These concentrations should be measured using the European gravimetric reference method defined in the CAFE Directive and as described in European standards (EN 12341:1998, EN 14907:2006 mixed in EN 12341:2014). Particle mass concentrations are then calculated from weighing filters under controlled conditions of temperature and relative humidity (i.e., 21 ± 1 °C and $50\% \pm 10\%$, respectively), before and after the filtration sampling step (McMurry, 2000). However, gravimetric analysis is an expensive time-shifted process that involves a large number of steps. This implies difficulty in resolving short-term urban PM episodes temporally and delay in public reporting. Indeed, real-time techniques allow information retrieval with temporal resolution of around 15 min, while the temporal resolution of gravimetric analysis is longer than one day. This is the primary reason why many European member states are relying on faster techniques by proving their equivalence to the gravimetric reference method (CEN/TS 16450:2013).

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The alternative techniques are based mainly on automated instruments allowing mass concentration measurements to be realized in near real time. Instruments based on optical methods can also be used, such as photometers (Gebhart, 2001; Thomas & Gebhart, 1994), optical particle counters (Görner, Simon, Bémer, & Lidén, 2012; Binnig, Meyer, & Kasper, 2007), and aerodynamic particle sizers (Sioutas, 1999; Hairston, Dorman, Sem, & Agarwal, 1996). However, these optical methods are dependent on particle properties such as size, shape, and refractive index (Eidhammer, Montague, & Deshler, 2008), which implies downstream use of calibration factors. Only a few optical methods are properly equivalent to the gravimetric method. This is the case for one optical analyser (FIDAS 200, PALAS, Germany) for which good agreement with the gravimetric reference method was obtained for PM_{10} and $PM_{2.5}$ mass concentration measurements in specific French site typology, i.e. urban background site (PALAS UK report, 2016). Beta gauges are also used and these allow measurements with high temporal resolution by measuring β-radiation attenuation through a filter, which is proportional to the total sample mass (Gehrig, Hueglin, Schwarzenbach, Seitz, & Buchmann, 2005; Chang & Tsai, 2003; Chung et al., 2001; Chang et al., 2001). Such β-radiation instruments are becoming increasingly involved in the French AQSNs, with the majority of PM_{10} and $PM_{2.5}$ mass concentration measurements now realized using the tapered element oscillating microbalance (TEOM) automated method (Patashnick & Rupprecht, 1991), which provides time-resolved mass measurements without the need for radioactive sources implemented in beta gauges. It has been shown that TEOMs underestimate $PM_{2.5}$ mass by 6%–30% compared with the gravimetric reference method, regardless of whether the oscillating element was maintained at 50 °C (Chow et al., 2006; Schwab, Felton, Rattigan, & Demerjian, 2006; Grover et al., 2005, 2006; Hitzenberger et al., 2004) or at 30 °C (Bressi et al., 2013; Grover et al., 2005, 2006; Butler, Andrew, & Russell, 2003). Price, Bulpitt, and Meyer (2003) highlighted that particle-bound water might be the major cause of this difference, knowing that TEOM temperatures are set initially to minimize interference from water evaporation/condensation on the filter and to provide stable and reproducible measurements (Patashnick & Rupprecht, 1991). However, semi-volatile compounds such as ammonium nitrate (NH_4NO_3) or semi-volatile organic compounds, which represent a considerable proportion of urban $PM_{2.5}$ (10%–20% of the total organic gas-phase emissions, Cross et al., 2013), can also be lost by volatilization from the filter (Jaques, Ambs, Grant, & Sioutas, 2004) and therefore enhancing this underestimation. Therefore, the Rupprecht and Patashnick Co. (R&P) filter dynamic measurement system (FDMS) was developed to measure particle mass concentrations including semi-volatile compounds. The FDMS module is attached upstream of the TEOM microbalance and it is currently used in the French regional AQSNs. A field study has shown that particle masses measured by the 30 °C-TEOM without FDMS were 50% lower than the TEOM-FDMS (Grover et al., 2005). Compared with the gravimetric reference method, which is not artefact-free and which can lead to volatilization losses, the TEOM-FDMS reported between 9% and 30% higher $PM_{2.5}$ mass concentrations (Bressi et al., 2013; Schwab et al., 2006; Grover et al., 2005) at urban and rural sites.

Currently, TEOM instruments represent about 80% of the total French PM analytical equipment deployed at urban, peri-urban, traffic, industrial, and rural stations (around 375 TEOM-FDMS). To ensure both the efficient operation of these instruments and the quality of the monitoring data with a proper QA/QC practice, a European Network of National Air Quality Reference Laboratories (AQUILA) has been established. In this European Network, the Laboratoire national de métrologie et d'essais (LNE) is implicated as a member of the French National Reference Laboratory, for monitoring air quality, named LCSQA, which is identified as an expert and reference laboratory for the French AQSNs, as required by European directives. In this context, and considering that no reference standard is actually available for PM mass measurement, a French protocol has been developed for flow-rate control and calibration verification (K_0 check, microbalance linearity) of TEOM instruments using three pre-weighed filters as calibration weights. Such calibration weights are characterized by masses of around 100 mg, with a mass difference of 5–10 mg between each of them, and are then not completely representative of quarter-hour atmospheric particle mass measurements. Indeed, typical urban atmospheric particle mass concentrations are around several dozens of $\mu g/m^3$ which correspond to the μg range in terms of particle mass by taking into account a flow rate of 3 L/min during 15 min. Moreover, these calibration weights do not account for any technical problems in relation to the sampling and microbalance filtration systems.

In this paper, we present the development and validation of a traceable and reproducible portable reference aerosol generator (PRAG) for TEOM-FDMS non-volatile particle mass calibration in a lower particle mass range compared with the calibrated weights. This system was developed for ease of use in field AQSNs monitoring stations by considering the entire TEOM-FDMS sampling system in a complementary way compared with the actual protocol. In this work, we present a metrological validation of this particle mass calibration system in terms of repeatability/reproducibility using the gravimetric reference method with downstream calibration tests on TEOM-FDMS.

Material and methods

Prior to the work reported here, different generation systems were tested and characterized to develop a particle mass calibration setup for TEOM-FDMS instruments (Gaie-Levrel, Motzkus, Macé, & Vaslin-Reimann, 2015; Gaie-Levrel et al., 2015; Gaie-Levrel, Bourrous, & Macé, 2016). The following sections present the selected setup, its characterization with the gravimetric method and its coupling with the TEOM-FDMS.

The portable reference aerosol generator (PRAG) system

For mass calibration purposes, a constant output atomizer (model 3076, TSI, USA) was found the most suitable generator in terms of both stable particle generation over time (>1 h) and low filter clogging compared with dry and electrical discharge generators. Fig. 1(a) presents the aerosol generation setup (Gaie-Levrel & Macé, 2016), which is composed of a clean-air tank connected to an atomizer generator. A diffusion dryer (model 3062, TSI) is used downstream of the atomizer outlet to remove water from the particles (relative humidity of around 95% and 50% before and after drying, respectively) and a four-way valve allows coupling with the instrument (TEOM-FDMS or beta gauges). The PRAG system is therefore a combination of cited commercially available components with minor technical modifications made to reinforce its robustness for transport. Before calibration, the valve is placed in position 1 (Fig. 1(a)), which directs the generated aerosols through an exhaust and allows coupling between the instrument and a HEPA filter. For the beginning of the calibration process, the valve is turned to position 2 (Fig. 1(a)). In this configuration, the generated aerosols are sampled by the instrument. At the end of the calibration procedure, the valve is returned to position1 and the measured particle mass and particle mass concentration can be read on the TEOM-FDMS.

For this study, KCl aerosols were generated by nebulizing 0.1 and 4.0 g/L aqueous solutions of potassium chloride (KCl, AnalaR Normapur, purity 99.995%) in Milli-Q water. A previous study of this project was dedicated to setup implementation by nebulizing