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June 2009

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Executive Summary

This Report presents the results of a study investigating the effect of humidity on the mass of filter samples of particulate matter (PM) collected in the UK, together with blank filters of relevance to UK measurements. It was carried out in parallel with samples and blank filters supplied from mainland Europe as part of a study coordinated by CEN TC 264 WG 15. The samples were taken through a series of different relative humidities (RH) ranging from 20% to 90%, with the temperature maintained close to 20°C, in a cycle designed to show:

- The effect and variability of mass changes with humidity on different types of blank filter relevant to the samples in the study and to other UK measurements;
- The scale of non-hysteretic effects caused by the conditioning humidity on the mass of selected UK PM samples;
- the scale of hysteretic effects on real UK samples that might lead to ambiguous results when the standard requirement (within EN 12341 and EN 14907) of 50 ± 5% RH is met, and hence the likely effect of changing the conditioning humidity to a lower value.

The blank 47mm diameter filters (4 of each type) were:

Emfab (as used on UK Equivalence trials, and since early 2009 on the UK Partisol sites),

Whatman QMA quartz (actually 5% glass – as used until recently on the UK Partisol sites),

Pallflex ultrapure quartz (as used on the UK Particles network for EC/OC and anions),

Cellulose ester (Pall-Gelman GN-4 Metricel, as used on the UK Metals network).

20 PM samples, of both PM_{10} and $PM_{2.5}$, on Emfab filters, were selected from those obtained from the 2008 Equivalence trial in Teddington primarily on the basis of high PM concentration, to make any humidity effects on the PM easier to see. Concentrations of chloride, nitrate and sulphate on these filters were measured after the humidity trial.

The Emfab filters gained around 10 µg in mass for a 10% rise in RH. This is comparable with earlier work [1].

The QMA quartz filters gained around 80 µg in mass for a 10% rise in RH. This is also comparable with earlier work [1]. These filters were at the same time observed to gain 150 to 230 µg in mass cumulatively over a period of about 6 weeks. This is again in line with observations reported to CEN WG 15, attributed to long-term absorption of moisture by new (dry) filters.

The Ultrapure quartz filters showed behaviour quite distinct from the QMA filters. They gained around 110 µg in mass for a 10% rise in RH, comparable with the QMA, but without any significant net gain of mass over the duration of the experiment.

The cellulose ester filters gained around 300 µg in mass for a 10% rise in RH, with evidence of hysteretic behaviour such that there can be differences of about 250 µg at 50% RH.

Using the rule of thumb [1] that filter mass changes become significant for practical PM monitoring purposes when they exceed 20 µg, and bearing in mind that humidity should be controlled in the range 45-55% RH, Emfab filters are confirmed as suitable for mass measurement, the scale and variability of effects on quartz reemphasises the difficulties in QA/QC when using quartz filters, while cellulose ester is shown to be a poor filter material for PM mass measurements.

From the PM samples:

Excessively high humidity during conditioning can lead to gross errors in PM measurement (greater than a factor of two), whereas excessively low humidity has a much smaller effect (of the order 10-15%); this non-linearity, observed in all samples, suggests that a lower conditioning humidity is intrinsically better for measurement uncertainty than a higher humidity;

Within the range of conditioning RH currently allowed within EN 12341 and EN 14907 (45 to 55%), observed variations for PM_{10} were 5-7%, and for $PM_{2.5}$ were 4-9%. These are significant contributions to the measurement uncertainty, and are generally larger for $PM_{2.5}$, as would be expected because most of the hygroscopic material will be present as fine particles (with the exception of sea salt).

The effects are not conspicuously different in scale between the summer episodes, the autumn samples, and the bonfire night samples, though there are distinct differences between different days.

The PM_{10} sample from 9 October (measured in duplicate), appeared to show hysteretic behaviour between around 50% and 70% RH, amounting to an ambiguity of about 15% in PM mass at 60% RH. Similar effects were seen in samples from a seaside site in Holland that were weighed as part of the concurrent CEN study, but not in any other samples. The compositional analysis does not show elevated chloride concentration in the coarse fraction of this sample, so that a simple explanation in terms of sea salt does not seem justified.

Together with the data from the CEN study, and the nonlinearity mentioned above, the observed hysteresis suggests that it would be beneficial to lower the target conditioning humidity from 50% to 40%.

1.0 Introduction

1.1 General

The water content of hygroscopic components of particulate matter (eg salt, nitrates, sulphates) can have a large effect on its total mass, ie PM_{10} and $PM_{2.5}$ results. The standard pre-weighing conditioning at 20±1ºC, 50±5% RH is aimed at harmonising the water content in all samples. However, this does not allow for the known hysteretic character of water absorption by the PM, such that material at 50% RH can be "wet" or "dry" depending on its previous history (see Figure 1 below).

There is a proposal within CEN to lower the standard conditioning RH to increase the chances that all samples are weighed "dry". This would bring European conditioning closer to that in the USA. However, it is not clear what the effect of this would be on real data, ie whether there would be a step change (and of what size), or whether there would only be a significant effect on a few "wet" samples.

The work in this Report extended the scope of a small experimental study funded by JRC Ispra (on behalf of CEN TC 264 WG 15) in which 20 loaded filters from across Europe were systematically taken in a cycle to high and low humidities in typically 10% RH steps between 20% and 90%, within NPL's humidity controlled glove box, weighing at each step. This was supplemented by the addition of 20 UK PM samples to assess the relevance of any conclusions to conditions in the UK.

1.2 Selection and identification of UK samples

Blank and sampled 47mm diameter filters were selected as follows:

Blank filters (4 of each):

- Emfab (Pall PTFE coated glass fibre), as used on UK Equivalence trials, and since early 2009 on the UK Partisol sites (identified as 3719 – 3722),
- Whatman QMA quartz (actually 5% glass) – as used until recently on the UK Partisol sites (identified as 3723 – 3726),
- Pallflex ultrapure quartz, as used on the UK Particles network for EC/OC and anions (identified as 3731 – 3734),
- Cellulose ester (Pall-Gelman GN-4 Metricel), as used on the UK Metals network (identified as 3727 – 3730).

All of the blank filters were taken "as new" from manufacturers' boxes.

20 PM samples, of both PM_{10} and $PM_{2.5}$, on Emfab filters, were selected from those obtained from the 2008 Equivalence trial in Teddington, primarily on the basis of high PM concentration, to make any humidity effects on the PM easier to see. All filters had been sampled on flow-calibrated 2.3 m^3/hr samplers (Derenda or Leckel), so that sampling volumes were all approximately 55 m^3. A change in mass of 55 µg on any sample therefore corresponds to a change in PM concentration of 1 µg/m^3. In many cases duplicate samples from the same day (required by the Equivalence procedure) were used, so that repeatability can be gauged.

The filters are identified in Table 1 below.

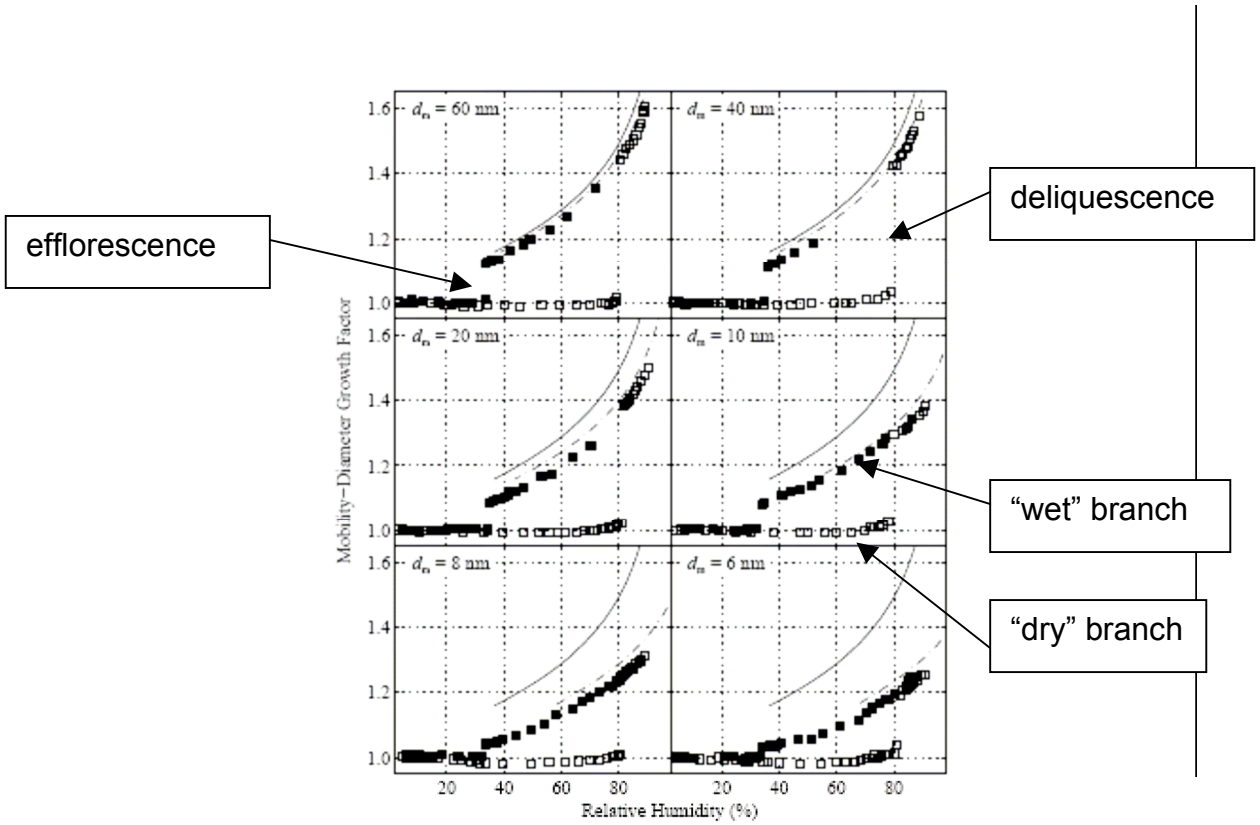


Fig. 5. Hygroscopic growth curves of ammonium sulphate aerosol particles generated by electrospray. Open symbols were recorded during deliquescence-mode measurements. Solid symbols were recorded during efflorescence-mode experiments and were analyzed by using either one- or two-peak fits, as necessary (cf. Figs. 3 and 4). Lines show the growth factors of models that omit (solid line) and include (dot-dashed line) the Kelvin effect (viz. models 1 and 2 described in the Appendix). Models are evaluated for $0<w_t<78\%$.

Figure 1, Data for ammonium sulphate particles of different sizes, taken from *Atmos. Chem. Phys. Discuss., 6, 7051–7073, 2006 Biskos et al*, exemplifying the hysteretic absorption of water by hygroscopic components of PM. (Creative Commons Attribution, NonCommercial and ShareAlike License)

1.3 Humidity cycle

The humidity cycle (agreed within CEN) was designed:

- to start at 50% RH, to be as close to the "reference" mass as possible at the start;
- to take all samples down to low humidity (in practice 30% RH), in an attempt to bring all samples into the "dry" state, if they were not in it already;
- to then take all samples through a full hysteresis loop from 30% to 90% RH and back to 30%.

The required sequence for % RH was:

50 - 45 - 40 - 35 - 30 - 40 - 50 - 60 - 65 - 70 - 75 - 80 - 90 - 80 - 70 - 60 - 50 - 45 - 40 - 35 - 30

The stated aim was to hold samples at each humidity for 48 hours before weighing. The intervals typically followed a sequence of 48 – 48 – 72 hours. This is not expected to have a significant effect on the results, as equilibrium should be reached in 48 hours. All samples were kept at 90% RH for a period of one week, after which they were reweighed before taking the humidity down again. An additional final weighing at close to 20% RH was added. The actual temperatures and relative humidities recorded in the 48 hours prior to each of the 21 weighings are shown in Table 2.

In 3 cases (weighings 4, 11 and 14), the humidity showed a distinct drift over the 48 hour period. In these cases, the results shown later use a value for humidity that is biased towards the end of the conditioning period: 35.0 instead of 37.4%; 83.0 instead of 79.9%; and 77.5 instead of 79.0%, respectively. These minor changes improve the appearance of the graphs at high humidities, where the mass changes are largest.

Filter id	Sample date	Size	PM µg/m^3	Cl^- µg/m^3	NO_3^- µg/m^3	SO_4^{2-} µg/m^3	Comment
3276	24 July 2008	PM_{10}	34.6	0.17	5.94	4.24	
3277	24 July 2008	PM_{10}	35.4				Summer elevated
3279	24 July 2008	$PM_{2.5}$	35.2	0.13	2.24	3.79	
3357	30 August 2008	PM_{10}	46.7	0.14	10.20	4.53	
3358	30 August 2008	PM_{10}	46.2				Summer elevated
3359	30 August 2008	$PM_{2.5}$	33.9	0.12	7.03	3.94	
3360	30 August 2008	$PM_{2.5}$	32.8				
3516	9 October 2008	PM_{10}	18.6	0.26	3.85	1.52	
3517	9 October 2008	PM_{10}	18.8				Autumn typical
3514	9 October 2008	$PM_{2.5}$	10.4	0.24	1.74	1.52	
3515	9 October 2008	$PM_{2.5}$	9.2				
3434	10 October 2008	$PM_{2.5}$	10.9				Autumn typical
3619	4 November 2008	PM_{10}	38.6	0.15	7.55	5.37	
3620	4 November 2008	PM_{10}	39.7				Bonfire night
3621	4 November 2008	$PM_{2.5}$	32.2	0.12	7.52	5.68	elevated
3622	4 November 2008	$PM_{2.5}$	32.0				
3623	5 November 2008	PM_{10}	36.5	0.28	5.06	5.56	
3624	5 November 2008	PM_{10}	37.4				Bonfire night
3633	5 November 2008	$PM_{2.5}$	30.7	0.15	3.93	4.78	elevated
3634	5 November 2008	$PM_{2.5}$	30.7				

Table 1: Identification and basic information about PM samples

1.4 Equipment and calibration

All filters were kept and weighed throughout the study with NPL's dedicated temperature and humidity controlled glove box.

Filters were weighed on a Mettler Toledo UMT-5 balance (0.1µg resolution, set to read at a resolution of 1 µg), calibrated using internal procedures in October 2008.

Temperature and relative humidity were continuously monitored with an Ebro Temperature and Humidity Logger, calibrated by NPL humidity section in March 2008.

weighing	date	%RH				T °C			
		Mean	Max	Min	SD	Mean	Max	Min	SD
1	11/3/09	49.0	49.6	47.5	0.5	20.1	20.5	20.0	0.2
2	13/3/09	46.1	47.5	42.3	0.8	20.1	20.5	19.9	0.1
3	16/3/09	44.2	45.4	37.1	1.0	20.3	20.5	20.2	0.1
4	18/3/09	37.4	42.3	31.9	3.0	20.4	20.7	20.0	0.3
5	20/3/09	31.0	31.9	27.8	1.2	20.4	20.5	20.3	0.1
6	23/3/09	36.6	39.2	36.1	0.9	20.1	20.7	20.0	0.2
7	25/3/09	48.8	52.7	46.5	1.2	20.4	20.7	20.2	0.1
8	27/3/09	60.5	65.1	57.9	1.5	20.1	20.7	20.0	0.2
9	30/3/09	61.2	69.3	58.9	2.2	20.1	21.5	19.9	0.2
10	1/4/09	69.7	73.4	65.1	2.0	21.4	22.7	20.3	0.9
11	3/4/09	79.9	83.8	73.4	2.6	21.8	22.7	21.6	0.2
12	8/4/09	90.3	91.0	90.0	0.5	21.7	21.9	21.6	0.1
13	15/4/09	91.0	92.1	90.0	0.2	21.7	21.8	21.6	0.0
14	17/4/09	79.0	80.7	76.5	1.6	21.8	21.8	21.7	0.0
15	20/4/09	68.0	72.4	65.1	1.4	21.8	21.8	21.6	0.0
16	22/4/09	59.5	61.0	57.9	0.6	21.7	21.9	21.5	0.1
17	24/4/09	49.1	51.6	43.3	2.4	21.5	21.9	20.5	0.2
18	27/4/09	45.2	46.5	42.3	0.8	21.6	21.6	21.4	0.0
19	29/4/09	39.8	41.3	37.1	1.1	21.1	21.1	21.0	0.0
20	5/5/09	30.7	31.9	27.8	0.8	21.1	21.2	21.1	0.0
21	8/5/09	17.3	15.5	16.4	0.7	20.2	20.5	20.0	0.1

Table 2: Temperature and relative humidity conditions in the 48 hours preceding each weighing. The SD columns are the standard deviations of the parameters over the 48 hour period, rounded to one decimal place.

1.5 Weighing procedure

The same weighing procedure as was developed for the UK Equivalence Trials was followed.

In this procedure, the effects of static are minimised by moving each filter past a static discharger before weighing, and by having a metallic disc on the weighing pan below the filter.

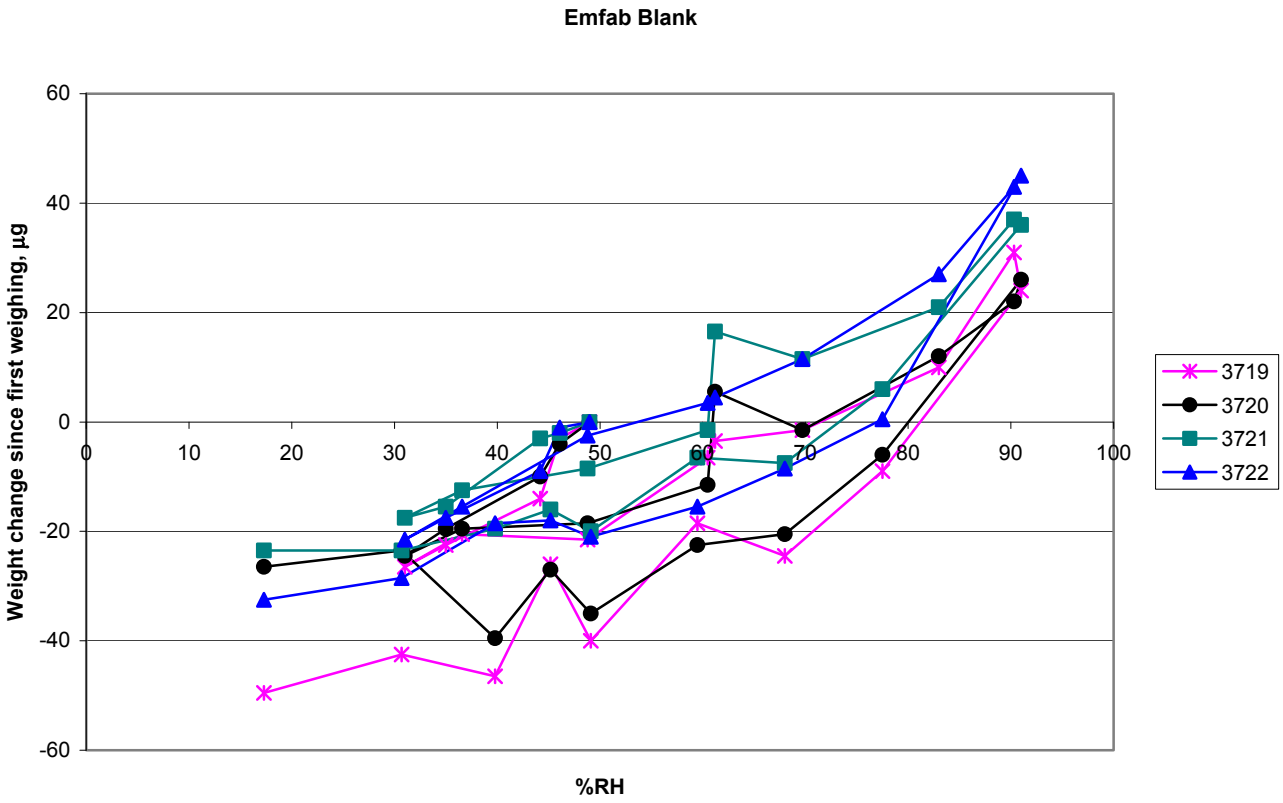
The effects of balance drift are minimised by measuring the weight of each filter relative to a metal tare weight of similar mass to the filters (100 mg), which is placed on the balance after every 4 filters. Further calibration and checks are carried out at the start and end of each weighing session.

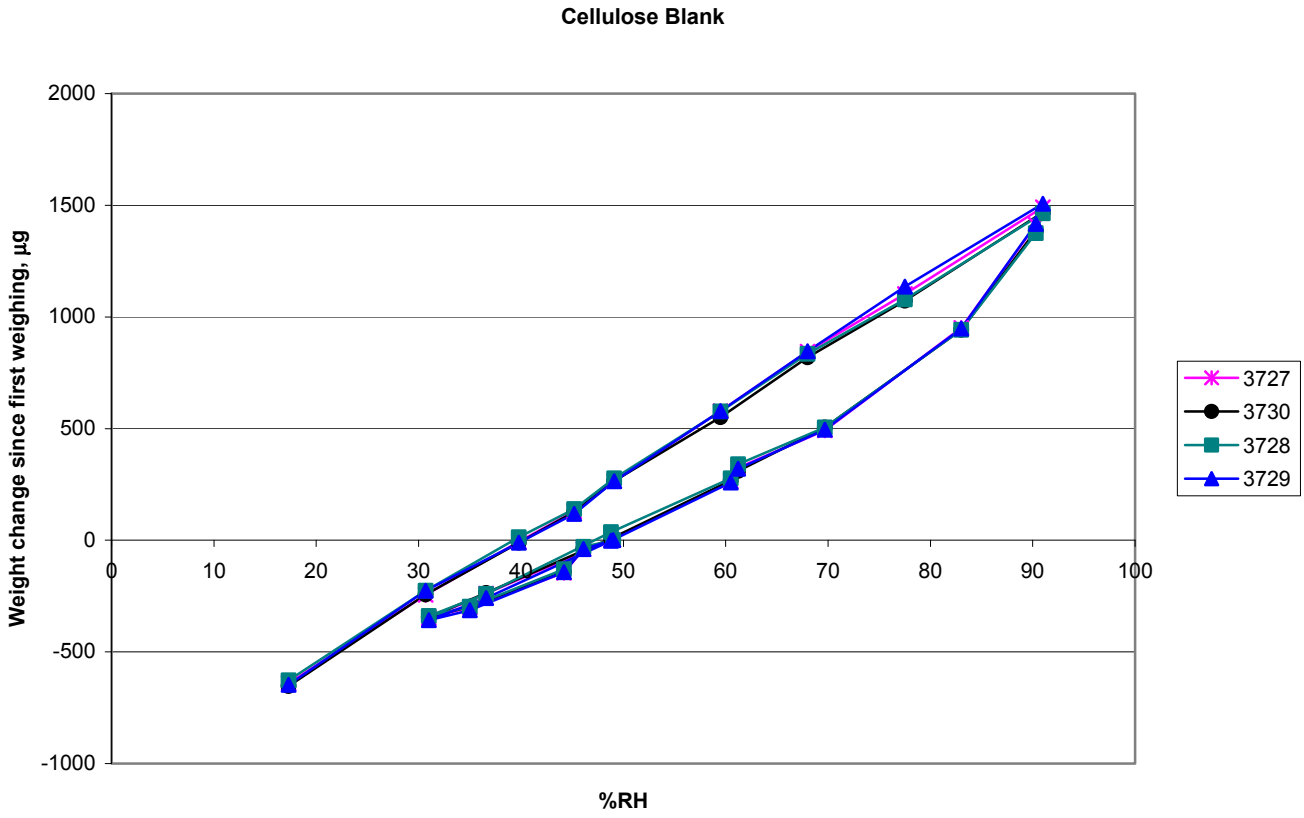
2.0 Results

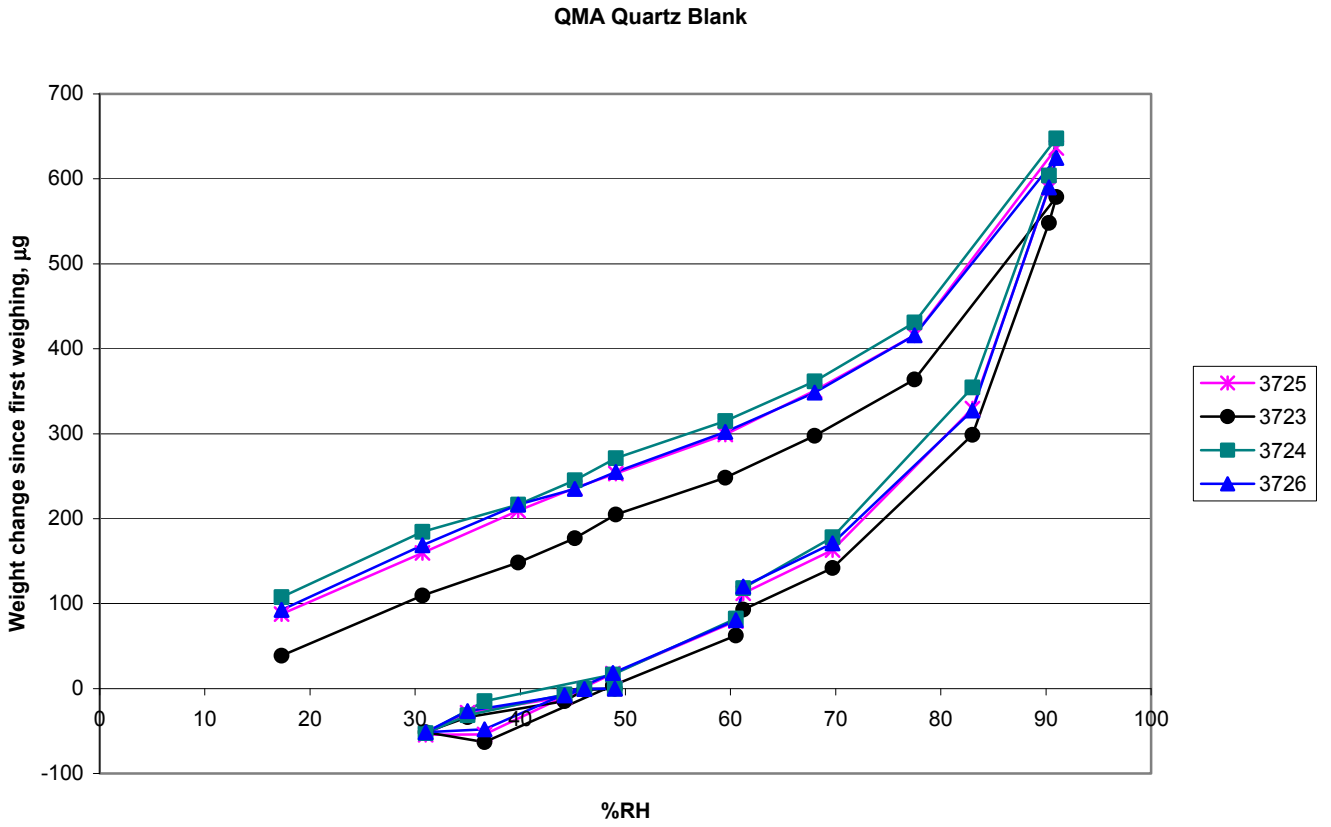
For all the results presented graphically, the ordering of the measurements can be inferred from the fact that the lowest humidity results (<20% RH) were made last.

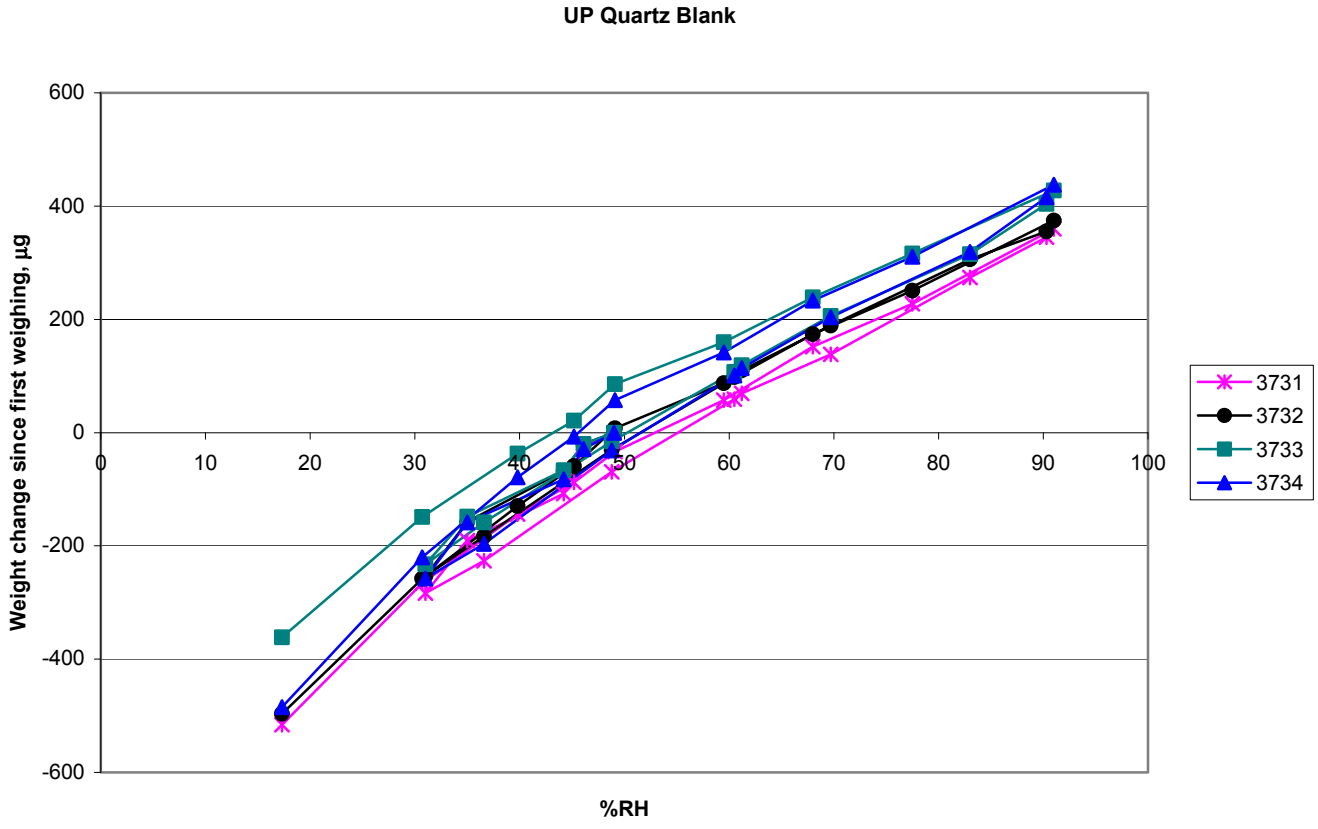
2.1 Blank filters

Results from the blank filters are shown graphically below:

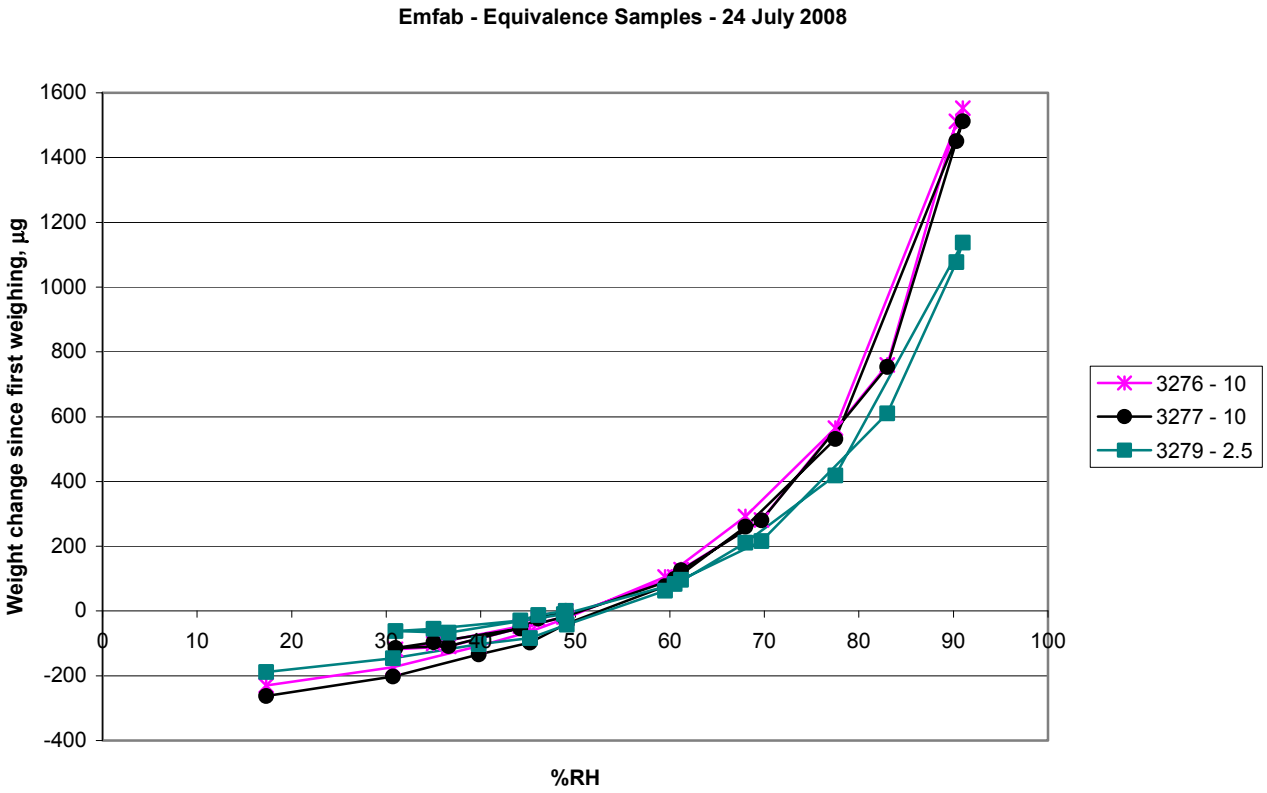


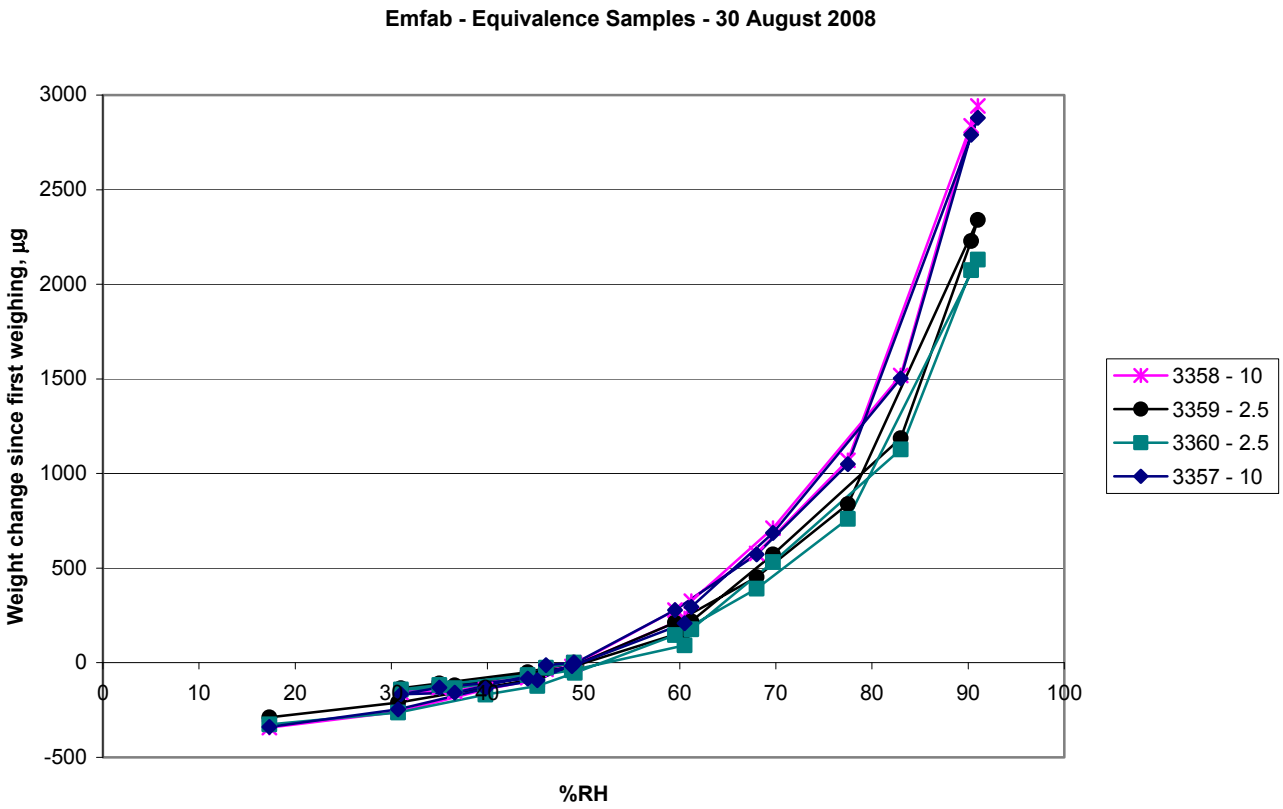

Cellulose Blank
Weight change since first weighing, µg
2000
1500
1000
500
0
-500
-1000
0
10
20
30
40
50
60
70
80
90
100
%RH
3727
3730
3728
3729

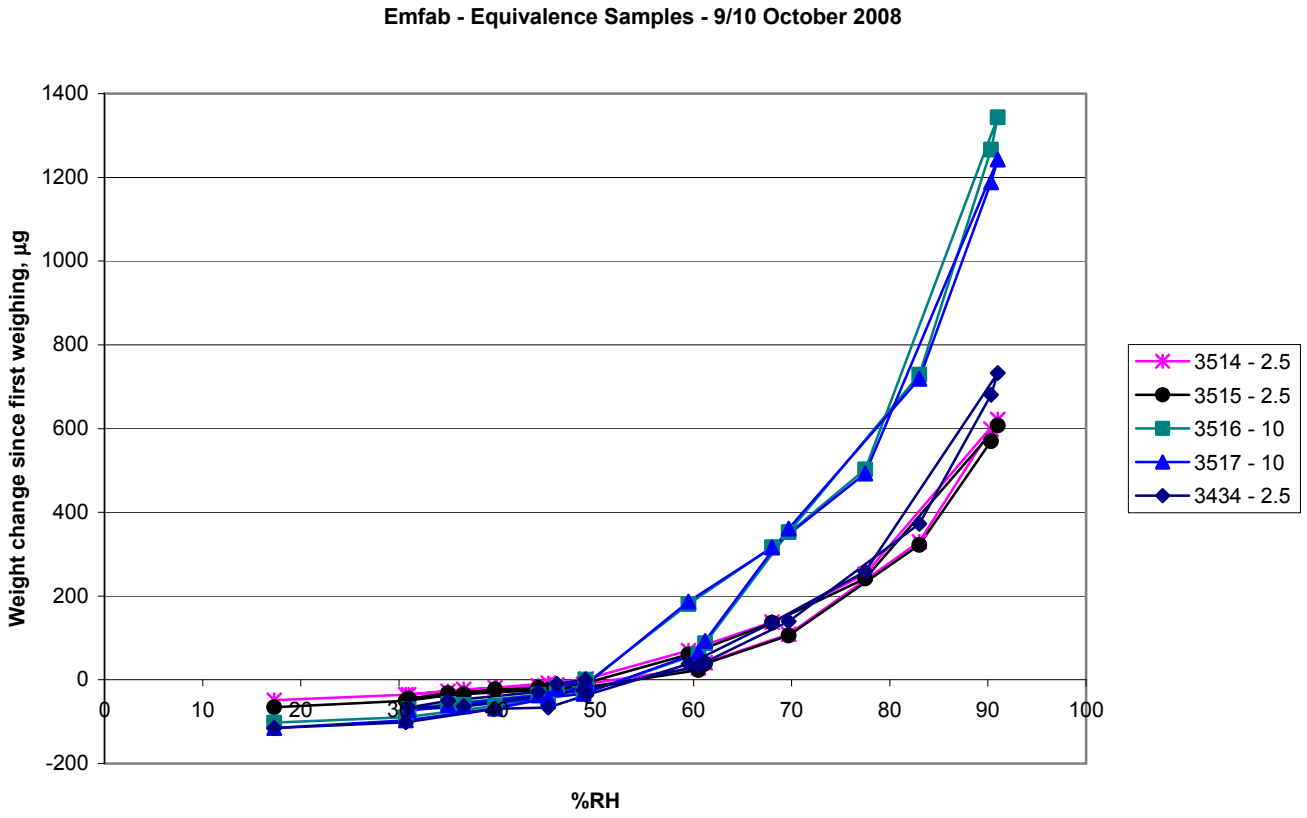

QMA Quartz Blank
Weight change since first weighing, µg
700
600
500
400
300
200
100
0
-100
0
10
20
30
40
50
60
70
80
90
100
%RH
3725
3723
3724
3726

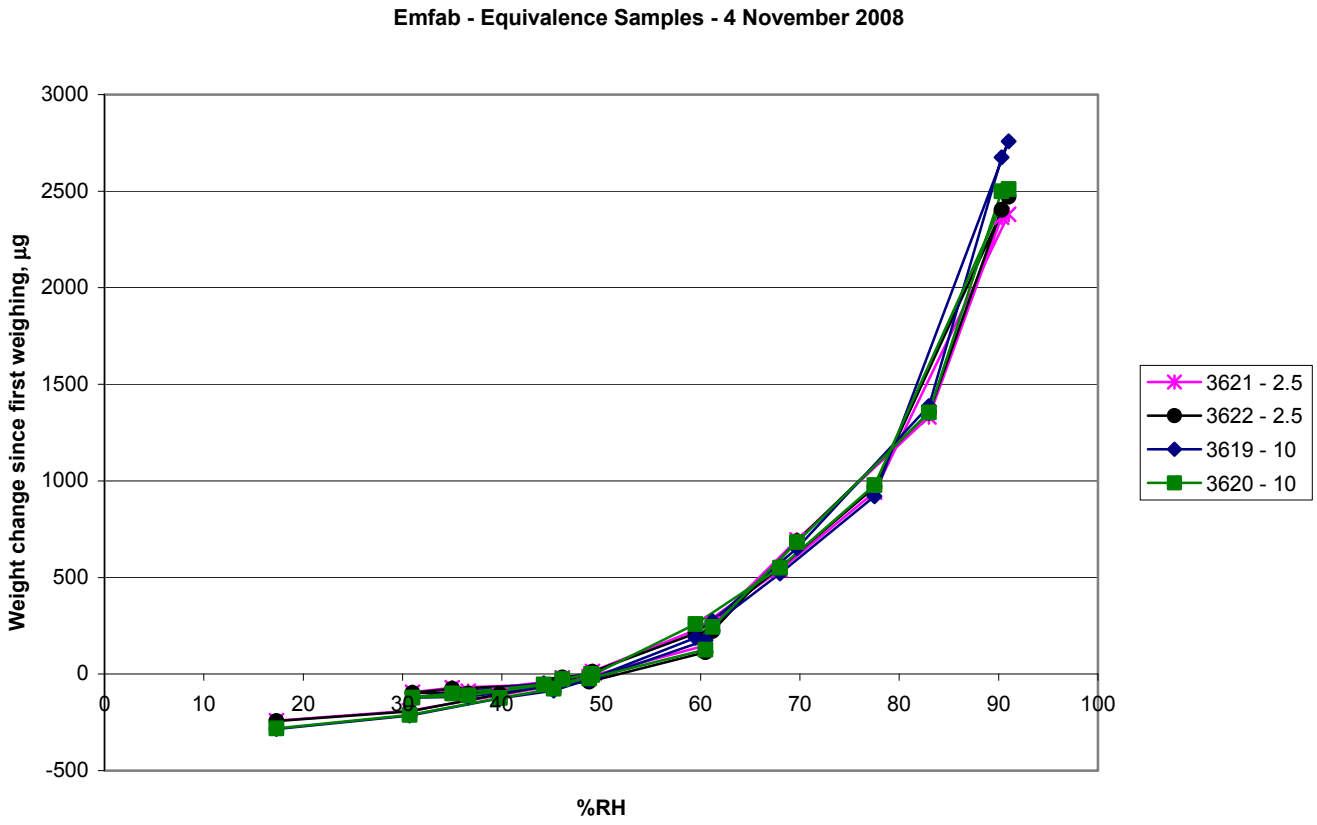

UP Quartz Blank
Weight change since first weighing, µg
600
400
200
0
-200
-400
-600
0
10
20
30
40
50
60
70
80
90
100
%RH
3731
3732
3733
3734

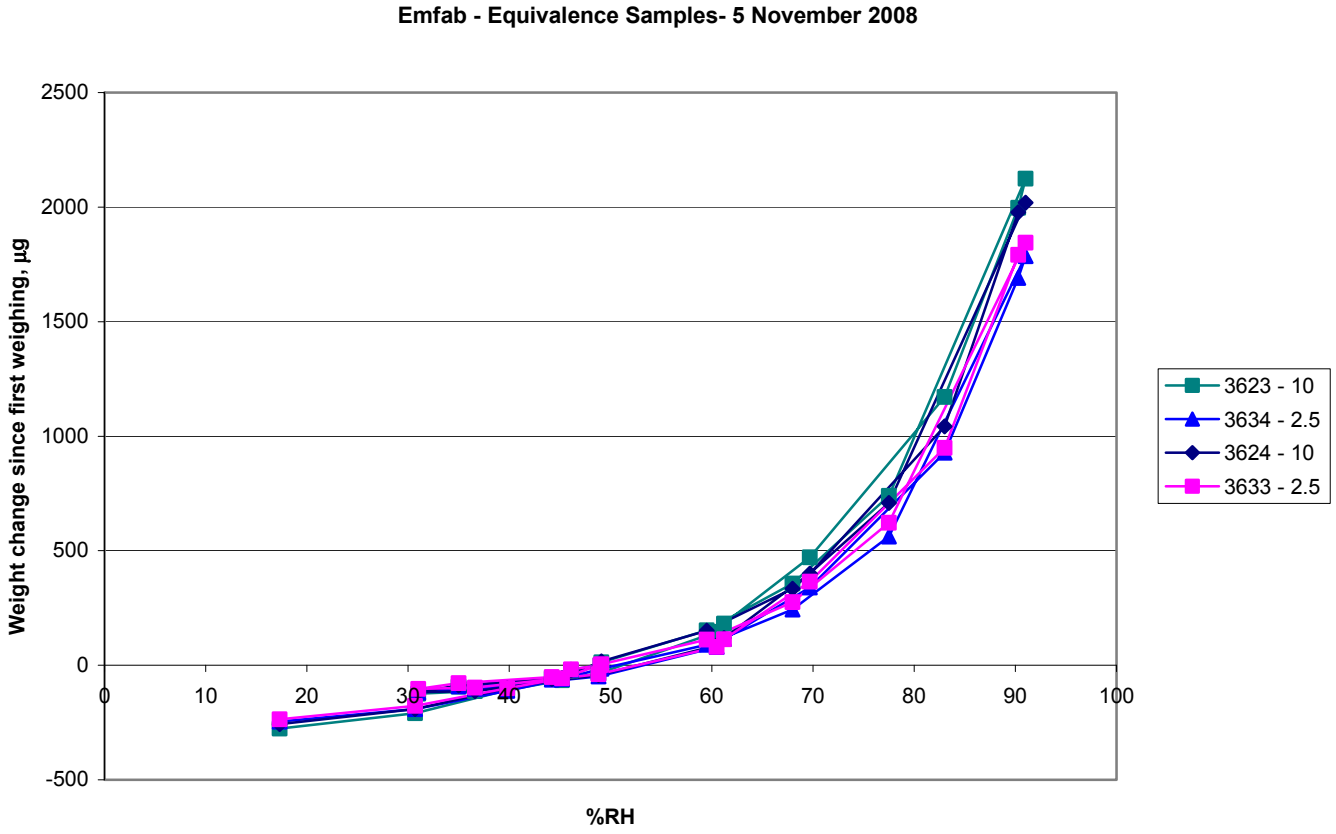
2.2 PM samples






Emfab - Equivalence Samples - 9/10 October 2008
Weight change since first weighing, µg
1400
1200
1000
800
600
400
200
0
-200
0
10
20
30
40
50
60
70
80
90
100
%RH
3514 - 2.5
3515 - 2.5
3516 - 10
3517 - 10
3434 - 2.5


Emfab - Equivalence Samples - 4 November 2008
Weight change since first weighing, µg
3000
2500
2000
1500
1000
500
0
-500
0
10
20
30
40
50
60
70
80
90
100
%RH
3621 - 2.5
3622 - 2.5
3619 - 10
3620 - 10



3.0 Discussion and conclusions

3.1 Blank filters

The Emfab filters gained around 10 µg in mass for a 10% rise in RH. This is comparable with earlier work [1].

The QMA quartz filters gained around 80 µg in mass for a 10% rise in RH. This is also comparable with earlier work [1]. These filters were at the same time observed to gain 150 to 230 µg in mass cumulatively over a period of about 6 weeks. This is again in line with observations reported to CEN WG 15, attributed to long-term absorption of moisture by new (dry) filters.

The Ultrapure quartz filters showed behaviour quite distinct from the QMA filters. They gained around 110 µg in mass for a 10% rise in RH, comparable with the QMA, but without any significant net gain of mass over the duration of the experiment.

The cellulose ester filters gained around 300 µg in mass for a 10% rise in RH, with evidence of hysteretic behaviour such that there can be differences of about 250 µg at 50% RH.

Using the rule of thumb [1] that filter mass changes become significant for practical PM monitoring purposes when they exceed 20 µg, and bearing in mind that humidity should be controlled in the range 45-55% RH, Emfab filters are confirmed as suitable for mass measurement, the scale and variability of effects on quartz reemphasises the difficulties in QA/QC when using quartz filters, while cellulose ester is shown to be a poor filter material for PM mass measurements.

3.2 PM samples

In all cases, the changes in mass greatly exceeded the mass changes expected from the Emfab filters, so that changes in the PM mass could be gauged with some confidence.

Repeatability

One advantage of using samples from the Equivalence trial is that in nearly all cases the samples are duplicated, allowing uncertainties in the weighing procedures to be gauged. In all cases, the duplicate samples agree very well, adding to the confidence that can be placed in the data.

Scale of effects

The PM_{10} and $PM_{2.5}$ UK samples can be considered as being of three distinct types –

- summer elevated (24 July and 30 August), PM_{10} 35 – 45 µg/m^3, $PM_{2.5}$ forming 70-85% of the PM_{10};
- autumn typical (9/10 October), PM_{10} 20 µg/m^3, $PM_{2.5}$ forming 50% of the PM_{10}; and
- bonfire night elevated (4 and 5 November), PM_{10} 40 µg/m^3, $PM_{2.5}$ forming 80% of the PM_{10}.

One notable feature is that the samples from the two different summer dates behave in distinct ways, as do the samples from the two November dates.

Table 3 gives a summary of non-hysteretic effects, scaled using the known values of PM on the samples.

Sample	PM mass gain at 90% RH (%)	PM mass loss at 20% RH (%)	PM sensitivity for a 10% RH change near 50% RH (%)
24 July PM_{10}	78	13	5
24 July $PM_{2.5}$	57	10	4
30 August PM_{10}	113	12	7
30 August $PM_{2.5}$	119	16	8
9 October PM_{10}	126	11	5
9 October $PM_{2.5}$	109	9	9
4 November PM_{10}	121	13	6
4 November $PM_{2.5}$	136	14	7
5 November PM_{10}	98	13	5
5 November $PM_{2.5}$	107	14	6

Table 3: summary of non-hysteretic effects, scaled using the known values of PM on the samples.

The main features are:

- excessively high humidity during conditioning can lead to gross errors in PM measurement (greater than a factor of two), whereas excessively low humidity has a much smaller effect (of the order 10-15%); this non-linearity, observed in all samples, suggests that a lower conditioning humidity is intrinsically better for measurement uncertainty than a higher humidity;

- with the range of conditioning RH currently allowed within EN 12341 and EN 14907 (45 to 55%), variations for PM_{10} were 5-7%, and for $PM_{2.5}$ were 4-9%. These are significant contributions to the measurement uncertainty, and are generally larger for $PM_{2.5}$, as would be expected because most of the hygroscopic material will be present as fine particles (with the exception of salt – see below);

- the effects are not conspicuously different in scale between the summer episodes, the autumn samples, and the bonfire night samples, though there are distinct differences between different days.

Hysteretic effects

With one exception, water absorption was not notably hysteretic on the samples studied.

The exception was the PM_{10} sample from 9 October (measured in duplicate), which appeared to show hysteretic behaviour between around 50% and 70% RH, amounting to an ambiguity of about 15% in PM mass at 60% RH. The hysteresis was not apparent in the $PM_{2.5}$ sample from the same day.

Similar effects were seen in samples from a seaside site in Holland that were weighed as part of the concurrent CEN study, but not in any other samples.

The analysis of the 9 October filters (Table 1) does not show a notable amount of chloride in the coarse fraction, so that a simple explanation in terms of sea salt does not seem justified.

As larger amounts of sulphate and nitrate were observed in many of the samples, and presumably account for a large fraction of the observed water absorption, it appears that these components usually absorb water reversibly. The specific cause of the hysteresis is therefore unclear.

Together with the data from the CEN study, and the nonlinearity mentioned above, the observed hysteresis suggests that it would be beneficial to lower the target conditioning humidity from 50% to 40%.

Conditioning period

The stability of the measurements at 90% RH, and the fact that the graphs are improved by using the RH data from about the last 12 hours of conditioning rather than the previous 48 hours, suggests that 48 hours is a more than adequate conditioning period for these samples.

Low humidity anomaly

In all samples except the samples from 9/10 October, the 30% RH measurements made on 20 March, after the initial lowering of humidity from 50% RH, are about 100 µg higher than the 30% RH measurements made on 5 May, after the subsequent lowering of humidity from 90%. This is very unlikely to be a weighing artefact, as the blank Emfab filters (and the 9/10 October samples) did not show the effect. It is also unlikely to be a humidity measurement error, as the sensitivity to humidity at 30% RH is low. This would merit further investigation.

Recommended further work

Both the low humidity anomaly and the hysteresis region would benefit from being examined in more detail.

Reference

1 Andrew S Brown, Rachel E Yardley, Paul G Quincey, David M Butterfield, Studies of the effect of humidity and other factors on some different filter materials used for gravimetric measurements of ambient particulate matter, Atmospheric Environment 40, 4670 - 4678.