

NPL REPORT AS 15

Measurement science issues relating to PM₁₀ and PM_{2.5} airborne particles

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September 2007

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Executive Summary

Airborne Particulate Matter (PM) is associated with major health effects in Britain and elsewhere. It also has a significant role in climate change. Current UK and European legislation sets limit values on health grounds for ambient concentrations of PM₁₀ (total mass per unit volume of air of particles with aerodynamic diameter less than 10 µm) and PM_{2.5} (the fraction less than 2.5 µm, called the fine fraction). However, it is well known that measurements of these quantities can vary by amounts of the order 50% depending on the method and instrument used, making compliance with legal obligations more problematic than for other important pollutants. Standardisation of manual measurements for EU purposes is being carried out through CEN. There has also been a recent EU-led exercise to define in practical terms how a non-standard method can be determined to be equivalent to the standard method. In a separate but related development, CEN has started work on standardisation of automated methods for measuring PM.

Both the standardisation process and the revision of the equivalence procedure are currently ongoing. This short Report aims to summarise:

- the legislative background
- the scientific background
- outstanding measurement issues in the definition of standard methods for PM₁₀ and PM_{2.5}
- the current position regarding equivalence and automated methods
- possible future developments.

The report considers only ambient (outdoor) air. PM measurements for vehicle and industrial emissions, occupational exposure, and indoor air have many related issues but are not specifically considered here.

Useful related documents have been appended.

Measurement science issues relating to PM₁₀ and PM_{2.5} airborne particles

1. The legislative background

1.1 Terminology and units

Airborne Particulate Matter (PM) is associated with major health effects in Britain and elsewhere. It also has a significant role in climate change. The metrics discussed in this report are PM₁₀ (total mass per unit volume of air of particles with aerodynamic diameter less than 10 µm) and PM_{2.5} (the fraction less than 2.5 µm, called the fine fraction). The difference between PM₁₀ and PM_{2.5} is called the coarse fraction. The units are µg/m³. On average the fine and the coarse fractions are similar in size, so that PM_{2.5} concentrations are around half those of PM₁₀.

1.2 European context

The need to regulate PM was first set out in European legislation within the Air Quality Framework Directive 96/62/EC, in 1996. This set out the broad outline of how the legislation for all air pollutants would operate. Specific legislation followed in the first “Daughter” Directive 1999/30/EC, in 1999, which was based on a 1997 Position Paper. These and other regulatory documents are available through the Europa website [1].

The position paper had proposed limit values – to be met at all locations used by the public – for PM₁₀ over two averaging periods, based on health studies. These were that the 98th percentile of the daily averages should not exceed 50 µg/m³, and the annual average should not exceed 20 µg/m³. These were relaxed in the Daughter Directive, on grounds of practicality, so that the daily average should not exceed 50 µg/m³ more than 35 times in a year (ie roughly the 90th percentile should not exceed 50 µg/m³), and the annual average should not exceed 40 µg/m³. The Directive referred to the European Committee for Standardisation (CEN) standard EN 12341 [2] as the reference method for PM₁₀ measurement. This Directive also put an obligation on Member States to monitor PM_{2.5} at an unspecified number of sites. As no standard method for PM_{2.5} was published at that time, Member States were allowed to use any method they saw fit.

It is notable that the legislation requires timely information about PM₁₀ concentrations to be provided to the public, but the reference method, based on the manual weighing of filters sampled for 24 hours, typically only provides data many days in arrears. The need for approved automated methods has always been apparent.

In the late 1990s it became clear that the commonly used automatic methods within Europe – the tapered element oscillating microbalance (TEOM, a patented technology) and instruments based on the attenuation of beta-radiation (known generically as beta gauges) gave significantly lower results than the reference method for PM₁₀ [2]. This is due to a large, variable component of the PM being semi-volatile, meaning that it is volatilised and therefore removed in the elevated temperatures, typically 50°C, at which the automated instruments operate.

This was addressed by a Guidance Report in 2001 [3] (written by a group led by Martin Williams and Peter Bruckmann), which proposed the use of “correction factors” based on parallel measurements of the automated and reference methods within each Member State. As an interim measure, Member States were to use a default factor of 1.3 for TEOMs and beta gauges until reliable local data were available.

In 2003 a second position paper was produced, this time by a group within the Clean Air for Europe (CAFE) programme [1]. Its main recommendation, in the context of measurement, was a move from PM₁₀ to PM_{2.5} as the principal metric for assessing exposure to PM. This was based on health studies, primarily carried out in USA. It proposed limit values for PM_{2.5} such that the 90th percentile of daily averages should not exceed 35 µg/m³, and the annual average should be within the range 12 to 20 µg/m³. On the subject of automated methods, it emphasised that Member States would need to demonstrate that their methods were “equivalent” to the reference method, and that the reference method for PM_{2.5} would be the CEN standard method then being developed (EN 14907) [4].

The practical meaning of equivalence was set out in a Guidance document [5], which had strong input from NPL, published in 2005. For PM, this set out the requirements for four independent parallel field comparisons, the possibilities for correction factors, and the statistical procedures for determining whether or not the candidate method is equivalent to the reference method, based on uncertainty considerations.

The 2003 position paper has led to a proposed new Air Quality Directive, COM(2005)447 [6], to replace the Framework and Daughter Directives. This is expected to be finalised in late 2007 or 2008. The current version places a limit value on the annual average concentration of PM_{2.5} at 20 µg/m³. There is no daily average requirement, but there is a new parameter based on Exposure Reduction. This involves an Average Exposure Indicator, which is a population-weighted national annual average for PM_{2.5} based on representative sampling. The current draft requires this Indicator to decrease by 15% over 10 years. The impetus for Exposure Reduction came from the UK, and it is designed to achieve a much greater overall health benefit for the same cost than the limit value approach, which has the effect of concentrating effort at pollution “hot spots”, which typically only affect a small number of people.

The proposed Directive requires PM_{2.5} measurements to be carried out in a way equivalent to the 2005 CEN manual filter weighing standard for PM_{2.5}, EN 14907, and expects the standard for PM₁₀, EN 12341, to be updated in a way that incorporates recent scientific developments, though within the constraints of political considerations described below.

1.3 United Kingdom

UK legislation in recent years has necessarily followed the EU Directives, though it is stricter in some regions, for example in Scotland (see below). The current UK Air Quality Strategy [7] was published in July 2007, and includes the proposed EU move from PM₁₀ limit values to a PM_{2.5} limit value (also called a concentration cap) and Exposure Reduction.

Some relevant extracts from the strategy are:

29. The current policy framework and the legislative requirement to meet EU air quality limit values everywhere in the UK tends to direct our attention to localised hotspot areas of pollution (where the objectives are not met). There is clear and unequivocal health advice that there is no accepted threshold effect, i.e. no recognised safe level for exposure to fine particles (PM_{2.5}). For this pollutant, the current policy framework is therefore not going to generate the maximum improvement in public health for the investment made, because it focuses attention on hotspots only, despite much more widespread adverse effects on health being likely.

30. We have therefore adopted an ‘*exposure reduction*’ approach for PM_{2.5} to seek a more efficient way of achieving further reductions in the health effects of air pollution by providing a driver to improve air quality everywhere in the UK rather than just in a small number of localised hotspot areas, where the costs of reducing concentrations are likely to be exceedingly high. This will act to make policy measures more cost-effective and is more likely to maximize public health improvements across the general population.

31. The exposure reduction approach is based on the principle that for pollutants with a low or zero threshold for adverse effects, it will generally be more beneficial to public health, and potentially more cost-effective to reduce pollutant levels across the whole population of an urban area or region rather than in a small area or “hotspot”. The framework of delivering this approach contains two inseparable parts:

- air quality objectives/limit values (often called “backstop objective” or “concentration cap”) to ensure some basic level or quality of air which all citizens should experience, embodying the “environmental justice” concept
- an objective based on reducing average exposures across the most heavily populated areas of the country (often called “percentage reduction” or “exposure reduction” objective), in order to generate further cost effective public health improvements over and above the basic level of protection generated by the objective above.

32. While the percentage reduction objective is a relative measure of improvement (in this case 15 per cent reduction in average concentrations in urban background areas across the UK between 2010 and 2020), the backstop objective (or concentration cap) is designed to deliver a **minimum level of protection applicable to all areas in a country** ($25\mu\text{g}\cdot\text{m}^{-3}$). In Scotland, where background levels of pollution are generally lower, the Scottish Executive has decided to retain the strategy’s 2010 PM_{10} objective in addition to introducing the exposure reduction approach.

In 2004-6 a series of Equivalence trials was carried out to determine whether automated PM_{10} and $\text{PM}_{2.5}$ instruments used in the UK were equivalent to the reference methods (described further in Section 4.1). These had considerable involvement from NPL in the implementation of the reference method (for example weighing all the filters), in providing and operating one of the sites, and in analysing the data. These trials form the basis for implementation of the Directives in Networks across the UK.

1.4 Political considerations

The inclusion of definite PM concentrations in prominent EU legislation leads to political considerations for these measurements, in addition to the scientific ones described below. Specifically, even if there are strong scientific grounds for redefining the standard method for PM_{10} , for example, it would not be politically acceptable for the change to be made if it led to significantly different concentrations being obtained, as this would logically mean that the limit values in the legislation would need to be changed, and this would require a major political effort.

It would also be politically unacceptable to allow a standard automated method to produce results distinctly different from the reference manual method. Because of this, standard automated methods are required to be directly linked to the reference method, however imperfect this may be. This is relevant because the TEOM instrument, for example, gives a very reproducible measure of non-volatile PM, but this is not acceptable for regulatory purposes because it under reads the less reproducible manual method by variable amounts.

Moreover, any attempt to move away from the manual gravimetric methods would be resisted on the grounds that the underlying health studies that led to the limit values were based on the existing methods, no matter how flawed, and far less evidence relating to the modified method would be available.

While there are good scientific reasons for defining measures of airborne particulate matter other than total mass, there are few spare resources for funding the long term monitoring programmes for these other measures that would lead to the necessary health studies.

This brief history of the legislative background highlights the importance of robust standard methods being available for PM_{10} and $\text{PM}_{2.5}$, and also of the need to incorporate automated methods into the measurement framework, either through standardised methods or a robust equivalence procedure.

2. The scientific background

The measurement of PM differs in major ways from the measurements of other air pollutants. Gaseous pollutants such as ozone and nitrogen dioxide have an unambiguous chemical definition, and fit into established ways of ensuring traceability to primary standards. Measurements of chemical

components of PM such as lead or benzo(a)pyrene also fit within established procedures for chemical traceability. Direct calibration of the analysis is possible, while issues with losses during sampling can be addressed by specific experiments and protocols.

It is historically unfortunate that the total mass of PM per unit volume of air has become the default measure of PM, and hence the parameter included in legislation. Mass measurement is of course easily traceable, but it has only become clear over recent decades just how variable measurements of this mass on a filter can be, due to water content, semi-volatile particles and other artefacts. There are no reliable calibration mixtures of airborne PM, and in any case they could not replicate the complicated and highly variable mixture of substances found in practice – including carbonaceous particles formed during combustion processes, sea salt, crustal material, organic material, some of which is formed through reactions within the atmosphere (secondary processes), and secondary inorganic particles such as ammonium nitrate and sodium sulphate. The definition of PM₁₀ and PM_{2.5} is therefore inherently method-dependent.

Ideally, any measurement method for PM₁₀ and PM_{2.5} must clearly address the following issues:

- 1 The allowable range of particle sizes – no size selection technique can deliver an exact cut-off at 10 µm, for example;
- 2 The allowable range of water content in the PM – this is especially important for deliquescent components such as ammonium sulphate and sodium chloride, whose mass changes dramatically with water content;
- 3 The allowable losses of semi-volatile material, such as ammonium nitrate and some organic compounds. Losses can occur during sampling, and in between sampling and weighing;
- 4 The allowable extent of chemical reactions during and after sampling, for example between reactive gases such as nitric acid and sulphur dioxide and the PM.

For historical reasons the definition of PM₁₀ and PM_{2.5} is based on manual methods involving the weighing of material collected onto filters (known as gravimetric methods). Because of this, other issues become inextricably linked to the operational definition of PM, notably:

- 1 The collection efficiency of the filter, both in allowing particles to pass through and inefficiency caused by partial blockage;
- 2 Allowable chemical reactions between gaseous pollutants with the filter;
- 3 Allowable changes in filter mass between the pre-sampling and post-sampling weighing, due for example to water absorption or detachment of filter fibres;
- 4 Practical problems with measuring a small change in mass in a filter over a period of weeks, such as balance drift or static electrical effects.

Most of these issues have all become more important over time, for the following reasons:

- 1 PM concentrations have fallen dramatically – by around a factor of 10 since the early 1960s (though they are still responsible for large numbers of premature deaths, and appear to have stabilised since around 2000) [8] – making all weighing errors more significant;
- 2 The emphasis has moved to lower size fractions, for example from PM₁₀ to PM_{2.5}, so that smaller quantities are measured, again making all weighing errors more significant;
- 3 The composition of PM has changed from being dominated by combustion sources, notably domestic and industrial coal burning, to being a more variable mixture with major components of secondary material such as organics and nitrates, which are much more susceptible to the problems of water content and semi-volatility.

- 4 The fact that the coarse fraction is dominated by crustal components, which are insoluble and non-volatile, compounds the previous two factors by making the PM_{2.5} fraction proportionately more susceptible to humidity and temperature.

As a small compensation, concentrations of reactive gases such as sulphur dioxide, nitrogen dioxide and nitric acid in the air have fallen.

3. Outstanding issues in the definition of standard methods for PM

PM₁₀ is effectively defined for European regulatory purposes by the CEN standard EN 12341:1998 – a gravimetric filter-based method. Scientific knowledge about PM has moved on considerably since 1998, so that we now realise that implementations of variations allowed within EN 12341:1998 can lead to substantial differences in results obtained.

These issues were partially addressed within the CEN standard for PM_{2.5}, EN 14907:2005, which, for example, included tighter control of the handling of sampled filters to reduce losses of semi-volatile material.

CEN Technical Committee 264 Working Group 15 is currently revising EN 12341, and has the opportunity to improve the reference method further, for example by tighter specification of the filter material, or by changing the specification for the humidity at which the filters are brought to equilibrium. Any changes must, however, be considered in the context of the regulatory implications of the standard, so that improvements in scientific quality must be balanced with the effect of a step change in reference method, and with associated costs.

The issues raised in the previous section are considered here briefly in turn:

- a) The allowable range of particle sizes – no size selection technique can deliver an exact cut-off at 10 µm, for example;

The sampled size distribution is determined by a combination of the inlet design (normally an impactor) and the flow rate of the air through it. The exact performance of different inlet designs is likely to become irrelevant for standardisation purposes because only one inlet design is expected to be included in the EN 12341 revision, in contrast to the three designs in EN 12341:1998 and two in EN 14907:2005.

Flow control, necessary both for the correct size fraction to be sampled and for the volume of air sampled to be known, is an important element of the measurement, but does not require significant further developments.

- b) The allowable range of water content in the PM – this is especially important for deliquescent components such as ammonium sulphate and sodium chloride, whose mass changes dramatically with water content;

This is a live topic that will be discussed further in Section 3.1 below.

- c) The allowable losses of semi-volatile material, such as ammonium nitrate and some organic compounds. Losses can occur during sampling, and in between sampling and weighing;

The measures to reduce excessive heating of the sample during and after sampling introduced into EN 14907 probably go as far as is practical without a radical change to the quantity measured, for example moving to non-volatile particles only.

- d) The allowable extent of chemical reactions during and after sampling, for example between reactive pollutants such as nitric acid and sulphur dioxide and the PM;

The reductions in concentrations of reactive gases make this less important than in the past, and there is probably little that can be changed without a radical revision to the method.

- e) The collection efficiency of the filter, both in allowing particles to pass through and inefficiency caused by partial blockage;

Sampling efficiency of clean filters is not an issue in practice, as they are generally very efficient at high particle size through impaction and at low particle size through diffusive processes. Blockage, however, is an issue, for example with PTFE filters (which take the form of membranes with pores), and some other filters that can become blocked when damp. This is discussed further in Section 3.1.

- f) Allowable chemical reactions between gaseous pollutants with the filter;

Historically this was an issue with reactive gases and glass fibre filters, but again the lower concentrations of reactive gases have made this a much less significant issue in practice.

- g) Allowable changes in filter mass between the pre-sampling and post-sampling weighing, due for example to water absorption or detachment of filter fibres;

This is a live issue that will be discussed in Section 3.1.

- h) Practical problems with measuring a small change in mass in a filter over a period of weeks, such as balance drift or static electrical effects.

These problems can be addressed using protocols that have been developed at NPL and elsewhere. A report on static effects [9] was produced in 2006. The weighing protocol developed at NPL for the UK Equivalence trials is appended.

3.1 Issues currently being addressed

3.1.1 Choice of filter material

One of the two key decisions facing the CEN Working Group revising the PM₁₀ standard is whether to change the specification for filters allowed within the standard method. At present only quartz filters are allowed within the PM₁₀ standard (EN 12341), while quartz, glass fibre, PTFE and PTFE-coated glass fibre are allowed within the PM_{2.5} standard (EN 14907).

Superficially it would make good standardisation sense to include only one filter type, and there is some pressure from other EU countries to stay with quartz filters. However, work at NPL [10] has highlighted the problems with quartz and glass fibre filters changing weight by significant amounts due to humidity.

This work has been extended by recent unpublished work at VMM in Belgium, and elsewhere, that shows quartz filters taken from the manufacturer's packaging taking several months to attain a stable weight (Figure 1). This is attributed to a combination of water absorption and absorption of organic material. As a rule of thumb, artefacts corresponding to a 20 µg mass change are significant.

Moreover, different manufacturers' quartz filters can behave in quite different ways, so the

designation “quartz” filter is clearly not specific enough for practical purposes. Glass fibre filters have similar humidity effects, and have greater variability of properties between manufacturers and batches.

Recent unpublished work at JRC Ispra has shown mass increases in quartz travel blanks up to 40 µg, believed to be attributable to the same problem.

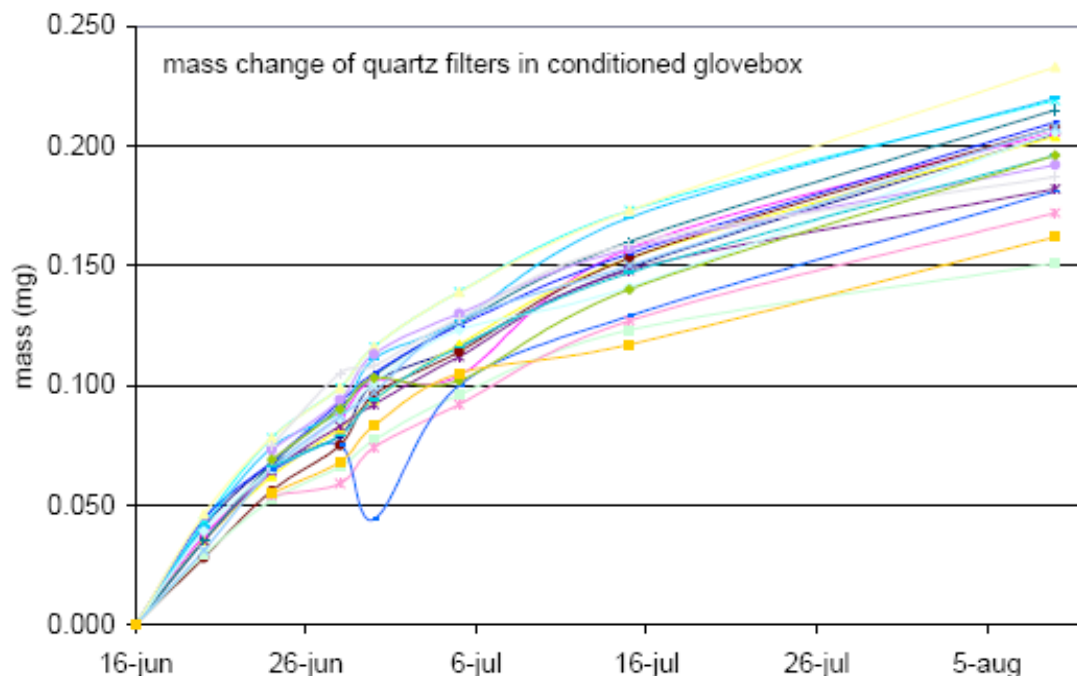


Figure 1: Weight gain over a two month period by a batch of similar quartz filters held at 20°C and 50% relative humidity (courtesy of VMM, Belgium, 2007)

There is no single filter type that is ideal. NPL has recommended PTFE-coated glass fibre [10], and this has been used in the UK Equivalence trials (described below), but this can become blocked in very damp conditions. There is therefore a clear problem for the CEN group in how to proceed.

Their aim is to specify the properties of the filter that are required (in terms of humidity effects, reactivity, etc), but there are not the resources to define validated tests, and there is likely to be no filter available that would pass all reasonable tests. Alternatively, this can be seen as an opportunity for filter manufacturers to produce a new type of filter with all the required properties. NPL has opened discussions with manufacturers in this area.

To summarise the advantages and disadvantages of the four filter types included in EN 14907:

quartz	good chemically, friable, humidity effect
glass fibre	less good chemically, humidity effect
PTFE	good chemically, no humidity effect, pores can block with PM and water
PTFE-coated glass fibre	good chemically, no humidity effect, flow through the (fibrous) filter can be impeded by excessive water

NB “quartz” and “glass fibre” come in many forms.

A supplementary issue is that many networks use the same filter samples for chemical analysis of the PM, and this places additional constraints on the filters. For example, subsequent analysis for organic and elemental carbon requires quartz filters to be used. However, specifying the best filter for

reference gravimetric measurements should not be compromised by the other uses to which filters could be put.

3.1.2 Humidity during pre-sampling and post-sampling filter conditioning

Filters are brought to conditions with controlled temperature and humidity before the pre-sampling and post-sampling weighing. This is to minimise effects of humidity both on the filters (as described above) and on the collected particulate matter. The present limits for both EN 12341 and EN 14907 are $20\pm1^{\circ}\text{C}$ and $50\pm5\%$ RH.

Regarding the significant effects of humidity on the mass of quartz and glass fibre filters, one suggestion is to bring filters to a “damp” state before bringing them down to 50% RH. Recent unpublished results, again from VMM in Belgium, show that this will take less time for the filter to reach equilibrium. However, this reduces, rather than eliminates, the problems associated with quartz and glass fibre filters.

A more fundamental problem is associated with hysteretic water absorption effects by soluble components of the PM such as sodium chloride, ammonium sulphate and ammonium nitrate.

The effect can mean a major difference in mass between PM when on the upper “wet” branch of the growth curve compared with the lower “dry” branch ($\sim 30\%$ of mass at 50%RH) – when the standard means that the PM could be on either branch.

Moreover, the variation of PM mass as the humidity changes is much larger on the “wet” branch than on the “dry” branch.

One simple solution to this problem would be to specify a lower humidity during conditioning, to guarantee that the PM was always on the lower branch of the growth curve. This is reflected by requirements in the US, where US EPA requires $30\text{--}40\pm5\%$ RH.

The situation was summarised in a short paper by Paul Quincey and Theo Hafkenscheid that is appended to this report (Annex 2). The decision as to whether to revise the conditions in EN 12341 will be made after further experimental work, due to take place in 2008.

4. The current position regarding equivalence and automated methods

4.1 Equivalence

The need for non-gravimetric measurement methods for PM_{10} and $\text{PM}_{2.5}$ has always been apparent. This was first systematically addressed by the 2005 Equivalence Guidance report [5], written with considerable NPL input.

The first major attempt to implement the procedures was carried out at four sites around the United Kingdom, including one at NPL in Teddington, with substantial NPL involvement in filter weighing and data analysis for the whole study [11]. The measurements were made over the period November 2004 to January 2006. The main conclusions were that the TEOM method did not pass the equivalence criteria with any simple correction factors or offsets, while a modified TEOM method called Filter Dynamics Measurement System (FDMS) passed for both PM_{10} and $\text{PM}_{2.5}$ without

corrections, and a beta attenuation instrument (BAM, from Met-One) met the criteria with a correction factor for PM₁₀, the only size fraction for which it was tested.

One notable feature to emerge from the study is a filter weighing protocol developed at NPL, which is appended as Annex 1.

The report [11] highlights deviations from the Guidance that were considered necessary and sensible. Experiences from the UK and elsewhere in Europe was pooled at a Workshop held at JRC Ispra on 2-4 May 2007.

Formal revisions to the Equivalence Guidance document will be made, but the mechanism for this is currently not clear. The summary of the Workshop by the Chair of the Equivalence Group (Theo Hafkenscheid) is appended as Annex 3.

A more limited set of Equivalence trials was carried out at NPL over the period June to August 2007, primarily to look at the effect of minor modifications to the FDMS instrument. The results for this are still being processed.

4.2 Automated methods

Although automated methods for PM can be used for EU regulatory purposes if Member States can demonstrate that they have passed the Equivalence criteria, there is a strong desire within the European Commission to formalise a CEN standard for automated PM measurements. This is a slightly unusual process, because the Commission have made it clear that a CEN standard for automated methods must not produce different concentrations to the reference gravimetric method, and therefore that the automated standard must be rooted in the gravimetric standard by essentially the same mechanism as the Equivalence procedure.

Discussions of the form of the CEN standard for automated PM measurements are at an early stage, within the CEN Working Group revising the PM₁₀ standard (CEN TC 264 WG 15). At the time of writing, it is likely to include:

- (1) a type approval process, including laboratory tests for such things as sensitivity to temperature and supply voltage, and field tests, in line with the field tests required by the current Equivalence guidance, but at a more limited number of sites (eg two rather than four);
- (2) rules on data treatment and validation, including standardisation of the treatment of low and negative concentrations, outliers, and averaging;
- (3) Ongoing quality assurance and quality control (QA/QC), to include periods of parallel operation with the standard method.

It will therefore extend the Equivalence procedure into the area of QA/QC (which the Equivalence procedure says is necessary), and cover the valuable practical matters relating to data handling. The laboratory type approval tests will add rigour to the operational requirements within the Equivalence procedure, and will bring the measurement of PM in line, to some extent, with the CEN standards for automated gaseous methods.

The critical element is the parallel field testing with the reference method. This should mean that a manufacturer can gain certification for an instrument to the CEN standard, and then a Member State would require only a limited set of extra tests to be declared equivalent for the purposes of official reporting to the Commission. The process of interlinking future revisions of the Equivalence procedures with the proposed CEN standard is not currently clear.

5. Possible future developments

While knowledge and methods for PM measurement have improved in recent years, significant measurement issues remain. With hindsight, total particle mass (below a certain size) was chosen for regulatory purposes as a parameter that was likely only to correlate loosely with the true causes of health effects, but which was easy to measure. It has turned out that not only is it a crude parameter for health studies, but it is also difficult to measure or even define. Because it is embedded in legislation, however, it is difficult to move to other, more suitable parameters.

Apart from the developments described above, there are two ways that regulatory measurements of PM in future may break away from the inherent restrictions of filter-based weighing.

One notable development is that within the proposed new Air Quality Directive COM(2005)447 [3] there is a requirement to measure the composition of PM_{2.5} at at least one site, to include nitrate, sulphate, ammonium, Organic Carbon (OC), Elemental Carbon (EC), Na⁺, K⁺, Cl⁻, Ca²⁺ and Mg²⁺. Although issues of volatility and chemical reactivity remain for nitrate, and OC and EC are operationally defined, these measurements are much less susceptible to problems from water absorption and filter weight changes than PM₁₀ and PM_{2.5}, and they would bring PM measurement much closer to other established techniques for analysis of air pollutants such as for metals. When these measurements become widespread and standardised, the emphasis on PM and its health effects should gradually move away from the simple total-mass parameters.

A second opportunity arises from the inclusion in COM(2005)447 of the Exposure Reduction requirement for PM_{2.5}. To comply with this, it is not strictly necessary to demonstrate equivalence to the reference PM_{2.5} method in an absolute sense, only to demonstrate continuity of measurements for a parameter “similar” to PM_{2.5}. This may open the way to some of the common automated methods such as TEOM, FDMS, beta attenuation and single particle light scattering having an official role in PM_{2.5} measurements, generating data that may provide an alternative to filter weighing methods in the longer term.

6. References

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Annex 1 –Weighing protocol (relevant extract)

6.2 Preparation for weighing

6.2.1 Mark all filters with a unique identifying number. Filters should be marked (on the side not sampled) with ink, pencil or a suitable stamp. After marking filters should be examined to ensure that there are no holes through the filter surface.

6.2.2 Exercise the balance by repeating the following procedure three times:

- (a) Place a 100mg metal mass piece onto the balance pan.
- (b) Wait until the reading is close to 100mg and remove the mass piece.
- (c) Remove the metal mass.

6.2.3 Remove circular disk of metal that is used to aid the discharging of static charges and zero the balance.

6.2.4 Perform an internal calibration of the balance.

6.2.5 Replace circular disk

6.2.6 Re-zero the balance.

6.2.7 Note the starting time, temperature and relative humidity in a weighing datasheet. An example of a weighing sheet may be seen in Appendix 1.

Note To assist in discharging static charges, a thin metallic disc (the same size or slightly larger than the filter) is placed the balance pan for all weighings. Anti-static devices (guns, fans, etc.) may also be used if they have been shown to operate successfully.

6.3 Weighing of sample filters

6.3.1. The resolution of the balance used for weighing must be better than or equal to 10 μ g.

6.3.2 Weighing a sample filter against a tare weight helps to correct for any changes in atmospheric conditions before and after sampling. A tare weight should weighed every four sample filters.

6.3.3 Frequent weighing of 50mg and 200mg check weights and the recording of the zero reading monitors any changes in the calibration of the balance. This performance check should be performed at the beginning and end of each weighing sequence, as well as after a maximum of each 30 sample filters.

6.3.4 A typical weighing sequence is given below:

- (1) Zero reading^{*}
- (2) 50mg check weight
- (3) 200mg check weight
- (4) Tare weight (100mg)[†]
- (5) Sample filter 1
- (6) Sample filter 2
- (7) Sample filter 3
- (8) Sample filter 4

- (9) Tare weight
- (10) Sample filter 5
- (11) Sample filter 6
- (12) Sample filter 7
- (13) Sample filter 8
- (14) Tare weight
- (15) Sample filter 9
- (...) ...
- (z-4) Sample filter n
- (z-3) Tare weight
- (z-2) Zero reading
- (z-1) 50mg check weight
- (z) 200mg check weight

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

- 6.3.5 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.
 - (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.

6.3.6 Filters are first weighed after an approximate 48 hour conditioning period and are then weighed again after another approximate 24 hour conditioning period. A filter weight is determined by a single weighing of the filter by the balance.

6.4 Data Analysis

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

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

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

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

6.4.2 The measured mass of the filter for the unloaded or loaded filter is the average of the two masses measured 24 hours apart. This is calculated by the use of the following equation:

$$m_{unloaded} \text{ or } m_{loaded} = \frac{(m_{t=0} + m_{t+24hr})}{2}$$

where:

- $m_{unloaded}$ = relative mass of unloaded filter (unsampled)
- m_{loaded} = relative of particulate loaded filter (sampled)
- $m_{t=0}$ = relative mass measurement performed after 48 hrs of conditioning
- $m_{t=24}$ = relative mass measurement performed after an additional 24hrs of conditioning.

Annex 2 – Short paper on the effect of humidity on PM

CEN TC 264 WG 15

Outline summary of knowledge regarding the effect of varying conditioning parameters for gravimetric filters

Paul Quincey; Theo Hafkenscheid
January 2007

1 Introduction

Following Resolution 196, this short document is required “to summarise the knowledge of uncertainty components, especially the effect of variations to conditioning parameters.”

2 Key uncertainty components

From Table 1 in EN 14907, the main uncertainty components needing further quantification are considered to be:

- 9.3.2.4 Loss of semi-volatile particulate matter between collection and weighing
- 9.3.2.5 Change in filter mass between the unloaded and loaded weighings due to water content
- 9.3.2.6 Variation in mass of particulate matter due to water content
- 9.3.2.9 Effects of static electrical forces during weighing
- 9.3.2.10 Contamination or loss of filter material between unloaded and loaded weighings.

The rest of this document will consider only 9.3.2.5 and 9.3.2.6, specifically the effects of changing the temperature and humidity conditions during filter conditioning.

3 Current T and RH conditions

	CEN	US EPA
T	$20 \pm 1 \text{ }^{\circ}\text{C}$	$20\text{-}23 \pm 2 \text{ }^{\circ}\text{C}$
RH	$50 \pm 5 \%$	$30\text{-}40 \pm 5 \%$

4 Effects of changing the conditioning temperature

A significant change in the required conditioning temperature is not considered practical or desirable.

Changing the tolerance for the temperature should be considered, but is secondary to the consideration of changing the relative humidity.

5 Effects of changing the conditioning relative humidity

There are four distinct potential effects of the humidity condition on the final result.

Effects on the filter material:

Hysteretic effects causing the filter mass at the pre-weighing to differ from the mass at the post-weighing, even if the humidity is the same, depending on the filter's humidity history.

Variations in filter mass because the humidity is different at pre- and post-weighings, within the prescribed tolerance.

Effects on the particulate matter:

Hysteretic hygroscopic effects allowing the PM mass to have two distinct values at the post-weighing, at the correct humidity, depending on the sample's humidity history (see Figure 1)

Variations in PM mass with humidity because of hygroscopic effects (see 6.2 below).

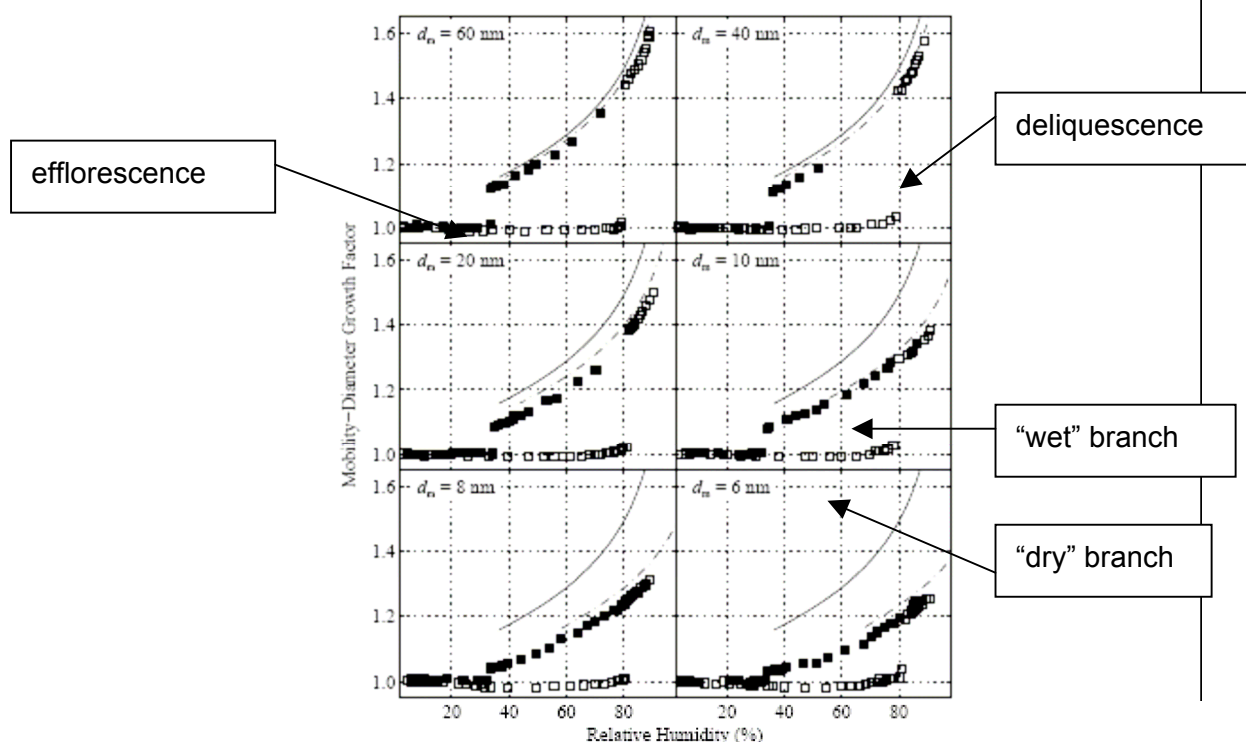


Fig. 5. Hygroscopic growth curves of ammonium sulphate aerosol particles generated by electrospray. Open symbols were recorded during deliquescence-mode measurements. Solid symbols were recorded during efflorescence-mode experiments and were analyzed by using either one- or two-peak fits, as necessary (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 $0 < w_r < 78\%$.

Figure 1, Data for ammonium sulphate particles of different sizes, from Atmos. Chem. Phys. Discuss., 6, 7051–7073, 2006 Biskos et al.

5 Discussion and preliminary quantification

6.1 Filter material

5.1 and 5.2 are of course highly dependent on the filter material. Brown et al (Atmospheric Environment 40 (2006) 4670-4678) found considerable variability even within filters of the same material, with potential errors of 100 μg ($\sim 2 \mu\text{g}/\text{m}^3$) for quartz and glass fibre filters. Effects for PTFE-coated glass fibre were much reduced ($< 0.1 \mu\text{g}/\text{m}^3$).

Well-defined specification of the filter material is considered to be a better way to control these uncertainty components than changing the filter conditioning parameters. This is being addressed by a separate WG document.

6.2 PM

The effects will of course depend on the composition of the PM. Sodium chloride, nitrates and sulphates are known to be significant components of PM with hygroscopic behaviour similar to that in the Figure 1.

The main points are:

- There is a major difference in mass between PM on the upper “wet” branch of the growth curve and the lower “dry” branch ($\sim 30\%$ of mass at 50%RH).
- The variation of PM mass as the humidity changes is much larger on the “wet” branch than on the “dry” branch.

To assess practical effects from a theoretical viewpoint it is clearly important to know the composition of the PM, whether the relevant components on the filters are in the “wet” or “dry” state, and any relevant thermodynamic factors affecting equilibrium between eg nitrates, sulphates and water. If the hygroscopic components are “dry”, changes in humidity during conditioning will have little effect on PM mass, while if “wet”, the effects are much greater (see 6.2.3 and 6.2.4 below).

6.2.1 Estimates of bound water content in measured PM_{10} from measurements

A mass closure study in the UK (Harrison et al, Atmospheric Environment 37 (2003) 4927-4933) found that the data from gravimetric PM samples correlated with sulphate and nitrate being in the hydrated state, but not chloride. This approach implies a typical urban background PM_{10} bound water mass content of around 7%, though of course this is highly variable with composition.

The figure of 7% can therefore be taken as an estimate of the decrease in mean UK urban background PM_{10} concentrations if samples are weighed “dry”, rather than at 50% RH. However, there will be a much larger effect at higher PM concentrations - up to 30% - as such elevations are often caused by secondary particles with a high proportion of sulphate and nitrate.

A US study in Pittsburgh (Rees et al, Atmospheric Environment 38 (2004) 3305-3318) found that bound water formed 8% of $\text{PM}_{2.5}$ mass in winter, and 16% in summer, when filters were conditioned at 35% RH. This was primarily attributed to ammonium bisulphate (NH_4HSO_4).

A US study in semi-rural North Carolina (Speer et al, J Aerosol Sci 34, 63-77) estimated that

on average 20% of the bound water was associated with organic compounds.

6.2.2 Estimates of bound water content in measured PM₁₀ from modelling

In principle the bound water content can be calculated from the PM composition and the relative humidity from thermodynamic considerations, for example using the Aerosol Inorganics Model (Clegg et al, J Phys Chem (1998) 102 2137-2154) or the GFEMN model (Ansari and Pandis, Atmospheric Environment (1999) 33, 745-757). Such models enable the measurements in 6.2.1 to be checked, and would allow the effect of changing the conditioning humidity to be calculated without the need for further experimental work.

It is clear that the water content calculation is not simple, depending for example on the degree of sulphate ammoniation and the relative amount of nitrate to sulphate (Frank, JAWMA (2006) 56 500-511). Moreover, the air flow through the filter during sampling may affect the equilibrium. While the agreement of such models with measured values is encouraging, there are still significant uncertainties in both the models and the measurements when applying the models to real samples. A very simple model is used in the examples below for illustrative purposes.

Further work is required before the bound water content can be calculated with confidence from the concentrations of hygroscopic components and the relative humidity history.

There are likely to be occasions when hygroscopic components of PM can be weighed either “wet” or “dry” within the scope of the current reference method, depending on the detailed circumstances, with a significant difference in PM mass. The WG should decide whether “wet” or “dry” is the correct mass for the purposes of the CEN standard.

6.2.3 Estimates of the effects of changing the humidity on PM mass

The effects will depend on whether the WG decides that “wet” or “dry” is the correct answer to the last question.

a) If the answer is “dry”:

Lowering the conditioning humidity to ~30% (or below the relevant efflorescence RHs) would guarantee consistent and correct results. There would be a small change to average results, but a significant change for a minority of filters with high hygroscopic content, due to loss of water (and possibly some ammonium nitrate). Uncertainties would be significantly reduced.

b) If the answer is “wet”:

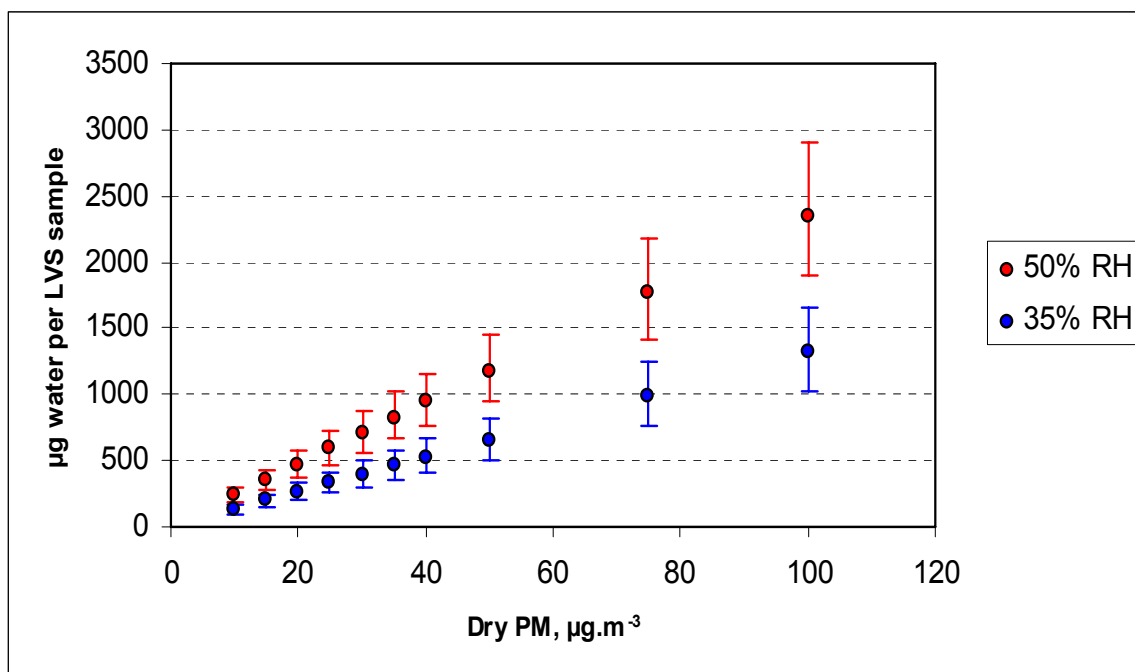
Lowering the conditioning humidity to ~35% (or above the relevant efflorescence RHs) would lead to similarly small reductions in average PM mass, with significant reductions in some cases due to loss of water (and possibly some ammonium nitrate), and lowering of measurement uncertainty.

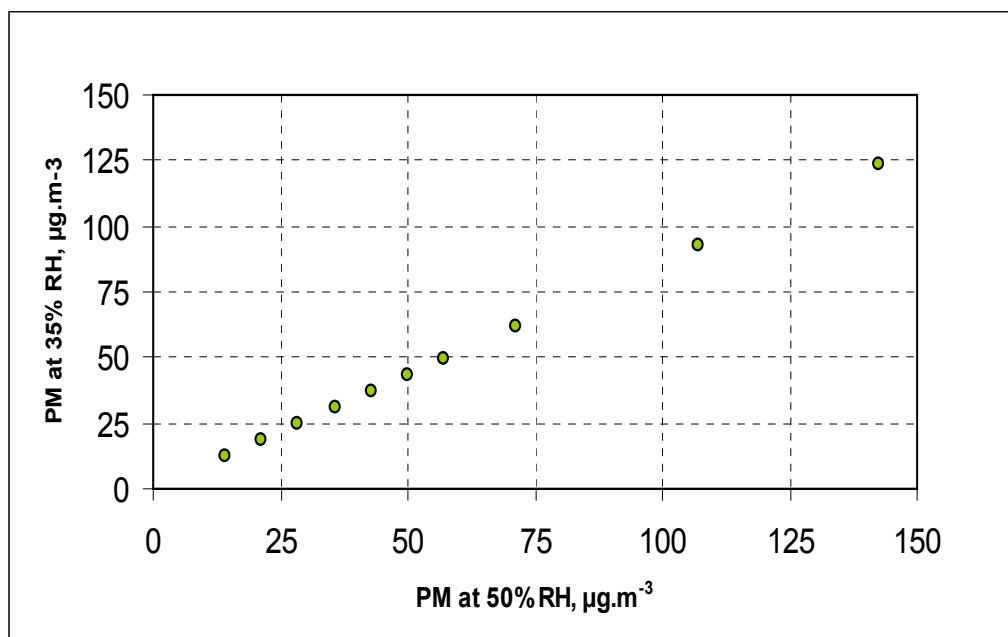
Lowering the conditioning humidity to ~30% (or below the relevant efflorescence RHs) would lead to incorrect (low) results.

Making reasonable assumptions for the ~35% RH case, we calculate the following for a

notional sample with a growth factor of 1.19 at 50% RH and 1.09 at 30% RH - *similar to pure ammonium sulphate in the "wet" state*:

- At 50% RH the fraction of the mass sampled consisting of water is 0,30; at 35% RH this fraction decreases to 0,19. The fraction of 0,30 is consistent with the value used for the hydration of sulphate in the mass closure study above.
- There is a 14% difference in the masses of PM calculated for conditions of 50 %RH and 35 %RH. The uncertainties resulting from possible variations around each single RH (± 5 %RH) are also quite large: $\pm 6,4\%$ for 50 %RH, and $\pm 4,7\%$ for 35 %RH.
- If the filter conditioning is performed at 35 %RH, the effect (for these extreme case samples) would be equivalent to the daily limit value of $50 \mu\text{g.m}^{-3}$ being increased to 57. The effect on the number of exceedances will depend on the distribution of the daily concentration values and the composition of the PM.



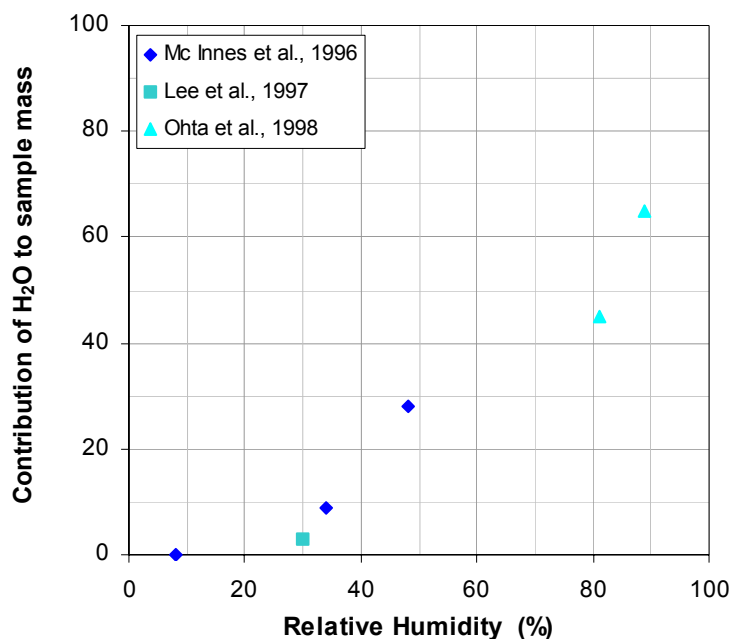


6.2.4 Measurements of the effects of changing the humidity on PM mass

There has been relatively little work done on weighing PM samples at different humidities. An unpublished study at JRC Ispra looking at PM_{10} from Ispra, Bologna and Madrid found that the PM mass changed by only 1 to 3 % when the humidity was raised from 20% to 50% RH. This is compatible with the hygroscopic components reaching the “dry” state while being conditioned at 20%. The Bologna sample masses increased by only 2 to 3% when RH was raised from 20% to 80%, whereas the Ispra and Madrid samples increased in mass by around 10% over this range.

Further data is available from the EMEP station at Ispra, where PM mass is routinely measured at both 50% RH and 20% RH. The differences in PM mass between the two cases are typically 8-12%. This change is the same whether the 50% RH case is measured first or second.

A related report EUR 20238 (2002) “Guidelines for concentration and exposure-response measurements of fine and ultrafine particulate matter for use in epidemiological studies” contains the following chart of water content versus relative humidity, based on US data, but the background to the data is not clear.



7 Conclusions

Lowering the relative humidity during filter conditioning has the potential to:

- Reduce the (presumably harmless) water content measured by gravimetric methods
- Reduce the measurement uncertainty associated with hysteretic water content

On the other hand, it may:

- Introduce a step change in the datasets (though this is likely to be small compared with the current measurement uncertainty)
- Increase the measurement uncertainty (if the chosen RH is close to the efflorescence RH)
- Make weighing more difficult in practice

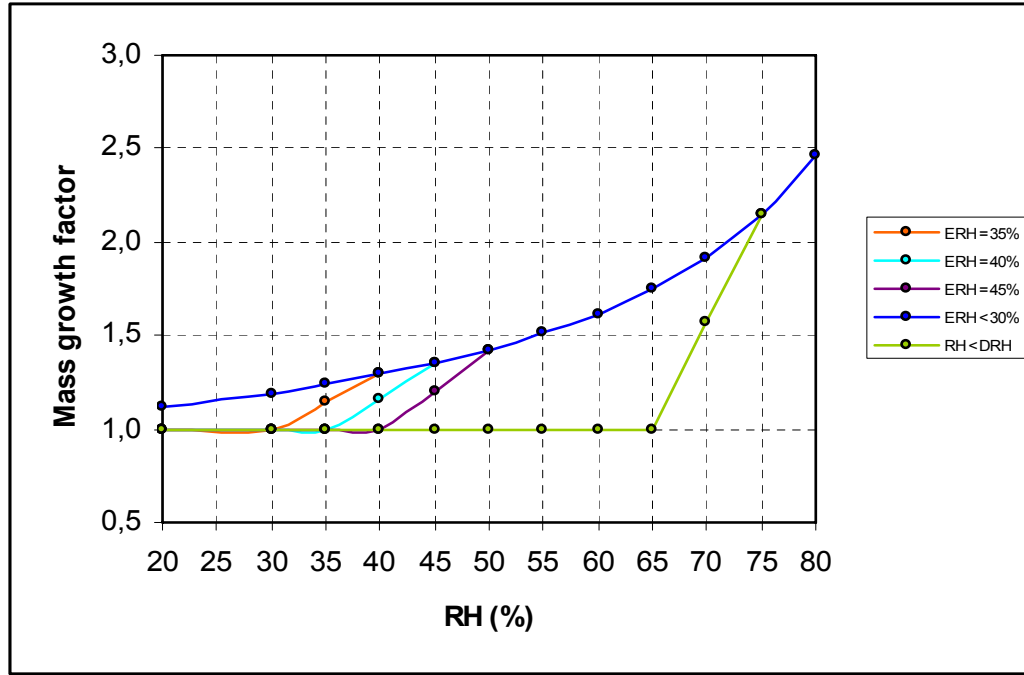
It is not possible to make quantitative estimates about the practical effect of changing the conditioning humidity without knowledge of:

- Particle composition – partial information for this is available
- Sampling T and RH conditions – information is available
- and
 - Either a validated model for predicting water content of PM samples
 - Or representative experimental results covering PM from across Europe.

The central issue could be addressed by assembling a representative collection of European filter samples (which could be routine filters from normal network sites, so that no special monitoring campaign is required), which had a known humidity history since sampling, and determining the mass change at different humidities. As a minimum the humidity would be taken

from 55% RH to 25% RH and back in 5% steps, so that both the preferred RH and the tolerance could be assessed. Whatever the final decision regarding CEN standard conditions for filter conditioning, this would provide valuable information about water content that does not seem to be available otherwise. We recommend that something like this should be included in the CEN experimental plan.

ANNEX – Further investigation of uncertainties at different humidities



Particle growth hysteresis curves for $DRH \approx 70\%$ and various ERH

From the above figure it may be inferred that – roughly speaking - a stable weighing result within the tolerance of the conditioning relative humidity (CRH) is obtained when the CRH is about $(ERH - 10)$, where ERH is the particle efflorescence relative humidity (in %). Hence, if $ERH \gtrsim 45\%RH$, then a CRH of $35\%RH$ will lead to stable results, whether or not the PM was on the “wet” or the “dry” branch of the hysteresis curve.

Assuming that the as-collected PM is on the “wet” branch of the hysteresis curve, however, if $ERH = 35\%RH$, then a CRH of $35\%RH$ will result in a huge weighing uncertainty due to the possible variation of the particle mass growth factor (MGF) between 1 and 1.3, the resulting relative uncertainty being $\approx 15\%$ – assuming a rectangular distribution of MGF for reasons of simplicity.

In this situation a $CRH = 50\% \pm 5\%$ would mean MGFs between 1.5 and 1.35,

Using the equation:

$$u^2(mgf) = (3\varepsilon)^2 (1 - rh)^{3\varepsilon - 1} u^2(rh)$$

where ε is the exponent for the “wet” branch in the equation $mgf = (1 - rh)^{-\varepsilon}$,

this gives a relative uncertainty of approximately $\pm 4\%$ – again, assuming a rectangular distribution of RH values for reasons of simplicity.

Annex 3 – Report on Equivalence Workshop May 2007

courtesy of Dr Theo Hafkenscheid, NMI, NL

Objective

The main objective of the workshop was to generate information for the improvement/revision of the Guidance Report for the Demonstration of Equivalence, aiming where possible at simplification and streamlining of procedures, and at a broad acceptance of conclusions.

Overview of discussion items

Broadly, the items discussed during the workshop can be categorized as follows.

- The general approach to equivalence demonstration, including interpretation of elements of the guidance report
- The practical approach to equivalence demonstration, with a main focus on particulate matter
- (Statistical) evaluation approaches used
- Ongoing QA/QC
- Practical experiences in different member states, including the use of new approaches
- Dissemination/sharing of information.

Summary of discussion and conclusions

Main focus

The main focus of the workshop has been on (items related to) the equivalence of automated continuous methods for measuring particulate matter. As a part of the discussion also items not strictly related to equivalence but relevant for its establishment have been discussed:

- The intrinsic uncertainty of the current realizations of the reference method for measuring PM (e.g. selection of type and brand of filter material; weighing conditions)
- Type approval of automated continuous methods.

Further discussion of these items is within the scope of the current activities of CEN/TC264 WG 15.

General approach to equivalence demonstration

Establishment of equivalence

The national competent authority – based on a validation study, considering the scope of the application of the equivalent method (e.g. site conditions, concentration levels, environmental and meteorological conditions) – authorizes the use of the equivalent method at the national level. The declaration of equivalence will include its scope (see above), and the period of validity of the claim.

Generalization/mutual acceptance/recognition of equivalence claims

The potential for a mutual acceptance of equivalence demonstrations between member states is limited by the scopes of the individual claims. For methods for which equivalence has been demonstrated over a broad range of conditions/scopes (see above) a broader claim of equivalence may be considered. The AQUILA forum may have an important role in this by providing advice on the generalization of claims.

Definition of a candidate equivalent method, particularly for PM

A candidate method may include corrections other than those derived from the evaluation of equivalence, e.g. corrections for effects of temperature and relative humidity if the uncertainties resulting from the corrections are included in the uncertainty budget of the candidate method.

In addition, more than one correction may be used for one candidate method if the scope of the associated equivalence claims is well defined, and if separate ongoing QA/QC suitably includes all differentiations.

A new approach is currently tested in the UK and France. The approach comprises a “dynamic” “remote” correction of hourly TEOM data using correlations with a regionally centered FDMS-TEOM. In this approach the candidate method is a “model system” rather than a method.

This approach should be accompanied with appropriate estimations of the uncertainties associated with these corrections.

In any case, the current equivalence protocol does not cover such approaches, and needs updating to include these new developments.

Practical approach to equivalence demonstration

Use of an equivalent method instead of a realization of the reference method

It has been proposed to use an already equivalent method as “reference” for comparison with a new candidate method. Here a distinction shall be made between a variation on the realization of the reference method (e.g. a sampler with automatic sample changer) and a different methodology.

In the former case the use of the equivalent method is acceptable as long as the effect of the variation is known and not significant.

In the latter case the concept of comparison with a “reference” may be invalidated because the measurement results of the different methodology will almost certainly have a bias towards the results of the reference method (it is assumed that the reference method is unbiased by definition). This requires a careful reconsideration of the statistics to be applied for the uncertainty evaluation. Moreover, the uncertainty of the equivalent method should be fully propagated into that of the new candidate method, most probably resulting in high uncertainties.

Obligation to evaluate equivalence for various data subsets (PM)

Questions have been raised as to the necessity to

- separately evaluate uncertainty for PM candidate methods for 7 different datasets, including subsets based on concentration ranges

- to pass the evaluation criteria for all separate datasets.

Sometimes practical limitations (e.g. low concentrations for specific sites) will prevent the full evaluation required.

This issue requires a reconsideration of the requirements of the current evaluation protocol.

Application of corrections

Questions have been raised as to whether corrections of slope and/or intercept should be applied when

- the slope / intercept are significantly different from 1 / 0 at the 95% confidence level; it has been proposed rather to use fixed ranges for each (cf. EN 12341)
- the uncertainty of the candidate method already fulfils the equivalence criterion.

In principle, ISO-GUM states that corrections shall always be applied in case of significant differences. In practice this may only be useful when the resulting uncertainty is positively affected.

Another factor to consider may be the uncertainty of the reference method itself.

For PM an additional issue may be the effect on the number of exceedances of daily limit value, although the uncertainty associated with the determination of this number is high already.

Statistical procedures

Removal of outliers

It has been proposed not to base the removal of outliers solely on technical grounds, but rather to use a statistical level of significance (e.g. 99%). An argument for using a statistical approach may be that in a large dataset a certain fraction of data from the manual standard method will be “aberrant” beyond demonstrability anyway.

Use of orthogonal regression forced through (0,0)

It has been proposed to use orthogonal regression forced through (0,0) when the intercept obtained by the general orthogonal regression procedure is not significantly different from zero.

In order to be able to accept this approach the effects on the slope of the regression (the calibration factor) should be understood. Possibly limitations should be set to the magnitude of the intercept.

A further question is how the uncertainty of the corrected results should be calculated.

At minimum the uncertainty of the correction factor shall be included in the uncertainty budget.

Use of different regression techniques

The introduction of a different regression method based on a criterion of symmetry along the correlation line instead of minimizing the sum of residual values has been proposed. Although it has been shown that when applying this criterion the Exploratory Regression method may have a better performance than the orthogonal regression technique, it is unclear whether this criterion provides a better correlation line for equivalence purposes because of an increased number of outliers and a potential underestimation of the uncertainty of the candidate method.

Ongoing QA/QC

The practical application of an equivalent method should always be accompanied by some form of ongoing QA/QC.

In the case of PM this may consist of periods of parallel measurements performed using a realization of the reference method.

It has been suggested to link the intensity of the QA/QC to the uncertainty level of the equivalent method.

If one candidate method is applied with different corrections the ongoing QA/QC should be such that all differentiations within the candidate method are suitably covered.

Experiences in Member States

A number of Member States presented their experiences – both orally and through posters – with the application of the approach to equivalence demonstration laid down in the current Guidance Report.

Dissemination of information

During the workshop it has been concluded that currently a “threshold” exists for sharing and exchanging information on equivalence trials and experiences. It has been suggested to open a website specifically for the exchange of information on equivalence.

Apart from serving as a medium for sharing information and discussion, the site may contain a list of equivalent methods plus scopes that have been “approved” by the AQUILA forum.