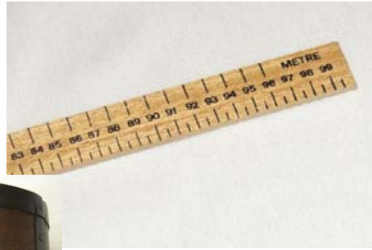
PM_{10} and $PM_{2.5}$
a measurement overview

or

How did we get into this mess
and how can we get out of it?

Paul Quincey

RSC-AAMG meeting
Air Quality – the Major Challenges
9th December 2009



The **Imperial (UK) gallon** was legally defined as 4.546 litres. This definition is based on the volume of 10 pounds of water at 62 °F.

The **US gallon** is legally defined as 231 cubic inches, and is equal to 3.785 litres. This is the most common definition of a gallon in the United States.

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The **US dry gallon** is one-eighth of a US Winchester bushel of 2150.42 cubic inches, thus it is equal to 4.405 litres. The US dry gallon is less commonly used.

Overview of presentation

(1) A short history of PM monitoring methods

(2) Current problems with European reference methods

(3) Some ways forward.

A short history of PM monitoring

UK historical: Black Smoke (1920s onwards)

Measures darkness, expressed as μg/m³.

But diesel soot is much darker than coal smoke.

Why not measure total PM mass?

US EPA 1971
Total Suspended Particulate

Real µg/m^3 via weighed filters

24 hour average: one exceedence of 260 µg/m^3 allowed per year

At a flow of 40 SCFM, air sample is 1632 m^3.

Limit PM mass is 424 mg.

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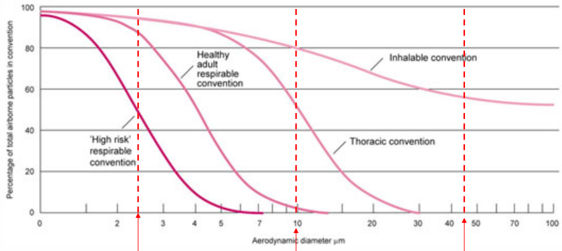
Early measurement emphasis (up to 1990s) – size-selective sampling inlets



ISO 7708

$PM_{2.5}$ cut off

PM_{10} cut off

~TSP cut off

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The move to PM_{10} and $PM_{2.5}$

US EPA 1987

PM_{10} 24 hour average: one exceedence of 150 µg/m^3 allowed per year

At a flow of 40 SCFM, limit PM mass is 245 mg.

US EPA 1997

$PM_{2.5}$ 24 hour average: 98th %ile 65 µg/m^3

At a flow of 40 SCFM, limit PM mass is 106 mg.

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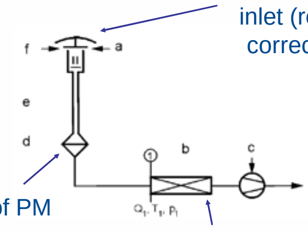
PM reference samplers



Size selective inlet (requires correct flow)

Collection of PM on filters

Flow control (for correct size selection and known sampled volume)

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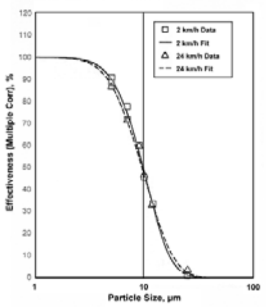
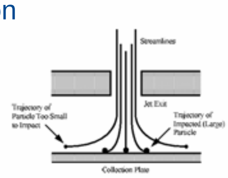
Size selection by impaction





$$d_{cut} = \sqrt{\frac{n \cdot 9 \cdot \pi \cdot \eta \cdot d_{jet}^{3} \cdot Stk}{4 \cdot C \cdot \dot{V} \cdot \rho_p}}$$

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European standard sampling inlets:

EN 12341:1998 (PM_{10})
3 designs (WRAC, "Hi-vol" 68 m^3/hr, "KFG" 2.3 m^3/hr)

EN 14907:2005 ($PM_{2.5}$)
2 designs ("Digitel" 30 m^3/hr, "KFG" 2.3 m^3/hr)

EN 12341 (PM_{10} and $PM_{2.5}$ revision)
(probably) 1 design each (2.3 m^3/hr)

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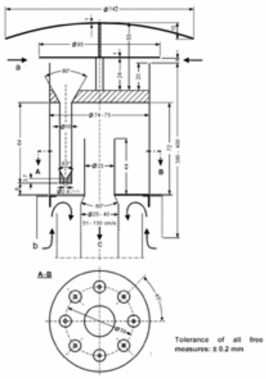
Inlet design convention



Sampling inlets summary:

Standardisation issues are solved by defining one inlet

Scientific issues remain

Emphasis has moved to other factors

The two parts of manual PM measurement

Size selective sampling onto a preweighed filter

Weighing the sampled filter

Recent emphasis - filter mass measurement

Typical basic parameters for a low volume sampler

Mass of 47 mm filter: 100 mg

Mass of PM: 0 – 2 mg

Acceptable uncertainty in Δm: 20 µg
(0.4 µg/m³ for reference samplers)

ie 0.02% change in the filter mass

Some factors affecting particle mass measurements

- Effect of water absorption by the filter material
- Effect of humidity on PM
- Loss of filter material
- Effect of sampling, storage and transport, eg on semi-volatile material (eg ammonium nitrate)
- Chemical reactions and gas absorption on the filter
- Effect of static electricity on the filter
- Balance drift…..

Constraints in EN 12341:1998 (PM_{10})

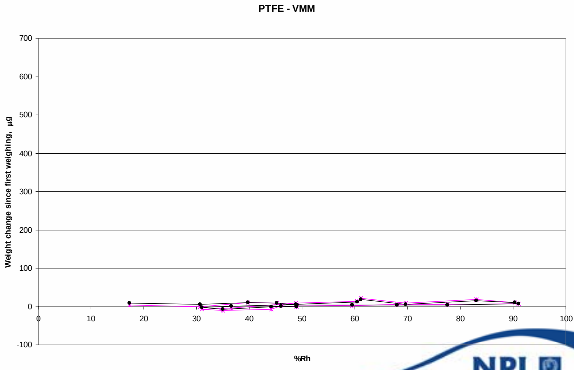
- standard conditions during weighing:

  20 ± 1 °C ; 50 ± 5 % RH

- filter material: quartz

  good for lack of reactivity; chemical analysis; cheaper than PTFE

Humidity dependence of PTFE filters



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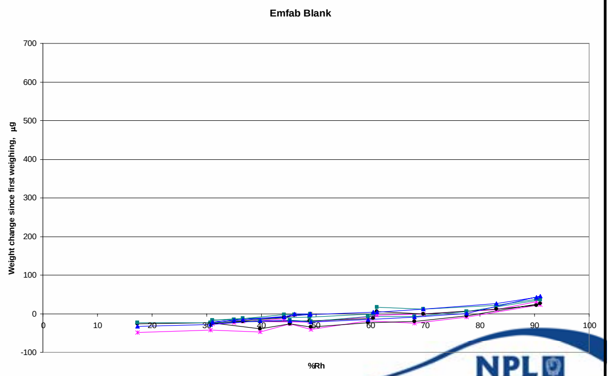
Humidity dependence of Emfab filters



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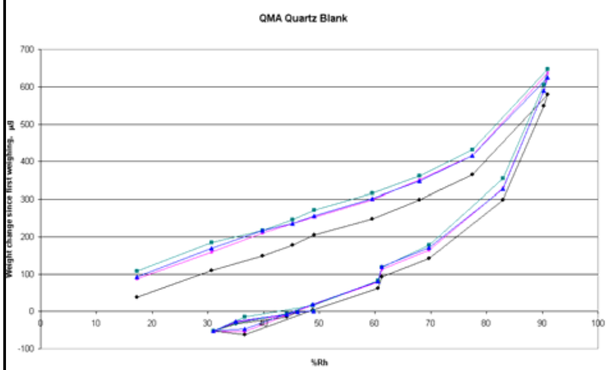
Humidity dependence of quartz filters



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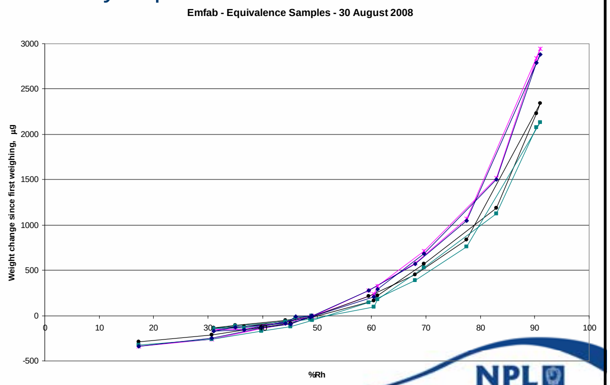
Humidity dependence of PM



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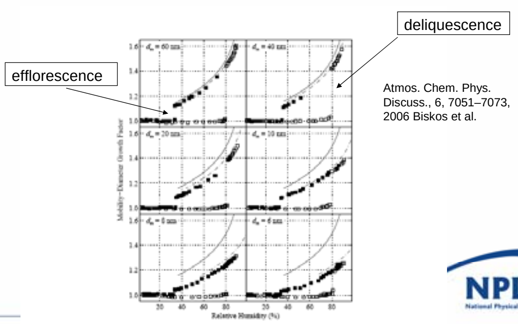
Water hysteresis effect on ammonium sulphate



Atmos. Chem. Phys. Discuss., 6, 7051–7073, 2006 Biskos et al.

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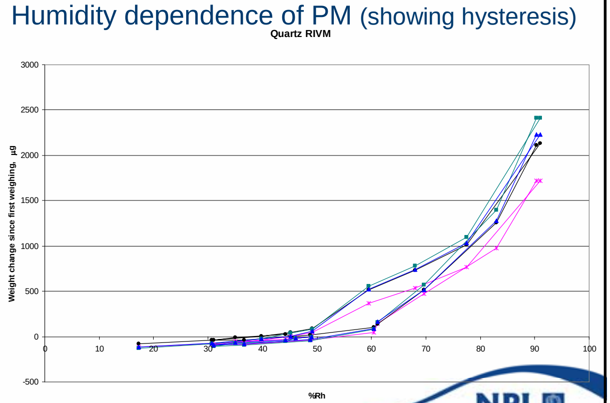
Humidity dependence of PM (showing hysteresis)



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Semi-volatile material

is another story …

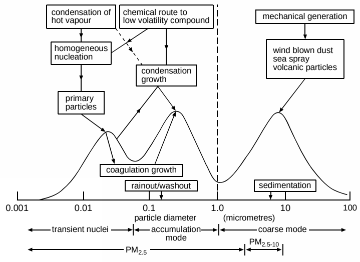
Constraints in EN 14907:2005 ($PM_{2.5}$)

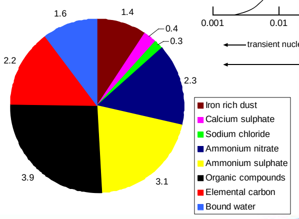
- standard conditions during weighing remained the same: 20 ± 1 °C ; 50 ± 5 % RH
  - but recommends lowering the conditioning humidity when the PM_{10} standard is revised
- filter materials: quartz, glass fibre, PTFE and PTFE-coated glass fibre
- sheath flow to avoid overheating during sampling
- requirements for temperature during storage and transport of samples
- criteria for repeatability of weighings

PM – a measurement summary

- the pollutant is not *objectively* defined:
- the pollutant is defined – imperfectly - by the reference *method*
  ie the desired water content, semi-volatile content and upper size cut-off are “whatever you end up with when you follow the method”

- the pollutant varies dramatically in time and location:
  both composition (affecting the water and semi-volatile content)
  and size distribution (affecting the size cut-off influence)





From AQEG (2005)

(Fine particles at urban background sites)

PM – a measurement summary (cont)

- cannot calibrate the whole measurement system directly with a traceable Reference Material (or range of Reference Materials) (aerosols)

- calibration for the reference method is via traceable sampling (flow) and mass, BUT this omits significant parts of the whole measurement. These have to be kept “under control”.

PM – a measurement summary (cont)

- unlike for gaseous pollutants, the Average Exposure Indicator requirement for long term $PM_{2.5}$ concentrations puts unusual demands on the measurement uncertainty, over a monitoring period when the monitoring instruments (and possibly methods) are likely to be changed.

e.g. to demonstrate a 1.2 µg/m^3 drop in the $PM_{2.5}$ AEI over 10 years.

PM – a measurement summary (cont)

- unlike for gaseous pollutants, but like the gallon, European PM_{10} is significantly different from US PM_{10} because:
  - Conditioning humidity is set at 30-40 ± 5 % rather than 50 ± 5 %
  - The reference filter material is PTFE, not quartz.

The ways forward

Refine the manual reference methods

Move to proxy but equivalent methods

Move to better defined parameters

Decisions in revision of EN 12341 and EN 14907

Filter materials:

quartz, good chemically, friable, humidity effect

glass fibre, less good chemically, humidity effect

PTFE, no humidity effect, pores can block

PTFE-coated glass fibre, no humidity effect, can be blocked by excessive water

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

Decisions in revision of EN 12341 and EN 14907

Custom-made new filter material ?

New filter suitability tests?
eg Dynamic Vapour Sorption →

New filter pre-conditioning?

Narrow and lower conditioning humidity range

Continuity (within Europe)

Proxy but equivalent methods

Core (non-volatile, minimum water) plus “other”

Automatic methods
eg TEOM-FDMS
beta attenuation
optical

Proprietary issues
Continuity (within Europe)

Better defined particle parameters

Size distribution, number and surface area concentration

Specific chemical components eg anions, cations, elemental/organic carbon

Specific properties eg oxidative capacity

Discontinuity (within Europe)

Closing remarks

Creative ideas are needed

Global agreement would be sensible

Thank you

NPL National Physical Laboratory

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