Atmospheric Aerosol Physics, Physical Measurements, and Sampling

Particle Mass Concentration Measurements

SAMLAC
San Juan, Puerto Rico
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Member of Leibniz Association

ECAC European Center for Aerosol Calibration

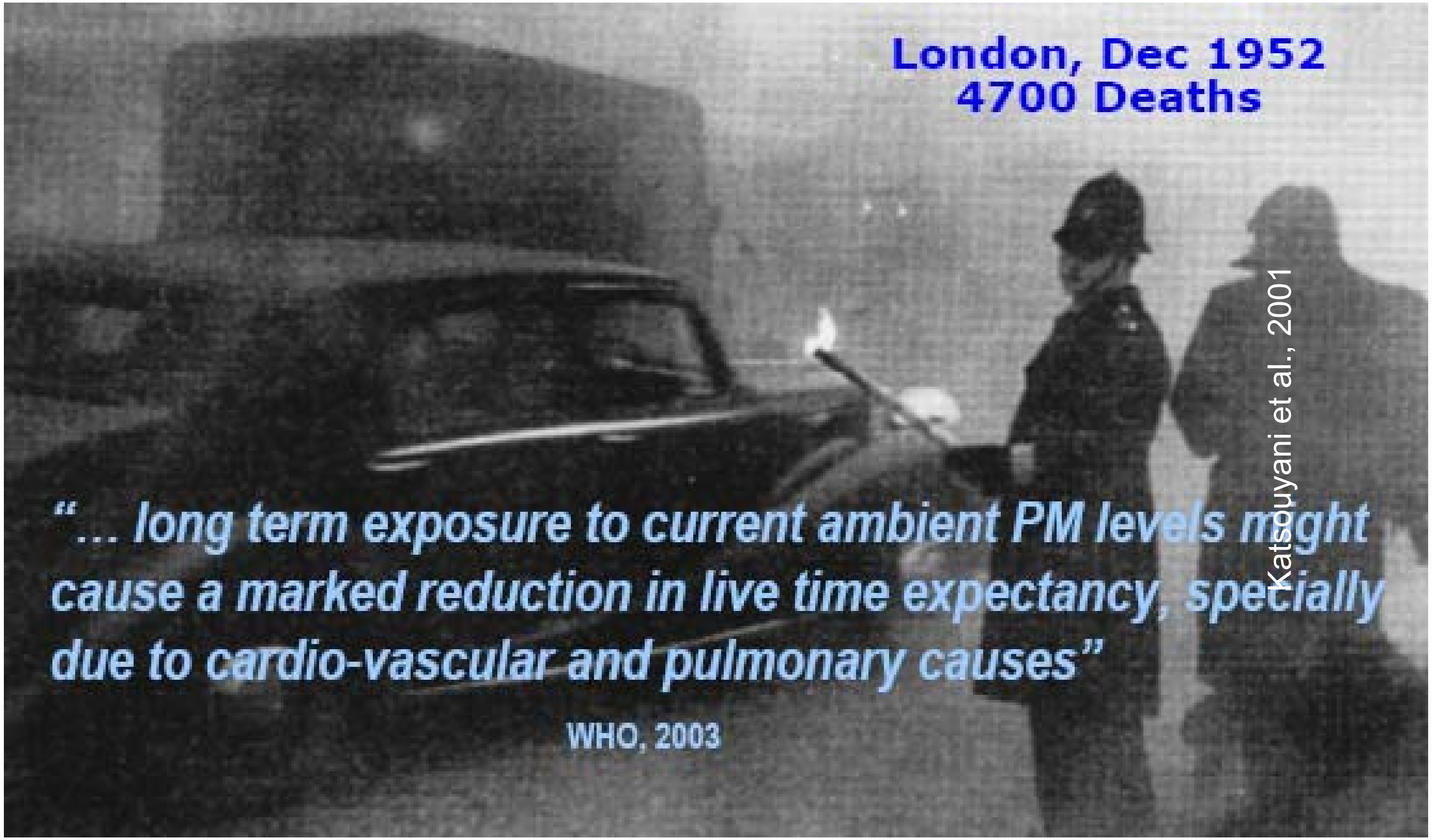
WCCAP World Calibration Centre for Aerosol Physics

TROPOS Leibniz Institute for Tropospheric Research

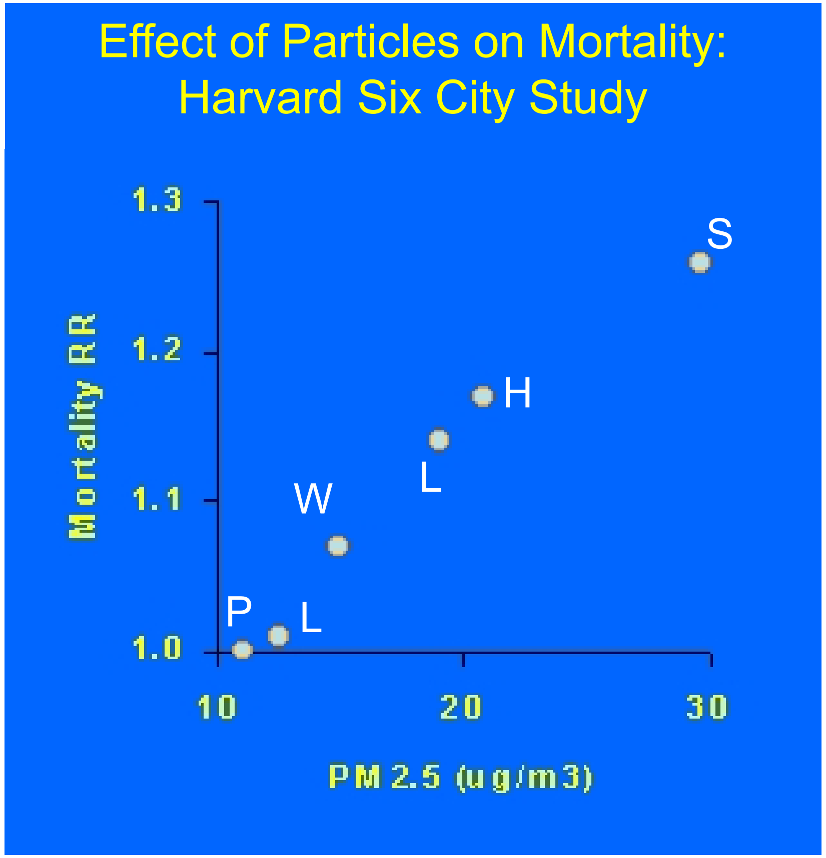
Background

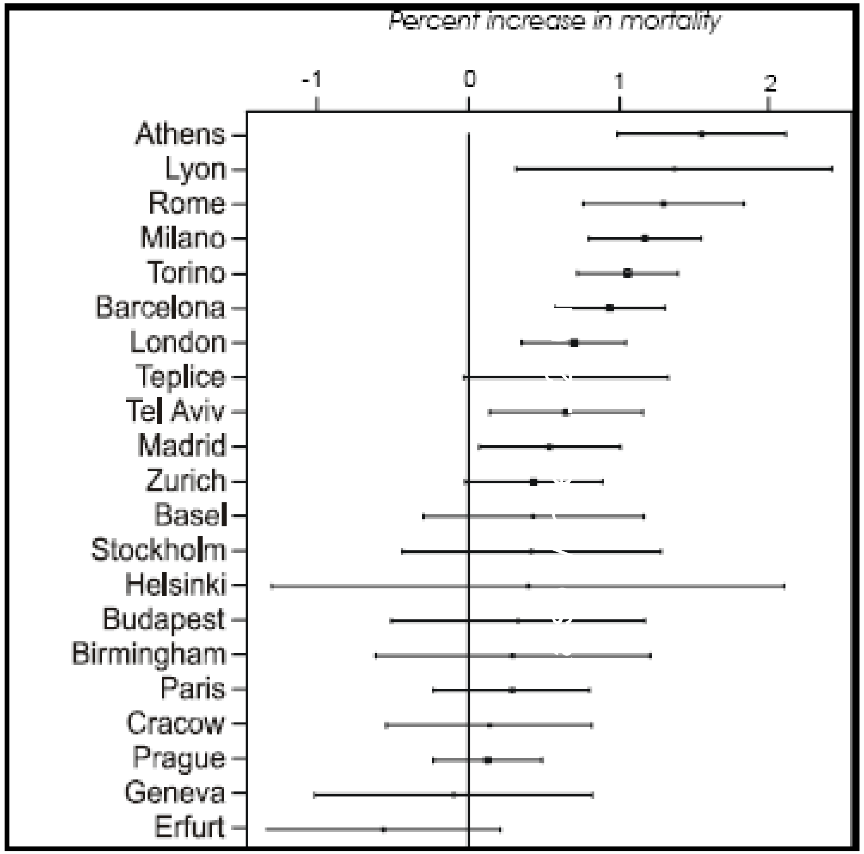
- Mass concentration measurements were the first routine measurements in networks addressing particulate ambient air pollution.
- Many epidemiological studies gave evidence that particle mass concentration is associated with adverse health effects.
- Because of these health effects particle mass concentrations are regulated (e.g. EU-Directive 2008/50/EC).
- Particle mass concentration is routinely monitored by environmental protection agencies.

Background


London, Dec 1952
4700 Deaths
Katsouyani et al., 2001
"… long term exposure to current ambient PM levels might cause a marked reduction in live time expectancy, specially due to cardio-vascular and pulmonary causes"
WHO, 2003

Background





Dockery et al., *N. Engl. J. Med.* **329**, 1753 (1993)

Particulate Matter$_{XX}$

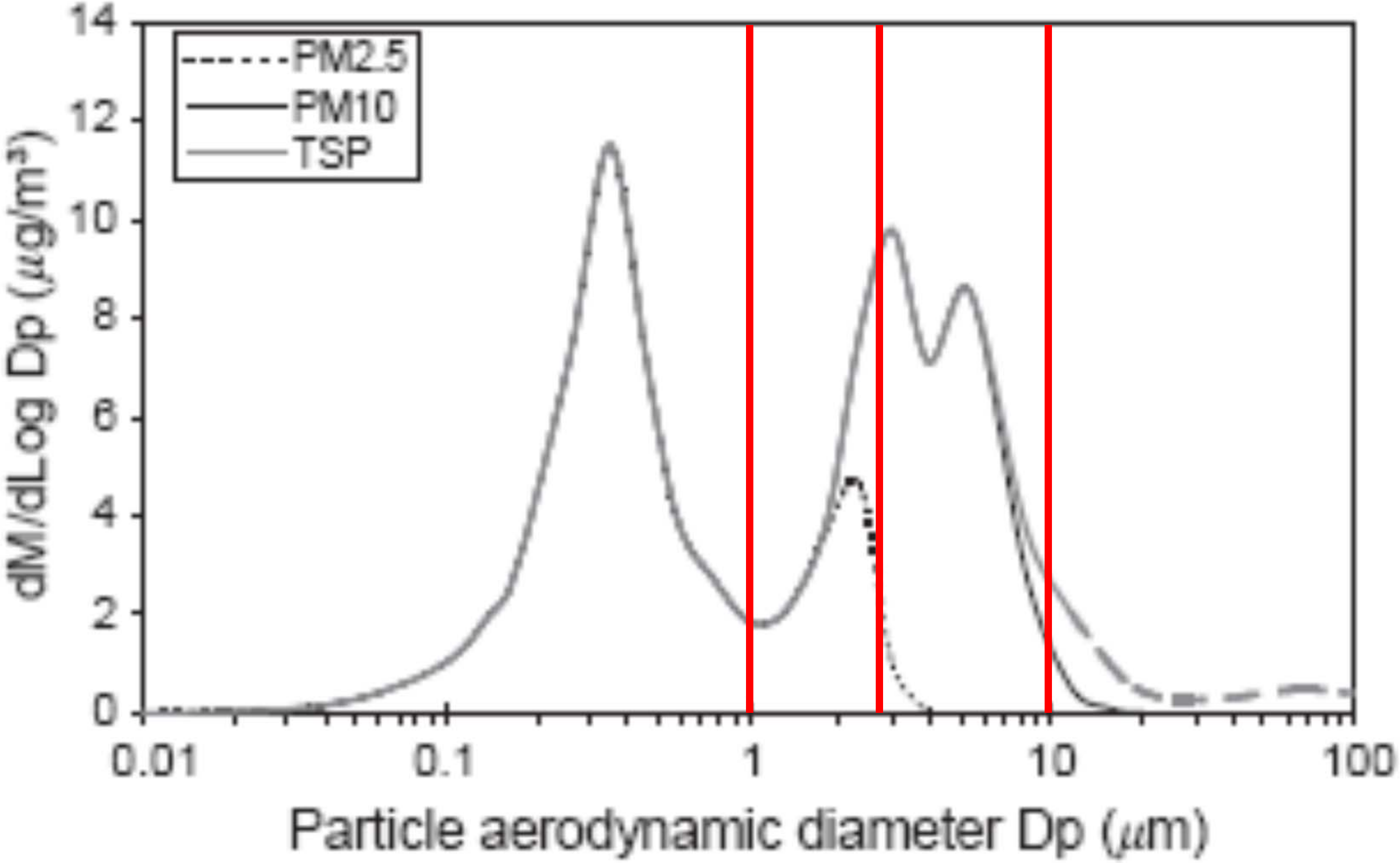
PM is often reported as particle mass concentration in µg/m³, where xx is the 50% cut-off diameter of a size selective inlet

PM10, PM2.5 or PM1

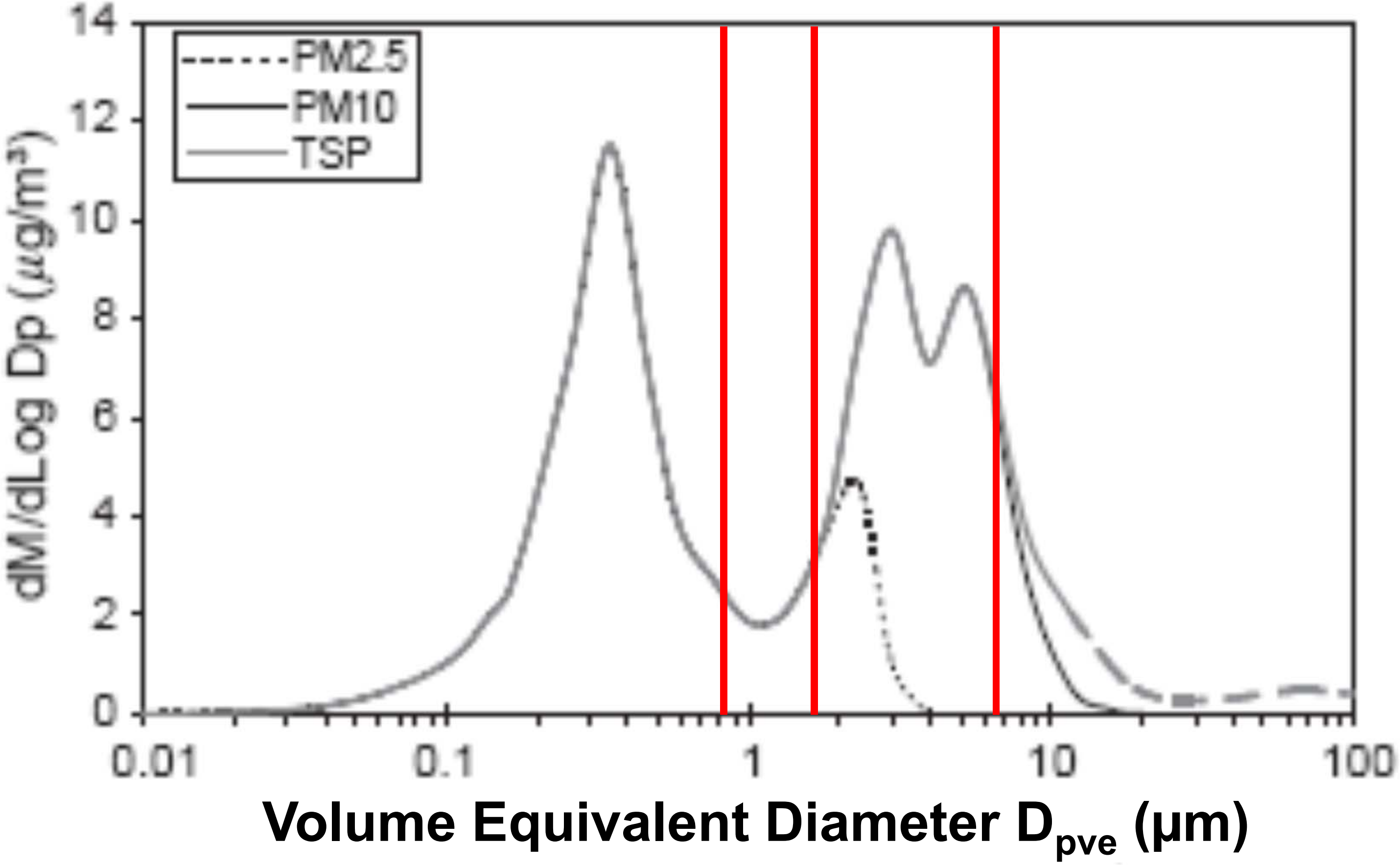
PM$_{XX}$ mass concentration can be determined by

- Filter sampling
- Beta- absorption
- Oscillating microbalance
- Light scattering

Example of Particle Mass Size Distributions



Example of Particle Mass Size Distributions



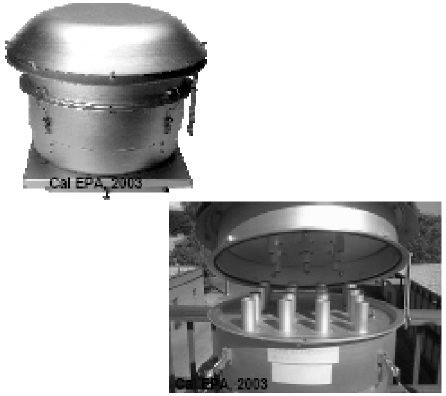
Filter Sampling

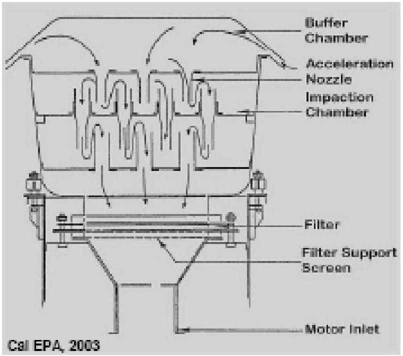
- Filter measurements provide direct access to the aerosol property.
- Mass concentrations are simply calculated from the deposited mass on a filter and the sampled air volume.
- Standard **reference** method for mass concentration measurements

Mass concentration	(M(loaded) – M(blank))/Volume
M(loaded)	Mass of the loaded filter
M(blank)	Mass of the blank filter prior to loading

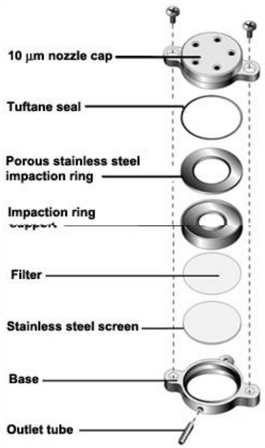
Manual filter samplers

A wide variety of manual filter samplers is available.



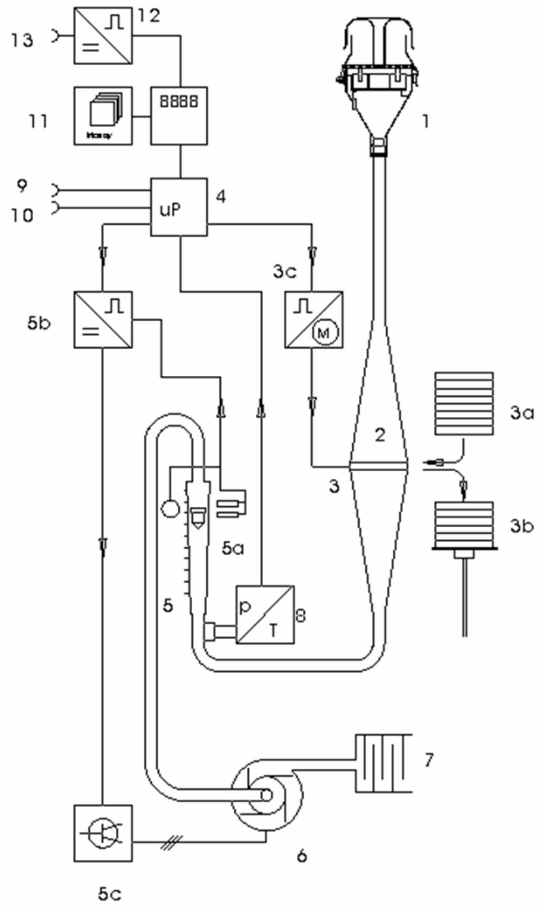


<u>Anderson High Volume Sampler</u>
Filter size: 20x25 cm
Air flow: 1013 l/min



<u>Personal Sampler</u>
Filter diameter: 37 mm
Air flow: 2 – 10 l/min

DIGITEL aerosol sampler DHA-80



Filter diameter: 15 cm

Air flow: 100- 1000 l/min

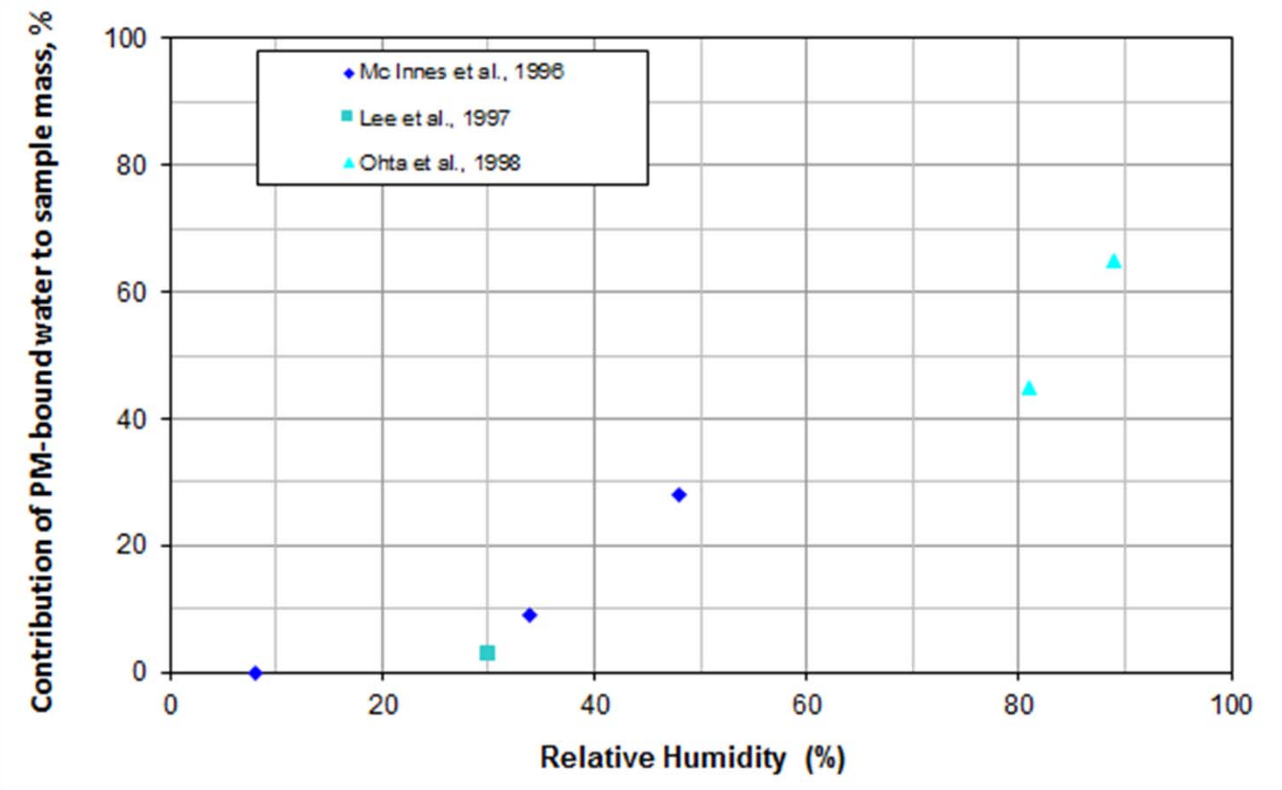
1 Pre-separator
2 Separator chamber
3 Current filter
3a Filter stock
3b Used Filter
3c Exchange electronics
4 Microprocessor control
5 Flow meter
5a Flow sensors
5b Flow control
5c Frequency converter
6 Blower
7 Noise baffle
8 Pressure and temperature measurement unit
9 Printer Interface
10 RS-232C Interface
11 PC Card Interface
12 Protection lightning print

Precision balances

Documents establishing the reference method

- CEN (2014) Ambient Air. Standard gravimetric measurement method for the determination of the PM_{10} or PM2,5 mass concentration of suspended particulate matter. Brussels (EN 12341).
- CEN (2017) Ambient air - Automated measuring systems for the measurement of the concentration of particulate matter (PM10; PM2,5). Brussels (EN 16450).
- EC (2001) Working group on particulate matter. Guidance to member states on PM_{10} monitoring and intercomparisons with the reference method. Draft Final Report, 16 March 2001
- EMEP (2000) EMEP-WMO Workshop on Fine Particles – Emissions, Modelling and Measurements, Interlaken, Switzerland, 22–25 November 1999. Kjeller, EMEP/CCC-Report 9/2000
- EPA (2011) NATIONAL PRIMARY AND SECONDARY AMBIENT AIR QUALITY STANDARDS, REFERENCE METHOD FOR THE DETERMINATION OF FINE PARTICULATE MATTER AS PM2.5 IN THE ATMOSPHERE. *Code of Federal Regulations, Title 40*, Appendix L to part 50.
- WHO Regional Office for Europe, Copenhagen (EUR/ICP/EHB1040102, E62010, 10-13.)
- WHO (1999) Particulate Matter (PM_{10} and $PM_{2.5}$). Results of Intercomparison Studies. Conference Held in Berlin 3-5 September 1998.

Contribution of PM-bound water



Aerosol water content expressed as mass percentage, as a function of relative humidity

Guidelines for concentration and exposure-response measurement of fine and ultra-fine particulate matter for use in epidemiological studies, EC-JRC and WHO, 2012

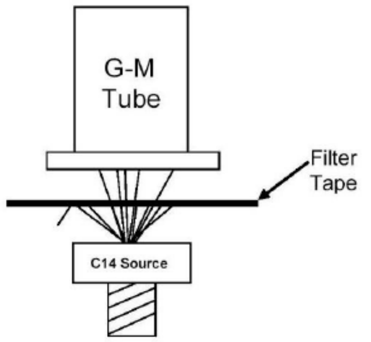
Summary gravimetric analyses

- Standard **reference** method
- Variety of samplers for different purposes
- Samples available for further analysis
- Reliable

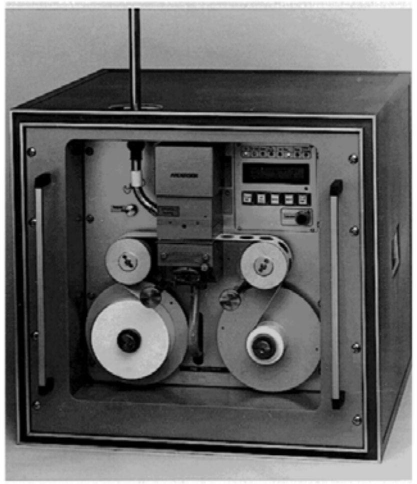
- Labor-intensive
- Filter handling and weighing
- Very limited time resolution
- No online data
- Sampling artefacts
- Possible contribution of water

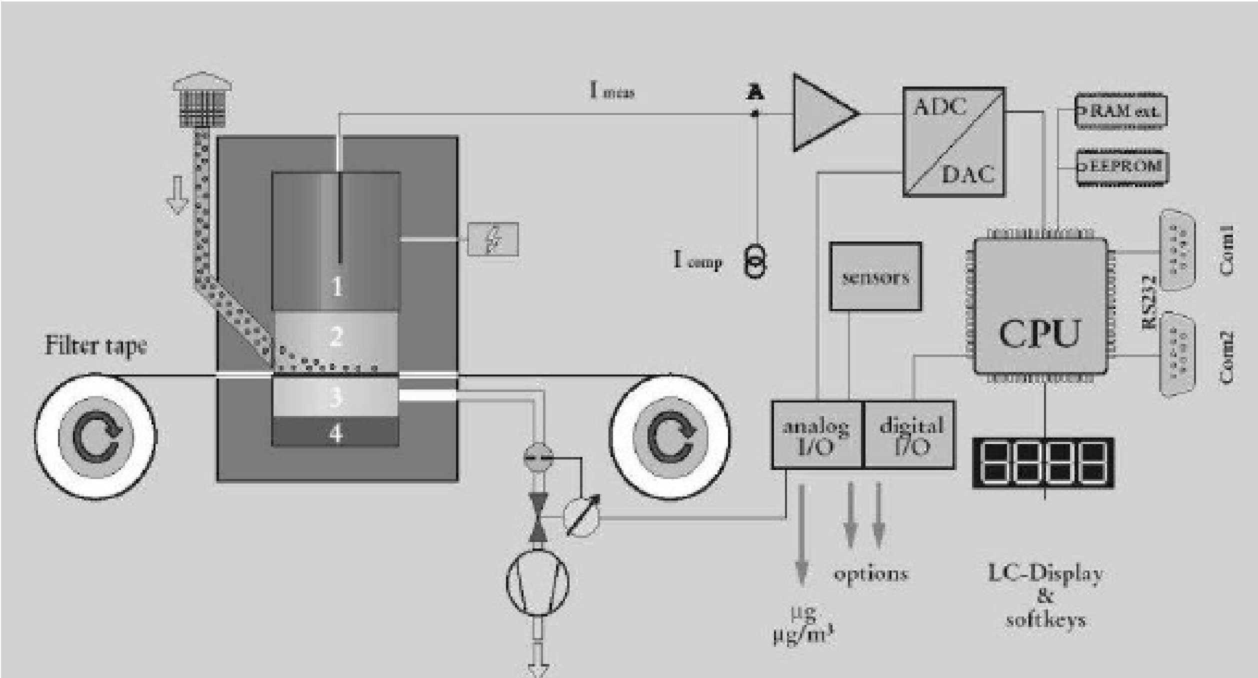
Beta-Absorption

Measurement of beta-Absorption of an aerosol layer deposited on a filter



Arnold, 1999





ESR Andersen, 2003

range of ^{14}C *b*-radiation in air: ~ 65 cm

Lambert-Beer-Law

$$I = I_0 \cdot e^{-\mu \cdot x}$$

I ... beta-Transmission of loaded filter
I_0 ... beta-Transmission of unloaded filter
μ ... Mass absorption coefficient
x ... Mass loading of the filter

$$m = F_{\mathrm{cal}} \cdot \ln\left(\frac{I_0}{I}\right)$$

Calibration factor F_{cal} is:

- proportional to the spot area **A**
- inverse proportional to the mass absorption coefficient μ

$$F_{\mathrm{cal}} = \frac{A}{\mu}$$

<u>Mass absorption coefficient for β radiation</u>

$$\mu/\rho = 0.008\, Z^{0.28}\, E_m^{-[1.57-(Z/160)]}$$ (Katz and Penfold, 1952)

$$\mu/\rho = 15.2\, Z^{(4/3)}\, A^{-1}\, E_m^{-1.485}$$ (Thummel, 1974)

Z … Proton number
A … Mass number
E_m … Maximum electron energy

Baron/Willeke, 2001

Compound	Z/A	μ (cm²/mg)[a]	μ (cm²/mg)[b]
$(NH_4)_2SO_4$	0.530	0.153	0.166
NH_4HSO_4	0.521	0.152	0.163
$CaSO_4 \cdot 2H_2O$	0.511	0.152	0.159
SiO_2	0.499	0.154	0.154
$CaCO_3$	0.500	0.154	0.154
Carbon	0.500	0.154	0.154
Fe_2O_3	0.476	0.163	0.144
NaCl	0.478	0.172	0.145
$PbSO_4$	0.429	0.193	0.126
$PbCl_2$	0.417	0.204	0.121
PbBrCl	0.415	0.206	0.120

a) experimentally determined
b) calculated

The mass absorption coefficient μ is material dependent.

- The mass load of the filter is measured in time intervals *τ.*
- The change of filter mass is calculated as:

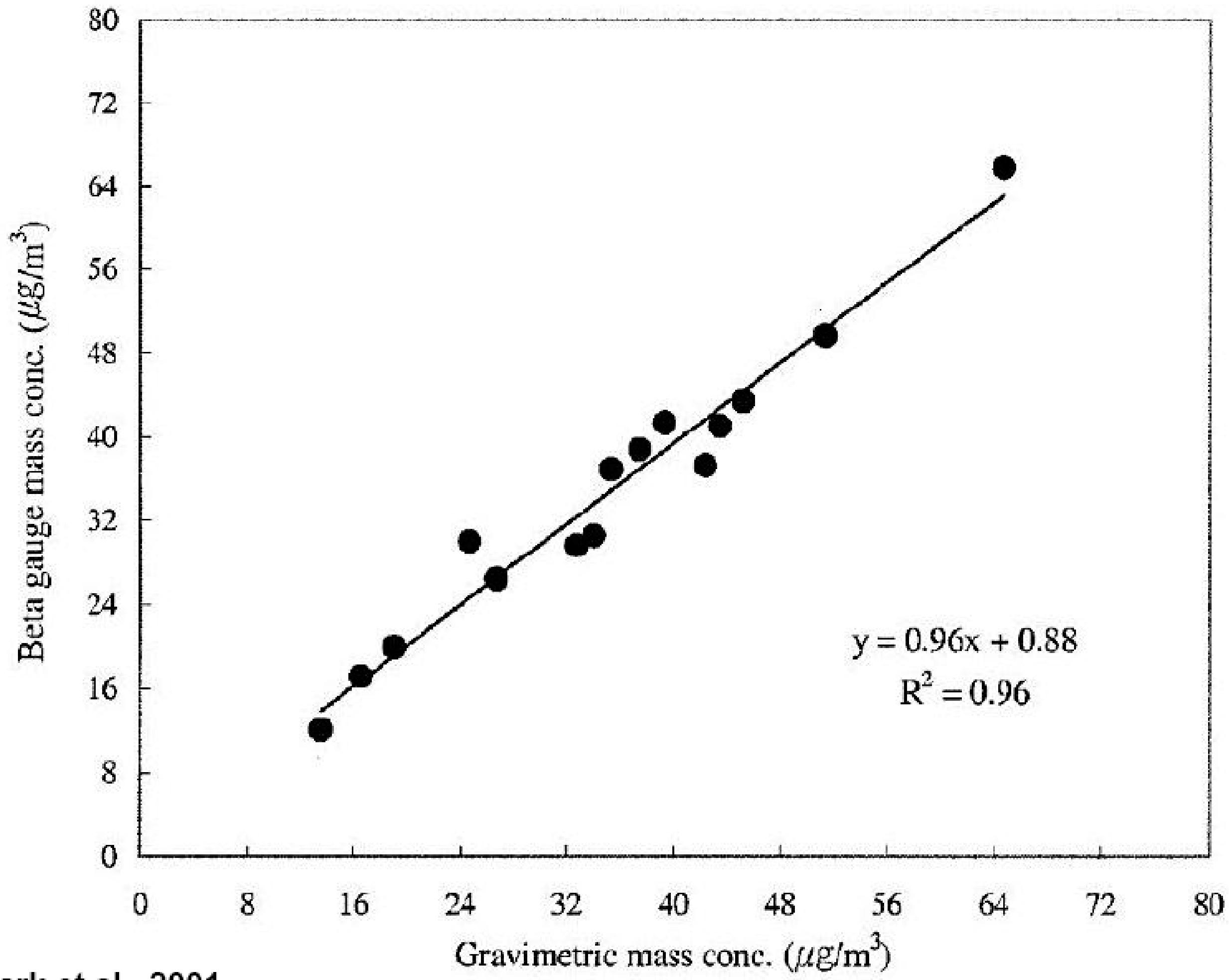
$$\frac{\mathrm{d}m}{\mathrm{d}t} = \frac{\sum (t_i - \overline{t}) \cdot m_i}{\sum (t_i - \overline{t}) \cdot t_i} = \frac{\Delta m}{\tau}$$

t_i … measurement time
$\overline{t}$ … average of measurement times
m_i … mass measured at measurement time

The mass concentration *C* is calculated knowing the average volumetric flow rate *Q*:

$$C = \frac{\mathrm{d}m / \mathrm{d}t}{Q}$$

Co-located filter and beta-gauge measurements



Park et al., 2001

Summary Beta-Absorption

Advantages

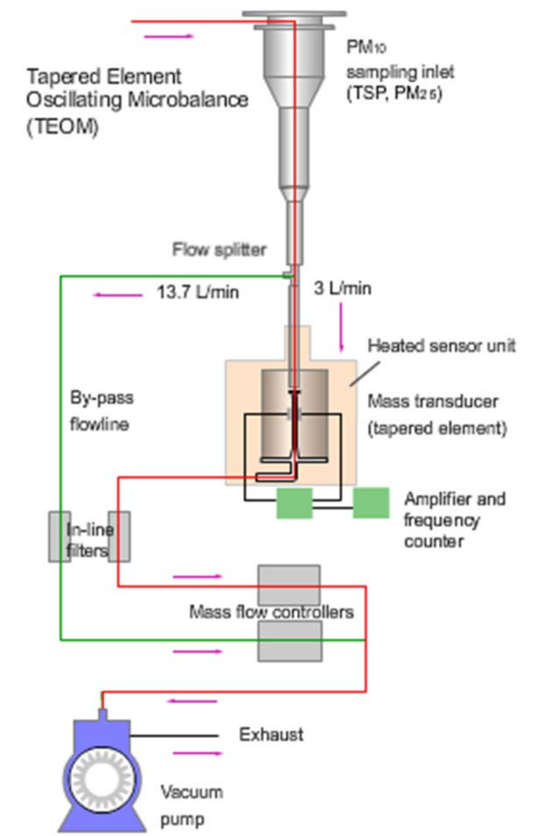
- Online measurement
- Long-term stability up to one year
- Good agreement with filter samplers
- US-EPA approved reference method

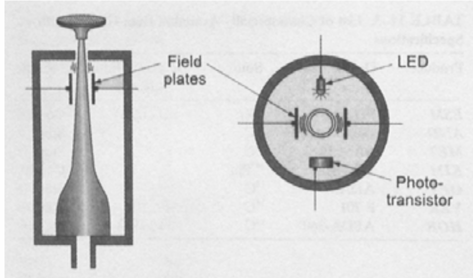
Disadvantages

- Moderate dependency on chemical composition of aerosol particles
- Filter typically not usable for chemical analysis
- Radioactive source may require a permit in some countries

Tapered Element Oscillating Microbalance (TEOM)

Frequency change of an oscillating filter with increasing mass load





The tapered element with the filter on top behaves like an oscillating pendulum.

$$f^2 = \frac{K_0}{m}$$

f … Eigen-frequency of the tapered element with filter
K_0 … Calibration constant
m … Mass

$$m = m_F + m_0 + \delta m$$

m_F … Mass of the blank filter
m_0 … Mass of the tapered element
δm… Deposited mass on the filter

The frequency of the pendulum decreases with increasing mass deposited on the filter.

An increase of the filter mass by δm causes a frequency change from f_i to f_f

$$f_i^{\,2} = \frac{K_0}{m_F + m_0}$$

$$f_f^{\,2} = \frac{K_0}{m_F + m_0 + \delta m}$$

Mass change can be calculated from the frequency change

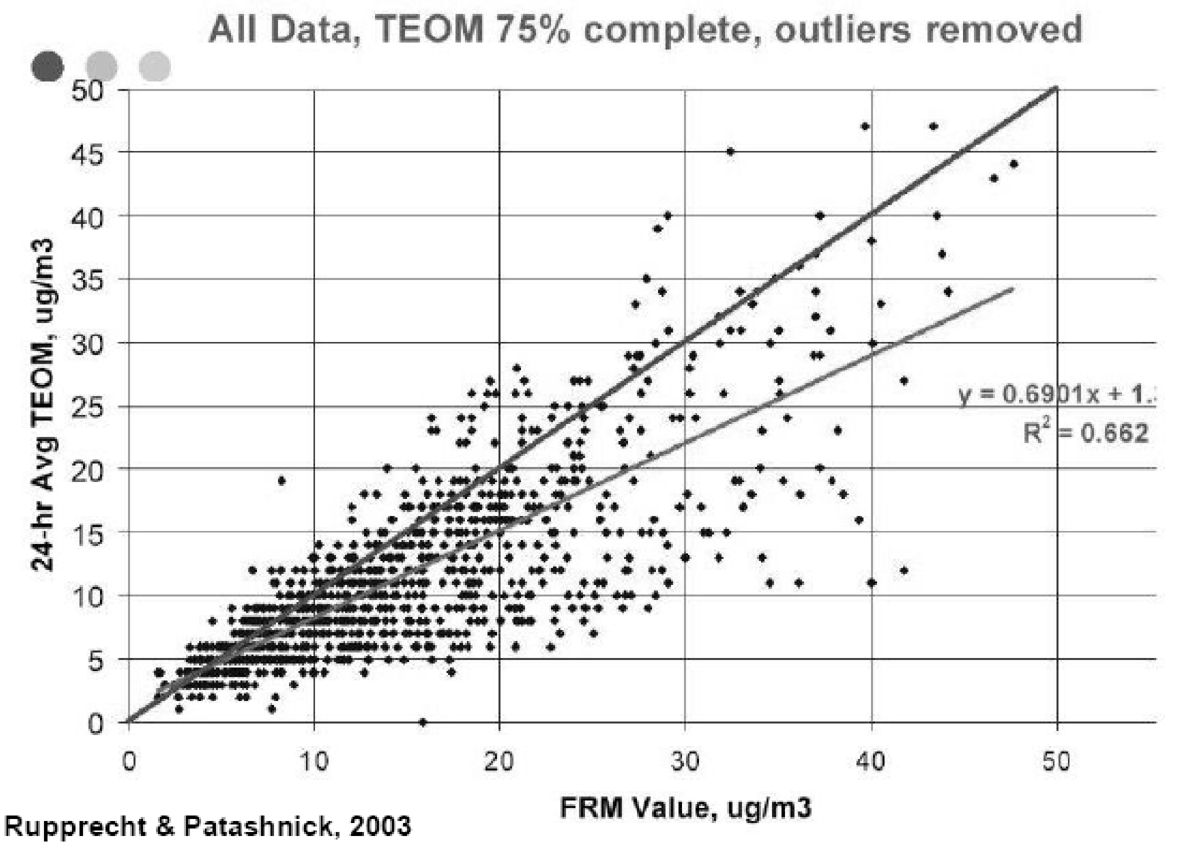
$$\delta m = K_0 \cdot \left(\frac{1}{f_f^{\,2}} - \frac{1}{f_i^{\,2}} \right)$$

And the mass concentration can be calculated to

$$C = \frac{\delta m \cdot \Delta t}{Q}$$

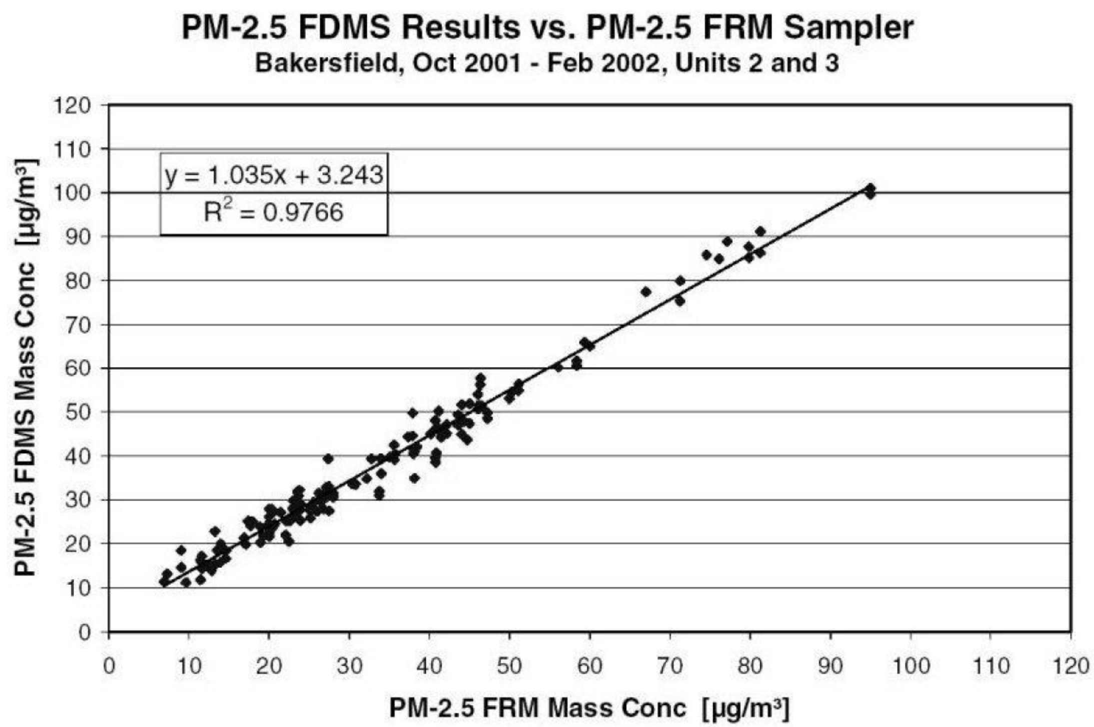
Δt… Time from f_i to f_f
Q… Volumetric flow rate

- Diurnal variation of RH causes variation of filter weight.
- Standard TEOM uses heated inlet at factory setting 35°C.
- Ammonium nitrate evaporates at this temperature.



Rupprecht & Patashnick, 2003

- Reduce temperature to 30°C
- Remove water with Nafion dryer (TEOM-SES)
- Alternating measurement between filtered air and aerosol (differential TEOM, TEOM-FDMS)



Rupprecht & Patashnick, 2003

Summary TEOM

Advantages

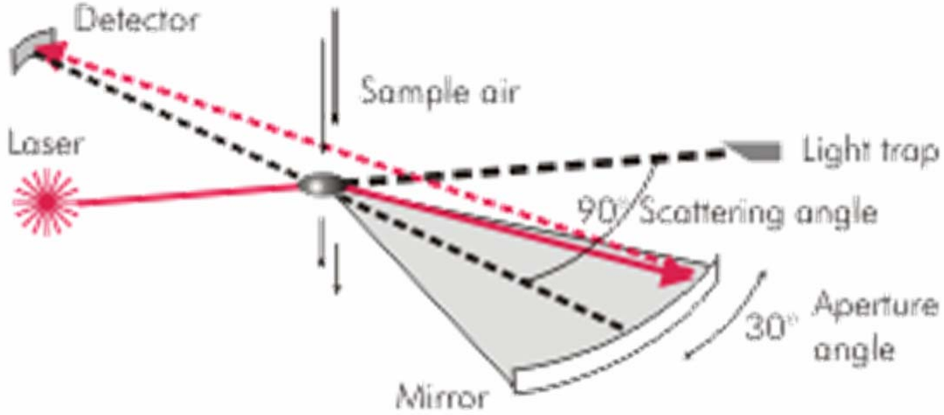
- Online measurement
- Long-term stability up to several months
- Good agreement with filter samplers if used with appropriate RH control or correction
- US-EPA approved reference method at 30°C

Disadvantages

- Standard TEOM measurements are influenced by chemical composition of the aerosol particles if used according to factory settings

Optical Instruments

- Measurement of light scattered by single aerosol particles in a measurement volume under a fixed angle
- Sizing by pulse height analysis



- The instrument is calibrated with well defined aerosol particles such as Latex particles
- Direct indication of particle mass concentration
- Light scattered from a measurement volume depends on many aerosol properties
    - Particle shape
    - Particle size distribution
    - Refractive index
- Particle density is assumed for conversion to mass concentration
- Light weight, inexpensive monitor
- The instrument is calibrated against reference