

NPL REPORT
DQL-AS 015

**Ambient Air Particulate
Matter: Quantifying Errors in
Gravimetric Measurements**

Andrew S. Brown,
Rachel E. Yardley,
Paul G. Quincey and
David M. Butterfield

NOT RESTRICTED

January 2005

NPL REPORT DQL-AS 015

**Ambient Air Particulate Matter:
Quantifying Errors in Gravimetric Measurements**

Andrew S. Brown, Rachel E. Yardley,
Paul G. Quincey and David M. Butterfield

NOT RESTRICTED

January 2005

© Crown Copyright 2005

Reproduced by permission of the Controller of HMSO

ISSN 1744-0602

National Physical Laboratory
Hampton Road, Teddington, Middlesex, TW11 0LW

Extracts from this report may be reproduced provided the source is acknowledged and the extract is not taken out of context

We gratefully acknowledge the financial support of the UK Department of Trade and Industry (National Measurement System Policy Unit)

Approved on behalf of the Managing Director, NPL
by Dr Stuart Windsor, Business Leader, Analytical Science Group

EXECUTIVE SUMMARY

This report details the results of a series of studies undertaken in order to improve filter gravimetry techniques and maximise the validity of a forthcoming UK-wide series of equivalence trials for particulate monitors.

The initial objectives of the study were to produce an optimised weighing protocol and to define the characteristics of the balances used, thus quantifying the major sources of error in the gravimetric technique. A further aim was to produce an uncertainty budget for the process.

Once established, the weighing protocol was used in investigations to select the filter material most suitable for ambient PM measurements. The effects of temperature and humidity; storage and transport; and inter-laboratory weighings on the mass of a variety of filter materials were studied.

It was found that the most important factors to consider when selecting a filter medium are variation of filter mass with temperature and relative humidity; structural integrity; flow resistance; chemical effects; particle sampling efficiency and static charge effects. Thorough consideration of these factors led to the selection of Emfab (PTFE-bonded glass fibre)

The project was funded by The Department for Environment Food and Rural Affairs (Defra) through Casella Stanger. The gravimetry facilities used at NPL were installed, commissioned and maintained with funding from the Department of Trade and Industry's Valid Analytical Measurement Programme (a Programme within the DTI's National Measurement System).

CONTENTS

Executive Summary	2
1. Introduction	4
2. Experimental	6
3. Balance Protocol	7
4. Effects of Temperature and Humidity on Blank filters	16
5. Effects of Temperature and Humidity on Loaded filters	20
6. Effects of Storage and Transport: Naphthalene & Ammonium Nitrate Spiking	23
7. Effects of Different Weighing Laboratories	28
8. Conclusions for Filter Material Selection	31
9. References	32
Appendix 1. NPL Filter Weighing Procedure	33
Appendix 2. Uncertainty Budget	37
Appendix 3. Full Results of Temperature & Humidity Experiments: After Correction	38

AMBIENT AIR PARTICULATES: QUANTIFYING THE EFFECTS ON GRAVIMETRIC MEASUREMENTS

1. INTRODUCTION

A series of studies has been undertaken in order to improve filter gravimetry techniques and maximise the validity of an extended series of equivalence trials for particulate monitors to be started in the late 2004.

A previous unpublished investigation at NPL studied the weighing of a small number of filters (quartz, glass fibre and PTFE) on a Mettler UMT5 balance, in particular the effect of factors such as repeatability, static charges and the effect of humidity on blank and loaded filters. This identified a need for a much broader examination of the sources of uncertainty in the weighing of particulates on filters.

The initial objectives of the work were to produce an optimised weighing protocol and to define the characteristics of the balances used, thus quantifying the major sources of error in the gravimetric technique. A further aim was to produce an uncertainty budget for the process.

The validated protocol was used in subsequent investigations into the effects of temperature and humidity, storage and transport, and inter-laboratory weighings on the mass of the filters. The study comprised five major components, namely:

1. Balance protocol and characteristics
2. Effects of temperature and humidity on blank filters
3. Effects of temperature and humidity on loaded filters
4. Effects of storage and transport: spiking with semi-volatile material
5. Effects of different weighing laboratories

There is a wide range of filter media available for particulate monitoring [1]. The more common types of filter used for this application are investigated here, namely quartz, PTFE, glass fibre (with and without binder) and Pallflex Emfab (PTFE-bonded glass fibre). The typical masses of 47 mm diameter filters of each of these materials are 135 mg, 105 mg, 87 mg and 90 mg respectively. The mass of particulate sampled over a 24 hour period at the lowest commonly used flow rate – $1 \text{ m}^3 \cdot \text{h}^{-1}$ – is $960 \mu\text{g}$ at an ambient concentration of $40 \mu\text{g} \cdot \text{m}^{-3}$, the annual EU limit value for PM_{10} .

Errors in the mass of the collected particulate of $50 \mu\text{g}$ can therefore lead to errors of around 5% at the limit value. This tolerance is increased to $115 \mu\text{g}$ for the EU standard low volume flow rate of $2.3 \text{ m}^3 \cdot \text{h}^{-1}$, but will be decreased for limit values for smaller size fractions such as $\text{PM}_{2.5}$.

The mass measurement of the small change in the filter mass is made more challenging by the necessity to obtain the pre-loaded and loaded masses several days apart. Systematic effects such as the mass dependence on humidity or balance drift need to be assessed and controlled, or significant errors in the mass difference will be introduced.

As a rule of thumb, factors affecting the weighing of a filter by more than 20 µg can be considered significant.

One of the main drawbacks of manual methods is the possible loss or increase in material collected on the filter after sampling but before weighing [1-4]. Ammonium nitrate has been reported to be lost from filters when the temperature exceeds 20°C. Section 6 studies the mass loss of ammonium nitrate- and naphthalene- spiked filters during storage and transport. In conjunction with this, Section 7 compares the data obtained when the same set of filters are weighed by two independent laboratories.

2. EXPERIMENTAL

2.1 Materials and Equipment

The types of filters used throughout the study are detailed in Table 1:

Manufacturer	Material	Name / code	Diameter
Whatman	Quartz microfibre	QM-A	47 mm & 8" x 10"
Whatman	Glass microfibre (no binder)	GF-A	47 mm
Schleicher & Schuell	Glass fibre (with binder)	GF10	47 mm & 8" x 10"
Pall Corporation	PTFE-bonded glass fibre	Emfab	47 mm
Pall Corporation	Quartz fibre	7202	47 mm
Munktell	Quartz microfibre	MK360	47 mm
Millipore	Glass fibre	APFA04700	47 mm

Table 1: List of ambient air monitoring filters used throughout the study. Note that all filters used were circular in shape, except for the 8" x 10" filters (rectangular).

All filter conditioning and weighings at NPL were carried out in a temperature and humidity-controlled cabinet (Glovebox Technology Ltd). Two balances were used, with resolutions of 0.1 µg (UMT5, Mettler) and 10 µg (AT261, Mettler) and the removal of static charges was assessed by use of an antistatic gun (Zerostat 3, Aldrich, USA) and an antistatic fan (Stat-Attack, UK).

For the experiments in Section 6, filters were spiked with solutions of ammonium nitrate (Analytical Reagent Grade, Fisher) in methanol (Spectrophotometric Grade, Acros Organics) and naphthalene (Scintillation grade, Acros Organics) in diethyl ether (Analytical Reagent grade, Fisher). All filters were stored and transported in 47mm diameter polystyrene filter holders (Gelman Sciences).

2.2 Ambient Air Sampling

Ambient air samples were collected by use of an Andersen high volume ('Hi-vol') sampler (Figure 1). Before sampling, the instrument was prepared in accordance to the manufacturer's instructions, and a leak test and flow calibration conducted using a certified, traceable flowmeter.

2.3 Experimental Procedure

Unless otherwise stated, filters were conditioned for at least 48 hours at 20°C and 50% relative humidity (RH). Where air samples were collected by the Hi-Vol sampler, a wad punch was used to cut appropriately sized samples from the 8" x 10" filter. All filters were marked (before sampling) with a unique identifying number.



Figure 1: Hi-vol air sampler

3. BALANCE PROTOCOL

A series of experiments was undertaken with the aims of fully characterising the balances used at NPL and ultimately producing a documented weighing protocol. This protocol would then be utilised in the remainder of the experiments in this study, and proposed as a recommended procedure for the forthcoming equivalence trial.

The effect of a number of parameters (e.g. balance ‘exercising’, positional effects, drift, repeatability and static charges) on the gravimetry process was investigated using both balances. In the initial investigations calibrated metal mass pieces were used, to avoid the complications introduced by filters. The balances were not switched off throughout the course of the experiments. The results of each investigation are reported and discussed below:

3.1 Exercising the balance

A metal mass piece was weighed consecutively ten times (a period of approximately two minutes elapsing between each reading), the balance being rezeroed in between each reading to eliminate drift. Each reading was recorded and used to assess the extent to which exercising is required before the true and stable mass is measured. A typical set of data for a 50mg calibration mass piece is shown in Figure 2):

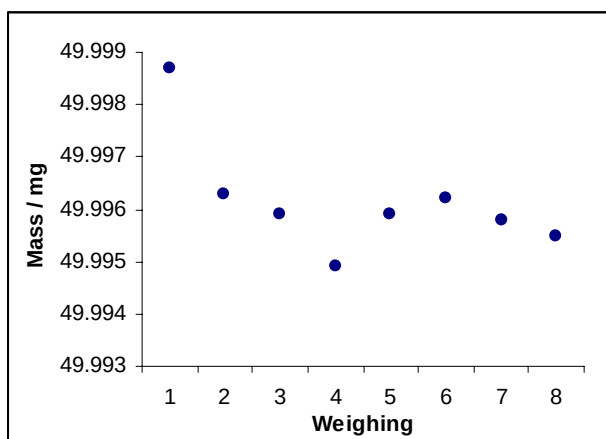


Figure 2: Plot showing typical repeated weighings of a 50mg calibrated mass piece (UMT5 balance). Each weighing is separated by a time period of approximate two minutes.

The results from both balances indicate that the readings stabilise after three or four repeat weighings. The data shows that taking measurements before exercising a balance (weighing 1) would incur an error in the region of $\pm 3 \mu\text{g}$ on the UMT5 balance, and $\pm 30 \mu\text{g}$ on the AT261 balance.

Therefore, in subsequent experiments, the balances were exercised by placing (and removing) a metal mass piece, of nominally the same mass as the filters, onto the weighing pan four times. This should be carried out whenever the balance has been idle for a period of 20 minutes or more, and should take place before performing an internal calibration.

3.2 Effects of Position

A 200 mg metal mass piece was placed in different positions on the balance (see Figure 3) and each reading was recorded. This was repeated a number of times (in a random order) to determine whether any relationship exists between the recorded mass and position on the pan. The balances were re-zeroed between each reading to eliminate drift.

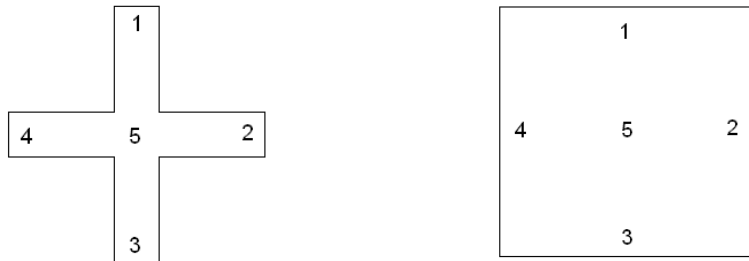


Figure 3: Schematic diagrams of the balance pans (left: UMT5; right: AT261). The numbers indicated the positions used to assess any effects of position

As the size of the more sensitive UMT5 balance pan has been designed to be the same size as 47 mm ambient air monitoring filters, no effects of position are possible when weighing filters. However when using a 200 mg metal mass piece, a positional variation of up to 5 μg was observed (UMT5 balance, Figure 4). The AT261 balance did not exhibit any significant variation in mass due to position, within its lower sensitivity (10 μg resolution).

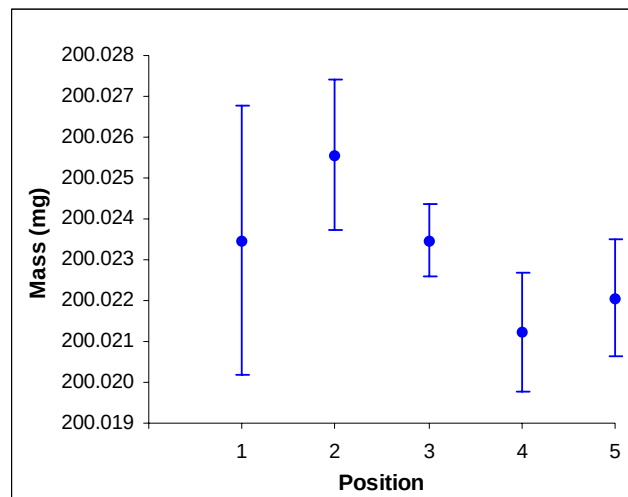


Figure 4: Effects of position (UMT5 balance, 200 mg mass piece). The data is shown as the mean and standard deviation of repeated measurements at each position.

3.3 Long- and short-term drift

The long-term drift of the balances was assessed by recording the balance readings every five minutes for a period of several hours using an empty balance pan (zero drift) and with a 100 mg metal mass piece (span drift). A typical pattern for the long-term span drift of the UMT5 balance is shown in Figure 5. The drift of the balance shows behaviour clearly distinct from the changing ambient temperature, an indication that the change in reading is not caused by external environmental effects on the buoyancy of the mass piece. Indeed, for a 100 mg stainless steel mass piece at 1030 mbar pressure, the buoyancy corrections are 15.30 μg and 15.15 μg at 20°C and 23°C respectively: a difference of only 150 ng (less than one thirtieth of a graduation on the left-hand x-axis in Figure 5).

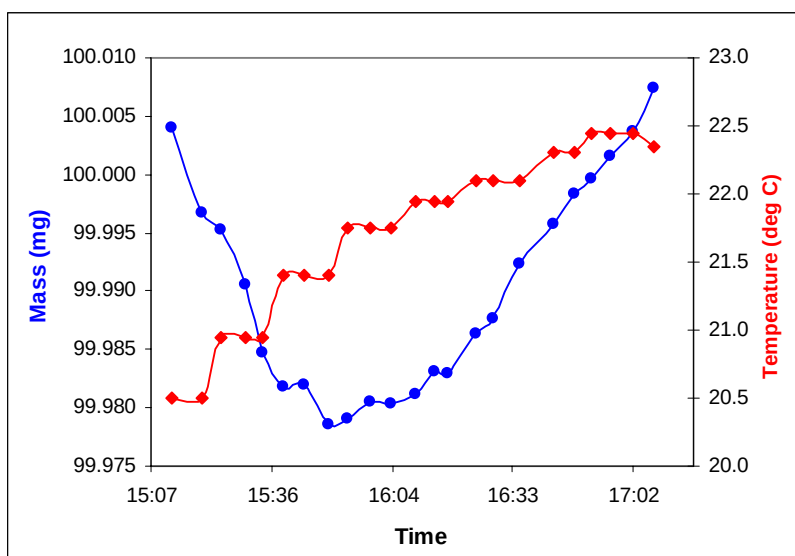


Figure 5: Typical long-term drift pattern (UMT5 balance, 100 mg span drift). The graph shows the mass of the 100 mg piece (blue) and the ambient temperature (red)

The short-term drift of each balance was assessed by placing a 100 mg mass piece on the balance and recording its mass every ten seconds for a period of ten minutes. Figure 6 shows a typical drift pattern for the UMT5 balance. Although there is a general trend for the reading to drift upwards at a constant rate (which may be corrected for by use of a tare filter), there are periodic excursions of 1 or 2 μg in the data (at intervals of approximately 50 s). When weighing a filter, it is therefore beneficial to allow the balance reading to stabilise fully before recording the mass.

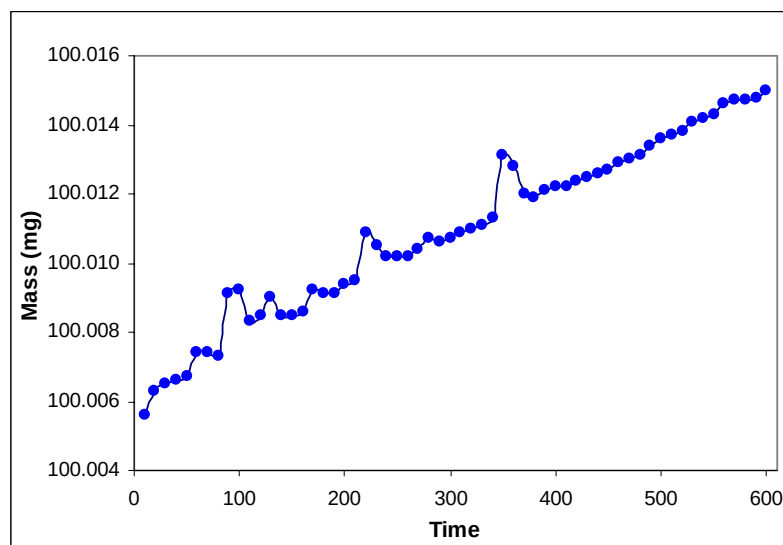


Figure 6: Typical short-term drift pattern (UMT5 balance, 100mg span drift) illustrating the random excursions observable on a timescale of approximately 50s.

Table 2 quantifies the drift recorded on both balances. (The UMT5 balance has two sets of data for its long-term drift, to characterise the negative and positive slopes in the above graph.)

	UMT5 Balance			AT261 Balance	
	Long-term Span drift	Long-term Zero drift	Short-term Span drift	Short-term Span drift	Long-term Zero drift
Duration (min)	37.3	49.0	9.8	186.1	171.0
Drift (μg)	-25.5	-36.0	9.4	1560	1300
Rate ($\mu\text{g}/\text{min}$)	-0.7	-0.7	1.0	8.4	7.6
Duration (min)	77.5	283.3	-	-	-
Drift (μg)	28.9	104.5	-	-	-
Rate ($\mu\text{g}/\text{min}$)	0.4	0.4	-	-	-

Table 2: Quantification of drift characteristics (UMT5 & AT261 balances)

The span and zero drift of the balances are shown to be approximately $\pm 1 \mu\text{g}.\text{min}^{-1}$ (UMT5 balance) and $\pm 8 \mu\text{g}.\text{min}^{-1}$ (AT261 balance). Investigations were carried out to ascertain whether the balance drift is related to the ambient temperature – no direct correlation was observed.

The results show that to keep errors below the nominal value of $20 \mu\text{g}$, drift cannot be allowed to go unchecked for more than around 20 minutes (on the UMT5) or 2 minutes (on the AT261).

3.4 Repeatability

3.4.1. Balance repeatability

‘Repeatability’ is defined as “measurement precision under repeatability conditions of measurement”. ‘Condition of measurement’ is in turn defined as “a set of conditions including the same measurement procedure, same operator, same measuring system, same operating conditions and same location, and replicated measurements over a short period of time”.

The repeatability of the balances was assessed by repeatedly weighing a 200mg metal mass piece. Three procedures were used to assess the repeatability of the balance and to distinguish repeatability from balance drift. These were:

1. To record repeated measurements with no corrections being applied.
2. To record the difference between measurements of the test mass and a tare mass piece (of the same nominal weight) weighed after every repeat.
3. To record the weights of the test mass with the balance being re-zeroed in between each weighing.

Table 3 summarises the results obtained on both balances.

Balance		1. No correction	2. Tare corrected	3. Re-zeroed
UMT5	Average mass	200.0 mg	24.3 μ g	200.0 mg
	St Dev (μ g)	11.6	2.1	1.1
	Range (μ g)	32.9	7.7	3.1
	Duration (min)	61	61	61
AT261	Average mass	200.3 mg	23.3 μ g	200.0 mg
	St Dev (μ g)	207.4	11.4	16.6
	Range (μ g)	560	40	50
	Duration (min)	62	62	62

Table 3: Repeatability characteristics of different balances and weighing methods. ‘Range’ is the difference between the maximum and minimum mass recorded.

For the above data, it can be concluded that the application of a correction, either by use of a tare mass piece, or by zeroing the balance between measurements, leads to an acceptable repeatability for the measurement by eliminating drift. The same conclusion was obtained when the experiment was repeated using a 100mg mass piece.

3.4.2 Filter mass repeatability

Studies were carried out on circular, 44 mm diameter, cuts of QM-A, GF-A and GF10 filters to determine whether weighing repeatability was most improved by use of the tare or re-zeroing methods. Each filter was weighed 10 to 15 times in succession, using each of the three methods detailed above. Static charges were allowed to dissipate fully before the mass was recorded. The typical standard deviations achieved for the different types of filters and weighing procedures are given in Table 4 (in μ g):

Filter	UMT5 balance			AT261 balance		
	1. No correction	2. Tare corrected	3. Re-zeroed	1. No correction	2. Tare corrected	3. Re-zeroed
QM-A	6.0	4.6	1.7	57.1	14.3	19.6
GF-A	10.1	1.0	3.4	59.3	8.9	24.5
GF10	11.4	7.4	3.0	95.8	5.3	28.0

Table 4: Standard deviations (in μg) of repeated weighing using different filter types, balances and weighing methods. The approximate masses of each filter type are QM-A: 134 mg; GF-A: 87 mg; GF10: 102 mg.

As was found when using a metal mass piece, the use of a tare correction or re-zeroing significantly reduces the standard deviation of each set of repeat measurements for all balances and filter types.

The tare corrected procedure is quicker than re-zeroing the balance, particularly in the case of the more sensitive balance. The tare corrected procedure was therefore selected as the most efficient way of controlling the effect of balance drift, and in subsequent experiments, a tare filter was weighed after every two sample filters. To ensure that the weight of these tare filters did not vary beyond acceptable limits, they were regularly weighed against other filters and metal mass pieces.

Use of the tare correction procedure keeps balance variations from run-to-run to an acceptable level, around 5 μg on the UMT5 balance.

3.5 Static Charges

In order to quantify the effects of static charges on the recorded mass of filters of different material, filters were artificially charged (using a static gun) and immediately placed on the balance pan. The mass of the filter was then recorded every ten seconds until a stable reading was attained. Three different methods designed to dissipate or neutralise static charges were then investigated:

- Use of a static gun
- Use of a static fan
- Weighing filters on aluminium foil

The results presented here are for artificially charged filters only; similar results have been found usually naturally charged filters during routine work in the laboratory. Artificially charged filters were selected for study in order to investigate the removal of very large quantity of static - effectively a worse case scenario.

Figure 7 shows the effect of static charges on the apparent mass of a typical filter (filter 760, Munktell quartz fibre). The filter was artificially charged and placed directly onto the balance pan; the mass being recorded every ten seconds. This process was then repeated, but with the filter being weighed on a piece of aluminium foil. Finally, the foil was removed and the filter re-weighed directly on the balance pan.

The initial weighing showed the static to cause a large instability in the balance reading, but this was almost entirely eliminated when the same filter was subsequently weighed on a piece of aluminium foil.

These results show that weighing filters on aluminium foil is a very simple and effective method for rapidly stabilising the effect of static charges. Similar results were obtained for filters of all materials studied (see below).

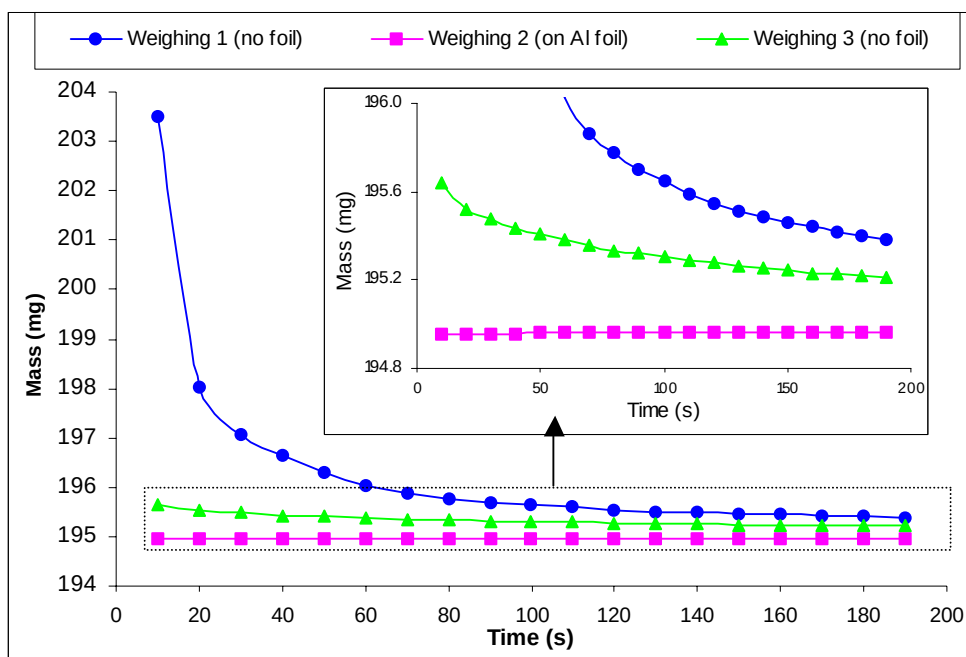


Figure 7: Effect of static charges on the observed mass of a quartz filter. In weighing 2 (on aluminium foil), the mass of the filter changes by only $1\mu\text{g}$ between $t = 90\text{ s}$ (the time where readings are recommended to be taken) and $t = 190\text{ s}$.

Table 5 shows data for different filter types and different techniques investigated to neutralise static. The data is presented in the form of mass change (in μg) for the first three sixty-second periods after placing the filter on the balance.

Filter Type	Filter ID	Weighing	Mass change (μg) during time period:		
			0-60s	61-120s	121-180s
Quartz	760	1 (initial)	7478.3	323.0	108.3
		2 (on Al foil)	11.2	0.2	0.5
		3 (no foil)	260.7	80.5	45.1
Glass Fibre	771	1 (initial)	1067.2	23.8	4.0
		2 (on Al foil)	3.0	1.0	0.4
		3 (no foil)	2.7	0.2	-
PTFE	775	1 (initial)	102.4	80.2	41.1
		2 (on Al foil)	29.2	4.1	1.4
		3 (no foil)	190.2	102.7	56.0
Pallflex Emfab	1022	1 (initial)	1886.4	0.7	-
		2 (on Al foil)	124.6	0.2	-
PTFE	774	1 (initial)	2361.0	1633.0	895.0
		2 (static fan)	95.2	1.3	1.1

Table 5: Data showing the effects of static charges on filters of different material and the removal of the charges by the use of aluminium oil or a static fan

The table shows that the use of aluminium foil is an effective method for the removal of static charges from filters. With these methods, acceptably stable balance readings can routinely be achieved for all filter types after 90 s (high resolution UMT5 balance) or 60 s (AT261 balance). Due to its inherent simplicity, the use of aluminium foil is proposed as the most efficient method. Storing the metal filters on aluminium foil and handling them with metal tweezers has also been shown to assist in discharging static.

The results of the above study were used to produce a balance protocol (see Appendix 1), defining the optimum weighing procedure for filters. The use of the protocol substantially reduces the expanded uncertainty inherent in the weighing of a single filter, such that for suitable filters the uncertainty is close to 20 μg with 95% confidence. The uncertainty budget is set out in Appendix 2.

3.6 Summary

- Balances should be exercised before use and whenever the balance has been idle for a period of 20 minutes or more. Taking measurements before exercising a balance has been shown to incur errors in the region of $\pm 3 \mu\text{g}$ (0.1 μg resolution balance) or $\pm 30 \mu\text{g}$ (10 μg resolution balance).
- Balances may drift considerably in the long-term, in the region of $\pm 1 \mu\text{g}.\text{min}^{-1}$ (0.1 μg resolution balance) and $\pm 8 \mu\text{g}.\text{min}^{-1}$ (10 μg resolution balance). For this reason frequent allowance for drift needs to be made. A tare correction has been found to be the most efficient way of eliminating drift: a tare filter (of the same material) should be weighed after every two sample filters.
- To allow for correction of any inadvertent change in the tare filter, a ‘check’ filter (of the same material) should be weighed against the tare filter at least once

every 30 weighings. The 'check' filter should also be weighed regularly against a calibrated mass piece.

- The effect of static charges can be most effectively removed by weighing filters on a piece of aluminium foil placed on the balance pan. Acceptably stable readings may then normally be achieved after 90 s (0.1 µg resolution balance). Storing the filters on aluminium foil and handling them with metal tweezers also assists in discharging static.

3.7 Recommendation

- The findings detailed above have been used to produce a balance protocol (see Appendix 1), defining the optimum weighing procedure for filters. It is recommended that this procedure be used in future studies. However, it should be noted that the advice given in it is based on data from the two balances used in this study only, so the suitability of these recommendations should be confirmed before applying them to different balances.

4. EFFECTS OF TEMPERATURE AND HUMIDITY ON BLANK FILTERS

It is well known that changes in ambient conditions, particularly temperature and relative humidity, can have a significant effect on the measured mass of ambient air monitoring filters. In order to study and quantify these effects, a lengthy series of experiments was undertaken weighing the mass of filters of different materials at different ambient conditions. A similar experiment using loaded filters is described in Section 5. The aims were to assist in recommending a filter type for high accuracy work, to assess the contribution to the particle mass uncertainty from this factor, and to assess whether the current recommended period for conditioning filters (usually 48 hours) is adequate.

4.1 Experimental

The following blank filters (44 mm diameter, except where stated) were used in the study:

- 15 QM-A filters
- 15 GF-A filters
- 15 GF10 filters
- 15 Emfab filters (47 mm diameter)

Each filter was weighed against a tare filter after conditioning for 48 and 72 hours under the conditions shown in Table 6. Each filter was therefore weighed eight times in total. The tare filters were the same size, same material and stored under the same conditions as the filters being tested.

Weighing	QM-A, GF-A & GF10 Filters		Emfab Filters	
	Temp / °C	RH / %	Temp / °C	RH / %
1 & 2	20	50	20	50
3 & 4	18	40	22	60
5 & 6	22	60	18	40
7 & 8	20	50	20	50

Table 6: Temperature and relative humidity (RH) conditions used during the study of the effects of environmental conditions on filter mass

The decision to weigh filters by reference to a tare of the same material at the same conditions means that the *actual* weight change of the filters in different conditions is not determined. What is measured is the *variability* in mass using the tare reference procedure, which was found to be the most suitable way of compensating for drift. This is the relevant parameter for assessing uncertainties in the data when this method is used.

4.2 Data Correction

As the mass of each filter was recorded against that of an appropriate tare filter and the study took over two weeks to complete, it was inevitable that the tare filters used would suffer some slight damage from constant handling. To monitor this, each tare filter was weighed on a daily basis against other ('check') filters of the same material; these in

turn were weighed periodically against calibrated metal mass pieces to ensure that their mass did not change over time.

Figure 8 shows the mass of the Emfab tare filter used in this experiment, relative to a check filter of the same size and material. The loss of mass of the tare filter over time was corrected for by fitting a trend line to the data for each filter type and using the equations of the lines used to produce mathematical ‘correction factors’. These correction factors were subtracted from the tare-corrected data of each individual filter, resulting in a set of data adjusted to account for any changes in mass of the tare filter. Further details of the data correction procedure are given in Appendix A1.8 and the full set of experimental data after correction is shown in Appendix 3.

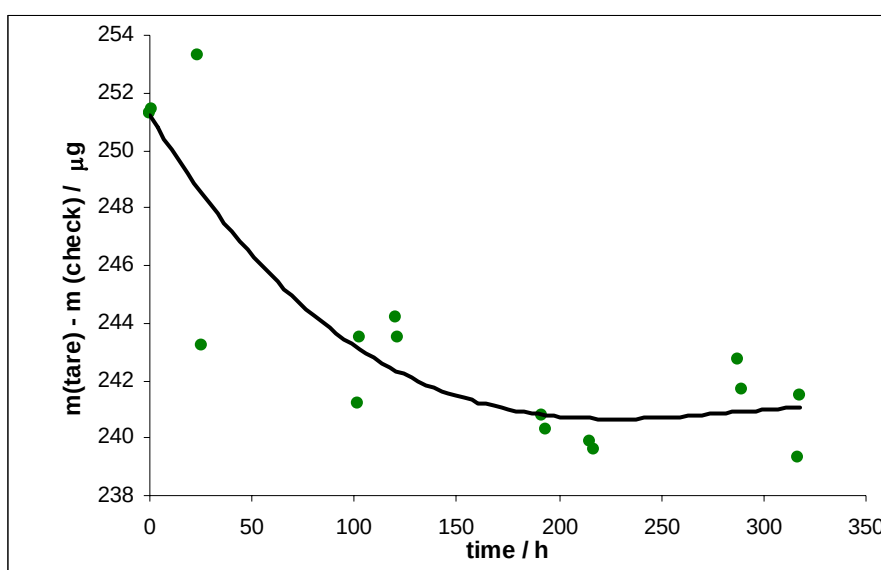


Figure 8: Variation in the mass of the Emfab tare filter (with respect to its ‘check’ filters) over a period of two weeks. The data was fitted with the polynomial curve shown to enable calculation of correction factors to account for losses of the tare filter

4.3 Results & Discussion

For each filter type studied, Figure 9 shows plots of the average blank filter mass (relative to the tare). In ideal circumstances weighings 1, 2, 7 and 8 should report the same mass, within the uncertainty of the experiment, as they were conditioned at the same temperature and relative humidity.

The mass differences are summarised in Table 7.

The plots and data show that there is a large variation in the behaviour of different types of filter. The Pallflex Emfab (glass fibre and PTFE) filters show remarkable stability; the masses recorded being virtually unaffected by any changes in temperature and relative humidity and highly repeatable from day-to-day. The results for the other filter types were worse by an order of magnitude.

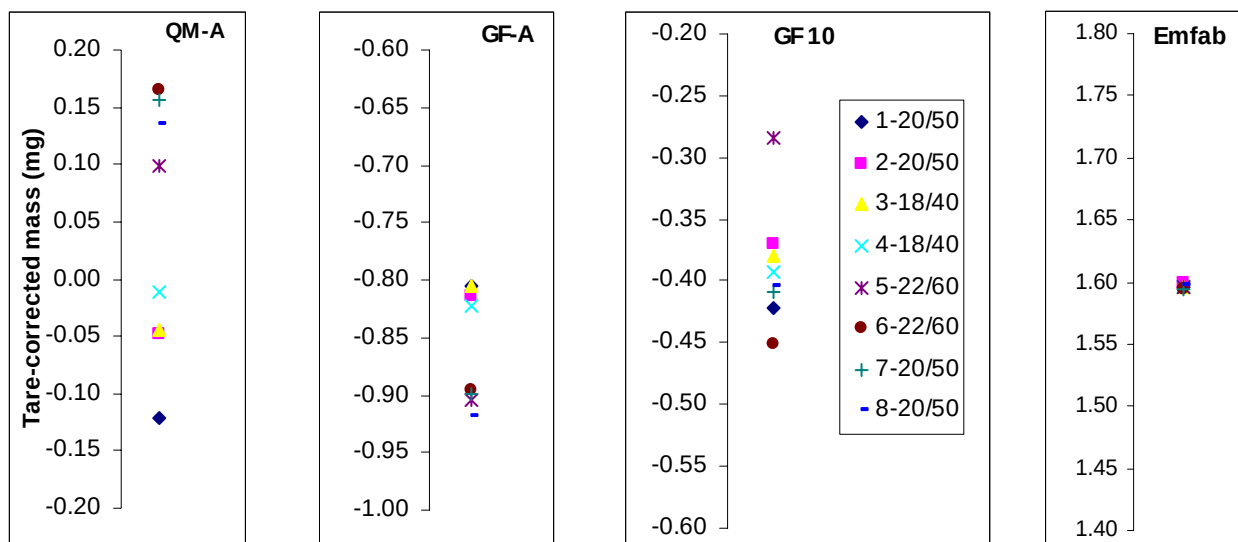


Figure 9: Average mass of the blank filters of each material (QM-A, GF-A, GF10 and Emfab) at each of the eight weighing conditions outlined in Section 4, plotted on the same scale. Note that for the Emfab filters only, weighings 3 & 4: 22 °C / 60% RH; weighings 5 & 6: 18 °C / 40% RH.

Filter Type	Range / μg	20°C / 50% W2-W1 / μg	18°C / 40% W4-W3 / μg	22°C / 60% W6-W5 / μg	20°C / 50% W8-W7 / μg
QM-A (blank)	287	74	34	66	-21
GF-A (blank)	114	-8	-18	8	-20
GF10 (blank)	82	51	-14	-	5
Emfab (blank)	4	3	0	-1	3

Table 7: Data showing the range and daily repeatability of the average masses of the blank filters for each material. The range is the difference between the maximum and minimum mass recorded; the subsequent columns show the difference in the consecutive daily weighings at the same temperature and RH conditions.

For all filter types, except QM-A, the difference between masses after conditioning for 48 and 72 hours is small. The Emfab filters again produce very stable results, with masses varying by no more than 3 μg from day-to-day. The data implied that the current recommendation of conditions filters for 48 hours prior to weighing is sufficient for these filters.

4.4 Summary

- A large variation in the behaviour of different types of filter is evident in this investigation. The Pallflex Emfab (glass fibre and PTFE) filters show remarkable stability, consecutive weighings reporting masses that differ by no more than 3 μg . This compares with around 100 μg for glass fibre filters and 300 μg for quartz filters.

- It is necessary to correct for damage to the tare and check filters when weighing filters over a extended period of time. Full details of the data correction procedure are given in Appendix A1.8.
- A period of 48 hours is sufficient to condition blank filters before weighing.

4.5 Recommendations

- From the results obtained from the study of blank filters, Pallflex Emfab filters are recommended for use for ambient air monitoring. In addition to their excellent repeatability, the filters are very robust in comparison with quartz or glass fibre filters and are therefore less liable to lose mass when handled.
- The application of corrections to account for damage to the tare and check filters is recommended. Full details of the data correction procedure are given in Appendix A1.8.

5. EFFECTS OF TEMPERATURE AND HUMIDITY ON LOADED FILTERS

To accompany the study of blank filters discussed in Section 4, a parallel investigation was carried out using loaded filters of the same material, in order to assess the effect of a real ambient air sample on the data.

5.1 Experimental

The following loaded filters (44mm diameter, except where stated) were used in the study:

- 12 QM-A filters – 24 hour sampling
- 12 GF-A filters – 24 hour sampling
- 12 GF10 filters – 24 hour sampling
- 12 GF10 filters – 72 hour sampling
- 12 Emfab filters (47 mm diameter) – 24 hour sampling

Ambient air samples were collected using a high volume ($67.8 \text{ m}^3 \text{ h}^{-1}$) sampler and cut using a 44mm diameter punch (QM-A, GF-A and GF10 filters), or a low volume ($2.3 \text{ m}^3 \text{ h}^{-1}$) sampler (Emfab 47mm diameter filters.) Two sampling periods (of 24 and 72 hours) were used for GF10 filters in order to simulate lightly and heavily loaded samples. The local PM_{10} content of ambient air [5] during the periods of operation of the high-volume sampler is shown in Figure 10:

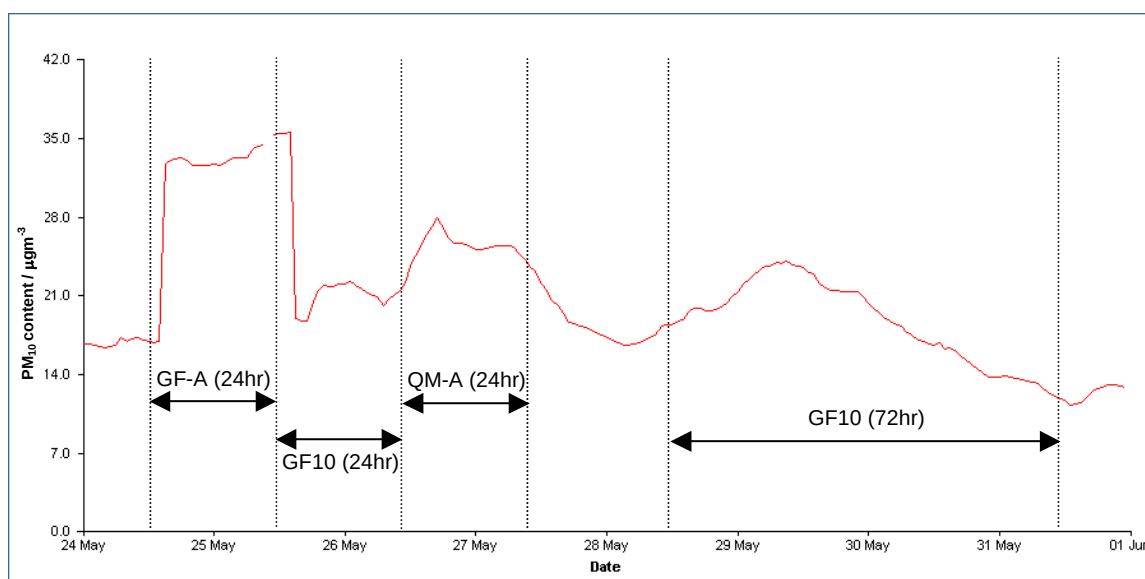


Figure 10: Measured PM_{10} content of ambient air at a monitoring station in the London Borough of Richmond-upon-Thames between 24 and 31 May 2004. Data is plotted as 24 hour rolling mean values in $\mu\text{g.m}^{-3}$; the sampling periods undertaken at NPL are indicated by the arrows on the chart

Each filter was weighed (against an appropriate tare) eight times after conditioning in the same environment as outlined in Section 4.1. Data corrections (detailed in Section 4.2) were applied to account for losses in the tare filters during the experiment.

5.2 Results & Discussion

Figure 11 shows plots of the average blank filter mass (relative to the tare) for each filter type under each weighing conditions:

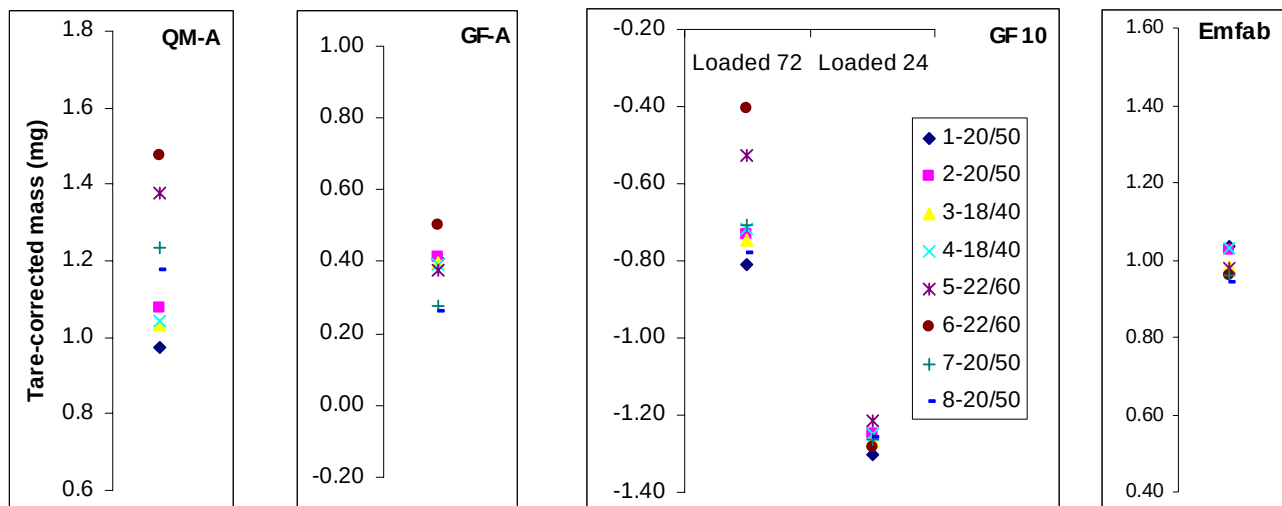


Figure 11: Average mass of the loaded filters of each material (QM-A, GF-A, GF10 and Emfab) at each of the eight weighing conditions outlined in Section 4.1, plotted at the same scale. Note that for the Emfab filters only, weighings 3 & 4: 22 °C / 60% RH; weighings 5 & 6: 18 °C / 40% RH.

The results are summarised in Table 8:

Filter Type	Range / μg	20°C / 50% W2-W1 / μg	18°C / 40% W4-W3 / μg	22°C / 60% W6-W5 / μg	20°C / 50% W8-W7 / μg
QM-A (loaded, 24h)	505	105	9	99	-57
GF-A (loaded, 24h)	242	3	-2	125	-19
GF10 (loaded, 72h)	403	79	30	120	-73
GF10 (loaded, 24h)	90	56	18	-67	4
Emfab (loaded, 24h)	94	-10	49	-19	-15

Table 8: Data showing the range and daily repeatability of the average masses of the loaded filters for each material (see Table 7 for further explanation) The times expressed as, for example, 'loaded, 24h', indicate the sampling period undertaken

For the QM-A and GF-A filters, the effects of conditioning on the particulates may be deconvoluted from the effects on the filter material. The range of results due to the effect of conditioning on the particulate matter only is calculated by subtracting the data in Table 7 from that in Table 8; the results are expressed (in μg and as a percentage of the average particulate mass collected during the sampling period) in Table 9.

Filter Type	Range / μg	PM ₁₀ concentration over sampling period / μgm^{-3}	Average particulate mass / mg	Range relative to average particulate mass
QM-A (24h)	218	22	1.1	19.8%
GF-A (24h)	128	35	1.2	10.7%

Table 9: Comparison of the range of masses of loaded filters (and the measured particulate mass) with the PM₁₀ content of ambient air recorded by the London Air Quality Network. The PM₁₀ concentration is stated as the 24-hour rolling average (or the sum of three 24-hour rolling average in the case of the 72 hour sample). No average particulate mass is reported for the GF10 filters due to the relatively high variability observed in the masses of the blank filters

As with the blank filters, a large variation in the behaviour of different types of filter is observed; here the Pallflex Emfab and GF10 filters show the best repeatability, followed by GF-A and QM-A. In all cases, it is noticeable that the repeatability is substantially larger than that for the blank filters, attributable to the variations in the particulate mass.

The effect of conditions on the observed mass of the particulates has been shown to be around 10-20% of the particulate mass. However, such data is only available from two of the samples studied.

The masses of the loaded filters (relative to the tare) increase with increasing temperature and humidity, the highest relative masses being recorded for weighings 5 and 6 (22°C and 60% RH). There is not such an evident effect for the filters when they are conditioned at 18°C / 40% RH and 20°C / 50% RH, which yield consistent results within the uncertainty of the experiment.

The day-to-day variability of the data (after 48 and 72 hours of conditioning) is also substantially greater than that of blank filters for all filter types. Although there is not an obvious correlation between recorded mass and conditioning time, the data implies that loaded filter may benefit from conditioning for a longer period than 48 hours.

The above two effects are more pronounced when the sample has a higher particulate loading: this can be seen by comparing the results for GF10 filters sampled for 24 and 72 hours. The variability on the data is much larger for the 72 hour sample than the blank tare.

5.3 Recommendations

- From the results obtained from the study of loaded filters, Pallflex Emfab or GF-10 filters both appear suitable for use for ambient air monitoring. When taking into account the results in Section 4 and the robustness of the filters, Pallflex Emfab are recommended.
- Loaded filters exhibit correlation between mass and conditioning temperature / humidity with variations in the particulate mass of 10-20% being observed in the range of conditions used.
- Loaded filters may need conditioning for more than 48 hours before weighing.

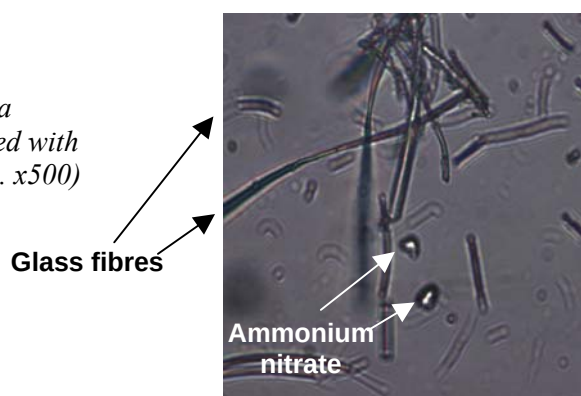
6. EFFECTS OF STORAGE AND TRANSPORT: NAPHTHALENE AND AMMONIUM NITRATE SPIKING

The loss of volatile and semi-volatile species from sampled filters has been well documented. In an attempt to quantify such losses, and to recommend conditions for the storage and transport of filters, investigations were carried using a series of filters artificially loaded with semi-volatile material. Two semi-volatile compounds, ammonium nitrate and naphthalene, were used. Filters were spiked with solutions of the two compounds in organic solvents (methanol and diethyl ether respectively). The solvent rapidly evaporates from the filter, leaving the semi-volatile material remaining in fine polycrystalline form.

6.1 Structure and Behaviour of Semi-Volatile Material Spiked onto Filters

Optical microscopy was used to study the structure and conformation of ammonium nitrate and naphthalene on the filter. After spiking and solvent evaporation, both substances were found to exist in polycrystalline structures with crystal diameters in the ranges of 1-3 μm (ammonium nitrate, see Figure 12) and 5-10 μm (naphthalene).

Figure 12: Optical microscope image of a section of a glass fibre (GF10) filter spiked with ammonium nitrate (magnification approx. x500)



Initial experiments were carried out to assess the volatility of the two compounds selected for study. When spiked onto filters in milligram quantities and stored at ambient conditions, all traces of naphthalene were lost within 1-2 hours (see Figure 13), the loss rate being approximately 2 mg.h^{-1} . Storing the spiked filters in a refrigerator slowed the evaporation of the naphthalene to approximately 0.5 mg.h^{-1} .

Similar experiments using ammonium nitrate spiked filters revealed ammonium nitrate to be far less volatile than naphthalene; ammonium nitrate spiked filters stored under ambient condition recorded no mass loss, even after a period of several days. When stored at elevated temperature, some mass loss was recorded, but only at temperatures greater than 50°C . The reason for the difference between this observation and the known volatility of ammonium nitrate in real samples is not clear.

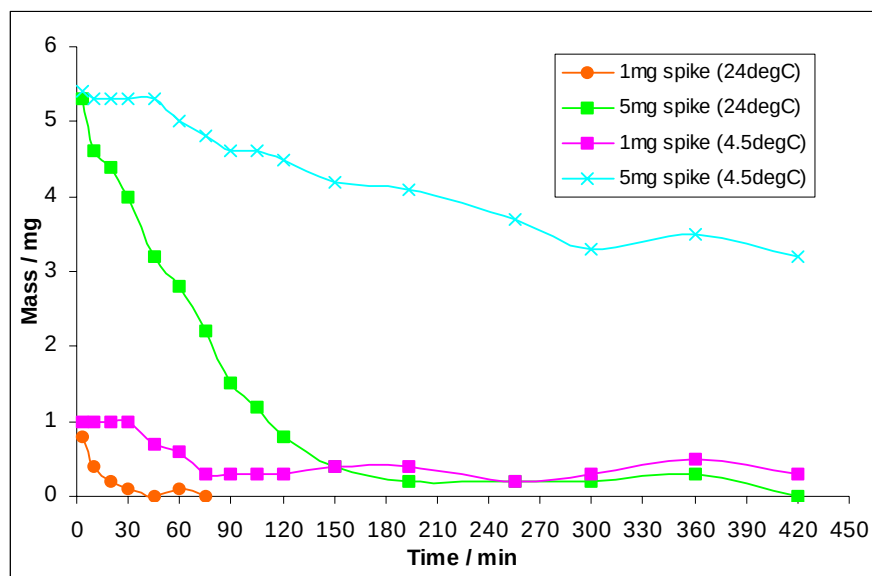
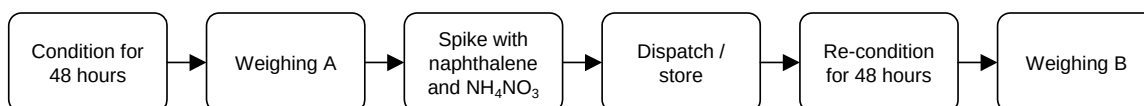


Figure 13: Graph showing the loss of naphthalene spiked onto filters with time. Filters were spiked with 1mg or 5mg of naphthalene and stored either in ambient conditions (24 °C) or in a refrigerator (4.5 °C)

6.2 Storage and Transport: Quartz & Glass Fibre Filters

To study the effects of storage and transport on filters, a series of blank and loaded QM-A and GF10 filters underwent the following process:



Some filters were spiked with nominally 1 mg of naphthalene and 2 mg of ammonium nitrate. The uncertainty in the spiked mass was expected to be about 20 µg, so that direct comparison between the spiked samples must be made only with caution. The filters were stored or transported under the following different conditions:

- Posted to Casella Stanger and immediately returned to NPL in sealed filter holders (see Figure 14)
- As (a), but in open, separated, filter holders
- Stored under controlled conditions (20°C / 50% RH) at NPL
- Stored in a refrigerator at NPL
- Thermally cycled (between 6°C and 35°C) daily at NPL

During transport, batches (a) and (b) were subject to a temperature range of 17 to 26°C, as measured by a portable thermometer. Upon return of these batches to NPL (three days after despatch), all filters were re-conditioned and re-weighed.

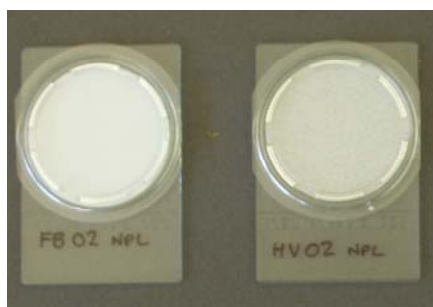


Figure 14: Photograph showing two filters in sealed holders (batch (a) of the five storage and transportation conditions investigated – see above for full details)

6.3 Transport: Emfab Filters

In a supplementary study, five blank and five loaded Emfab filters were weighed and NPL, despatched in the post and re-weighed upon return (after conditioning at 20°C and 50% RH). The filters were not spiked with semi-volatile material. The temperature conditions experienced during transport were recorded and found to diurnally vary between approximately 22°C and 27°C.

6.4 Results and Discussion

For the quartz filters, the differences (in μg) between the masses recorded in weighings A and B are given in Table 10(a). To compensate for a small change in the mass of the tare filters during the experiment, the tare correction described in Appendix A1.8 was applied to the data.

Batch	Conditions	Recorded mass change / μg			
		Blank, spiked	Blank	Loaded, spiked	Loaded
(a)	Posted in sealed filter holders	+ 1912	- 76	+ 1841	- 127
		+ 1891	- 22	+ 2007	
(b)	Posted in open, separated, filter holders	+ 1962	- 154	+ 1901	- 173
		+ 1965	- 65	+ 1888	
(c)	Stored at 20°C and 50% RH	+ 1938	- 75	+ 1944	- 121
		+ 2006	- 78	+ 1969	
(d)	Stored in a refrigerator	+ 1925	- 16	+ 1981	- 83
		+ 1943	- 60	+ 1962	
(e)	Thermally cycled (6°C to 35°C) daily	+ 1888	- 97	+ 1968	- 134
		+ 1921	- 108	+ 1976	

Table 10(a): Results of filter storage and transport experiments (QM-A filters). The data shows the difference (in μg) between the masses of the filter recorded before and after transport or storage (weighings A and B in the above flow chart)

From the above data, it is clear that all the spiked filters exhibited a mass increase of approximately 2 mg from the initial weighing. This is thought to be due to the

ammonium nitrate remaining on the filter throughout the experiment, implying that ammonium nitrate spiked in this fashion is non-volatile. It is expected that no traces of the naphthalene remain.

All of the non-spiked filters (columns 'Blank' and 'Loaded' in Table 10(a)) are shown to lose mass (shown as negative figures) between the two weighings. The losses are lowest for filters stored in a refrigerator, and highest for those posted in open holders, indicating that storage and transport conditions are crucial to ensure accurate weighing. The mass losses observed with the blank filters are attributable to the loss of filter material – an expected problem with quartz filters.

The same data for the GF10 glass fibre filters is presented in table 10(b):

Batch	Conditions	Recorded mass change / μg			
		Blank, spiked	Blank	Loaded, spiked	Loaded
(a)	Posted in sealed filter holders	+ 2161	- 14	+ 2252	-5
		+ 2129	+ 16	+ 2224	
(b)	Posted in open, separated, filter holders	+ 2166	- 24	+ 2207	- 28
		+ 2091	- 39	+ 2218	
(c)	Stored at 20°C and 50% RH	+ 2095	-10	+ 2167	-3
		+ 2173	+ 45	+ 2180	
(d)	Stored in a refrigerator	+ 2126	- 22	+ 2181	-1
		+ 2143	n/a	+ 2181	
(e)	Thermally cycled (6°C to 35°C) daily	+ 2124	-8	+ 2243	0
		+ 2112	- 20	+ 2202	

Table 10(b): Results of filter storage and transport experiments (GF10 filters). The data shows the difference (in μg) between the masses of the filter recorded before and after transport or storage (weighings A and B in the above flow chart)

Unlike the QM-A filters, the GF-10 filters display little discernable trend between the five batches. This indicates that under the conditions of this experiment (including conditioning for 48 hours before re-weighing), storage and transport conditions have little effect on the volatility of ammonium nitrate and naphthalene, and on the stability of the collected mass on these filters.

A greater mass of semi-volatile material was lost from the QM-A filters than the GF10 filters. This implies that semi-volatile material is bound more tightly to the GF10 filter fibres.

The results for the Emfab filters are shown in Table 11 in the form of the mass difference between the two weighings (before and after transport):

	Recorded mass change / μg	
	Blank	Loaded
Individual Filters	- 21	-39
	-30	-41
	-20	-77
	-20	-14
	-28	-35
Average	-24	-41

Table 11: Results of filter transport experiments (Emfab filters). The (non-spiked) filters were weighed before despatch and on return to NPL. The temperature conditions experienced during transport were recorded and found to vary diurnally between approximately 22 °C and 27 °C.

The blank Emfab filters experienced approximately the same change in mass during transport as the GF10 filters (Table 10). The loaded filters however, show an average loss of 41 μg during transport, a larger loss than for the GF10 filters. This is most likely caused by an increase in the quantity of semi-volatile material lost due to the elevated temperatures experienced during transport (the average temperature was approximately 2°C higher than for the GF10 filters). A more direct comparison is difficult as the filters were loaded and transported at different times.

6.5 Summary

- The observed losses from QM-A filters are lowest for those stored in a refrigerator, and highest for filters posted in open holders. This was found with both blank and loaded filters and is therefore likely to be caused partly by loss of filter material during transport. The GF10 and Emfab filters exhibit much smaller mass changes and are therefore the most robust filter types for transporting through the post.
- The losses of semi-volatile material observed with the QM-A filters imply that such compounds are bound more tightly to glass fibres than quartz fibres.
- Storage and transport conditions have little effect on the volatility of artificially-spiked ammonium nitrate and naphthalene on GF10 filters.

6.6 Recommendation

- Both GF10 and Emfab filters have been successfully transported by post without significant mass change using sealed plastic containers. These types of filters and storage containers are recommended when transportation is required

7. EFFECTS OF DIFFERENT WEIGHING LABORATORIES

The variability of filter weighings between laboratories was studied with the aim of determining whether variability from weighing at different laboratories was comparable with the variability caused by transport to a central weighing laboratory.

7.1 Experimental

The following filters were used in the study:

- 5 QM-A filters – blank
- 5 QM-A filters – loaded (24 hour sampling)
- 5 GF10 filters – blank
- 5 GF10 filters – loaded (24 hour sampling)

The filters underwent the following procedure:

Weighing A: NPL (24 June 2004)

Transport: NPL to Casella Stanger, Runcorn (25-28 June 2004)

Weighing B: Casella Stanger (7 July 2004)

Transport: Casella Stanger to NPL (22-26 July 2004)

Weighing C: NPL (29 July 2004)

Weighings were carried out using each laboratory's in-house procedure after conditioning of the filters for at least 48 hours at 20°C / 50% RH. All filters were transported in sealed plastic filter holders, accompanied by a temperature logger.

7.2 Results and Discussion

Each filter was weighed against a tare filter of the same material. For each sample, the average filter mass at each weighing (with Weighing A: NPL re-defined as zero) is given in Table 12:

Filter Type	Mass of filter with respect to tare / μg		
	Weighing A (NPL)	Weighing B (Casella S.)	Weighing C (NPL)
QM-A (blank)	0	-27	+3
QM-A (loaded)	0	+23	-104
GF10 (blank)	0	-2	+4
GF10 (loaded)	0	+29	-39

Table 12: Average filter mass recorded at each of the three weighing define above. All values are presented with Weighing A: NPL re-defined as zero.

The temperature profile experienced by the filter during transport is shown in Figure 15:

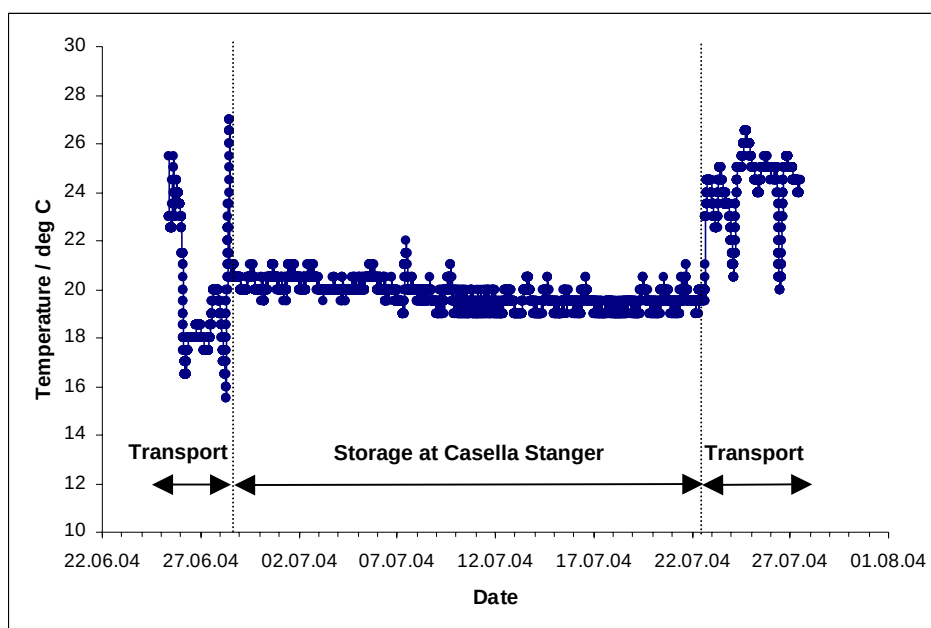


Figure 15: Temperature profile experience by the filters during transportation from NPL to Casella Stanger and return to NPL.

The data in Table 12 shows a very good agreement between the Weighings A (NPL) and B (Casella Stanger), the maximum variation being only 29 μg , implying that the outward transportation did not affect the mass of the blank or loaded filters to any appreciable extent.

A more interesting effect is observed between Weighings B (Casella Stanger) and C (NPL), after the return transport. Here, there is again little variation in the mass of the blank filters, but much larger changes are observed in the masses of the loaded filters, particularly the loaded GF10 filters, which exhibit an average mass loss of 104 μg . As the two laboratories have already demonstrated comparability of weighings and the effect is not observed with blank filters, it is likely that the mass loss is due to the loss of volatile material during return transport to NPL. Figure 15 shows the average temperature during return transport to be approximately 24°C, compared to only 19°C during initial transport to Casella Stanger. This increase in temperature is therefore likely to be the cause of the loss of volatile material.

7.3 Summary

- Independent weighing of a series of filters by two laboratories yielded results within the experimental uncertainties for those filter types.
- Loss of particulate material was observed on quartz filters when transported at an average temperature of 24°C.

7.4 Recommendations

- It is recommended that weighing facilities local to the monitoring sites should be utilised where available, as the disadvantages of using more than one weighing laboratory are outweighed by the benefits of more easily controlled storage and reduced transport.
- If transportation of loaded filters is essential, all filters should be stored in sealed containers and not exposed to temperatures above 20°C. However, prevention of other unexpected events during transport is difficult to ensure.

8. CONCLUSIONS FOR FILTER MATERIAL SELECTION

The study covered a number of factors to assist in the selection of a filter material for use in ambient air monitoring studies. The most important factors to consider when selecting a filter medium can be summarised as:

1. Variation of weight with temperature and relative humidity – Sections 4 & 5
2. Structural integrity (including resilience to transport) – Section 7
3. Flow resistance (tendency for the filter to become blocked with sampled material)
4. Chemical effects (e.g. adsorption of gases, nitrate retention, etc.)
5. Particle sampling efficiency
6. Static charge effects

Other effects that may be important for specific applications are blank levels (for chemical analysis), thermal stability (when sampling hot exhausts) and cost and availability. All the filters used in this study are routinely available from commercial suppliers; the costs of the filters vary between approximately 15p (GF10) to 110p (Emfab) per filter.

The four main types of filter material (PTFE, quartz, glass fibre with binder and Emfab) can be assessed against the six criteria listed above:

Criterion	Filter Material			
	PTFE membrane	Quartz	Glass fibre with binder	Emfab
1	Very good	Moderate	Moderate	Very good
2	Very good	Poor	Good	Good
3	Poor	Good	Good	Good
4	Good	Moderate	Moderate	Good
5	Good	Good	Good	Good
6	Poor	Moderate	Moderate	Moderate

Table 13: Summary table assessing the four most widely-used filter materials against the six criteria listed above. Some of the assessments are made using information from References [1] and [6].

We therefore conclude that the Emfab filter is most suitable for ambient PM measurements.

9. REFERENCES

- [1] CHOW, J.C., Measurement methods to determine compliance with ambient air quality standards for suspended particles, *J. Air Waste Manag. Assoc.*, 1995, **45** (5), 320–382.
- [2] CHOW, J.C., ENGELBRECHT, J.P., FREEMAN, N.C.G., HASHIM, J.H., JANTUNEN, M., MICHAUD, J-P., SAENZ DE TEJADA, S., WATSON, J.G., WEI, F., WILSON, W.E., YASUNIO, M., ZHU, T., Chapter one: Exposure measurements, *Chemosphere*, 2002, **49**, 873-901
- [3] KIRCHSTETTER, T.W., CORRIGAN, C.E, NOVAKOV, T., Laboratory and field investigation of the adsorption of gaseous organic compounds onto quartz filters, *Atmos. Environ.*, 2001, **35**, 1663-1671
- [4] TSAI, C-J., PERNG, S-N., Artifacts of ionic species for hi-vol PM₁₀ and PM₁₀ dichotomous samplers, *Atmos. Environ.*, 1998, **32**, 1605-1613
- [5] Data from The London Air Quality Network (www.londonair.org.uk)
- [6] HARRISON, D., Personal Communication

APPENDIX 1. NPL FILTER WEIGHING PROCEDURE

A1.1 Purpose

A1.1.1 This procedure describes a method for the accurate measurement of the particulate mass on ambient air monitoring filters.

A1.1.2 All filters are weighed on high-accuracy single-pan balances in a temperature and relative humidity-controlled environment. The mass of filters is reported relative to the mass of tare filters of the same material. Corrections may need to be applied to account for any loss of the tare material during the course of the weighing process.

A1.2 Scope

A1.2.1 The procedure is suitable for the weighing of ambient air filters of any material, up to 47mm in diameter.

A1.2.2 The procedure has been developed at NPL using two single pan balances: Mettler UMT5 (0.1 µg resolution) and Mettler AT261 (10 µg resolution). The procedure is strictly valid for use with these balances only; the performance of any other balances should be investigated and characterised fully before use.

A1.3 Filter Storage and Conditioning

A1.3.1 To prevent the loss of volatile- and semi-volatile species, all sampled filters should be stored in a refrigerator between sampling and conditioning.

A1.3.2 Prior to weighing, filters should be conditioned at the required temperature and relative humidity for a period of 48 hours (for blank filters) or 72 hours (for loaded filters).

A1.3.3 Filter conditioning and weighing should take place in an atmosphere-controlled cabinet. The cabinet must be capable of controlling temperature and relative humidity to better than within $\pm 1^{\circ}\text{C}$ and $\pm 5\%$ RH of the respective set values. Standard conditions within EN 12341 are $20 \pm 1^{\circ}\text{C}$ and $50 \pm 5\%$ RH.

A1.3.4 The temperature, relative humidity and atmospheric pressure should be logged continuously.

A1.3.5 All filters should be stored on aluminium foil to assist the discharge of static. Metal tweezers should be used when handling all filters.

A1.4 Preparation for weighing

A1.4.1 Mark all filters with a unique identifying number. Filters should be marked (on the side not sampled) with ink, pencil or a suitable stamp.

A1.4.2 Select suitable tare and check filters. These should be of the same material, type and size as the sample filters.

A1.4.3 Exercise the balance by repeating the following procedure three times:

- (a) Place a 1 g metal mass piece onto the balance pan.
- (b) Wait until the reading is close to 1g and remove the mass piece.

A1.4.4 Perform an internal calibration of the balance.

A1.4.5 To assist in discharging static charges, place a circular piece of aluminium foil (the same size or slightly larger than the filter) on the balance pan. Anti-static devices (guns, fans, etc.) may also be used if they have been shown to operate successfully.

A1.4.6 Re-zero the balance.

A1.4.7 Note the starting time, temperature, relative humidity and atmospheric pressure in a weighing datasheet.

A1.5 Weighing of Check filter against metal mass piece

A1.5.1 To ensure that the mass of the check filter does not change with time, weigh the check filter against a calibrated metal mass piece of a similar mass (typically 100 mg).

A1.5.2 The metal mass piece should be weighed three times and the check filter weighed twice. Use the following sequence: Mass piece, check filter, mass piece, check filter, mass piece.

A1.5.3 Follow the procedure below for each individual weighing:

- (a) Place the metal mass piece or filter on the foil-covered pan. Close the door of the balance.
- (b) Wait for 90 s (Mettler UMT5 balance), 60 s (Mettler AT261 balance), or a period of time deemed suitable after a full assessment of the short-term drift characteristics of the balance used.
- (c) Record the mass (and number) of the filter in a weighing datasheet.
- (d) Open the balance door and remove the mass piece or filter from the pan.

A1.6 Weighing of sample filters

A1.6.1. Weighing a sample filter against a tare filter automatically corrects for any changes in atmospheric conditions before and after sampling, thus rendering buoyancy effects, and humidity effects on the filter, negligible. A tare filter should be weighed every two sample filters.

A1.6.2 Any changes in the mass of the tare filter are monitored by frequent weighing of the tare filter against a check filter. A check filter should be weighed at the beginning and end of each weighing sequence, as well as after a maximum of each 30 sample filters.

A1.6.3 A typical weighing sequence is given below:

- (1) Check filter *
- (2) Tare filter †
- (3) Sample filter 1
- (4) Sample filter 2
- (5) Tare filter
- (6) Sample filter 3
- (7) Sample filter 4
- (8) Tare filter
- (9) Sample filter 5
- (...) ...
- (z-2) Sample filter n
- (z-1) Tare filter
- (z) Check filter

* The check filter should be re-weighed after (at a maximum of) every 30 sample filters, and at the end of the experiment.

† The tare filter should be re-weighed after every two sample filters, and at the end of the experiment.

A1.6.4 Follow the procedure below for each individual weighing

- (a) Place the filter on the foil-covered pan. Close the door of the balance
- (b) Wait for the period of time deemed suitable in Section A1.5.3(a)
- (c) Record the mass (and number) of the filter in a data weighing sheet
- (d) Open the balance door and remove the mass piece or filter from the pan.

A1.7 Data Analysis

A1.7.1 The mass of each sample filter should be reported with respect to the tare filter. This is calculated by use of the equation:

$$m_{rel} = m_{filter} - \frac{(m_{tare,bef} + m_{tare,aft})}{2}$$

Where: m_{rel} = mass of sample filter relative to the tare filter

m_{filter} = mass of sample filter

$m_{tare,bef}$ = mass of tare filter recorded before weighing of sample filter

$m_{tare,aft}$ = mass of tare filter recorded after weighing of sample filter

A1.7.2 If necessary, a correction should be applied to account for changes in the mass of the tare filter (see Section A1.8). If a correction is applied, the result is reported as the corrected mass of the filter relative to the tare filter, $m_{corr,rel}$:

$$m_{corr,rel} = m_{rel} - correction$$

A1.8 Calculation of correction factor

A1.8.1 As described in Section A1.6, monitor the mass of the tare filter relative to the check filter ($m_{tare} - m_{check}$) at regular intervals.

A1.8.2 Plot $m_{tare} - m_{check}$ against time and fit a quadratic function to the data.

A1.8.3 Calculate the correction factor by use of:

$$correction = (m_{tare} - m_{check})_{t=0} - (at^2 + bt + c)$$

A1.8.4 Apply the correction as described in section A1.7.2

A1.8.5 As described in Section 1.5, the check filter is weighed against a metal mass piece before each series of weighings. If any significant change in the weight of the check filter is discovered, the check filter should be replaced before any further weighings are carried out.

APPENDIX 2. UNCERTAINTY BUDGET

A2.1 Introduction / Scope

An example uncertainty budget is given below for weighing the mass of particulate matter on a 47 mm diameter PTFE coated glass fibre filter using NPL's Mettler UMT5 balance. The uncertainty calculated is that for the difference between the mass of loaded and the mass of an unloaded filter, i.e. the mass of particulate matter sampled.

Uncertainty budgets for weighings carried out with different filters on other balances will contain similar components, but the values assigned to these components may be very different than those stated here.

A2.2 Components of uncertainty budget

The following components are expected to contribute to the uncertainty for the mass of particulate sampled:

Component	Contribution to uncertainty (1 σ)
Effect of temperature and humidity on filter ^(a)	2 μg
Effect of temperature and humidity on particulate matter ^(b)	10 μg
Loss of semi-volatile material after sampling ^(c)	10 μg
Buoyancy effects	Negligible
Static effects	Negligible
Filter contamination	Negligible
Balance calibration	10 / $\sqrt{3}$ μg
Balance drift ^(d)	2 μg

^(a) Variation in mass recorded over the allowed range of temperature and humidity conditions (see Table 7)

^(b) An indicative value estimated from the data in Section 5, assuming 1 mg of particulate matter

^(c) An indicative value estimated from the data in Table 10.

^(d) The zero and span drifts of a UMT5 balance have been determined to be approximately $1\mu\text{g min}^{-1}$ (see Table 2). The assigned uncertainty assumes a period of two minutes between the weighings of the sample and tare filters.

A2.3 Combination of Uncertainties

The combined uncertainty for the mass of particulate matter is calculated by summing the components in the above table in quadrature. This gives $u(m) = 15.5 \mu\text{g}$.

The expanded uncertainty using a coverage factor of $k = 2$, thus providing a level of confidence of approximately 95% is therefore $U(m) = 31 \mu\text{g}$.

APPENDIX 3. FULL RESULTS OF TEMPERATURE & HUMIDITY EXPERIMENTS: AFTER CORRECTION

Symbols refer to the weighing number, temperature and RH stated in the legend.

QM-A, GF-A and Emfab data: 12 loaded (24h) and 15 blank filters; GF10 data: 12 loaded (72h), 12 loaded (24h) and 15 blank filters

