PM$_{10}$ and PM$_{2.5}$ - development of new national and international measurement methods

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1   Introduction

PM$_{10}$ and PM$_{2.5}$ (particulate matter below 10 🏭 and 2.5 🏭 in diameter respectively) are a combination of a large number of different chemical species emitted from several different sources. The lack of a clear chemical definition has led to many problems in areas such as measurement and source apportionment.

PM$_{10}$ and PM$_{2.5}$ arise as direct emissions from some sources, both natural and from human activities, and also as a result of interactions of pollutants in the atmosphere. Potential sources from human activities include coal-fired power plants, industry, agriculture and road transport. Some of the particles are solids: by-products of combustion, or incombustible matter; whereas others are secondary aerosols such as sulphate and nitrate species or semi-volatile organic compounds (SVOCs).

The chemical and physical nature of fine particulate emissions are considered to change considerably after emission into the atmosphere, varying with factors such as location, temperature, humidity and the presence of other pollutants. The study of PM$_{10}$ and PM$_{2.5}$ in the atmosphere involves not only the measurement of these species at the source and in ambient air, but also requires complex chemical modelling programmes to relate the two values.

The sampling and analysis of any pollutant is of fundamental importance. A species can neither be understood nor managed without accurate and reliable measurement. The measurement of PM$_{10}$ and, to a greater extent, PM$_{2.5}$ is known to be prone to significant artefacts and inaccuracies. This has led to what may be regarded by some as a lack of valid data and a poor understanding of the chemistry of particulate matter. Hence there are problems in relating ambient concentrations to health effects and ultimately difficulties in applying a successful control and management plan for PM$_{10}$ and PM$_{2.5}$. However, new and improved sampling techniques and expanding monitoring networks throughout Europe and the USA should increase our knowledge and understanding.

2   Definitions

As mentioned above, unlike other pollutants such as SO$_2$ and NOx, PM$_{10}$ and PM$_{2.5}$ are not a single chemical species. Rather they are a heterogeneous mix of many different and often reactive elements and compounds including ammonium, nitrates, sulphates, organic compounds and mineral species. It is also possible that viable species such as fungi, bacteria, pollen, yeast and viruses will contribute to PM$_{10}$ and PM$_{2.5}$ samples in many locations. Since the mix of species is so complex and variable in its chemical and physical characteristics, a strict definition or set of

identification criteria is not yet possible. In fact, particulate matter is the only air pollutant regulated by the US EPA that does not specify a chemical composition. Although a single definition or set of identification criteria would be beneficial to all aspects of PM_{10} and $PM_{2.5}$ research, it is unlikely that a specific chemical definition will ever be produced. It is more likely that this species will remain defined by the sampling methodology.

With this in mind, it is important to remember that there are two major sub-groups of fine particulates, each with very different chemistry and measurement requirements. These are:

-       primary particles - the fraction which is in particulate form at stack gas temperature and can be caught in standard particulate measurement systems;
-       secondary particles - the fraction in gaseous or aerosol form which *MAY* form particulates in the plume or downwind.

Primary particles are relatively easy to capture, although doing so accurately and precisely at low concentrations can be difficult.

The precursors of secondary particles can be captured using systems such as impinger trains, denuders or dilution systems. However, it can never be known exactly how these species would behave in the ambient air, for example:

-       they could produce secondary particles on their own through aerosol formation;
-       they could adhere to primary particles to create larger particles;
-       they could react with other species in ambient air to create combined secondary particles;
-       they could remain in gaseous form until washed from the atmosphere.

Although secondary particulates can be created and measured by impinger methods, it should not be assumed that these secondary particulates are truly representative of those that actually form in the plume from a source. The information should serve only as a guide to possible reaction products and should be used in source apportionment ONLY if suitable atmospheric modelling is included.

The following section describes the sampling systems available for measuring primary and secondary fine PM.

3   Sampling

There are a large number of sampling systems available for PM_{10} and $PM_{2.5}$, each with its own advantages and disadvantages. Most have at least one characteristic that can be a source of artefact formation or sample loss. However, all of these share a single common limitation - the inlet. Since the inlet determines which particles are excluded and which pass through to the collection system, the inlet is actually defining the particle cut-off size and thus the species captured. The correct use of the inlet - the flow rate and the general operation of the system by the sampling professional - is vital to the accuracy of any PM_{10} or $PM_{2.5}$ sampling.

Size selective inlets for stacks which are based on sampling effectiveness curves are defined by their 50% cut point size, where half of the particles of that size pass through the inlet and the other half is deposited within the inlet. Inlets based on cyclones or impactors are used to screen particle in both stack and ambient sampling systems.

Once the sample has passed the inlet, the material must be collected in a form that can be weighed and/or analysed further. The following sections briefly review the options currently available.

3.1   Systems for primary particles

One of the most common methods of particle collection is a **filter.** A selection of filter materials is available and the selection depends on what species are to be targeted and which analysis methods will be used (Dzubay and Stevens, 1991). Between sampling and final weighing, the filter is exposed to various ambient conditions of temperature and humidity which could lead to additional variation in the measured concentration of semi-volatile materials (Allen and others, 1997). Storage and treatments such as equilibration also lead to loss of some chemical species. Because the sample sizes collected from PM_{10} and $PM_{2.5}$ studies are so small, weighing and handling of filters can also be a major source of error (QUARG, 1996).

The use of **impactors** as pre-screening inlets is common. However, cascade impactors can be used as classifiers to divide particles into sub-groups by size. The samples are weighed and, if necessary, can be removed for further chemical analysis. Because of the use of jets within the sampling system the method is not truly isokinetic. Cascade impactors are bulky and heavy, especially those which have a large number of separation stages. They are therefore not ideal for use on stacks, although this could also be said of cyclones which are commonly used in stacks. Cascade impactors can, however, cope with high temperatures.

Cyclones are most commonly used as size-selective inlets but are occasionally used as collection systems, especially in stack studies. However, according to a review by the US National Mining Association (NMA, 1997), cyclones do not give such sharp classification characteristics as impactors. They are more difficult to design for an exact cut-size than either impactors or virtual impactors.

In addition to manual methods for primary particles, it is also possible that **automated systems** could be standardised for $PM_{10/2.5}$ measurement. For example, the tapered element oscillating microbalance (TEOM) is based on an oscillating filter and can measure particulates in real-time on a first principles basis, offering very accurate and reliable measurement. An upstream impactor or cyclone can be used to pre-collect larger particles for the measurement of PM_{10} or $PM_{2.5}$.

3.2   Systems for secondary particulates

The definition of condensable particulates is complex as condensation will depend on the sampling conditions. The US EPA defined condensable particulate matter (CPM) by the measurement method, Method 202 (*see* below). CPM is therefore material which passes through a filter (at a specified temperature) and is collected by a cooled **impinger train**. The impinger contents are recovered and extracted with methylene chloride (to determine organic material). The methylene chloride and water fractions are then reduced to dryness and the condensable material is determined gravimetrically.

The measurement of CPM in impinger systems is prone to artefacts. It is common for CPM to be overestimated due to the formation of sulphate and ammonia salts. For example, a study on coal-fired units with high sulphate emissions (2000 ppm) produced a value for PM_{10} of which 41% was due to artefact formation on both the filters and impingers. Even on gas-fired boilers with 1-10 ppm SO2, 25-100% of the condensible particulate matter measured may be artefact (England, 2004).

There are alternative systems to impinger trains but these are used more often for research purposes than emissions monitoring. These include systems such as **denuders**. A typical diffusion denuder is a chemically coated cylindrical tube that captures gases that diffuse to the walls and react with the coating. Annular denuders collect gaseous species by moving air through an annular space between two concentric glass cylinders coated with appropriate chemical substrate.

The results from studies using denuder systems arguably provide more information on the aerosol species which may be present, particularly in $PM_{2.5}$ studies. The capture of these species prior to the filter stage helps to ensure that no reactions are induced between the individual chemical species which may occur on filters. The main reason for using a denuder system is to distinguish gas phase species from aerosols by first removing the gases and collecting the aerosols on the filter. This allows the distinction to be made between, for example, HNO_3 and NH_4 which would both be measured as NO_3^- in solution.

Denuder systems offer the potential to be amongst the most useful sampling methods for PM_{10} and $PM_{2.5}$ with respect to speciation and chemistry. However, they are batch methods and are expensive and complex compared to the other options.

Dilution systems are becoming popular, especially for use in source apportionment studies. In dilution systems both primary and secondary particles are measured together. Dilution systems are discussed below.

3.3 Systems for total fine particulates

Total fine particulates, both primary and secondary particles, can be measured by a combination of methods such as a cyclone or impactor system run in conjunction with an impinger system. However, as discussed above, these systems are prone to artefacts.

Dilution systems are becoming more popular, especially for use in source apportionment studies. The sample is collected from the stack and diluted with clean air. It is proposed that the controlled dilution will represent the chemical and physical reactions that may take place in the plume and therefore some understanding is obtained as to what secondary species are formed from any individual source. The diluted gases are analysed using ambient measurement systems and therefore the results are directly comparable with other ambient measurements from the same area.

There are many different dilution based systems being developed by research bodies around the world: Nuclear Environmental Analysis Inc, Southern Research Institute, California Institute of Technology, University Research Glassware Inc, California Air Resources Board, Desert Research Institute, GE Energy and Environmental Research Organisation and the Canadian Centre for Mineral and Energy Technology. The US EPA has also developed its only dilution based method (*see* below).

4 Current standard measurement methods

Several countries have produced or are in the process of producing their own standard methods for $PM_{10/2.5}$. These are as follows:

Germany:
VDI 2066: Messumg der Emissionen von PM_{10} und $PM_{2.5}$ an gefurten Quellen nach dem Impaktionsverfahren
(Dust measurement in flowing gases - measurement of PM_{10} and $PM_{2.5}$ emissions.)
Currently in draft only.
Principle: Use of in-stack multistage impactors for the collection of $PM_{10/2.5}$ particulate matter. Most of the work has been with the GMU Jonas II three stage impactor developed by the University of Duisburg and the North Rhine Westphalia State Environment Agency.

USA:

US EPA Method 201: Determination of PM_{10} emissions - Exhaust Gas Recycle Procedure

http://www.epa.gov/ttn/emc/promgate/m-201.pdf

Principle: An in-stack cyclone is used to separate PM greater than PM_{10}, and an in-stack glass fibre filter is used to collect the PM_{10}. To maintain isokinetic flow rate through the cyclone, a clean, dried portion of the sample gas at stack temperature is recycled into the nozzle. The particulate mass is determined gravimetrically after removal of uncombined water.

US EPA Method 201A: Determination of PM_{10} emissions - Constant Sampling Rate Procedure

http://www.epa.gov/ttn/emc/methods/method201a.html

Principle: A gas sample is extracted at a constant flow rate through an in-stack sizing device, which separates particulate matter greater than PM_{10}. Variations from isokinetic conditions are maintained within well-defined limits. The particulate mass is determined gravimetrically after removal of uncombined water.

US EPA Method 202: Determination of condensible particulate emissions from stationary sources

http://www.epa.gov/ttn/emc/methods/method202.html

Principle: This method applies to the determination of condensible particulate matter emissions from stationary sources. It is intended to represent condensible matter as material that condenses after passing through a filter an as measured by this method. This method can be used with Method 201 or 201A if the probes are glass-lined. The condensible particulate matter is collected in the impinger portion of a Method 17 type sampling train. The impinger contents are immediately purged with nitrogen (N_2) to remove dissolved sulphur dioxide (SO_2) gases from the impinger contents. The impinger solution is then extracted with methylene chloride ($MeCl_2$). The organic and aqueous fractions are then taken to dryness and the residue weighed. The total of both fractions represents the condensible particulate matter.

CARB M501: California Air Resources Board - Determination of size distribution of particulate matter from stationary sources

http://www.arb.ca.gov/testmeth/vol1/vol1.htm

Princple: Cascade impactor

US EPA CTM 39: (Conditional Test Method) - Measurement of $PM_{2.5}$ and PM_{10} emissions by dilution sampling (constant rate sampling procedures)

http://www.epa.gov/ttn/emc/ctm/ctm-039.pdf

Principle: This method expands on the particle sizing capabilities of EPA Method 201A with the addition of a $PM_{2.5}$ sizer (cyclone) behind (or replacing) the PM_{10} sizer. Furthermore, the capabilities of quantifying and characterising the condensible particulate matter are improved and expanded with the removal of the in-stack 47mm, the addition of a system to dilute and cool the sample gas and the addition of a 142mm filter to collect filterable the $PM_{2.5}$ and the particulate matter condensed through the dilution and cooling of the sample gas. This method was designed specifically to allow for the collection of particulate matter samples for developing speciation profiles to be used in conjunction with the ambient air sampling network. The calculations and set-up are essentially the same as for Method 201A, with additional calculations required for the $PM_{2.5}$ sizer, the dilution setup and the use of a venturi for monitoring the sampling rate.

ASTM D22.03: Dilution method

Principle: This method is a dilution-based method similar to US EPA CTM 39 above.

5   Proposed new ISO/CEN standard

Unlike any other measurement system, measurement systems for PM define the pollutant. This means that there is no calibration material or system available to

validate the methodology. It is therefore vitally important that the results of any particulate measurement study make it clear which sampling method was used and which species (particulate and/or condensible species) were included in the measurement. Sampling conditions must be controlled to avoid the formation of artefacts because some of the sample may be reaction products and/or temperature or moisture sensitive species.

A new joint working group has been established within CEN and ISO to determine a standard for the measurement of fine particulates at stationary sources. At the initial meeting of this working group it was decided to split the standard into two distinct parts:

- WG 20: for the measurement of primary $PM_{10/2.5}$ in stacks;
- WG 21: for the measurement of total $PM_{10/2.5}$ in stacks - dilution method.

WG 20 will look at the options available for in-stack measurement of $PM_{10/2.5}$. It is clear from Section 4 above that several different options are available, each with their own advantages and disadvantages. Rather that select one method (such as impactors over cyclones or vice versa), the most appropriate option may be to set a performance based standard. Such a standard could therefore also include automated methods. However, a performance based standard would need to be written such that it was clear that results from different measurement techniques are often not directly comparable. That is, measurements from a source or source type should be made with either impactors or cyclones - not both.

Theoretically, measurements made from a source or source type could be characterised such that a proportionality factor could be used. That is, if the $PM_{10/2.5}$ fractions can be shown to remain relatively constant in relation to the total particulate measurement, then total particulate measurements could be used as a proxy for $PM_{10/2.5}$ measurements. However, this approach needs to be validated and would only be viable if the factor were shown to be constant and if the source were shown to be of a constant nature.

At the moment, WG 20 is not considering the measurement of precursors. This would be the topic of a separate working group.

WG 21, on dilution methods, will compare and contrast the different dilution-based method being developed. The final, performance based standard, will determine the minimum requirements for such systems.

6   Conclusions

$PM_{10/2.5}$ are a complex and reactive mix of pollutants. Several different types of monitoring system are available for $PM_{10/2.5}$ and all of these are known to have associated problems and inaccuracies. However, the measurement of $PM_{10/2.5}$ must be standardised in order to ensure that data are comparable. There are currently several national standards for the measurement of primary $PM_{10/2.5}$ based on filters, cylones and impactors. New standards are also under development in the USA for the determination of total $PM_{10/2.5}$ using dilution techniques. New CEN/ISO performance based standards are currently being developed which will help ensure that, no matter which of these methods are used, they are used in the most appropriate manner for the promotion of reliable, quality data.

7   References

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