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Repeatability and intermediate precision of a mass concentration calibration system

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ABSTRACT

Many aerosol instruments require calibration to make accurate measurements. A centrifugal particle mass analyzer (CPMA) and aerosol electrometer can be used to calibrate aerosol instruments that measure mass concentration. To understand the sources of uncertainty in the calibration method, two CPMA-electrometer systems were tested to measure the repeatability and intermediate precision of the system, where the repeatability is the standard deviation of several measurements using the same system over a short period of time, and the intermediate precision is the standard deviation of several measurements using different instruments with different calibrations over a long period of time. It was found that the repeatability of the CPMA and the aerosol electrometer were both 0.8%, while the intermediate precision was 1.3% and 2.2%, respectively. The intermediate precision of the aerosol electrometers determined here compares well with a broader study by national metrology institutes which determined an intermediate precision of ∼1.7%. By propagation of uncertainty, it is expected that a CPMA-electrometer system would have repeatability of 1.1% and an intermediate precision of ∼2.1%. This compares favorably to thermal-optical analysis methods which aim to measure black carbon mass concentrations for instrument calibration, which have a repeatability in the range of 8.5–20% and reproducibility in the range of 20–26% for elemental carbon. Thus, the CPMA-electrometer method may be a good alternative to existing instrument calibration procedures.

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1. Introduction

There are a wide variety of instruments that measure the mass concentration of an aerosol in real-time or semi-continuously. These instruments use a range of operating principles including, but not limited to, beta radiation attenuation (Weingartner et al. 2011), oscillating frequency shift techniques (e.g., tapered-element oscillating microbalance or quartz crystal microbalance; Weingartner et al. 2011), optical techniques based on scattering or extinction (e.g., photometers and nephelometers; Sorensen et al. 2011), optical techniques based on absorption for black carbon measurement (e.g., photoacoustic and laser induced incandescence; Arnott et al. 2003; Snelling et al. 2005), aerosol mass spectrometers (Pratt and Prather 2012) and a variety of instruments that calculate or estimate the mass of an aerosol from measurement of the size distribution and measuring or estimating the relationship between the size and mass of the particles (Weingartner et al. 2011). Many of these instruments require calibration to make accurate mass measurements.

Calibration is often accomplished by parallel measurement with a filter where the mass of aerosol collected on a filter and the gas volume sampled is measured and the filter measurements are used to calibrate the integrated response of the real-time instrument. This methodology can be problematic for the calibration of very sensitive instruments which would require very long sampling times to collect adequate mass on the filter. Gravimetric calibration may also be inaccurate as the filter may be subject to sampling artifacts such as adsorption of vapor onto the filter, volatilization of semi-volatile compounds from filtered particles, and chemical reactions which may occur between filtered particles, the gas, and filter substrate (Zhang and McMurry 1987).

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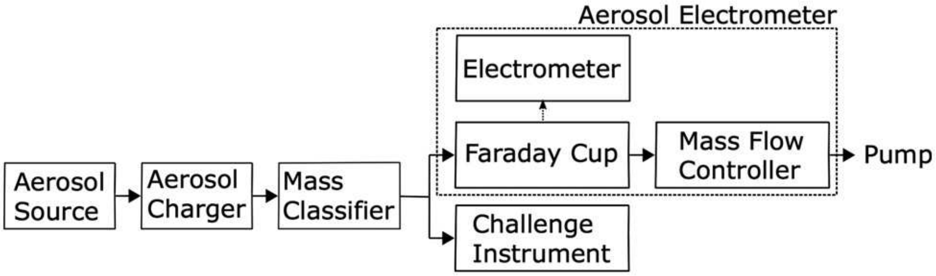

Figure 1. Schematic of calibration system using mass to charge ratio for classifying the aerosol.

Absorption- or laser-induced-incandescence based black carbon mass concentration instruments are often calibrated with thermal-optical analysis (TOA) such as the NIOSH 5040 method (NIOSH 2003). For example, the Society of Automotive Engineers (SAE) E-31 committee has recommended a variant of the NIOSH 5040 for the calibration of black carbon mass concentration instruments for future regulations of aircraft emissions (SAE ARP6320). In this method particles are collected on a quartz-fiber filter which is subsequently placed in the thermal-optical analyzer. In the analyzer the filter is heated in an oxygen-free environment, volatile particulate matter is evaporated, oxidized, passed through a methanator, and the mass of organic carbon is measured with a flame ionization detector (FID). Then the remaining particulate is heated with oxygen to oxidize the elemental carbon to carbon dioxide which is passed through a methanator and measured by the FID. It is assumed that elemental carbon determined from TOA is equivalent to black carbon in this calibration even though there is likely a material dependence on each of the measurements. This technique is preferable to simple gravimetric calibration because it is much more sensitive so a lower amount of particulate is needed on the filter. However, these black carbon instruments may have relatively low detection limits ($\sim 1\,\mu g/m^3$), at which very long sampling times are required to acquire filter samples for calibration (on the order of hours or days) where artifacts related to organics and humidity can be more pronounced than normal.

As an alternative to gravimetric or thermal-optical calibration, Symonds, Reavell, and Olfert (2013) have proposed a calibration system using a particle mass analyzer and an electrometer. The system is composed of: an aerosol source, a unipolar aerosol charger, a particle mass classifier (e.g., centrifugal particle mass analyzer [CPMA; Olfert and Collings 2005] or an aerosol particle mass analyzer [APM; Ehara, Hagwood, and Coakley 1996]) and an aerosol electrometer as shown in Figure 1. In this system the test aerosol is electrically charged in a unipolar charger (e.g., corona charger) to impart a high level of charge on the aerosol. The aerosol is then classified by mass-to-charge ratio in the particle mass classifier by balancing centrifugal and electrostatic forces through the use of an electrostatic field generated between concentric rotating cylinders through which the aerosol is passed (in the CPMA the inner cylinder rotates slightly faster than the outer cylinder to improve the penetration efficiency of the mass classifier). The aerosol exiting the particle mass classifier is then measured by the instrument to be calibrated and an aerosol electrometer, which consists of a Faraday-cup, an electrometer, and a flow controller.

The mean particle mass, m, exiting the mass classifier for a given charge state, i, is

$$m_i = \frac{ieV}{r_c^2 \omega_c^2 \ln\left(\frac{r_2}{r_1}\right)}, \tag{1}$$

where r_1 and r_2 are the radii of the classifier inner and outer cylinders, r_c is the mean radius, V is the voltage, and ω_c is the rotational speed of the gas at the mean radius (Olfert and Collings 2005).

The total mass concentration passing though the particle mass classifier is

$$M_{\text{total}} = M_0 + m_1(N_1 + 2N_2 + 3N_3 + \ldots), \tag{2}$$

where M_0 is the mass concentration of uncharged particles, m_1 is the mass set point of the mass classifier (the mass of a particle that has one charge on it), and N_i is the number concentration of particles with i charges (Symonds, Reavell, and Olfert 2013). Similarly, the current flow, I, measured by the electrometer is

$$I = Qe(N_1 + 2N_2 + 3N_3 + \ldots), \tag{3}$$

where Q is the volume flow rate through the aerosol electrometer and e is the elementary charge (1.602×10^{-19} C). Equations (2) and (3) can be combined to give:

$$M_{\text{total}} = M_0 + \frac{m_1 I}{Qe}. \tag{4}$$

The total mass through the system includes all charged particles and all uncharged particles. However, though the use of a corona charger and high speeds of the CPMA, the number of uncharged particles can be limited such that they will have a negligible effect on the measurement (Symonds, Reavell, and Olfert 2013). An electrostatic precipitator can be used to remove all charged particles and the uncharged fraction can be measured by the instrument to confirm the uncharged concentration is negligible. This calibration method has been demonstrated by comparison to gravimetric measurements (Symonds, Reavell, and Olfert 2013) and by calibration of black carbon instruments (Dickau et al. 2015).

In choosing a calibration system, it is important to consider the uncertainty in the calibration method. The instrumental bias (the difference between the arithmetic mean of a large number of test results and a reference value; Joint Committee for Guides in Metrology, JCGM 200:2012) of calibration techniques is often difficult to assess. Often the variability of a method is used to understand at least some of the uncertainty in a calibration system. This is often expressed in terms of its repeatability and reproducibility. The repeatability of a system is defined by JCGM 200:2013 and ISO 5725-3 (1994) as the standard deviation of many measurements where the same equipment and operator are used to make repeated measurements over a short time period. The reproducibility is defined as the standard deviation of many measurements with different equipment, calibrations, and operators over a long time period (JCGM 200:2013; ISO 5725-3 1994). Thus, repeatability and reproducibility describe the minimum and maximum variability expected from a particular measurement system. Intermediate precision refers to the variability of measurements when only some of the four precision conditions (time, calibration, equipment, operator) are different (JCGM 200:2013; ISO 5725-3 1994).

In previous work, the uncertainty of the CPMA-electrometer system was estimated by using the propagation of uncertainty on Equations (1) and (4) and estimating typical uncertainties in the measurement of current, flow rate, classifier voltage, rotational speed, and radii (Symonds, Reavell, and Olfert 2013). In this way, Symonds, Reavell, and Olfert (2013) found the standard uncertainty (coverage factor, $k = 1$) of the CPMA to be 1.4% and the uncertainty of the entire system to be approximately 2%.

The purpose of the work reported here was to experimentally investigate the uncertainty of the CPMA-electrometer system by determining the repeatability, intermediate precision, and where possible, the instrumental bias, of each component of two different CPMA-electrometer systems. The components of interest are the mass flow controller (MFC) that measures and controls the flow in the Faraday cup (Q in Equation (4)), the Faraday cup and electrometer that measures the current (I), and the CPMA (m_1). The intermediate precision throughout this work refers to the condition where the precision conditions of time and equipment were different; while the instruments were factory-calibrated at different times, they were not re-calibrated between tests, and the operator was the same in all tests. The repeatability, intermediate precision, and instrumental bias of the flow controllers and electrometers where determined by calibration with standard techniques. The instrumental bias of the aerosol electrometer and CPMA could not be determined as such techniques do not yet exist, however, the repeatability and intermediate precision were determined by comparing the measurements between the two devices. The repeatability and intermediate precision of the CPMA-electrometer system is compared to calibration using thermal-optical analysis which is of particular interest in the aviation industry.

2. Experimental setup

Each component of the two CPMA-electrometer systems (designated as System 1 and System 2) was tested to determine the repeatability and intermediate precision. Also, for the MFCs and the electrometers, measurements were made against a known standard to determine the instrumental bias of those components. The following sections describe the experimental procedure to test each component.

2.1. Mass flow controllers

Mass flow controller 1 (GFC37, Aalborg, Orangeburg, NY) and MFC 2 (MC-5SLPM-D, Alicat, Tucson, AZ, USA) were tested by measuring the controlled flow with a bubble flow meter (Gilibrator-2, Sensidyne) which was considered to be a transfer standard. The mass flow rate is calculated by also measuring the temperature and pressure of air entering the bubble flow meter. The mass flow controllers were calibrated on the first day of testing with the bubble flow meter and then tested each day for at least 5 days. The flow meters were only tested at a set point of 4.0 standard L/min (SLPM; referenced to 0 °C and 1 atm) as this is the typical flow rate through the Faraday cup when the CPMA-electrometer system is used for calibration.

2.2. Electrometers

The instrumental bias of electrometer 1 (6514, Keithley, Solon, OH, USA) and electrometer 2 (6517B,

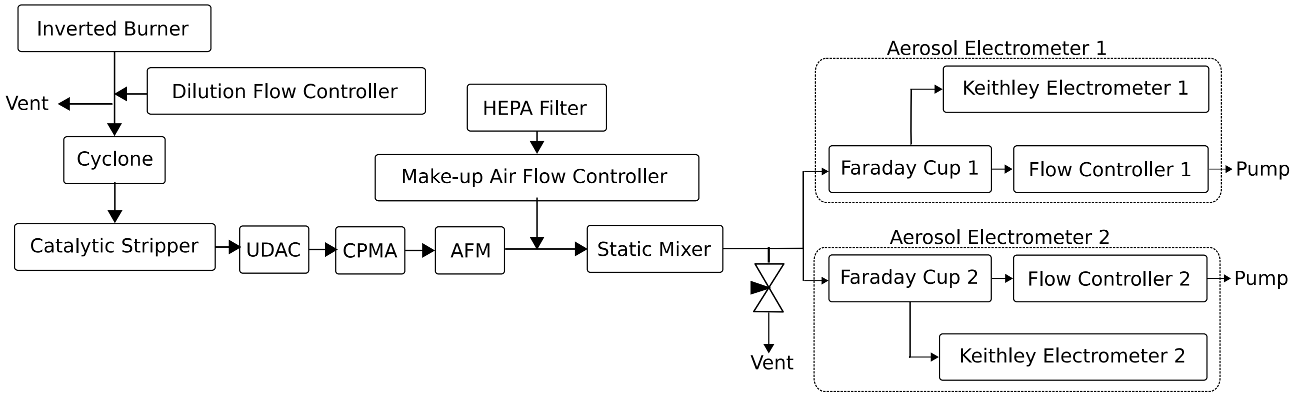

Figure 2. Schematic for aerosol electrometer testing.

Keithley) was found by calibrating each of the two devices with a reference standard at the National Research Council Canada metrology laboratory. This was achieved by applying a known voltage, from a high accuracy voltage source, across a known resistor, and measuring the current that is produced. For the calibration the voltage was varied from 0 to 0.20 V (instrumental bias less than 0.01%); the resistor used was a 10 GΩ resistor (instrumental bias less than 0.01%) resulting in a traceable current range from 0 to 20 pA.

2.3. Aerosol electrometers

A Faraday cup is a device which captures particles; where the charge induced by the charged particles is measured with an electrometer. The combination of the Faraday-cup, electrometer, and flow controller is often called an aerosol electrometer. Particle capture inefficiencies or leakage current caused by the Faraday cup may result in erroneous currents measured by the electrometer. A method to determine the instrumental bias of the Faraday cup by measuring an accepted standard is not known. The repeatability and intermediate precision of the two aerosol electrometer systems were determined by comparing the simultaneous measurement of a stable charged particle source.

Figure 2 displays the testing schematic that was used for the aerosol electrometer comparison. An inverted burner (Stipe et al. 2005) was used to generate a stable source of soot particles. The burner had a methane fuel flow rate of 1.4 SLPM, combustion air at 16.6 SLPM, and dilution air at a flow rate of 200 SLPM. The burner was provided ample time (>1 h) to warm up and provide a stable particle distribution. A cyclone (BGI, NJ, USA) and catalytic stripper (Catalytic Instruments, Rosenheim, Germany) were used to remove large particles (cutoff of 1 µm) and ensure volatile material was removed. The soot was then passed through a unipolar diffusion aerosol charger (UDAC; Cambustion, Cambridge, UK). Upon charging, the flow traveled through a CPMA (Cambustion, Cambridge, UK). The CPMA was used to classify the particle distribution with a mass to charge ratio of 0.25 fg per charge and a normalized full-width half maximum resolution of ~0.2 (or inverse resolution of 5). Additional, particle-free make-up air was added downstream of the CPMA to provide sufficient flow for the aerosol electrometers. A static mixer (3/8-40-3-12-2, Koflo, Cary, IL, USA) was used to ensure the aerosol was well mixed before the flow was split between the two Faraday cups. The Faraday cups were identical and were a custom design consisting of a high-efficiency particulate air (HEPA) filter which was shielded in an aluminum enclosure. The Faraday cup was isolated with custom-machined ultra-pure PTFE seals. Electrometers 1 and 2 measured the current from Faraday cup 1 and 2; respectively. The flow through each Faraday cup was 4.0 SLPM. The concentration of particles (and thus, the current measured by the electrometers) was varied by adjusting the amount of make-up air after the CPMA giving a range of currents from ~0.7 up to ~9 pA. A vent and a control valve were used downstream of the static mixer to vent excess flow to maintain 4.0 SLPM flowing through the CPMA as measured by an aerosol flow meter (AFM, Cambustion, Cambridge, UK). The current measured by each electrometer was recorded simultaneously with an averaging time of 1 s for more than 3 min at each measurement point. The data was collected over four days to determine the repeatability and intermediate precision.

The bias of the flow split between the two electrometers (i.e., concentration biases due to poor mixing or different particle losses in the lines to each electrometer) was evaluated by following the methodology of Annex G in ISO 27891. It was found that the bias

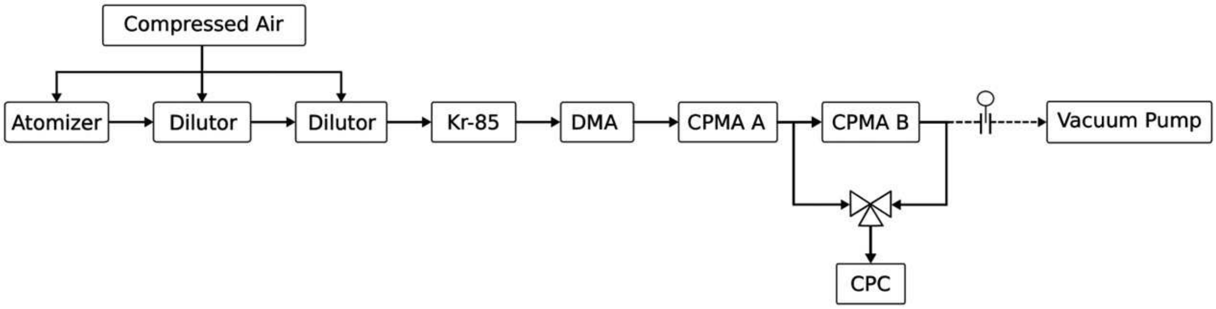

Figure 3. Schematic of tandem CPMA experiment.

correction factor was 1.000 ± 0.001, thus no correction was applied to the data.

2.4. Centrifugal particle mass analyzer

A tandem CPMA-CPMA setup was used to determine the repeatability and intermediate precision of the CPMA as seen in Figure 3. Particles were generated using an atomizer (Model 3076, TSI Inc., Shoreview, MN, USA) with an ∼1% (vol.) solution of bis (2-ethylhexyl) sebacate (DOS) in ethanol. The aerosol was then diluted by a factor of approximately 64 using two ejector diluters (DI-1000, Dekati Ltd, Kangasala, Finland), in series to evaporate the ethanol. This solution was selected as it generates spherical particles with a known density (910 kg/m^3) so no assumptions were needed on the effect of morphology on the transfer function of the CPMA.

A potentially complicating factor in a tandem CPMA experiment is that uncharged particles may pass through the classifier when the rotational speed of the CPMA is low and the centrifugal force on small particles is very low. To prevent these particles from entering the CPMA, a Kr-85 neutralizer (TSI, Model 3077A) and a DMA (TSI, Model 3080) were used upstream of the tandem CPMAs to charge particles and eliminate any uncharged particles. The particle size distribution entering the first CPMA, which will be referred to as CPMA A, should be broad, thus the resolution of the DMA was set to allow a broad range of particles through. The aerosol flow rate through the DMA and tandem CPMA system was 0.3 LPM, 1.5 LPM, or 4 LPM depending on the test point. The DMA sheath flow was set to 1 LPM, 2 LPM, and 5 LPM, respectively for the previously stated aerosol flows resulting in a broad distribution entering CPMA A. For measurements taken at 0.3 LPM and 1.5 LPM the aerosol flow rate through the CPMAs was regulated using the internal flow control of the CPC (Model 3776, TSI). For measurements at 4 LPM the CPC was set to a flow rate of 1.5 LPM and a vacuum pump with a critical orifice was used to regulate a makeup flow of 2.5 LPM, thus generating a net flow of 4 LPM through the tandem CPMAs.

Once the particles were classified by the DMA, the aerosol enters CPMA A which was set at a constant mass set point of 0.01 fg, 0.1 fg, 1 fg, 10 fg, or 100 fg (assuming the particles are singly charged). The DMA set point was chosen to select the equivalent diameter for each mass set point (27 nm, 60 nm, 128 nm, 275 nm, 593 nm) to maximize the number of particles entering CPMA B. CPC measurements were then taken downstream of CPMA A to determine the steady state particle concentration leaving CPMA A (N_1). The CPC was then connected downstream of CPMA B, and CPMA B was stepped through a range of mass set points and the CPC measured the particle concentration exiting CPMA B (N_2). CPMA B was stepped through the range six times and on different days to determine the repeatability and intermediate precision.

The CPMAs were tested at each particle mass (0.01–100 fg) and each flow rate (0.3–4 LPM), at a normalized full-width half-maximum resolution of 0.33, 0.2, or 0.1, if the operating condition was within the operating window of the CPMA (i.e., some operating conditions could not be tested because they would exceed the maximum or minimum voltage or rotational speed of the CPMA). Some set points at high rotational speeds (e.g., 0.01 fg) were not tested though they were within the operating window of the CPMA as the temperature of the CPMA would rise excessively (>60 °C), potentially causing some evaporation of the DOS particles. In some experiments at 0.01 fg the mass measured by CPMA B was substantially lower than the mass set point of CPMA A, indicating that particle evaporation was occurring. Thus, limiting the temperature of the CPMA (by starting the test when the CPMA was cool) reduced the likelihood of the aerosol from partially evaporating and changing mass.

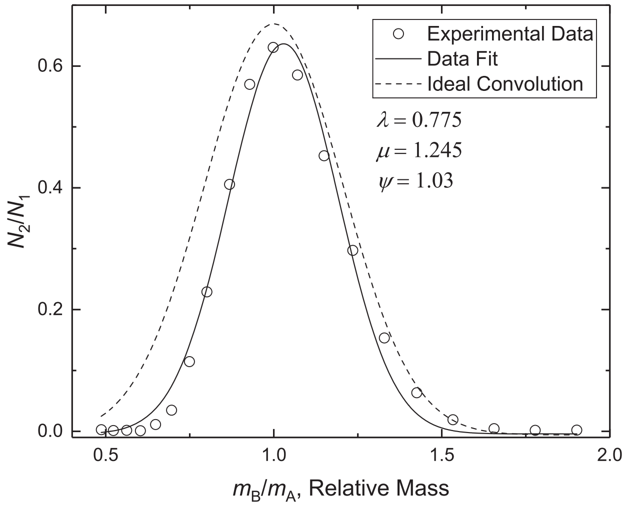

Figure 4. Example data set and fitting output. Set point of 10 fg with a resolution of 0.33 and flow rate of 1.5 LPM. The solid line represents the convolution with the optimized fitting parameters accounting for non-idealities of the CPMA transfer functions. The dashed line represents the ideal theoretical convolution (i.e., $\lambda = \mu = \psi = 1$).

The relative difference between the mass classification of the two CPMAs was determined by following a methodology similar to Johnson et al. (2018) which is based on the methodology of Martinsson, Karlsson, and Frank (2001). Briefly, in this method, the relative concentration was calculated at each CPMA B set point (N_2/N_1) and plotted (Figure 4). Then a Matlab script was used to calculate the theoretical normalized concentration by convolving the triangular transfer functions of the two devices given the operating conditions of both CPMAs. Three parameters were introduced to represent the non-idealities of the CPMA transfer functions. These include: (i) the area parameter (λ) which accounts for the penetration efficiency of the classifiers, (ii) the width parameter (μ) which accounts for the broadening of the transfer function, and (iii) the offset parameter (ψ) which is the ratio of the peak mass of the transfer function of CPMA B to the peak mass of the transfer function of the CPMA A. It was assumed that the width parameter (μ) was identical between the two CPMAs. The offset parameter, ψ, is the parameter of interest for this work as it indicates the difference in the mass classification between the two CPMAs. The three parameters were adjusted using χ^2 minimization until they provided a good fit with the experimental data. An example is shown in Figure 4 which shows the experimental data, the convolution with the fitting parameters optimized to the experimental data accounting for non-idealities of the CPMA transfer functions (solid line), and the ideal theoretical convolution ($\lambda = \mu = \psi = 1$; dashed line). In this example, CPMA A was set to 10 fg and the fit of the data reveals that $\psi = 1.03$, which means CPMA B measured a peak mass of 10.3 fg. As expected, the area parameter (λ) was less that one meaning that there are particle losses, such as diffusion and impaction in the classifier inlet and outlet, which were not accounted for in the ideal transfer function. Also, the width parameter (μ) was greater than one meaning the classification was narrower (i.e., higher resolution) than expected, which may have been due to flow irregularities.

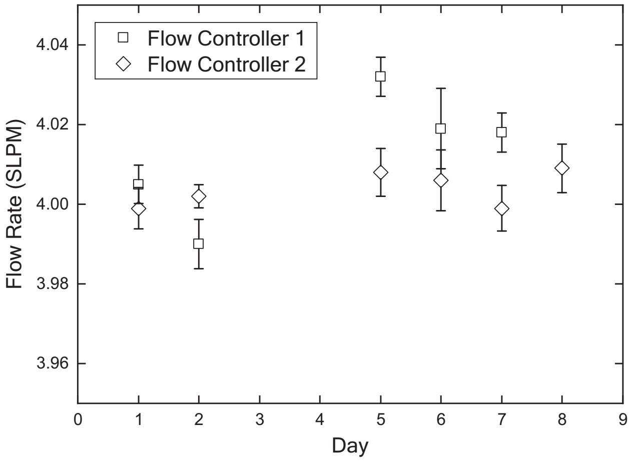

Figure 5. Repeatability, intermediate precision, and instrumental bias measurements for two flow controllers. Error bars represent the standard deviation (repeatability) for each test. Each daily average consists of 10 individual measurements.

Experiments were conducted when CPMA 1 (serial number C313) and CPMA 2 (serial number C220) were each in the CPMA A (upstream) and CPMA B (downstream) positions.

3. Experimental results and discussion

3.1. Flow controllers

The repeatability, intermediate precision, and instrumental bias results for the flow controllers over a period of 8 days is shown in Figure 5. The set point for each device was set to 4.0 SLPM each day and the flow was measured 10 times with the bubble flow meter. The repeatability is defined as the standard deviation of the measurements for one day and is indicated with the error bars in the figure. The repeatability for both systems for all measurements is expressed as the mean of the individual repeatabilities (ISO 5725-2) and is 0.0058 SLPM (0.15%). The intermediate precision of the flow controllers is the standard deviation of all measurements from both flow controllers, which was 0.012 SLPM (0.3%). The instrumental bias of each flow controller is the difference

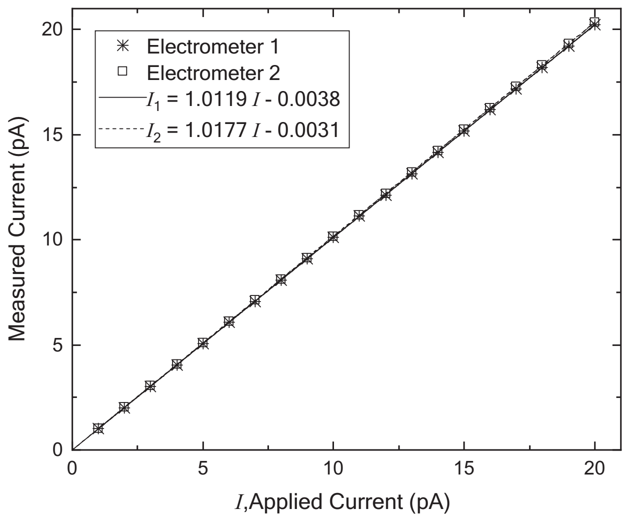

Figure 6. Calibration of electrometers against a reference method.

between the accepted value (4.000 SLPM) and the mean of all the readings of each flow controller, which is found to be 0.013 SLPM (0.3%) and 0.004 SLPM (0.1%) for flow controller 1 and 2, respectively. These are all relatively small values, making the flow controllers a relatively small source of uncertainty in the CPMA-electrometer calibration method.

3.2. Electrometers

The electrometers (without Faraday cups) were calibrated against a reference standard to determine the instrumental bias of each electrometer and also to understand the relative bias between the electrometers. Figure 6 shows the calibration curve of both electrometers. From this data the instrumental bias of electrometer 1 and electrometer 2 are 1.2% and 1.8%, respectively. The repeatability of the electrometers is 0.08%. The intermediate precision was 0.3%; however, the electrometers were only calibrated on one day so this intermediate precision does not include the effects related to time-different behavior of the devices.

3.3. Aerosol electrometers

The two aerosol electrometer systems were compared to each other to assess the performance of the Faraday cups since there is no known method to determine the efficiency of Faraday cups individually. Thus, the aerosol electrometers were tested simultaneously, in parallel, to determine the repeatability and intermediate precision of the systems.

The repeatability of one of the systems was measured daily by measuring seven current levels between ~0.7 and 9 pA. Over the four days of testing the repeatability was found to be 0.8%. Note that the repeatability of the aerosol electrometer will be a function of the repeatability of the flow controller, electrometer, the stability of the particle source, and the time-dependent behavior of the efficiency of the Faraday cup. As the repeatability of the flow controllers and electrometers is relatively low (<0.3% and <0.08%, respectively), the dominant source of the repeatability would be the stability of the particle source or the time-dependent behavior of the efficiency of the Faraday cup.

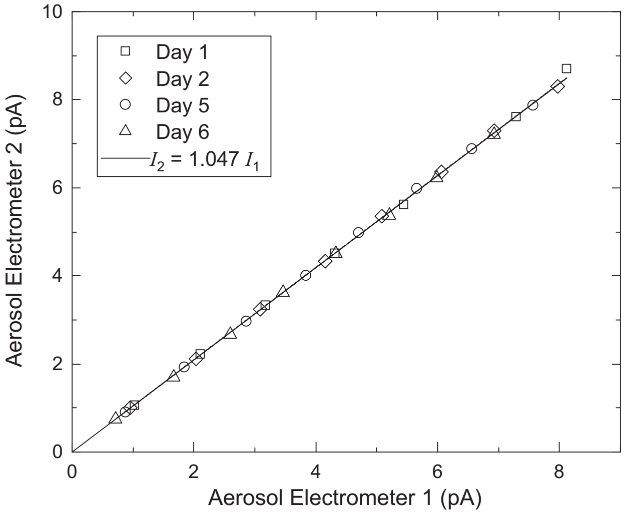

Figure 7. Comparison of aerosol electrometer measurements over several days of measurements.

The intermediate precision is found by comparing the simultaneous measurements of the two systems. Figure 7 displays a plot of the current readings made by the aerosol electrometers over four days of testing. The fit of the data shown in Figure 7 shows that aerosol electrometer 2 reads higher by 4.7% on average. The bias between the aerosol electrometers is also quantified by the intermediate precision and the intermediate precision of the systems (over all days) is found by calculating the standard deviation of the normalized difference between simultaneous measurements with respect to the mean value of the simultaneous measurements. This calculation shows the intermediate precision of the aerosol electrometers is 2.2%. In this case the stability of the particle source is expected to have a relatively small effect on the intermediate precision since the aerosol electrometers measure the same particle source simultaneously. Furthermore, the intermediate precision of the flow controllers and electrometers is relatively low (0.3% in each case), which suggests the largest source of the precision uncertainty in the aerosol electrometer is the difference in the efficiencies of the two Faraday cups.

Aerosol electrometers are also widely used in the calibration of condensation particle counters and their use is defined in ISO 27891:2015. As part of the development of the ISO standard, a large group of national metrology institutes and expert labs intercompared seven aerosol electrometers (five TSI 3060B, one GRIMM 5.705, and one self-made) over a range of particle sizes (20–200 nm) and concentrations (0–17,000 cm^{-3} corresponding to currents about 0–45 fA) as described by Högström et al. (2014). The study did not assess the intermediate precision of the flow controllers or electrometers, but only the aerosol electrometers as a whole. It was found that the agreement between all aerosol electrometers was very good except for one TSI 3060B whose measurements were very different at low concentrations (up to 40% lower than the mean reading at currents <10 fA). Neglecting this one aerosol electrometer, the intermediate precision of the remaining aerosol electrometers was 1.7% (in this case, the measurements were time-, equipment-, and operator-different, but not calibration-different). The precision uncertainty determined by Högström et al. (2014) is slightly lower than the one determined in our study (2.2%). As the Högström et al. (2014) study involves a greater number of aerosol electrometers and aerosol properties (size and concentration), it would be a better representation of the intermediate precision of these devices. Furthermore, a few national metrology institutes have stated their calibration capabilities of aerosol electrometers have a relative expanded uncertainty ($k = 2$, 95%) of 2% (Bureau International des Poids & Mesures 2019).

Also note that the current measured using a CPMA-electrometer calibration system tends to be much higher than aerosol electrometer measurements in CPC calibration (on the order of pA rather than fA), so one might expect the aerosol electrometer measurements to have improved intermediate precision at higher currents.

3.4. Centrifugal particle mass analyzer

Figure 8 displays the results of the difference between the two CPMA set points (offset parameter, ψ). Each data point for a device is calculated when the respective CPMA was in position B as identified in Figure 3. Although CPMA flow rate and resolution were also examined, it was found that there was no systematic difference in those results, so the results are shown as a function of the mass set point of CPMA A and the data points represent the mean of the measurements at all flow rates and resolutions. Ideal CPMA performance would occur when $\psi = 1$ (i.e., the set points of the CPMAs are identical). As each CPMA is tested in each position, it is expected that the data should be symmetric around a value of 1 (i.e., when the CPMA positions are switched it is expected that the magnitude of the offset to be the same but in the opposite direction). For particle masses greater than or equal to 1 fg, CPMA 1 has mass offset that is slightly larger than 1 while CPMA 2 gives an offset that is slightly less than 1, and they are approximately symmetric about 1, as expected.

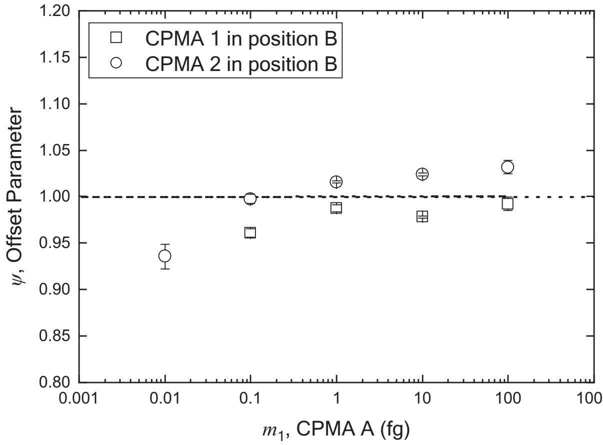

Figure 8. Mass offset measurement for the transfer function of the two CPMA's. Measurements were made with each respective CPMA in position B as identified by Figure 3. The error bars on the plots represents the uncertainty in the mean of the measurements with 95% confidence.

For the set points of 0.1 fg and 0.01 fg, the offset of the CPMAs is below 1. This is likely caused by particle evaporation occurring within the second CPMA as the particle mass will decrease as it travels though the CPMA in position A and then the CPMA in position B. A decreasing mass through the system is represented by a decrease in the offset parameter. This might be expected as the smaller mass set points have higher rotational speeds and thus the devices operate at higher temperatures (up to 60 °C) making it possible that for the lower set points the DOS may have begun to evaporate and thus reduce the mass of the particles.

Figure 9 displays the repeatability of both CPMAs when they were in position B. From this figure it can be found that all of the data except for 3 points out of 47 fall below 2%. The repeatability for both systems for all measurements is expressed as the mean of the individual repeatabilities (ISO 5725-2) and is 0.8%.

The intermediate precision of the CPMAs (over all days, mass set points, flow rates, and resolutions) is found by calculating the standard deviation of the normalized difference between simultaneous

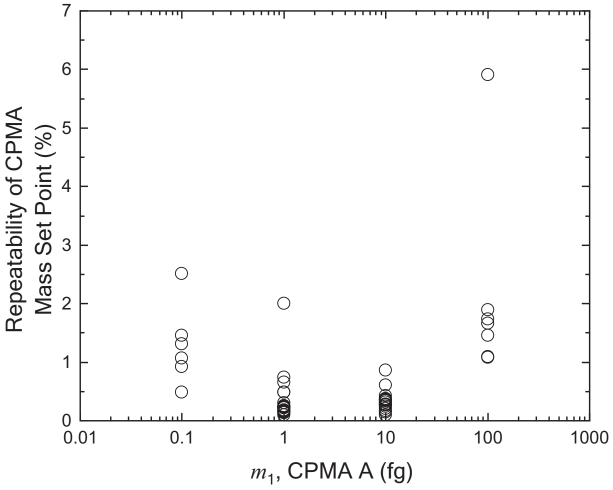

Figure 9. Repeatability of the CPMAs while in position B in the tandem CPMA-CPMA experiment. Each point represents the repeatability (standard deviation) of six consecutive measurements.

Table 1. Summary of instrumental bias, repeatability, and intermediate precision of elements in the mass calibration system.

Element	Instrumental bias	Repeatability	Intermediate precision
Flow controller	0.3%	0.15%	0.3%
Electrometer	1.7%	0.08%	0.3%
Aerosol electrometer	–	0.8%	2.2%
CPMA	–	0.8%	1.3%

measurements with respect to the mean value of the simultaneous measurements. This results in an intermediate precision of 1.3%.

4. Conclusions

A summary of the instrumental bias (where applicable), repeatability, and intermediate precision of the elements of the CPMA-electrometer calibration system is shown in Table 1. In general, the repeatability and intermediate precision of each element is quite low. The aerosol electrometer is composed of a Faraday cup, electrometer, and flow controller, and thus it is expected that the intermediate precision of the aerosol electrometer is higher than both the flow controller and electrometer. This also suggests that the largest source of the intermediate precision is the difference in the efficiencies of the two Faraday cups.

The intermediate precision of the CPMA was 1.3% including all data between 0.01 to 100 fg. For very high CPMA rotational speeds, it appeared that particle evaporation caused the mass indicated by two CPMAs to differ. It is recommended that either a nonvolatile particle sources is used in calibration or a cooling jacket is placed around the cylinders of the CPMA to maintain aerosol temperature as is currently being used on the aerodynamic aerosol classifier (Tavakoli, Symonds, and Olfert 2014) which is produced by the same manufacturer (Cambustion Ltd).

The repeatability and intermediate precision of the entire CPMA-electrometer system cannot be determined experimentally unless there is an instrument with a repeatability much less than the CPMA-electrometer system. However, the repeatability and intermediate precision can be estimated by using the principles of the propagation of error on Equation (4). Assuming that the repeatability and intermediate precision of the flow controller and electrometer are included in the repeatability and intermediate precision of the aerosol electrometer, then the estimated repeatability and intermediate precision of the entire CPMA-electrometer system is 1.1% and 2.6%; respectively. If the intermediate precision of aerosol electrometers is assumed to be 1.7% as determined by Högström et al. (2014), then the intermediate precision of the CPMA-electrometer system would be 2.1%.

The uncertainty analysis by Symonds, Reavell, and Olfert (2013) found the standard uncertainty (coverage factor, $k = 1$) of the CPMA to be 1.4% which only included estimates in the uncertainties in the voltage, rotational speed, and radii of the cylinders. Symonds, Reavell, and Olfert (2013) estimated that the standard uncertainty in the aerosol electrometer to be 1.5% resulting in a combined uncertainty of approximately 2% for the CPMA-electrometer system. The intermediate precisions measured here are very close to these values; however, as the intermediate precisions do not account for any biases between the measurements and the true value, the total uncertainty in the CPMA-electrometer will be higher than the estimate of Symonds et al.

Although the CPMA-electrometer calibration system could be used to calibrate any aerosol mass concentration instrument with a range of particle materials, it is initially being considered as an alternative to the thermal-optical analysis method in the calibration of black carbon mass concentration instruments. NIOSH 5040 (2003) states the method has a repeatability of 8.5% at 23 $\mu g/m^3$, which is much higher than the expected repeatability of the CPMA-electrometer system (1.1%). A more comprehensive study of two different TOA protocols by 17 European labs (Panteliadis et al. 2015) reported repeatability and reproducibility of 9% and 12% for NIOSH 870 and 11% and 15% for the EUSAAR2 protocol (Cavalli et al. 2010) for total carbon. While for elemental carbon, they reported repeatability and reproducibility of 20% and 26% for NIOSH 870 and 15% and 20% for EUSAAR2 protocol. The reproducibility of the CPMA-electrometer system was not determined in our study because all experiments were performed by the same operator, however, as the intermediate precision of the CPMA-electrometer system is 2.1%, it is likely that the reproducibility would be much less than the thermal-optical method.

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References

Arnott, W. P., H. Moosmüller, P. J. Sheridan, J. A. Ogren, R. Raspet, W. V. Slaton, J. L. Hand, S. M. Kreidenweis, and J. L. Collett. 2003. Photoacoustic and filter-based ambient aerosol light absorption measurements: Instrument comparisons and the role of relative humidity. *J. Geophys. Res.* D1:4034. doi:10.1029/2002JD002165.

Bureau International des Poids & Mesures. 2019. Calibration and measurement capabilities. Accessed January 24, 2019. https://www.bipm.org/exalead_kcdb/exa_kcdb.jsp?_p=AppC&_q=charge+concentration&x=95&y=11.

Cavalli, F., M. Viana, K. E. Yttri, J. Genberg, and J.-P. Putaud. 2010. Toward a standardised thermal-optical protocol for measuring atmospheric organic and elemental carbon: the EUSAAR protocol. *Atmos. Meas. Tech.* 3 (1):79–89. doi:10.5194/amt-3-79-2010.

Dickau, M., T. J. Johnson, K. Thomson, G. Smallwood, and J. S. Olfert. 2015. Demonstration of the CPMA-electrometer system for calibrating black carbon particulate mass instruments. *Aerosol Sci. Technol.* 49 (3):152–158. doi:10.1080/02786826.2015.1010033.

Ehara, K., C. Hagwood, and K. J. Coakley. 1996. Novel method to classify aerosol particles according to their mass-to-charge ratio: Aerosol particle mass analyzer. *J. Aerosol Sci.* 27 (2):217–234. doi:10.1016/0021-8502(95)00562-5.

Högström, R., P. Quincey, D. Sarantaridis, F. Lüönd, A. Nowak, F. Riccobono, T. Tuch, H. Sakurai, M. Owen, M. Heinonen, et al. 2014. First comprehensive inter-comparison of aerosol electrometers for particle sizes up to 200 nm and concentration range 1000 cm^{-3} to 17,000 cm^{3}. *Metrologia* 51 (3):293–303. doi:10.1088/0026-1394/51/3/293.

ISO. 1994a. *Accuracy (trueness and precision) of measurement methods and results—Part 1: General principles and definitions*; ISO 5725-1. Geneva, Switzerland: ISO.

ISO. 1994b. *Accuracy (trueness and precision) of measurement methods and results—Part 3: Intermediate measures of the precision of a standard measurement method*; ISO 5725-3; Geneva, Switzerland: ISO.

ISO. 2015. *Aerosol particle number concentration—Calibration of condensation particle counters*; ISO 27891; Geneva, Switzerland: ISO.

Joint Committee for Guides in Metrology. 2012. International vocabulary of metrology—*Basic* and general concepts and associated terms; JCGM 200:2012.

Johnson, T. J., M. Irwin, J. P. R. Symonds, J. S. Olfert, and A. M. Boies. 2018. Measuring aerosol size distributions with the aerodynamic aerosol classifier. *Aerosol Sci. Technol.* 52 (6):655–665. doi:10.1080/02786826.2018.1440063.

Martinsson, B. G., M. N. A. Karlsson, and G. Frank. 2001. Methodology to estimate the transfer function of individual differential mobility analyzers. *Aerosol Sci. Technol.* 35 (4):815–823. doi:10.1080/027868201753227361.

NIOSH. 2003. US Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health. Diesel particulate matter (as elemental carbon). Method 5040. Issue 2. *NIOSH manual of analytical methods*. 4th ed. Cincinnati, OH: NIOSH.

Olfert, J. S., and N. Collings. 2005. New method for particle mass classification—The Couette centrifugal particle mass analyzer. *J. Aerosol Sci.* 36 (11):1338–1352. doi:10.1016/j.jaerosci.2005.03.006.

Panteliadis, P., T. Hafkenscheid, B. Cary, E. Diapouli, A. Fischer, O. Favez, P. Quincey, M. Viana, R. Hitzenberger, R. Vecchi, et al. 2015. ECOC comparison exercise with identical thermal protocols after temperature offset correction—Instrument diagnostics by in-depth evaluation of operational parameters. *Atmos. Meas. Tech.* 8 (2): 779–792. doi:10.5194/amt-8-779-2015.

Pratt, K., and K. Prather. 2012. Mass spectrometry of atmospheric aerosols-Recent developments and applications. Part II: On-line mass spectrometry techniques. *Mass Spectrom. Rev.* 31 (1):17–48. doi:10.1002/mas.20330.

SAE. 2018. *Procedure for the continuous sampling and measurement of non-volatile particle emissions from aircraft turbine engines*; Aerospace Recommended Practice ARP6320. Warrendale, PA: Society of Automotive Engineers.

Snelling, D. R., G. J. Smallwood, F. Liu, O. L. Gulder, and W. D. Bachalo. 2005. A calibration-independent laser-induced incandescence technique for soot measurement by detecting absolute light intensity. *Appl. Opt.* 44 (31): 6773–6785. doi:10.1364/AO.44.006773.

Sorensen, C. M., J. Gebhart, T. J. O'Hern, and D. J. Rader. 2011. Optical measurement techniques: Fundamentals and applications. In *Aerosol measurement: Principles, techniques, and applications*, eds. P. Kulkarni, P. A. Baron, and K. Willeke, 269–313. 3rd ed. Hoboken, NJ: Wiley.

Stipe, C., B. Higgins, D. Lucasa, C. Koshland, and R. Sawyer. 2005. Inverted co-flow diffusion flame for producing soot. *Rev. Sci. Instrum.* 76 (2):023908. doi:10.1063/1.1851492.

Symonds, J. P. R., K. St. J. Reavell, and J. S. Olfert. 2013. The CPMA-electrometer system—A suspended particle mass concentration standard. *Aerosol Sci. Technol.* 47(8): i–iv. doi:10.1080/02786826.2013.801547.

Tavakoli, F., J. P. R. Symonds, and J. S. Olfert. 2014. Generation of a monodisperse size-classified aerosol independent of particle charge. *Aerosol Sci. Technol.* 48(3):i–iv. doi:10.1080/02786826.2013.877121.

Weingartner, E., H. Burtscher, C. Huglin, and K. Ehara. 2011. Semi-continuous mass measurement. In *Aerosol measurement: Principles, techniques, and applications*, eds. P. Kulkarni, P. A. Baron, and K. Willeke, 255–269. 3rd ed. Hoboken, NJ: Wiley.

Zhang, X. Q., and P. H. McMurry. 1987. Theoretical analysis of evaporative losses from impactor and filter deposits. *Atmos. Environ.* 21 (8):1779–1789. doi:10.1016/0004-6981(87)90118-1.