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REVIEW ARTICLE

Ambient air particulate matter PM_{10} and $PM_{2.5}$: developments in European measurement methods and legislation

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Abstract

The measure of airborne particulate matter PM_{10} is effectively defined for European regulatory purposes by the European Committee for Standardisation (CEN) standard EN 12341:1998 – a gravimetric filter-based method. However, compared with the reference methods written for other pollutants, specifically to address the needs of the Air Quality Directives, EN 12341 falls short in areas such as ongoing Quality Assurance and Quality Control. Also, scientific knowledge about PM has moved on considerably since 1998, so that we now realize 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 paper outlines the present position of the EN 12341 revision and recent changes to EU Air Quality legislation.

Keywords: *Particulate matter; gravimetry; PM10; PM2.5; air quality monitoring*

Introduction

Airborne particulate matter (PM) is associated with major health effects worldwide. It also has a significant role in climate change. Current UK and European legislation sets limit values on health grounds for ambient concentrations of PM_{10} (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 pollutants. Standardization 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 standardization of automated methods for measuring PM.

Both the standardization process and the revision of the equivalence procedure are currently ongoing. This short paper aims to summarize the legislative background, the scientific background and outstanding measurement issues in the definition of standard methods for PM_{10} and $PM_{2.5}$. The paper 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.

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The European legislative background

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 1999 in the first 'Daughter', Directive 1999/30/EC, which required that the daily average should not exceed 50 μg m^{-3} more than 35 times in a year, and the annual average should not exceed 40 μg m^{-3}. The Directive referred to the CEN standard EN 12341 (CEN 1998) as the reference method for PM_{10} measurement. This Directive also put an obligation on member states to monitor $PM_{2.5}$ at some 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 PM_{10} concentrations to be provided to the public, but the reference method, based on the manual weighing of filters sampled for 24 h, 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 PM_{10}. This is primarily due to a large, variable component of the PM being semivolatile, meaning that it is volatilized 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 (EC 2001), 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 became available.

In 2004 the second of two position papers was produced by a group within the Clean Air for Europe (CAFE) programme (CAFE 2004). Its main recommendation, in the context of measurement, was a move from PM_{10} to $PM_{2.5}$ as the principal metric for assessing exposure to PM. This was based on health studies, primarily carried out in USA. The reference method for $PM_{2.5}$ would be the CEN standard method then being developed (CEN 2005).

The practical meaning of equivalence was set out in a guidance document, published in 2005 (EC 2005). For PM, this set out 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 2004 position paper has led to a recently agreed Air Quality Directive, 2008/50/EC (EC 2008), to replace the Framework and several Daughter Directives. PM_{10} limit values remain the same. There is a limit value on the annual average concentration of $PM_{2.5}$ of 25 μg m^{-3}, to be met by 2015. There is no daily average $PM_{2.5}$ requirement, but there are new requirements based on an average exposure indicator, which is a population-weighed national 3-year average for $PM_{2.5}$ based on representative sampling. The Directive requires this indicator to decrease by a fixed percentage (dependent on initial concentration) over 10 years. There is also an obligation for the indicator to be below 20 μg m^{-3} by 2015. The average exposure indicator approach 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.

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

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, semivolatile 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 sulphate and sodium nitrate. The definition of PM_{10} and $PM_{2.5}$ is therefore inherently method-dependent.

Ideally, any measurement method for PM_{10} and $PM_{2.5}$ must clearly address the following issues:

- The allowable range of particle sizes – no size selection technique can deliver an exact cut-off at 10 μm, for example;
- 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;
- The allowable losses of semivolatile material, such as ammonium nitrate and some organic compounds. Losses can occur during sampling, and between sampling and weighing;
- 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 PM_{10} 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:

- The collection efficiency of the filter, both in allowing particles to pass through and inefficiency caused by partial blockage;
- Allowable chemical reactions between gaseous pollutants and the filter;
- Allowable changes in filter mass between the pre-sampling and post-sampling weighing, due for example to water absorption or detachment of filter fibres;
- 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 become more important over time, for the following reasons:

- PM concentrations have fallen dramatically – by around a factor of 10 since the early 1960s (although they are still responsible for large numbers of premature deaths, and appear to have stabilized since around 2000) (AQEG 2005) – making all weighing errors more significant;
- The emphasis has moved to lower size fractions, for example from PM_{10} to $PM_{2.5}$, so that smaller quantities are measured, again making all weighing errors more significant;
- 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 volatility.
- The fact that the coarse fraction is dominated by crustal components, which are generally insoluble and non-volatile, compounds the previous two factors by making the $PM_{2.5}$ fraction proportionately more susceptible to humidity and temperature.

Issues currently being addressed

Choice of filter material

One of the two key decisions facing the CEN Working Group revising the PM_{10} standard is whether to change the specification for filters allowed within the standard method. At present only quartz filters are allowed within the PM_{10} 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 be good standardization practice to include only one filter type, and there is some support for retaining the quartz-only specification. However, work at NPL (Brown et al. 2006) has highlighted 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 (Vercauteren 2007, pers. commun.), and elsewhere, that shows quartz filters taken from the manufacturer's packaging taking several months to attain a stable weight, with weight changes of around 200 μg. This is attributed to a combination of water absorption and absorption of organic material.

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.

There is no single filter type that is ideal. NPL has favoured PTFE-coated glass fibre (Brown et al. 2006), and this has been used in UK equivalence trials, 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. To summarize 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.

N.B. '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.

Humidity during pre-sampling and post-sampling filter conditioning

Filters are brought to conditions of controlled temperature and humidity before the pre-sampling and post-sampling weighing. This is to minimize 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 ± 1°C and 50 ± 5% RH.

This requirement brings a potential problem associated with hysteretic water absorption 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 'wet' branch of the growth curve compared with the 'dry' branch (~30% of mass at 50% RH). Under the conditions of the standard, the PM can 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 'dry' branch of the growth curve. This is reflected by requirements in the US, where US EPA requires 30–40 ± 5% RH.

The decision as to whether to revise the conditions in EN 12341 will be made after further experimental work, due to take place in 2009.

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.

One notable development is that within the new Air Quality Directive 2008/50/EC (EC 2008) there is a requirement to measure the composition of $PM_{2.5}$ for at least one site, to include nitrate, sulphate, ammonium, organic carbon (OC), elemental carbon (EC), Na^+, K^+, Cl^-, Ca^{2+} and Mg^{2+}. 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 PM_{10} 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 standardized, the emphasis on PM and its health effects may gradually move away from the simple total-mass parameters.

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