Thermally induced filter bias in TEOM mass measurement

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Researchers at the National Institute for Occupational Safety and Health (NIOSH) have long used stationary tapered element oscillating microbalances (TEOMs®) in laboratory settings. They have served to assess the mass concentration of laboratory-generated particulates in experimental dust chambers and they provide a reference method for comparison with other particulate-measuring instruments. Current NIOSH research is focused on further adapting TEOM technology as a wearable personal dust monitor (PDM) for coal mining occupations. This investigation's goal is to help identify, quantify, and provide means for resolving certain TEOM-related error. The present research investigated bias caused by thermal effects on filter assemblies. New filters used in the PDM for 8 h tests show an average positive bias of 25.5 μg, while similar tests of equivalent filters used in two 1400A model TEOMs show an average positive bias of 34.3 μg. The derived bias values allow correction of previously collected biased data. Also, pre-heating the filters for 24 h at 46 °C shows significant bias reduction, with PDM pre-heated filters subsequently averaging −3.3 μg and 1400A TEOM filters averaging 5.9 μg. On a single-point comparison to gravimetric sampling, a 25.5 μg bias is only significant at low mass loadings. At 2.5 mg, this bias represents a negligible 1% of the mass measurement. If ordinary linear regression is used, the bias is still insignificant. However, if the more valid weighted linear regression is used, it gives more weight to the smaller dependent variable values, which are more impacted by the bias. Consequently, what is 1% bias on a single high-mass value can translate into a larger bias percentage at high-mass values when performing a weighted regression on data that include a large number of low-mass values.

1. Introduction

1.1 Background

Among the various instruments developed to quantify concentrations of airborne particulate matter, those based on the tapered element oscillating microbalance (TEOM®) have gained wide acceptance in a variety of applications. Beginning in 1981, the TEOM technique was commercialized by Rupprecht & Patashnick Co. (R&P), Albany, NY, now part of Thermo Fisher Scientific, Inc. (hereafter referred to as Thermo), Waltham, MA. This class of instruments is capable of nearly continuous time-resolved measurements directly related to the particulate mass, independent of other particulate properties, such as composition, density, size, and color. With an external display, TEOM instruments can serve as direct-reading near-real-time particulate monitors. Varied applications[1] for TEOM-based monitors have included particulate measurement for the ambient environment,[2] industrial stack emissions,[3] engine exhaust,[4] and as discussed below, occupational exposure assessment.

The Pittsburgh Research Laboratory of the National Institute for Occupational Safety and Health (NIOSH) has long used stationary TEOM instruments in laboratory settings to monitor and control experiments with airborne particulate, typically of coal, mineral, or diesel origin. They have been used to assess the mass concentration of laboratory-generated particulate in experimental dust chambers and they provide a reference method for comparison with other particulate-measuring techniques or instruments. Further advancing this instrument category, recent NIOSH contract research has miniaturized, stabilized, and reconfigured TEOM technology into a worker-wearable personal dust monitor (PDM) that also provides a data file for dust levels over a work shift. Performance of this new TEOM-based PDM has been documented by NIOSH researchers through extensive testing.[5] In this current investigation, both pre-commercial (not for general sale) Model 3600 wearable PDMs and Thermo Model 1400A stationary TEOMs were used. The Model 1400A instruments have US EPA certification for continuous PM-10 particulate monitoring. Details on the principles[6] for and operation[7] of these instruments are available elsewhere: therefore only the instrument details most relevant to this research are reviewed here.

1.2 TEOM device descriptions

The core component of any TEOM mass sensor is a vibrating hollow tube called the tapered element (TE). It is secured at its base but free to oscillate at the opposite end. The TE is set into oscillation at its resonant frequency and an electronic feedback system maintains the oscillation amplitude. A small replaceable filter assembly is mounted on its free end, which collects particulate in the air stream that passes into the mass sensor chamber. As particulate collects on the filter, the TE oscillation frequency decreases and the collected mass is determined *via* the relationship

$$\Delta M = K_0\left[\frac{1}{f_t^2} - \frac{1}{f_0^2}\right] \qquad (1)$$

where

ΔM = mass change/g;

f_0 = measured initial frequency/Hz;

f_t = measured frequency at time t/Hz;

K_0 = characteristic constant of each individual instrument.

The manufacturer or user calibrates each TEOM unit with a K_0 value, a proportionality constant between mass accumulation at the end of a specific TE and its frequency change. Concentration is then calculated from the dust mass, time, and flow rate data for the test.

The PDM is a combined respirable dust monitor and cap lamp, configured to have dimensions and weight (3.0 kg) similar to those of a current lead-acid miner's cap lamp battery. PDM components include: cyclone sample inlet tube, Higgins–Dewell (HD) cyclone, internal air heater, pump, TEOM dust sensor, sampler and cap lamp lithium-ion batteries, electronic control and memory boards, display screen, and Windows®-based interface software. The PDM system further includes a docking station, used to communicate with personal computer software for programming operations, retrieving stored instrument data files, and also recharging batteries for the next work shift.

The HD cyclone design operated at 2.2 L min^{-1} airflow has previously been reported to have low bias relative to the International Organization for Standardization (ISO) convention.[8] The fraction of dust considered respirable is an important part of measuring a worker's risk from dust exposure. The ISO has recommended[9] that the definition of respirable dust follow the convention described by Soderholm.[10]

The PDM inlet is attached to the side of the cap lamp, which is well within the worker's breathing zone. An external conductive silicone rubber tube (0.48 cm internal diameter and 152 cm length) is bound with the cap lamp cord in a shared fabric sleeve and is used to draw particulate-laden air at constant 2.2 L min^{-1} airflow. The conductive tube has been shown not to cause significant loss of respirable particulate.[11] At the external tube's junction with the instrument main body, the HD cyclone size-fractionates the particulate and transmits the respirable portion of a sample through heated zones inside the PDM. Heating the air sample minimizes the influence of humidity on mass readings. Ambient and internal temperatures, relative humidity (RH) and flow rate are measured by various sensors, with measurements recorded to the instrument data file, along with dust mass measurements. At the end of the instrument's internal sampling train is the TEOM, the TE oscillating end mounted with the specialized filter assembly. The TEOM sensor and filter sample are typically heated to a constant 46 °C in the PDM.

The TE is a very narrow-diameter steel tube in the TEOM module of the PDM (and is a larger glass tube for the Model 1400A). The TEOM filter assembly, a key component for this research, is mounted directly on the TE free end with a customized tool. The filter collects dust in an open-face manner in the small chamber of the TEOM, while a pump draws air through the filter by way of the TE tube. Therefore, the circular face of the filter is the TE inlet and the base of the TE tube is the outlet.

Any event or process that affects TE frequency will be interpreted in instrument calculations as a change in collected dust mass. Under ideal conditions, collection of dust mass alone changes the TE frequency and is the sole process guiding TEOM results. In reality, a variety of secondary processes can affect TE frequency and lead to errors. Researchers have noted that temperature fluctuation, humidity collection, flow pulsation, and filter pressure drop are among the parameters that can affect TEOM performance.[12] Even when operational parameters are held steady, moisture accumulation within collected dust, or heat-induced loss of volatile material adsorbed onto or associated with sampled dust, are regarded as major sources of error in some applications. To compensate for these errors, it is common for correction factors[13] to be applied to TEOM measurements in cases where loss of volatiles has occurred.

Various approaches, including user recalibration,[14] have been taken to counter TEOM problems. One post-test procedure to address error with stationary TEOMs has involved a calculated moisture correction, based on water mass transfer from air to particulate.[15] To counter humidity-related errors by refining experimental technique, fresh TE filter assemblies are stored in small auxiliary chambers that are part of the TEOM module in Model 1400A instruments. These chambers provide extended periods of warming for the filter assemblies. This warming has been described as stabilizing filter moisture-related properties [Rupprecht and Patashnick Co., 1996, p. 3–2].[7a] Boxes of new filter assemblies can also be stored in the larger housing for the TEOM module. However, storage in the housing provides lesser degrees of filter heating, due to lower temperatures. No such chambers are part of the PDMs. Instead, PDMs rely on automatic 0.5 h initial warm-up periods, attempting to stabilize both TEOMs and newly installed filter units.

Additional approaches to address measurement errors have involved creation of more complex instruments. In one case, two TEOMs are used in parallel,[16] one acting as a reference for the other. In another case, dust flow to a single TEOM is periodically interrupted,[17] so it can act as its own intermittent reference instrument. These methods do not identify and resolve specific causes of TEOM error, but only compensate for them as a whole. They rely on more complex instrumentation to compensate for fundamental error sources and also rely on basic assumptions that may not be entirely true. When paired TEOMs are used, it assumes one filter assembly will behave the same as another. When a TEOM acts as its own reference, it typically assumes that the recorded drift during reference measurement periods can be attributed to dust mass loss, rather than to other effects.

Thermally related phenomena have been noted in the past,[4,12,17] but not fully characterized or explained. In an active instrument, the filter may experience, to minor degrees, all categories of heat-induced change to which filter materials are subject. This can include processes such as oxidation, degradation, relaxation, and deformation.[18] In this article, all discussion of TEOM filters refers to complete filter assemblies, unless the context indicates that the fibrous filtration material is the topic. Because the TEOM is an extremely sensitive mass balance, any change in filter mass or shape will affect TE frequency and induce inaccuracies into dust mass measurements. Therefore, if the filter continues to be used in its current form, it will remain a source of some error. Furthermore, a reliable way to address or reduce bias caused by changing filter characteristics would certainly be very useful. It is the goal of this investigation to help identify, quantify, and provide means for resolving certain sources of TEOM-related error. The present research has focused on bias caused by thermal effects on filter assemblies. Comparison was made between the two types of TEOM instruments to determine if the filter thermal bias was a much more universal issue than one occurring only in the mining industry.

2. Materials

The PDM filter assembly, a key component for this research, is unique to Thermo TEOM instruments. Filter assemblies are provided by the manufacturer as fully fabricated units, having masses of approximately 110 mg, a nominal 16 mm diameter, and a 14 mm filtration diameter.

Each filter assembly is constructed from three sonically welded components. The primary material composing the filter assemblies is a polypropylene (PP) polymer. The largest component is a circular PP base with a hollow axial hub, which attaches to the exposed TE end. The second component is a small circular fibrous filter which mounts on the PP base, and the final component is a PP ring used to seal the rim of the fibrous filter onto the base. There are two compositional variants for the filter-holding PP components: clear and white. All PDM filter assemblies used in this research had clear PP components, with no colorant additives. All 1400A filter assemblies had white PP components, tinted (for cosmetic reasons) with 0.5% titanium dioxide pigment.

Mounted between PP base and ring, the filter material currently used by Thermo for both the PDMs and 1400-series TEOMs is EMFAB TX40H120WW, from Pallflex Products Corp. (Putnam, CT; a division of Pall Gelman Sciences). The filter medium is borosilicate glass fiber, with polytetrafluoroethylene (PTFE) binder, cured above 370 °C. A woven fiberglass fabric is also incorporated as a reinforcing backing. The fiberglass and PTFE filter is designed to be hydrophobic, minimizing the collection of airborne moisture.

3. Methods

3.1 PDM tests

PDM tests were performed in four phases to quantify the average bias and determine to what degree the bias can be alleviated. Phase 1 investigated the average value for the thermally induced bias (hereafter referred to as thermal bias) of new (unused and unheated) filter assemblies. This was accomplished by performing zero-drift tests. The filters were selected for testing without regard to manufacturing lot number. Phase 2 investigated the effect on bias by filter pre-heating. Phase 3 investigated the magnitude of the thermal bias with PDM internal heaters inactive, as independent confirmation of the heating-related phenomenon. Phase 4 investigated and compared average values for the thermal bias for new filters from two different lot numbers.

3.1.1 Phase 1: zero-drift thermal bias. Testing used PDM instruments that were thoroughly cleaned prior to testing. Cleaning procedures, which went beyond the routine process recommended, involved multiple flushings of the cyclone inlet tube with compressed air, swabbing the TEOM chamber with isopropyl alcohol, and subsequent flushing with canned air. The instruments were then run for 6 h using a new filter assembly and a HEPA filter on the instrument inlet. Following this procedure, new filters, selected without regard to lot number, were placed in the PDMs. PDM inlets were connected to a manifold where all sampling air was drawn through a HEPA filter. Two to four PDMs were used per test run, programmed to sample for 8 h and record data at 1 min intervals. Internal TE temperature was set at 46 °C.

Usually, the PDM is programmed so that frequency and mass change for any measurement period must exceed a pre-set threshold before a new value different from the preceding measurement will be recorded. Under normal settings, thermal bias will not usually be recorded, because it will typically be below the specified threshold. However, the bias will still be transparently recorded as part of actual dust measurements, because the threshold value will be exceeded as collected dust mass increases. Frequency and mass values, when recorded, will reflect the changing state of the filter. In programming the PDMs for these tests, the threshold feature was disabled to accurately track all frequency and mass changes.

For the first forty PDM tests, three HD gravimetric cyclone samplers were also connected to the manifold. In this arrangement, all samplers were drawing the same air, presumably free of particulate matter. The gravimetric samplers were used to verify real particulate matter was not being collected by the PDMs. The average mass change of three HD control filters was used to correct the gravimetric values for uncontrollable variations between pre- and post-weighings.

For each test, the instruments were located in climate-controlled rooms of 22.3 ± 0.6 °C (72.1 ± 1.2 °F) temperature and 54.6 ± 4.4% relative humidity. Similar tests were run for 24 h periods to examine the asymptotic stabilization of filters during use. The mass gain for the initial 8 h was also used from these data for inclusion with the other 8 h tests. Although the PDM zeroes itself after the warm-up period, the entire time duration that the filter is being conditioned by heat must include the initial 0.5 h warm-up. Therefore, test run times of 8 or 24 h are actually 8.5 or 24.5 h, respectively, in terms of effects on the filter assembly.

3.1.2 Phase 2: filter pre-heating. It was noted in the description of the PDM that the sampled air is heated internally.

This procedure ensures the temperature at the PDM filter is maintained to 46 °C during sampling. For this phase of the work, filters were pre-treated before use by heating in an oven controlled to 46 °C for 24 h. Filters were then allowed to cool to controlled room temperature naturally, with testing proceeding similarly to Phase 1.

3.1.3 Phase 3: PDM heaters inactive.

To further examine the degree to which the internal PDM heaters contribute to the thermal bias, 8 h zero-drift tests were performed on new filters with the heaters inactive.

3.1.4 Phase 4: filter lot comparison.

Test procedures were identical to those described for Phase 1, with the exceptions that gravimetric sampling was not performed and new filters were selected from two specific lot numbers. It was not necessary to perform 24 h tests because the PDM is typically used for 8 h sampling only.

3.2 1400A TEOM

Two Model 1400A TEOMs were used in these tests. The sensor unit inlets were thoroughly cleaned and cartridge-type HEPA filters were then inserted into the external instrument inlets. Both TEOMs were set to operate at 2.2 L min^{-1} and programmed to operate at 46 °C, similar to the PDM. Prior to each test, new filters were installed in both TEOMs.

Both new and pre-heated filters were tested. Filters used in these tests were not pre-conditioned in the TEOM mass transducer. The present test results will show that this pre-conditioning has little, if anything, to do with moisture and may instead create thermal relaxations in the filter.

Each test lasted at least 24 h. However, in order to reasonably compare the thermal bias of the 1400A TEOM with the PDM, the 1400A recorded mass was read 8.5 h after installation of a fresh filter. In some cases, the 1400A was not run for 24.5 h as with the PDM because the test duration is dependent upon the time at which the instrument stabilizes and begins proper operation. Therefore, only 24 h values are reported for the 1400A.

Table 1 PDM thermal bias data using new filters[a]

Bias mass/μg				
8 h			8 h	24 h
27.5	18.6	29.7	35.2	—
20.0	25.8	12.0	29.6	—
14.9	33.1	12.0	25.8	—
13.6	35.3	15.5	18.5	—
19.0	39.8	8.1	17.7	—
25.3	24.6	24.1	14.8	—
17.3	39.1	23.9	17.1	—
24.4	35.7	29.4	12.0	—
38.4	19.5	29.9	27.9	—
34.6	37.0	24.4	29.8	—
20.9	31.6	15.4	33.5	—
27.4	24.1	7.5	23.5	—
22.8	56.6	19.4	35.2	—
30.1	22.9	20.7	27.8	37.4
24.2	31.7	30.6	39.9	47.4
30.6	35.0	31.5	25.8	37.9
24.2	25.7	11.5	33.2	47.3
24.3	25.9	16.7	24.4	37.8
14.3	18.6	20.9	30.3	41.5
21.5	36.7	27.1	25.1	37.5
34.4	21.7	30.6	—	—

[a] Filters randomly chosen from manufacturing lot numbers.

4. Results

4.1 PDM

4.1.1 Phase 1: zero-drift thermal bias.

Table 1 presents the results of eighty-three 8 h tests and seven 24 h tests of new filters. It is noticed that all mass values are positive, indicating systematic error. In Table 2, the 8 h tests show that new PDM filter bias averaged 25.5 μg [95% CI: (23.6, 27.4)] with a range of 49.1 μg while the 24 h tests show an average bias of 41.0 μg [95% CI: (36.4, 45.6)] with a range of 10.0 μg. Fig. 1 shows a typical plot of 1 min mass readings for a new filter over an 8 h test. It is noticed that the mass gain rate is greatest during the first 2 h and that the trend appears to approach an asymptotic value. All tests exhibited this asymptotic behavior. It is observed from Table 2 that the 24 h range is substantially less than the 8 h range, being 10.0 and 49.1 μg, respectively. This

Table 2 Thermal bias 95% CI summary statistics

		Mass/μg				
	N	Mean	Stdev	CL_{lower}	CL_{upper}	Range
PDM						
8 h, new filters[a]	83	25.5	8.5	23.6	27.4	49.1
8 h, pre-heated filters[a,b]	23	−3.3	3.2	−4.7	−1.9	12.6
8 h, internal heaters inactive[a,c]	22	0.8	15.5	−6.2	7.8	62.2
24 h, new filters[a]	7	41.0	4.6	36.4	45.6	10.0
8 h, new filters, lot no. 1	22	26.8	5.2	24.4	29.1	21.9
8 h, new filters, lot no. 2	22	20.0	6.1	17.2	22.7	21.9
Model 1400A TEOM						
8.5 h, new filters	13	34.3	6.2	30.4	38.2	23.4
8.5 h, pre-heated filters[b]	10	5.9	7.2	0.5	11.3	24.0
24 h, new filters	13	43.8	12.1	36.1	51.4	35.1
24 h, pre-heated filters[b]	10	9.0	5.8	4.6	13.4	22.8

[a] Filters chosen randomly from multiple manufacturing lot numbers. [b] Filters pre-heated for 24 h at 46 °C. [c] Internal average temperature rise of approximately 12 °C above ambient.

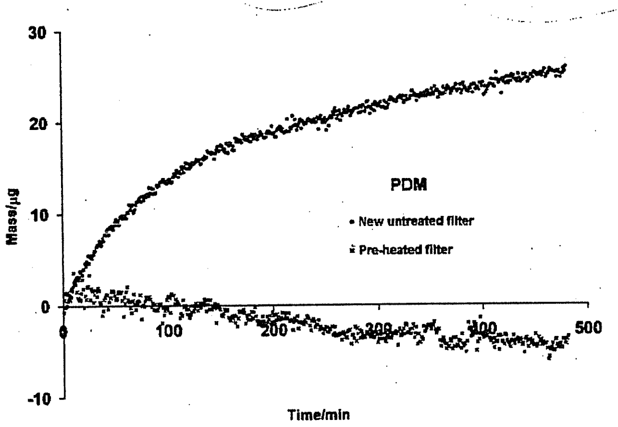

Fig. 1 Typical PDM 8 h thermal bias.

may be a consequence of the 24 h tests being closer to an asymptotic value than the 8 h tests.

The thirty-six gravimetric samples used for the first forty PDM filter tests yielded an average mass change of −1.9 µg, indicating that no particulate matter was in the air sampled by the PDMs. This value is well within the 7 µg measurement precision of the NIOSH weighing facility.

4.1.2 Phase 2: filter pre-heating. Table 3 presents the results of twenty-three tests with pre-heated filters. Table 2 shows that the pre-heated filter bias averaged −3.3 µg [95% CI: (−4.7, −1.9)] with a range of 12.6 µg. Pre-heated filter tests shows a clear alleviation of the thermal bias, with only a slight negative bias remaining. Fig. 1 presents the graphical comparison of typical data from the two types of filters. In all cases, the pre-heated filters produce a minor initial rise, followed by a slowly decreasing mass value over time.

4.1.3 Phase 3: PDM heaters inactive. Table 3 presents the results of twenty-two tests with the PDM internal heaters inactive. The only heat source available to affect the new filters was that generated solely from PDM operation. For these tests, the average internal temperature rise was approximately 12 °C above ambient conditions, half the rise when the heaters were active. Table 2 shows that the average bias is 0.8 µg [95% CI: (−6.2, 7.8)] with a range of 62.2 µg. Although there is a substantial range of bias, it is apparent that reduced heating of the new filters produces significantly less average bias. In these tests, the PDMs slowly reached internal temperatures of 33–36 °C. TEOMs are typically set to maintain temperatures in the 30–50 °C range. The test results suggest that the variety of operating temperatures employed merit further examination for thermally-related bias and variance, which may have different magnitudes at various temperature settings.

Table 3 Heating effect on PDM bias data[a]

8 h bias mass/µg			
Pre-heated filters		Inactive heaters[b]	
−6.4	3.2	15.9	−11.4
−0.3	−7.6	13.3	−8.8
−1.5	−1.7	17.7	−28.8
−9.4	−5.1	33.4	−23.7
−4.7	−5.0	16.7	−16.1
−6.5	−5.3	4.7	−3.7
−2.3	−1.8	8.8	0.8
−3.5	−5.9	0.5	−0.8
−0.8	−5.2	7.1	−1.6
−2.4	2.8	6.8	−23.5
−5.1	−1.4	15.3	−5.5
0.4	—	—	—

[a] Filters randomly chosen from multiple manufacturing lot numbers. [b] Internal average temperature rise of approximately 12 °C above ambient.

Table 4 PDM thermal bias of two filter lots

8 h bias mass/µg			
Lot no. 1 filters		Lot no. 2 filters	
21.9	24.9	22.9	20.6
24.8	39.0	23.5	16.5
31.0	26.9	13.1	11.2
30.4	29.0	21.4	24.3
23.8	31.5	20.1	13.4
28.5	24.2	17.3	23.2
17.1	27.2	21.3	33.1
21.9	31.2	12.9	21.9
21.6	35.4	11.5	32.9
24.5	29.8	19.3	22.9
24.7	19.9	23.6	12.7

4.1.4 Phase 4: filter lot comparison. Test results for twenty-two filters from each of two lots are shown in Table 4. As shown in Table 2, filter lot no. 1 bias averaged 26.8 µg [95% CI: (24.4, 29.1)] with a range of 21.9 µg while lot no. 2 averaged 20.0 µg [95% CI: (17.2, 22.7)] with a range coincidentally also of 21.9 µg. To test whether there is a difference in filter lots, a two-tailed *t*-test was performed assuming unequal variances, as shown in Table 5. The results show there is a significant difference in the bias associated with the two lots tested [99% CI for difference: (2.2, 11.4)].

4.2 1400A TEOM

Results for twenty-three tests using new and pre-heated filters are summarized in Table 6. A review of Table 6 for both 8.5 h and 24 h tests reveals the same positive thermal bias associated with new PDM filters. Here also, pre-heating alleviates most of this bias, in all but one test. Referring to Table 2, the 8.5 h tests of new TEOM filters show an average bias of 34.3 µg [95% CI: (30.4, 38.2)] with a range of 23.4 µg. Pre-heating the filters reduced the average bias to 5.9 µg [95% CI: (0.5, 11.3)] with a

Table 5 CI *t*-test assuming unequal variances

	Lot no. 1	Lot no. 2
Mean/µg	26.8	20.0
Variance	26.8	37.2
Observations	22	22
Hypothesized mean difference	0	
d.f.	42	
t_{stat}	3.99	
$P(T \leq t)$ two-tail	0.0003	
t Critical two-tail	2.70	
99% CI for difference of means/µg =	(2.2, 11.4)	

Table 6 Model 1400A TEOM thermal bias data

TEOM no. 1 mass/µg				TEOM no. 2 mass/µg			
New		Pre-heated		New		Pre-heated	
8.5 h	24 h	8.5 h	24 h	8.5 h	24 h	8.5 h	24 h
28.7	48.8	2.7	8.9	25.8	25.7	1.8	6.9
30.1	33.1	3.3	9.2	34.6	57.7	2.3	6.7
28.8	50.4	3.9	8.5	35.1	58.1	3.0	7.2
36.9	60.8	25.8	20.2	49.2	52.0	6.4	−2.6
36.0	29.2	6.2	14.4	29.4	31.7	4.0	10.7
36.7	42.2	—	—	34.2	32.4	—	—
40.9	47.0	—	—	—	—	—	—

range of 24.0 µg. The 24 h tests of new filters show an average bias of 43.8 µg [95% CI: (36.1, 51.4)] with a range of 35.1 µg. Pre-heating the filters reduced the average 24 h bias to 9.0 µg [95% CI: (4.6, 13.4)] with a range of 22.8 µg. Fig. 2 shows typical 24 h plots for new and pre-heated filters. Although individual filters showed differing bias traces, general time trends for new and pre-heated filters were similar to those in Fig. 1.

5. Discussion

5.1 Source of bias

The bias exhibited by new filters can be considered the sum of all filter-related bias sources, positive and negative, within the PDM or 1400A. Test results demonstrate a net positive bias for both instruments. Because testing was performed in a climate-controlled environment, ambient temperature and humidity variations are not contributory to the measured bias. The dominant source of positive bias appears to be associated with thermal treatment of a new filter during actual usage. The data obtained with the internal PDM heaters inactive clearly show a substantially reduced average bias. Also, the fact that pre-heating filters essentially removes this bias is compelling evidence the bias is associated with the filter itself. As mentioned earlier, sources of this filter bias can include oxidation, degradation, relaxation, and deformation. Although the exact source of the bias cannot be determined, it would not appear that oxidation is responsible. Oxidation would likely provide a weight gain to the filter. However, the gravimetrically measured, reference-corrected, mean mass change of six pre-heated filters was −7.3 µg, equivalent to the laboratory weighing precision. Although this value is not comparable in magnitude or direction to the measured bias of new filters, it does suggest the possibility of some small, but real, filter mass loss.

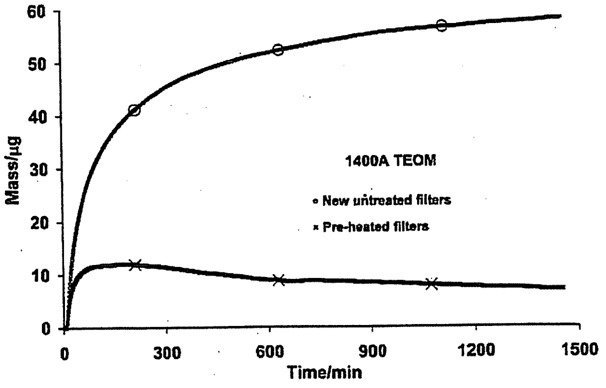

Fig. 2 Typical 1400A TEOM 24 h bias.

In all cases, the pre-heated PDM filters exhibit a slowly decreasing mass value over time. The end result is typically a slight negative bias, small compared to the positive thermal bias. Although the source of this negative bias is not known, another possibility is the effect of the constant negative pressure applied to the filter assembly for the test duration. This negative pressure, which is a function of the selected air flow rate, would have the tendency to depress or compress the filter and shorten the TE pendulum length slightly, resulting in a frequency increment and a virtual mass loss. However, investigation of this effect was not undertaken in this study because design of the PDM does not permit significantly reducing the differential pressure across the filter.

The effect of the pre-heating treatment appears to persist for at least three to four days, the time period during which treated filters were used. If this were not the case, tests with pre-heated filters, which were stored at controlled room temperature before use, would not exhibit bias reduction so fully. It is not known if the treatment effect is permanent or irreversible.

The data show that the 1400A TEOM filters exhibit the same generic final bias as the PDM filters. It is also observed for the 1400A TEOM pre-heated filters that there is an initial rise in mass reading followed by decreasing mass, similar to the PDM. These results are not surprising, because the filters are nearly identical. Although the filter media itself is identical for the PDM and 1400A, there is the earlier-noted difference in the composition of PP in which the filter material is mounted. This may account for the differing biases between the new filters, as well as the fact that pre-heating the 1400A TEOM filters did not reduce the bias to the same level as the pre-heated PDM filters. However, it may be significant that the 8 h bias reductions between new and pre-heated filters for the two types of instruments are very similar: respectively, 28.8 µg and 28.4 µg for the PDM and the 1400A.

5.2 Bias impact on gravimetric comparisons

For single-point mass comparison to gravimetric dust sampling, 25.5 µg bias is only of significance at low mass loadings. For a 2.5 mg sample, the 1% bias is negligible. However, this is not always the case. For example, TEOM measurements are often compared to gravimetric samples by linear regression over a range of masses. If the ordinary linear regression is used, this bias is still ignorable. However, there is a critical error in this approach. A fundamental assumption of ordinary linear regression analysis is constant additive variance of the dependent variable across the range of the independent variable. This assumption is rarely met in dust mass sampling, with the variance usually increasing with the square of the independent variable. This behavior is typical of data collected with dust sampling instrumentation[19] and is referred to as constant coefficient of variation (CV) or multiplicative error. Constant CV will usually occur except at very low dust loadings. In relationships with multiplicative error, large dependent variable values will have large residuals, which will significantly overwhelm the small dependent value residuals. As a result, the total sum of squares will be erroneously influenced by the large dependent variable values and lead to a regression bias. Therefore, the large dependent variable values should accordingly be given less "weight" in the analysis.

One common means of dealing with this type of error is weighted least squares linear regression. Using this method naturally provides more weight to the smaller variable values. Unfortunately, these are the very values where the bias is a more significant percentage of the value itself. Consequently, what is a 1% bias on individual high-mass values can translate into a larger bias percentage for high-mass values in a weighted regression that includes a large number of low-mass values. Therefore, the estimated bias reported in this work could produce a larger change in regression slope across all values of the independent variable. The estimated bias values derived in the present work allow for the correction of previously collected data over the full range of the independent variable, which would prevent regression-derived bias.

5.3 General low mass sample considerations

Because filter thermal bias is seen in both the PDM and 1400A TEOM, it is a reasonable generalization that all TEOMs utilizing PP filters may exhibit similar bias. This is a concern, because TEOM technology is used extensively in air quality monitoring. In many instances, the sample masses are small and bias magnitudes seen in the present work may have an impact if new filters are used without pre-heating. Generally, TEOM instruments provide measurement accuracy that is better with high-mass samples than with those of low mass. The bias documented by this research may provide an explanation. The degree of bias is dependent on the heating history of the filter unit, and accuracies for low-mass samples, therefore, have greater vulnerability to filter-related bias. If low-mass samples are anticipated in TEOM use, reducing instrument error by utilizing fully heat-conditioned filter units would be the best technique.

Additionally, that the bias develops differently over time for new and pre-heated filters is an important consideration. It is a phenomenon dependent on whether or not users of TEOMs rigorously adhere to manufacturer recommendations to condition filters within the mass transducer housing. Unfortunately, the PDM does not have the same capability to precondition the filter as the 1400A TEOM. Therefore, PDM filters need to be pre-heated separately before use, if it is determined that the bias must be eliminated from a measurement. In either case, reasonable bias correction of previous data can be performed with the average bias values presented here. It is only necessary that there is known heating experience for the filters that were used to collect the earlier data.

5.4 TEOM calibration issues

In addition to errors in test measurements, time-progressive bias can be expected to affect TEOM calibration. Each TEOM is calibrated in a procedure where cumulatively more mass is added step-wise to a filter assembly. The tendency to manifest a virtual positive mass (actually a lowering of TEOM frequency) will bias the calibration. Fortunately, the calibration bias will be small, because the virtual mass, which progresses over the range 0–25 μg, occurs while working with much greater real masses, progressing over the range 500–4000 μg. It is also a common practice to later perform calibration checks on TEOMs, using a single pre-tested filter unit. The accuracy of calibration checks may be impaired, depending on the heating history of a test filter and what size mass was added to it as a calibration quantity. Again, the effect is likely to be small, because the real mass involved will be much larger than the bias that develops. However, in the interest of optimizing instrument accuracy, all calibration procedures would best be performed with fully pre-heated assemblies, substantially negating the biasing effect.

6. Conclusions

Both PDM and 1400A filter assemblies exhibit positive thermal bias, which increases more rapidly during the first 2 h and continues approaching some asymptotic value after 24 h. In this research, average bias values were 25.5 μg (8 h) and 34.3 μg (8.5 h) for the PDM and 1400A TEOM filters, respectively. This filter bias may occur for all TEOM-based instruments using similar polypropylene filters. Approximate bias correction can be applied to measurements previously acquired using TEOM-based technology. This bias can largely be eliminated by pre-heating the filters. Although not yet an optimized process, pre-heating the filters for 24 h at 46 °C shows significant bias reduction, with PDM pre-heated filters subsequently averaging −3.3 μg and 1400A TEOM filters averaging 5.9 μg.

There was a statistically significant mean difference of 6.8 μg between biases for two lots of new filters tested, but preheating filters can be reasonably expected to reduce inter-lot differences through a reduction in bias variance.

7. Disclaimer

Mention of any company or product does not constitute endorsement by NIOSH. The findings and conclusions in this report are those of the authors and do not necessarily represent the views of NIOSH.

References

1 H. Patashnick, M. Meyer and B. Rogers, in *Mine Ventilation: Proceedings of the North American/9th US Mine Ventilation Symposium*, Kingston, Canada, 2002, ed. E. De Souza, A. A. Balkema Pub., Lisse, Netherlands, 2002, pp. 625–631.

2 (*a*) H. Patashnick and E. G. Rupprecht, *J. Air Waste Manage. Assoc.*, 1991, **41**, 1079–1083; (*b*) G. P. Ayers, M. D. Keywood and J. L. Gras, *Atmos. Environ.*, 1999, **33**, 3717–3721.

3 J. C. F. Wang, B. F. Kee, D. W. Linkins and R. W. Lynch, *J. Air Pollut. Control Assoc.*, 1983, **33**, 1172–1176.

4 (*a*) M. S. Gilbert and N. N. Clark, *Int. J. Engine Res.*, 2001, **2**, 277–287; (*b*) H. Moosmuller, W. P. Arnott, C. F. Rogers, J. L. Bowen, J. A. Gillies, W. R. Pierson, J. F. Collins, T. D. Durbin and J. M. Norbeck, *Environ. Sci. Technol.*, 2001, **35**, 781–787.

5 (*a*) J. C. Volkwein, R. P. Vinson, L. J. McWilliams, D. P. Tuchman and S. E. Mischler, *Performance of a New Personal Respirable Dust Monitor for Mine Use*, DHHS (NIOSH) Pub. 2004–151, Report of Investigation 9663, 2004; (*b*) J. C. Volkwein, R. P. Vinson, S. J. Page, L. J. McWilliams, G. J. Joy, S. E. Mischler and D. P. Tuchman, *Laboratory and Field Performance of a Continuously Measuring Personal Respirable Dust Monitor*, DHHS (NIOSH) Pub. 2006–145, Report of Investigation 9669, 2006.

6 (*a*) H. Patashnick, *US Pat.*, 3 926 271, 1975; (*b*) H. Patashnick and G. Rupprecht, *US Pat.*, 4 391 338, 1983; (*c*) G. Rupprecht and D. R. Hassel, *US Pat.*, 4 696 181, 1987; (*d*) D. R. Hassel and R. Basch, *US Pat.*, 5 488 203, 1996; (*e*) D. R. Hassel, *US Pat.*, 6 080 939, 2000.

7 (*a*) *Operating Manual, TEOM Series 1400a Ambient Particulate (PM-10) Monitor (AB Serial Numbers)*, Rev. B, Part No. 42-003347, Rupprecht and Patashnick Co., Albany, NY, USA, 1996(*b*) *Operating Manual, TEOM Series 3600/3700 Personal Dust Monitor*, Rev. A, Part No. 42-009904, Rupprecht and Patashnick Co., Albany, NY, USA, 2004.

8 A. D. Maynard and L. C. Kenny, *J. Aerosol Sci.*, 1995, **26**, 671–684.

9 *Air Quality—Particle Size Fraction Definitions for Health-Related Sampling, Standard 7708*, International Organization for Standardization, Geneva, Switzerland, 1995.

10 S. C. Soderholm, *Ann. Occup. Hyg.*, 1989, **33**, 301–320.

11 T. M. Peters and J. C. Volkwein, *Appl. Occup. Environ. Hyg.*, 2003, **18**, 458–465.

12 (*a*) R. Whitby, R. Johnson and R. Gibbs, *Soc. Automot. Eng.*, Paper 850403, 1985; (*b*) D. A. Okrent, *Soc. Automot. Eng.*, Paper 980409, 1998; (*c*) M. Gilbert, M.S. Thesis W. Virginia Univ., 2002; (*d*) N. A. Kelly and C. Morgan, *J. Air Waste Manage. Assoc.*, 2002, **52**, 1362–1377; (*e*) J. C. Volkwein, D. P. Tuchman and R. P. Vinson, in *Mine Ventilation: Proceedings of the North American/9th US Mine Ventilation Symposium*, Kingston, Canada, 2002, ed. E. De Souza, A. A. Balkema Pub., Lisse, Netherlands, 2002, pp. 633–639.

13 (*a*) D. Muir, *Atmos. Environ.*, 2000, **34**, 3209–3211; (*b*) A. M. King, T. Pless-Mulloli, J. Merefield and I. Stone, *Atmos. Environ.*, 2000, **34**, 3211–3212; (*c*) D. Green, G. Fuller and B. Barratt, *Atmos. Environ.*, 2001, **35**, 2589–2593.

14 P. R. Shore and R. D. Cuthbertson, *Soc. Automot. Eng.*, Paper 850405, 1985.

15 R. P. Jarrett, N. N. Clark, M. Gilbert and R. Ramamurthy, *Powder Technol.*, 2001, **119**, 215–228.

16 H. Patashnick, G. Rupprecht, J. L. Ambs and M. B. Meyer, *Aerosol Sci. Technol.*, 2001, **34**, 42–45.

17 (*a*) C. Asbach, T. Kuhlbusch and H. Fissan, Proceedings of QA/QC in the Field of Emission and Air Pollution Control Conference, Prague, 2003; (*b*) P. A. Jaques, J. L. Ambs, W. L. Grant and C. Sioutas, *Aerosol Sci. Technol.*, 2004, **38**(S1), 49–59.

18 H. P. Frank, *Polypropylene*, Gordon and Breach Sci. Pub., New York, USA, 1968, pp. 58–93.

19 National Institute for Occupational Safety and Health, *The Precision of Coal Mine Dust Sampling*, National Technical Information Service, Springfield, VA, USA, Accession No. PB85-220721, 1984.