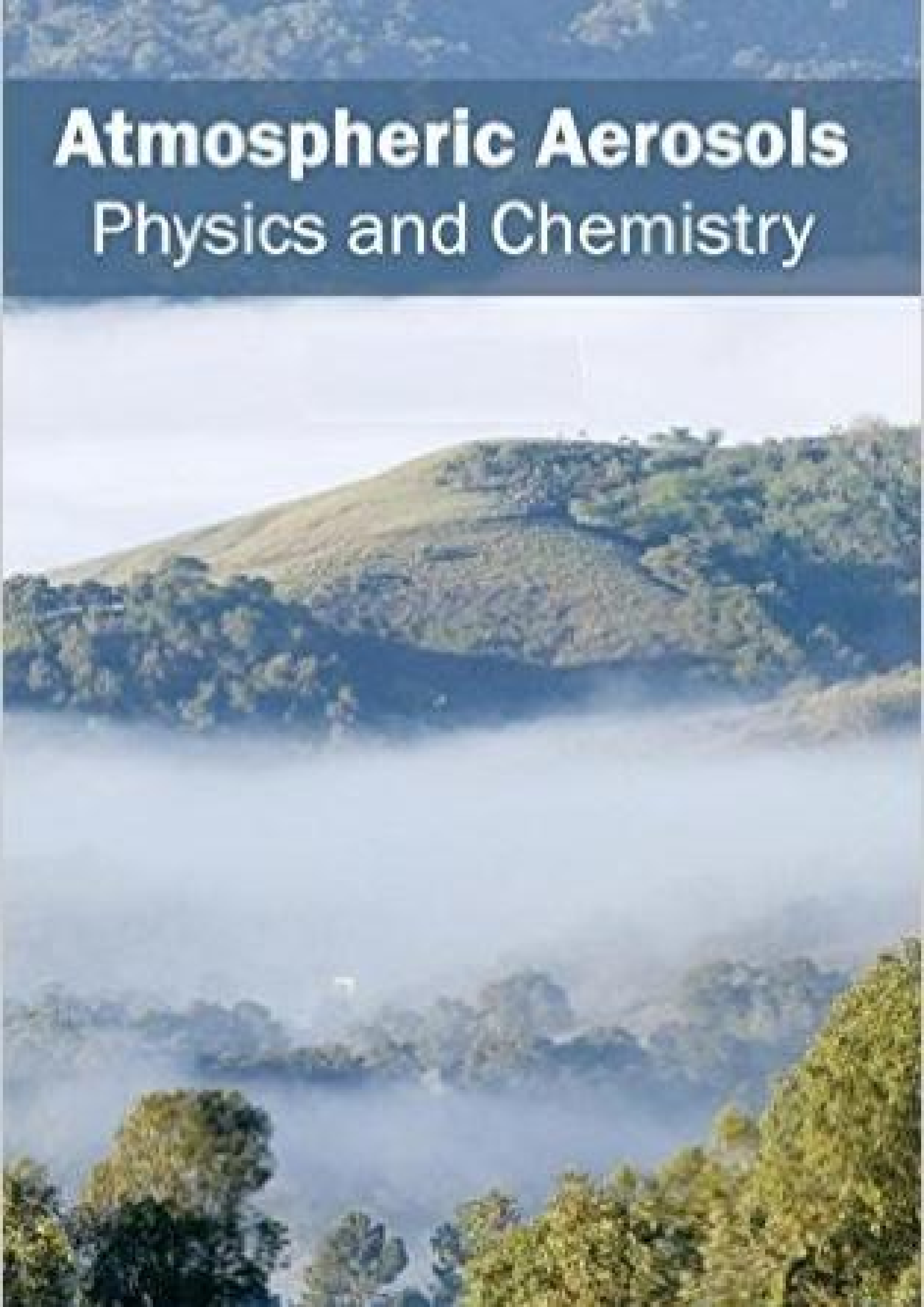
Atmospheric Aerosols

Physics and Chemistry



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PART I - 1. ATMOSPHERIC PROCESSES, ROLE OF AEROSOLS

Lecture topics:

- Atmospheric processes - role of aerosols
- Characterisation of aerosol particles
- Forces and interactions
- Instrumentation and measurements
- Health effects of particles
- Applications
- Standards and guidelines
- Aerosols in indoor and outdoor environment
- Motor vehicle emissions
- Other

Aims of the lecture series:

- To provide students with a broad understanding of all aspects related to environmental aerosol science, with a focus on physics.
- To show the scientific depth and complexity.
- To present applications and current directions.

Furthermore this lecture will cover:

- Air pollution and its sources
- Airborne particles
- Effects of the pollutants – thus need for control and management
- Outdoor and indoor particles

Fig. I-1.1 Forest fire[i]

Why study environmental aerosols?

Reason 1: Because particles constitute one of the most important pollutant affecting human health. Evans et al 1984: "We are of the opinion that the cross-sectional studies reflect a casual relationship between exposure to airborne particles and premature mortality... However, we are in the minority in taking this view."

Dockery et al 1993: ".... Quote from indoor air paper: the unknowns.

Reason 2: Approaches taken in environmental aerosol studies could be used in any other area of environmental studies or in any other type of interdisciplinary studies.

Reason 3: Understanding of aerosol processes and interactions can be used in the most advanced areas of industry and technology such as material synthesis, microelectronics, and pharmacy.

Reason 4: For the challenge of it - if you do not do it, the others might do it, or nobody will do it!

Classification of airborne pollutants

i) According to chemical composition or their properties sulphur, nitrogen, carbon containing substances, toxic substances, etc.

Volatile (VOC) and semi-volatile organic compounds (sVOC), includes polynuclear aromatic compounds (PAH), aldehydes, organic acids, etc.

Sulphur dioxide (SO_2), Nitrogen oxides (NO_x), Carbon monoxide (CO), Carbon dioxide (CO_2), Photochemical oxidants, Hydrocarbons (CH_4, C_4H_{10}, C_3H_8, etc.), Hydrogen sulphide and fluoride: (H_2S) and (HF), others;

i) According to physical properties, whether these pollutants occur in a gaseous form, particle form (solid or liquid), or are even as radioactive compounds.

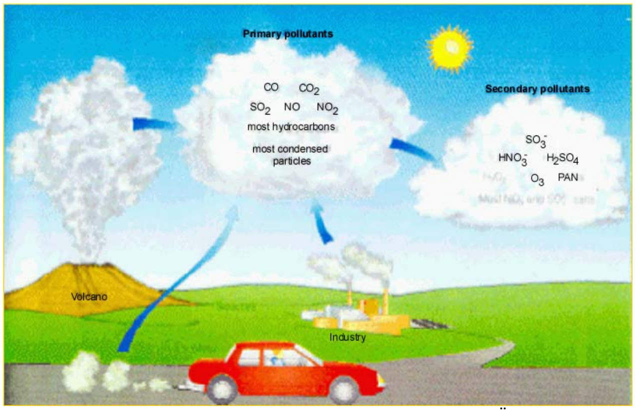


Fig. I-1.2. Primary and secondary pollutants[ii]

i) According to formation mechanisms:

Primary pollutants: emitted directly from sources; e.g.: nitric oxides, hydrocarbons, etc.

Secondary pollutants: formed in the atmosphere by chemical interactions among primary pollutants and normal atmospheric constituents; e.g.: ozone, photochemical aerosols, etc.

I - 2. Dynamic nature of atmospheric processes

Gases are produced by:

- chemical processes in the atmosphere
- biological activity
- volcanic exhalation
- radioactive decay
- human activity

Gases are removed from the atmosphere by:

- chemical reactions in the atmosphere
- biological activity
- physical process in the atmosphere
- by deposition and uptake by the oceans and earth

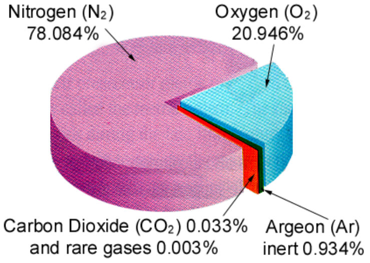


Fig. I-2.1. Composition of tropospheric air[iii]

Atmospheric pollutant **concentration units** are:

- $\mu g/m^3$
- parts-per-million by volume (ppm)

Parts-per-million by volume is defined as the species ***i*** mass concentration and can be calculated as follows:

concentration of species $i = \frac{c_i}{c} \cdot 1 \cdot E^6$ [ppm]

$$c_i = \frac{1 \cdot E^6 \cdot m_i}{M_i} \quad [mol/m^3]$$

concentration of species $i = \frac{R \cdot T}{p \cdot M_i} \cdot c_i$ [$\mu g/m^3$]

c_i and c concentration of species i medium and air at p and T		[mol/m^3]
M_i is the molecular weight of species i		[g/mol]
$c = p/R \cdot T$		
p, atmospheric pressure	$101.3 \cdot E^3$	[N/m^2] = [Pa]
T, temperature		[K]
R, gas constant	8.314 510	[J/(mol·K)]

Average time of gas molecules introduced into the atmosphere ranges from **minutes** to **million years** atmospheric cycles

Gas	avg. **concentration** [ppm]	approx. **residence** time	**Cycle**	**Status**
Ar	9340	-	No cycle	Accumulation during earth's history
Ne	18	-	No cycle	Accumulation during earth's history
Kr	1.1	-	No cycle	Accumulation during earth's history
Xe	0.09	-	No cycle	Accumulation during earth's history
N_2	780-840	10^6 years	Biological & microbiological	?
O_2	209-460	10 years	Biological & microbiological	?
CH_4	1.65	7 years	Biogenic & chemical	Quasi-steady state or equilibrium
CO_2	332	15 years	Anthropogenic & biogenic	Quasi-steady state or equilibrium (?)
CO	0.05-0.2	65 days	Anthropogenic & chemical	Quasi-steady state or equilibrium
H_2	0.58	10 years	Biogenic & chemical	Quasi-steady state or equilibrium
N_2O	0.33	10 years	Biogenic & chemical	Quasi-steady state or equilibrium
SO_2	$1 \cdot E^{-5}$-$1 \cdot E^{-4}$	40 days	Anthropogenic & chemical	Quasi-steady state or equilibrium
NH_3	$1 \cdot E^{-4}$-$1 \cdot E^{-3}$	20 days	Biogenic, chemical, rainout	Quasi-steady state or equilibrium
NO & NO_2	$1 \cdot E^{-6}$-$1 \cdot E^{-2}$	1 day	Anthropogenic, chemical, lightning	Quasi-steady state or equilibrium
O_3	$1 \cdot E^{-2}$-$1 \cdot E^{-1}$	?	Chemical	Quasi-steady state or equilibrium
HNO_3	$1 \cdot E^{-5}$-$1 \cdot E^{-3}$	1 day	Chemical, rainout	Quasi-steady state or equilibrium
H_2O	variable	10 days	Physico-chemical	Quasi-steady state or equilibrium (?)
He	5.2	10 years	Physico-chemical	Quasi-steady state or equilibrium

Atmospheric cycles involve physical, chemical and biological processes; the main global cycles are:

- water cycle (evaporation from the sea 85%, transpiration from land 14.5%, run off 6%, precipitation 36%, evaporation on land 0.001%, movement of water vapour 5%);
- sulphur cycle (of biogenic and anthropogenic origin; e.g. fossil fuel combustion; volcanic activity, etc.);
- nitrogen cycle (of biogenic and anthropogenic origin; e.g. agriculture, etc.);
- carbon cycle (of biogenic and anthropogenic origin; e.g. fossil fuel combustion; volcanic activity, etc.);
- halogen compounds cycle (biogenic and anthropogenic origin; e.g. industry, volcanic activity, etc.);
- phosphorous cycle (of biogenic and anthropogenic origin; e.g. industrial agriculture, etc.);

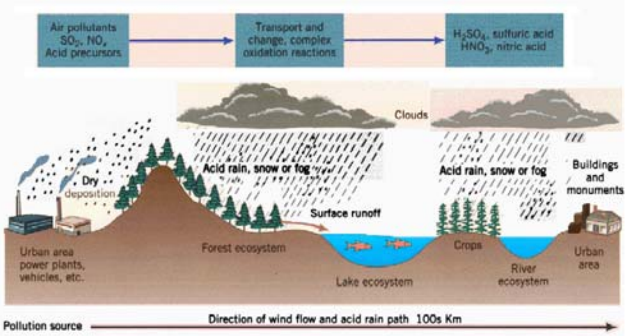
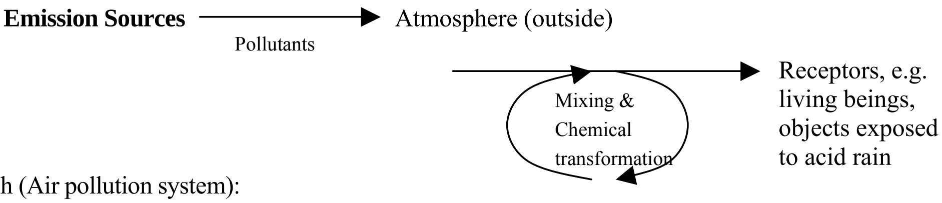
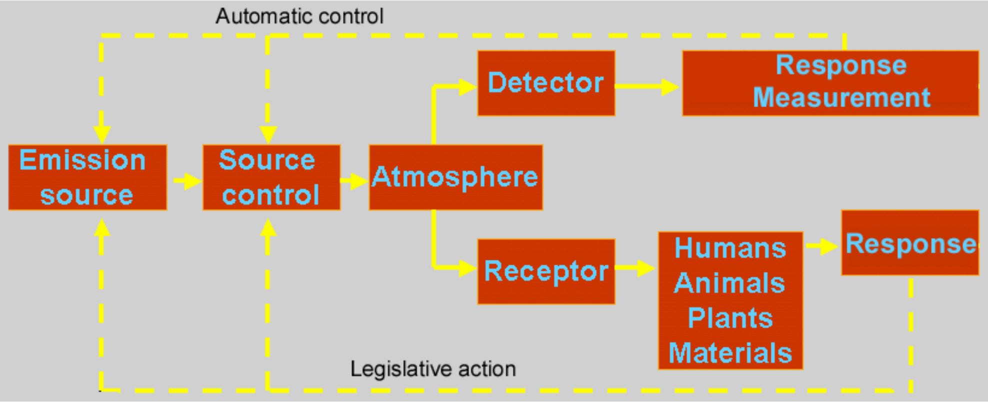


Fig. I-2.2. Part of the global water cycle; the masses of water vapour accumulated over the oceans (as well as over land) and drifted over the continents become enriched with suspended pollutants; along with wind patterns ranging from local, meso-, macro-scale, these pollutants are washed out far away from the source of origin.[iv]

I - 3. Air pollution – classical view of chemical pollutants



A more complex approach (Air pollution system):



Air pollution sources:

- transportation
- electric power generation
- refuse burning
- industrial and domestic fuel burning
- industrial processes
- consumer products

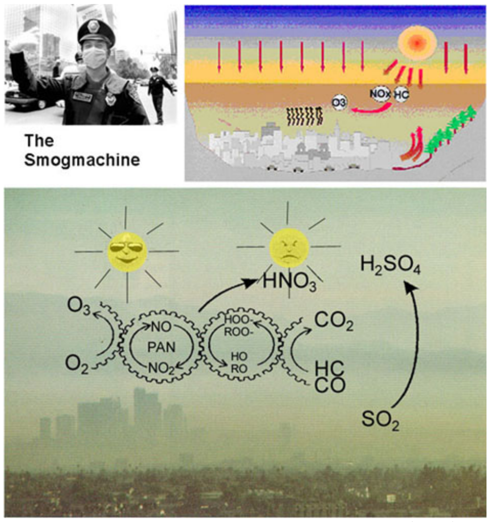


Fig. I-3.1 The urban Smog Machine; otherwise harmless gaseous substances change reactivity under the influence of UV-radiation of the sun.[v]

Classification of air pollutants - according to physical state:

- gaseous form
- particulate form (solid or liquid particles)

According to chemical composition (Major groupings include):

- sulphur-containing compounds
- nitrogen-containing compounds
- carbon-containing compounds
- halogen-containing compounds
- toxic substances
- radioactive compounds

According to formation mechanisms:

- Primary pollutants emitted directly from sources; e.g.: nitric oxide and hydrocarbons.
- Secondary pollutants formed in the atmosphere by chemical interactions among primary pollutants and normal atmospheric constituents; e.g.: ozone, organic nitrates, oxidized hydrocarbons and photochemical aerosol.

http://www.sbg.ac.at/ipk/avstudio/pierofun/funpage.htm

PART II - 1. CHARACTERISATION OF AEROSOL PARTICLES

Aerosol fundamentals:
- definitions
- sources
- physical properties
- chemical composition
- morphology

Definitions of:

Aerosol: an assembly of liquid or solid particles suspended in a gaseous medium long enough to enable observation or measurement. Generally, the sizes of aerosols are in the range from 0.001 to 100µm. **Dust**: solid particles formed by crushing or other mechanical breakage of a parent material. These particles generally have irregular shapes and are typically around 0.5µm. **Fog & mist**: liquid aerosol particle of 10µm – 100µm ion diameter. **Fume**: particles that are usually the result of vapour condensation with subsequent agglomeration usually <0.05mm. **Particle**: small discrete objects.

Particulate: a particle.

Smog: an aerosol consisting of solid and liquid particles, created at least in part, by the action of sunlight or vapour; thus <2µm. **Smoke**: a solid or liquid aerosol, the result of incomplete combustion or condensation of supersaturated vapour; typically <1µm

Nature of Aerosols:

Natural sources: soil and rock debris, forest fires, sea salt, volcanic debris, biogenic (pollen, viruses, bacteria, etc.)*Anthropogenic sources*: fuel combustion and industrial processes, industrial processes fugitive emissions, non-industrial fugitive emissions, transportation, etc.

The investigation of airborne pollutants is basically entered within **Environmental sciences**. Its main aspects are:
- interdisciplinary by nature;
- science of the interactions;
- crosses the boundary between science and non science;

Factors characterising airborne particles
- the nature of the pollutants present in the air
- the concentration levels of pollutants
- the particle size spectra

The terminology related to atmospheric particles slightly extends the definition of an **aerosol**: it is an assembly of liquid or solid particles suspended in a gaseous medium long enough to enable observation or measurement; generally, the sizes of aerosol particles are in the range from 1nm (molecular size) to 100µm (particle diameters >100µm are removed from the atmosphere due to gravitational settling).

Comparison of **sizes**:
- H_2O molecule - 0.15nm
- Pb atom - 0.5nm
- Biphenyl (complex organic molecule) - 0.7nm
- Sand grain - few µm to 200µm
- Human hair 50 to 100µm

Sources of atmospheric particulate matter

Natural outdoor sources:
- Soil and rock debris
- Forest fires (combination of smoke, dust, and gas; smoke travels far, while dust settles quickly)
- Sea salt
- Volcanic debris (dust and some smoke that are ejected high into the atmosphere)
- Particles formed from gaseous emissions of H_2S, NH_3, NO_X and HC

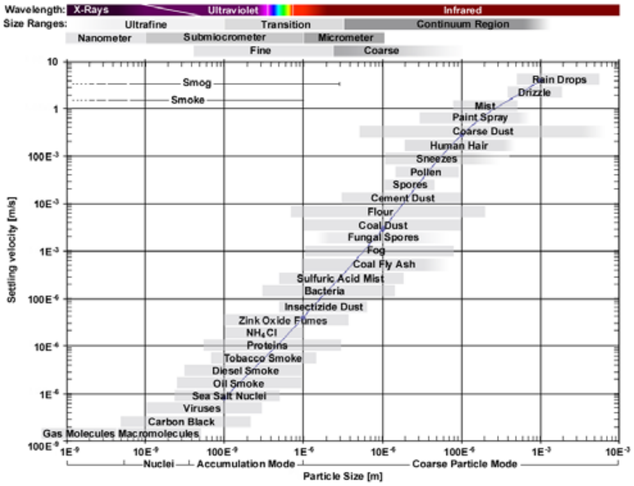


Fig. II-1.1 Sizes of Airborne Particles; superimposed are the settling velocities in still air at 0°C and 101.3kPa for particles having a density of $1g/cm^3$ as a function of particle diameter[vi].

Indoor sources:
- occupants i.e. skin, hair, etc.
- cooking
- building materials, especially mineral fibres, sick building syndrome;
- tobacco combustion
- combustion appliances
- maintenance products

Anthropogenic outdoor sources:
- Fuel combustion and industrial processes
- Industrial process fugitive emissions (wind erosion of storage piles, and unpaved plant roads, materials handling, loading and transfer operations)
- Non-industrial fugitive emissions (traffic entrainment of dust from public roads, agricultural operations and constructions)
- Transportation

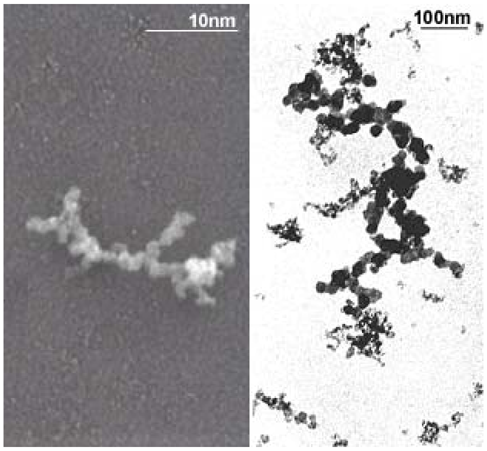


Fig. II-1.3: Micrograph of petrol (left) and soot (right) particle agglomerate[vii]

II - 2. Properties of aerosol particles

Physical	**Chemical**
density number (count) size (diameter) surface area mass size distribution shape degree of agglomeration electrical charge	phase distribution stability/reactivity organic/inorganic solubility (aqueous) acidity/alkalinity

Particle size and shape: it determines particle behaviour (<u>aging, transport, deposition</u>); particle size and shape

Classification of particle sizes (very subjective classification based on EPA-standards; recent trends tend to be more aware of the inhalability of ultrafine particles):

Fine particles < 2.5∝m
- ultra fine particles < 0.02µm (< 0.1µm)
- sub-micrometer particles < 1µm

Coarse particles > 2.5∝m

The fine and coarse particles:
- originate separately
- are transported separately
- are removed from the atmosphere by different mechanisms
- require different detection techniques
- require different control techniques
- have different chemical composition
- have different optical properties

Chemical composition of particles: Chemical composition of particles relates to particle formation and post-formation processes and is thus very different for particles in different size ranges.

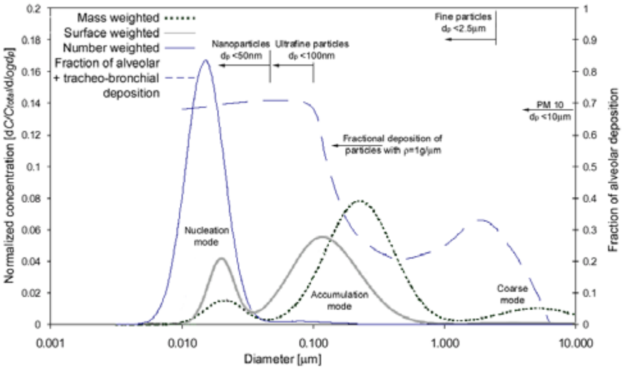


Fig. II-2.1 Normalized and weighted distribution curve of diesel exhaust. Mass-, surface-, and number weighted particle-size distributions shown with alveolar deposition fraction. The accumulation mode is the typical size range of an aging aerosol[viii] Particle number (or volume, surface area or mass) per logarithmic interval of size: $dN/d\log D_p$

- Fine: sulfates, organic compounds, ammonium, nitrates, carbon, lead, and other trace elements, etc.;
- Coarse: crystallic materials, Si-, Fe-, Al- compounds, sea salt, plant particles, etc.

II - 3. Bio-aerosols (are an important source of aerosols as they often trigger allergic reactions): These are airborne particles, large molecules or volatile compounds that are living, contain living organisms or were released from living organisms. Another definition describes them as primary Biological Aerosol Particles describe airborne solid particles (dead or alive) that are or were derived from living organisms, including micro-organisms and fragments of all varieties of living things.

• viruses	(0.02 to 0.3µm)
• bacterial cells	(0.5 to 30µm)
• fungal spores	(0.5 to 30µm)
• pollen	(10 to 100µm)
• protozoa	(>10µm)
• skin scales	(0.1-1mm)
• hair	(0.1mm)
• domestic dust mite	(appr.10µm)
• excreta or fragments of insects	(<1mm)

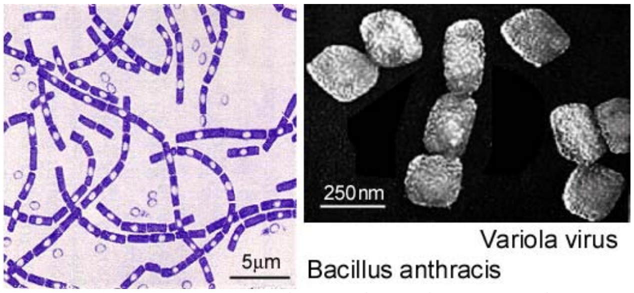


Fig. II-3.1 Bioaerosols. Viruses and Bacteria are among the most dangerous viable species.

Sources of bioaerosols

Indoor sources:

- Occupational environment where organic materials are handled (industrial and non-industrial);
- Microbial growth in air-handling systems of buildings, such as heating, ventilation and air conditioning systems; e.g. *Legionella* spp.
- Building occupants: humans and pets;
- Hospital environments;
- Bathrooms (showers)
- Indoor plants;

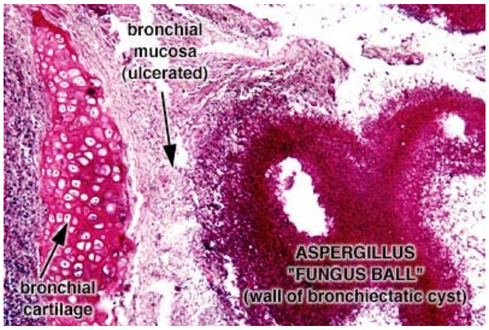


Fig. II-3.2 Bioaerosols. Aspergillus incorporated in bronchial linage of human lung[ix].

Outdoor sources:

- Surfaces of living and dead plants (fungal spores, bacteria), composting facilities;
- Natural and anthropogenic waters such as sewage lagoons or cooling towers (mainly bacteria);
- Aerosolation of water;
- Building exhaust and sanitary vents;
- Anthropogenic activities especially agriculture and wastewater treatment process;

Physical characterisation of bioaerosols: Concentration of micro-organisms which can be cultured and is expressed as the number of colony forming units for unit volume of air: **[cfu/m^3]**

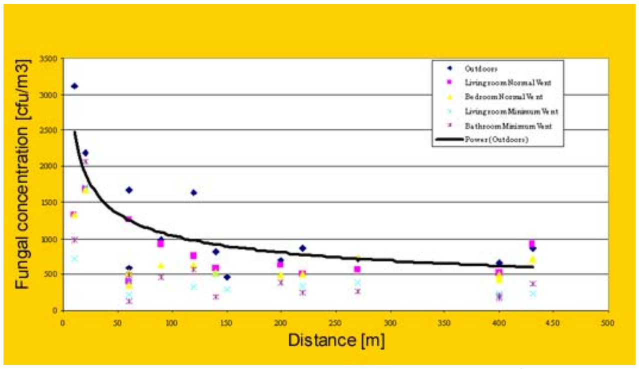


Fig. II-3.3 Fungal spore concentration in the vicinity of a park

http://www.sbg.ac.at/ipk/avstudio/pierofun/funpage.htm

II - 4. Particle equivalent diameter

Particle equivalent diameter is the diameter of a sphere having the same value of a physical property as the irregularly shaped particle being measured.

Equivalent diameter relates to particle behaviour (such as inertia, electrical or magnetic mobility, light scattering, radioactivity or Brownian motion) or to particle properties (such as chemical or elemental concentration, cross-sectional area, volume to surface ratio).

Aerodynamic (equivalent) **diameter** is the diameter of a unit-density sphere (1g/cm^3) having the same gravitational settling velocity as the particle being measured.

Particle size definitions that depend on observation of particle properties or behaviour

Relation between physical diameter and aerodynamic diameter:

$$d_a = d_p \cdot \sqrt{\frac{C_{c(d_p)}}{C_{c(d_a)}}} \cdot \sqrt{\frac{\rho_p}{\rho_0}} \qquad [\mathrm{m}]$$

simplified:

$$d_a = d_p \cdot \sqrt{\frac{C_{c(d_p)}}{C_{c(d_a)}}} \cdot \sqrt{\rho_p} \qquad [\mathrm{m}]$$

For particles of density close to unity (1g/cm^3) or for particles above 1µm:

$$d_a = d_p \cdot \sqrt{\rho_p} \qquad [\mathrm{m}]$$

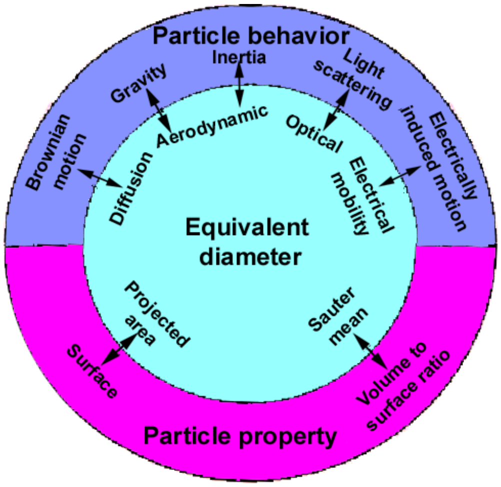


Fig. II-3.1 Particle Size Definitions. These depend on observations of particle properties or behaviour[x]

d_a aerodynamic diameter	[m]
d_p physical particle diameter	[m]
C_c Cunningham slip correction factor	[-]
ρ_p, particle density	[g/m^3]
ρ_0, std. particle density	1 [g/cm^3] = 1000 [g/m^3]

The parameters often used, especially for particles of complex shapes (for example agglomerates) include:

- mass equivalent diameter, for which the particle is compressed into a spherical particle without voids;
- envelope-equivalent diameter, for which the particle voids are included in the sphere;

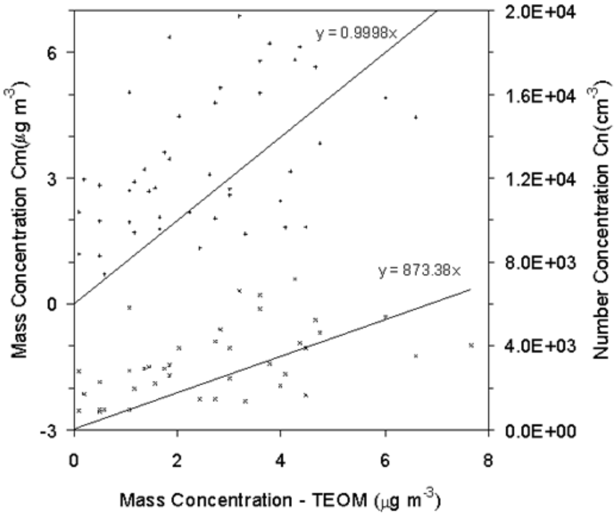


Fig. II-3.2 Number concentration versus particle mass. Particle number concentration is only transferable into mass concentration with known density[xi]

II - 5. Particle size distribution - particle size spectrum:

- Monodisperse aerosol - single sized particles with a very narrow standard deviation;
- Polydisperse aerosol - mixture of variety of particle sizes (characterized by a broad standard deviation);

The spread of particle size distribution is characterised by an arithmetic (lin) or geometric (log) standard deviation.

Size characterisation:

Mode size - size with the maximum number of particles;
Mean size - average of particle spectrum;
Median size - equal *number of particles* above and below this size;
Often used: count median diameter (CMD), number or mass median diameter (NMD) or mass median diameter (MMD).

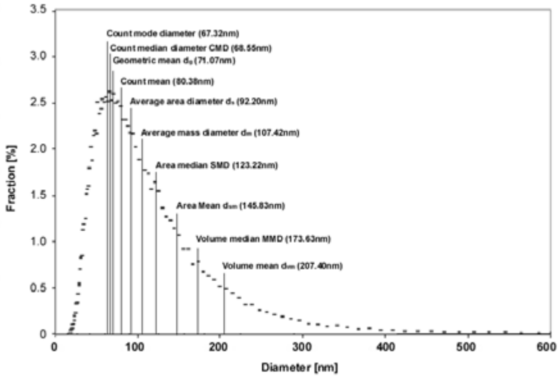


Fig. II-3.2 Particle Size Characterization. Typical size distribution of a polydisperse aerosol (NaCl crystals)[xii]

a) **Particle size distribution**: Particle size distributions are usually presented as frequency, histograms, or cumulative distributions. The simplest size distribution is the **Normal (Gaussian) Distribution**: As most distributions exhibit a skewed (large shoulder with a long tail) function, the normal distribution is rarely used to describe most aerosol particle size distributions. It is presented here to understand its concept, which will be applied in the Log-normal distribution later on.

$N(d_p)\mathrm{d}d_p$ = number of particles per unit volume of air having diameters in the range d_p to $d_p + \mathrm{d}d_p$. The total number of particles of all sizes per unit volume of air:

$$N = \int_0^\infty n\left(d_p\right) d d_p \qquad [1/\mathrm{m}^3]$$

$$y(d_P) = \frac{1}{\sigma\sqrt{2\pi}} \cdot e^{-\frac{(d_P-\mu)^2}{2\sigma^2}}$$

N, number of particles per unit volume	[1/m^3]
n, number of particles	[-]
d$_p$, particle diameter	[m]
σ, standard deviation	[-]
μ, mean value (of particle size)	[-]
π, circle constant	3.414 [-]

Log-Normal Distribution: for many man-made sources, the observed particulate matter distribution approximates a log-normal distribution.

$N(\ln d_p)\,\mathrm{d}\ln d_p$ = number of particles per unit volume of air having diameters in the range $\ln d_p$ to $\ln d_p + \mathrm{d}\ln d_p$. The total number of particles per unit volume of air of all sizes:

$$N = \int_{-\infty}^{\infty} n\left(\log d_p\right) d \log d_p \qquad [1/\mathrm{m}^3]$$

$$n(d_p) = \frac{N}{\sqrt{2\cdot\pi}\cdot d_p\cdot\ln\sigma_g}\cdot e - ^{\frac{\left(\ln d_p - \ln\bar{d}_{pg}\right)^2}{2\cdot\ln^2\sigma_g}}$$

The log-normal distribution is the distribution that results when the distribution of ln(x) is Gaussian (normal); Log-normal size distributions are most commonly used in aerosol physics because:

- most aerosol sources generate particles displaying log-normal distributions (more than 80% of particles by number are smaller than 0.1 μm);
- it is convenient as the particle diameters range for several decades;

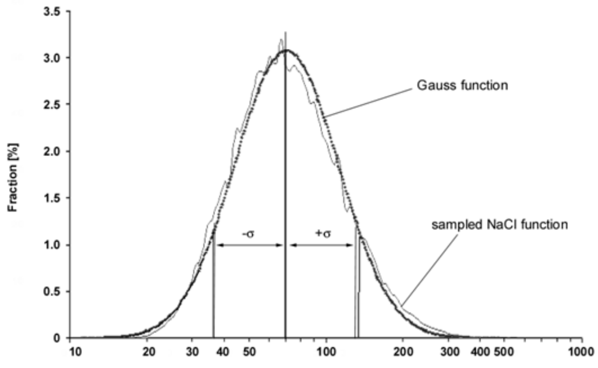


Fig. II-3.3: **Frequency distribution plotted against logarithm of particle size**; it displays a symmetric (i.e. bell-shaped) distribution with the population mean μ and its standard deviation σ[ξιιι].

b) Particle shape characterisation

Form factor is a measure of irregularly shaped particles (χ = 1 for spherical particles), and is defined as:

$$\chi = \frac{4\cdot\pi\cdot Area}{P^2} \qquad [\mathrm{m}]$$

A, surface area	[m^2]
P; perimeter	[m]

Shape factor is the inverse of the form factor (usually applied for fibrous particles) ans is defined as the **aspect ratio**:

$$\beta = \frac{L}{w}\,[-] \qquad [-]$$

L, length	[m]
w, width	[m]

PART III - 1. FORCES AND INTERACTIONS

a) Particle forces: sub-micrometer particles tend to stick together while larger ones do readily detach.

Adhesion Forces: particles adhere to each other and to surfaces; most adhesion forces are linearly dependent on particle diameter (thus, large particles are more readily detached than small ones).

London (van de Waals) forces: weak forces that are attractive in nature and act over a short distance relative to particle dimensions (other forces such as H-bonding and π-orbital are also commonly observed).

Electrostatic forces: most particles 0.1μm carry same small net charge facilitating agglomeration as opposing forces attract each other. Dipole forces may facilitate hydratation of aqueous particles resulting in agglomerates. Surface tension (of a liquid layer on a particle surface) is then the main force holding such a composite together.

Detachment Forces

- Centrifugal force: related to particle rotation and proportional to particle mass and thus volume (d^3)
- Vibration: also proportional to (d^3)
- Detachment by air currents: proportional to exposed surface (d^2)

Rebound: particle collision with a surface - deformed upon collision

Externally applied forces

- Gravitational force
- Aerodynamic drag
- Electrostatic force
- Diffusion (if there is a concentration gradient - very important for particles smaller than 0.2 μm)
- Inertial forces (used for example for deposition by impaction)
- Thermophoretic (if there is a temperature gradient)

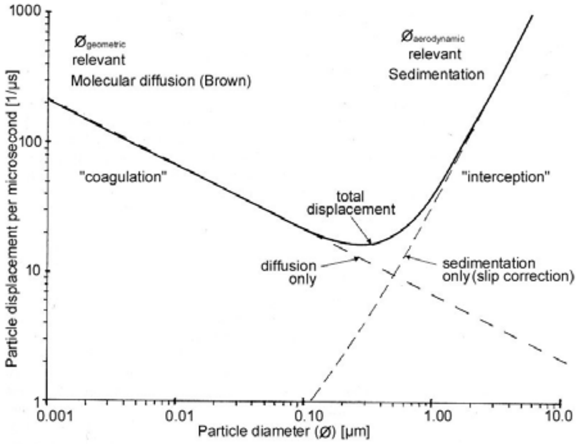


Fig. III-1.1: **Interaction of Aerosols**; according to an aerosol's density, it can sediment, intercept, impact, or diffuse across space and time.[ξιϖ]

b) Particle motion (describes the gas-particle relation; characterises the particle diameter in regards to the medium in which it is suspended (compare with fig. II-1.1 *Sizes of Airborne Particles*):

Free <u>molecular regime</u>: sub-micrometer particles, especially < 0.1μm, are affected by the motion of individual gas molecules;

The <u>continuous regime</u>: larger particles can be treated as being submersed in a continuous gaseous medium (characterised by a Knudson number >1, see next page);

The <u>transition (or slip) regime</u>: intermediate size particles can usually be treated by an adjustment of equations from the continuum regime (requires Cunningham slip correction factor, next page);

Reynolds Number: describes the onset of turbulence and is the ratio of the inertial force of the gas to the friction force of the gas moving over the surfaces:

$$Re = \frac{\rho_g \cdot v \cdot d_P}{\eta} \qquad [-]$$

v, velocity of the gas	[m/s]
η, dynamic gas viscosity [Pa·s] = [N·s/m^2] =	[g/(m·s)]
ρ_g is gas density	[g/m^3]
d_P, characteristic diameter of the particle	[m]

At normal temperature and pressure (NTP which is 20°C at 101kPa corresponding to 1atm) Re can be simplified to:

$$Re = 6.5 \cdot v \cdot d_P \qquad [-]$$

A distinction between the flow Reynold's number (Re_f) and particle Reynold's number (Re_p) must be made; from experiments for circular ducts is was found that **laminar flow** occurs when $Re_f < 2000$ (friction forces dominate), whereas **turbulent flow** for $Re_f > 4000$ (interactive particle forces dominate). The gas flow is sensitive to the "previous" history for Re_f in the intermediate range. From experimental work with suspended particles it is known that laminar flow occurs when $Re_p < 0.1$.

The gas flow in a tube with laminar flow characteristics at boundary layer (near the wall surface) result in a relative velocity of zero, whereas at the centre of the tube the gas velocity is twice the average velocity in the tube. At least about ten tube diameters are required to enable laminar flow patterns within a tube.

From the kinetic gas theory it is known that gas molecules move about in a random fashion (Brownian motion), which result in collisions with the walls of their container and with each other, interfering with laminar flow patterns.

Gas Diffusion coefficient it is the result of the Brownian motion and results in net movement from regions of higher to regions of lower concentrations. A general note: remember always to correct for temperature, pressure, volume, etc, when measurements are conducted for conditions different to standard

$$D = -\left(\frac{3\cdot\sqrt{2}\cdot\pi}{64\cdot N\cdot d_{molec}^{2}}\right)\cdot\sqrt{\frac{R\cdot T}{M}} \qquad [\mathrm{m^2/s}]$$

Flux J: $J = -D\cdot\frac{\partial N}{\partial x}$ [m/s]

The average velocity of a gas molecule:

$$\bar{v} = \bar{v}_r\cdot\sqrt{\frac{T\cdot M_r}{T_r\cdot M}} \qquad [\mathrm{m/s}]$$

Mean free path (λ):

$$\lambda = \lambda_r\cdot\frac{101.3}{P}\cdot\frac{T}{293.15}\cdot\frac{1+S/293.15}{1+S/T} \qquad [\mathrm{m}]$$

Gas viscosity

$$\eta = \eta_r\cdot\frac{T_r+S}{T+S}\cdot\left(\frac{T}{T_r}\right)^{3/2} \qquad [\mathrm{N\cdot s/m^2}]$$

N number of gas molecules per unit volume		[1/cm^{-3}]
d_{molec}, molecular collision diameter		[m]
R, gas constant	8.315	[J/(mol·K)]
D, diffusion in a concentration gradient		[m^2/s]
(D_{air} at NTP) = 0.18cm^2/s)		
(D for air: 3.7·E^{-8} cm^2/s)		
x, distance		[m]
T, temperature		[m]
T_r = 293K		
$\bar{v}_r$, particle velocity		[m/s]
reference values for air at NTP: $\bar{v}_r$ = 463 m/s		
M, molecular weight of gas molecule		[g/mol]
M_r = 28.9 g/mol		
λ_r, mean free path		[m]
S, Sutherland interpolation constant		[-]
η_r, viscosity of gas		[Pa·s]

Particle diffusion likewise connected to Brownian motion, it is dependent on the size and shape of the aerosol particle, resulting in slower diffusion of larger particles than smaller ones.

$$D = \frac{k\cdot T\cdot C_c}{3\cdot\pi\cdot\eta\cdot d_p} \qquad [\mathrm{m^2/s}]$$

The root mean square distance that a particle can travel in time t is

$$x_{rms} = \sqrt{2\cdot D\cdot t} \qquad [\mathrm{m}]$$

For example: x_{rms} a particle travels in 10s, equals 0.1cm for a particle of diameter 0.01μm, and 2.3·E^{-3}cm, for a particle of diameter 1 μm.

D, particle diffusion coefficient		[m^2/s]
k, Boltzman constant	1.381·E^{-23}	[J/K]
T, temperature		[K]
C, Cunningham slip correction factor		[-]
η, viscosity of gas		[Pa·s]
t, time		[s]

Knudsen number: it relates the gas molecular mean free path to the physical dimensions of the particle (usually its radius). The mean free path of a particle, defined as the distance between collisions of gas molecules, is depended on temperature and pressure. Thus, the Knudson number (again a dimensionless quantity), relates the gas molecular mean free path to the physical dimension of the particle; thus, *Kn* is an indicator of particle size:

$$Kn = \frac{2\cdot\lambda}{d_p} \qquad [-]$$

Kn <<1, continuum flow
Kn >>1, free molecular flow
0.4 < Kn < 20, slip regime

Cunningham slip correction factor: for particle sizes in the slip regime, it is convenient to assume that the particle is still moving in the continuum gas flow (λ, β and γ are empirical material parameters^{xv}):

$$C_c = 1 + Kn\cdot\left[\alpha + \beta\cdot e^{-\gamma/Kn}\right] \qquad [-]$$

α, 1.142 (solid particles)	[-]
β, 0.558 (solid particles)	[-]
γ, 0.999 (solid particles)	[-]

Caution when using slip coefficient constants from the literature!
C_c = 1 in the continuum regime (see previous page)
C_c > 1 in the transition regime (especially for particles <100nm)

Peclet number: describes the amount of convective transport of particles towards an object; the larger **Pe**, the less important diffusion;

$$Pe = \frac{v\cdot d_c}{D} \qquad [-]$$

v, upstream gas velocity towards the surface	[m/s]
d_c, significant dimension of the particle of collecting surface (such as filter)	[m]

Aerodynamic drag on particles: a particle drag force, F_{drag}, relates the resistive pressure of the gas to the velocity pressure; i.e. relative motion between the particle and the surrounding gas.

$$F_{drag} = \frac{\pi \cdot C_d \cdot \rho_g \cdot \chi \cdot v^2 \cdot d_p^2}{8 \cdot C_c} \qquad [N]$$

Dependence of C_d on particle velocity

$$C_d = \frac{24}{Re_p} \qquad Re_p < 0.1$$

$$C_d = \frac{24}{Re_p} \cdot \left(1 + 0.0916 \cdot Re_p\right) \qquad 0.1 \le Re_p \le 5$$

$$C_d = \frac{24}{Re_p} \cdot \left(1 + 0.158 \cdot Re_p^{2/3}\right) \qquad 5 \le Re_p \le 1000$$

$$Re = \frac{\rho_g \cdot v \cdot d}{\eta} \qquad [-]$$

Thus - Stokes law:

$$F_{drag} = \frac{3 \cdot \pi \cdot \eta \cdot \chi \cdot v \cdot d_p}{C_c} \qquad [N]$$

C_c Cunningham slip correction factor	[-]
χ, dynamic shape factor for spherical particles $\chi = 1$	[-]
C_d drag coefficient	[-]
Re_p, Reynolds number of particle in air pollution application, Re is generally < 0.1	[-]
ρ_g gas (medium) density	[g/m^3]
v, particle speed	[m/s]
C_d is the drag coefficient	[-]
η, viscosity of medium	[Pa·s]
χ, dynamic shape factor	[-]
C_c Cunningham slip correction factor	[-]
d_p physical particle diameter	[m]

Particle motion in gravitational field

$$F_{grav} = m_p \cdot g = \left(\rho_p - \rho_g\right) \cdot v_g \cdot g \approx \rho_p \cdot v_p \cdot g \qquad [N]$$

For spherical particles:

$$V_p = \frac{\pi \cdot d_p^3}{6} \qquad [m^3]$$

$$F_{grav} = \frac{\pi}{6} \cdot d_p^3 \cdot \rho_p \cdot g \qquad [N]$$

m_p particle mass		[g]
g gravitational constant	9.81	[m/s^2]
ρ_p particle density		[g/m^3]
ρ_g gas density		[g/m^3]
V_p particle volume		[m^3]
π, circular constant	3.14	[-]

and gravitational settling velocity (terminal velocity): $F_{grav} = F_{drag}$
and in Stokes regime:

$$\frac{3 \cdot \pi \cdot \eta \cdot \chi \cdot v \cdot d_p}{C_c} = \frac{\pi}{6} \cdot d_p^3 \cdot \rho_g \cdot g$$

$$v_{grav} = v_{ts} = \frac{\rho_p \cdot d_p^2 \cdot g \cdot C_c}{18 \cdot \eta} \qquad Re_p < 0.1$$

For negligible slip, at NTP: $V_{grav} = 0.003 \cdot \rho_p \cdot d_p^2$

The Stokes diameter relates to the diameter of a spherical particle with the same density and settling velocity as the particle in question.

Relation b/w Stokes and aerodynamic diameters[xvi]:

$$\rho_p \cdot d_s^2 = 1 \cdot d_a^2 = d_a^2 \qquad [1/m]$$

ρ_p particle density	[g/m^3]
d_s, stokes diameter	[m]
d_a aerodynamic diameter	[m]

In still air in a room the initial and final (N_0 and N(t) after an elapsed time t) the number of particles homogenously spreads in the room is:

$$N(t) = N_0 \cdot \left(1 - \frac{v_{grav} \cdot t}{H}\right) \qquad [-]$$

H, room height	[m]
v_{grav}, gravitational settling velocity	[m/s]
t, time	[s]

NB: still conditions are rarely achieved; gravitational settling is more important for larger particles, and negligible (compared to other processes) for smaller particles.

c) Particle motion in an electric field: For a particle with a total charge equal to n times the elementary unit of charge e, the electrostatic force is (Note: Electrostatic forces are particularly effective for sub-micrometer particles):Applications: electrostatic precipitators; size classification

$$F_{elec} = n \cdot e \cdot E$$

Terminal velocity in electric field: $F_{elec} = F_{drag} \Rightarrow$

$$\frac{n \cdot e \cdot E \cdot C_c}{3 \cdot \pi \cdot \eta \cdot d_p} = \frac{3 \cdot \pi \cdot \eta \cdot \chi \cdot v \cdot d_p}{C_c}$$

$$v_{elec} = \frac{n \cdot e \cdot E \cdot C_c}{3 \cdot \pi \cdot \eta \cdot d_p} \qquad [\mathrm{m/s}]$$

Mechanical particle mobility B:

$$B = \frac{C_c}{3 \cdot \pi \cdot \eta \cdot d_p} \qquad [\mathrm{s/g}]$$

$$v_{elec} = n \cdot e \cdot E \cdot B \qquad [\mathrm{m/s}]$$

Particle electrical mobility Z:

$$Z = n \cdot e \cdot B \qquad [\mathrm{m^2/(V \cdot s)}]$$

$$v_{elec} = Z \cdot B \qquad [\mathrm{m/s}]$$

e, unit charge		[A·s] = [C]
n, number of unit charges		[-]
E, electrical field strength		[V/m]
C_c Cunningham slip correction factor		[-]
π, circular constant	3.14	[-]
χ, dynamic shape factor		[-]
d_p physical particle diameter		[m]
η, viscosity of medium		[Pa·s]
V_{elec}, electric field velocity		[m/s]

d) Particle motion in other force fields (are generally much weaker than gravitational or electrostatic forces); these forces are caused by the presence of a:

- thermal gradient (thermophoresis and photophoresis)
- electromagnetic radiation pressure
- acoustic pressure
- diffusiophoresis

e) Physical and chemical processes

Changes in the particulate phase result from:

- external forces
- physical and chemical processes

Importance of physical and chemical processes

- essential contribution to the earth's hydrological cycle
- formation of photochemical smog
- key to shaping the atmospheric aerosol size distribution
- aerosol exposure
- instrument operation (condensation particle counters)
- industrial aerosol processing
- generation of test aerosols

Physical and chemical processes:

- affect particle size and composition
- involve mass transfer to or from the particle

Physical and chemical processes include:

- condensation/evaporation
- nucleation (homogenous and heterogenous)
- coagulation
- reactions

Fundamentals behind this process are rooted in the partial pressure of vapour is the pressure the vapour would exert if it were the only component present. The vapour pressure (or saturation pressure) is a condition required for mass equilibrium (no net transfer of molecules at the liquid surface); this definition applies to flat surfaces; e.g. vapour pressure of water at a temperature T, is:

$$p_s = 1 \cdot E^{8.1-1750\,/(T-38)} \qquad [\mathrm{Pa}]$$

p_s, saturation pressure [Pa]
for temperatures between 273 - 330K

Saturation ratio for curved surfaces (particles)

$$S_R = \frac{p_{vapour}}{ps_{vapour}} \qquad [-]$$

Saturation ratio: $S_R = 1$, mixture saturated
$S_R > 1$, mixture supersaturated
$S_R < 1$, mixture unsaturated
p_{vapour}, partial pressure of vapour [Pa]

Kelvin effect describes the equilibrium between particle growth and evaporation; greater pressure is required to maintain mass equilibrium for curved surfaces than for flat surfaces. It is of essential importance when operating under supersaturated conditions such as in a CPC where particle growth is obtained by cooling the gas to such conditions. The Kelvin equation is:

$$S_R = e^{4 \cdot \gamma \cdot M\,/(\rho_p \cdot R \cdot T \cdot d_p)} \qquad [-]$$

γ, surface tension		[N/m²]
M, molecular weight of particle		[g/mol]
ρ_p, density of the liquid		[g/m³]
R, gas constant	8.315	[J/(mol·K)]

Nucleation of a particle undergoing a condensation process under supersaturated conditions.
Homogenous nucleation (self nucleation) is the process of droplet formation in the absence of condensation nuclei. For this process to occur: $2 < S_R < 10$ (S_R, Saturation ratio for curved particles).
Heterogenous nucleation occurs in the presence of condensation nuclei (usually sub-micrometer airborne particles), as with insoluble or soluble nuclei. Heterogenous nucleation occurs in the following manner:

Insoluble nuclei
supersaturation conditions
↓
formation of an adsorbed layer of vapour molecules on particle surface
↓
the nucleus "looks like" a droplet
↓
if the diameter is larger than Kelvin diameter for the particular conditions, vapour condenses

Soluble Nuclei for example are NaCl nuclei; important factors that must be present to make this process possible:

- strong affinity for water (hydrophilic, hygroscopic);
- favourable conditions for initial formation of droplets;
- particle growth can occur for lower saturation ratios;
- the droplet contains dissolved salt (mass of salt in the droplet is constant during the nucleation/condensation process).

Condensation: diffusion controlled process for supersaturated conditions. The growth rate for pure liquids and droplets with insoluble nuclei is valid for $d_p < \lambda$.

$$\frac{d(d_p)}{dt} = \frac{2 \cdot (p - p_d)}{\rho_p \cdot \sqrt{2 \cdot \pi \cdot R \cdot T / M}} \qquad \text{for } d_p < \lambda$$

$$\frac{d(d_p)}{dt} = \frac{4 \cdot D_v \cdot M \cdot (p - p_s)}{\rho_p \cdot d_p \cdot R \cdot T} \qquad \text{for } d_p > \lambda$$

Time for particle growth from d_1 to d_2:

$$t = \frac{\rho_\gamma \cdot R \cdot T \cdot (d_2^2 - d_1^2)}{8 \cdot D_v \cdot M \cdot (p - p_s)} \qquad [\text{s}] \text{ for } d_1 > \lambda$$

d_p physical particle diameter		[m]
t, time		[s]
p, partial pressure of vapour in the particular environment		[Pa]
p_d, partial pressure of vapour at droplet surface		[Pa]
note: p_d calculated from Kelvin EQ for $d_p > \lambda$		
ρ_p particle density		[g/m^3]
D_v, diffusion constant w/n a given system		[m^2/s]
M, molecular weight		[g/mol]
R, gas constant	8.315	[J/(mol·K)]
T, temperature		[K]
λ, mean free path		[m]

Evaporation: this is the opposing process to condensation and occurs under unsaturated conditions. Corrections needed for:

- cooling of the droplet surface due to evaporation;
- complications in the calculation of mass transfer by diffusion within one mean free path;

$$\frac{d(d_p)}{dt} = \frac{4 \cdot D_v \cdot M}{R \cdot \rho_p \cdot d_p} \cdot \left(\frac{p_\infty}{T_\infty} - \frac{p_d}{T_d} \right) \cdot \frac{2 \cdot \lambda + d_p}{d_p + 5.33 (\lambda^2 / d_p) + 3.42 \cdot \lambda}$$

The rate of decrease:
∞ - conditions removed from the particle
d - conditions at the particle surface

NB: in environmental systems, any processes in which condensation/evaporation are involved, or which proceed in the presence of vapours, are the most difficult to quantify, and often the experiments do not agree with the theory (if the theory exists).

Coagulation: this is a diffusion controlled aerosol growth process which results from particle collisions; it can occur as thermal coagulation (governed by Brownian motion) or by kinematic coagulation (governed by external forces).

Monodisperse coagulation (Smoluchowski coagulation): The following assumptions have to be made:

- particles should be monodisperse (rarely true);
- particles stick if they contact one another (agglomeration / accumulation mode which is usually the case);
- particles grow slowly (depends on conditions);

Rate of particle number decrease due to coagulation (Smoluchowski's equation):

$$\frac{dN}{dt} = -K \cdot N^2 \qquad [1/\text{s}]$$

For particles larger than the gas mean free path (which is usually the case):

$$K = 4 \cdot \pi \cdot d_p \cdot D = \frac{4 \cdot k \cdot T \cdot C_c}{3 \cdot \eta} \qquad [\text{m}^3/\text{s}]$$

K, coagulation (rate) constant		[m^3/s]
N, number concentration		[1/m^3]
D, diffusion constant in a given system		[m^2/s]
k, Boltzman constant	$1{,}381 \cdot E^{-23}$	[J/K]
T, temperature		[K]
C_c Cunningham slip correction factor		[-]
η, viscosity of medium		[Pa·s]

Coagulation coefficients for selected particle sizes at 20°C:

Particle Diameter [μm]	Coagulation Coefficient [cm³/s]
0.05	$150\cdot E^{-9}$
0.1	$86\cdot E^{-9}$
0.5	$40\cdot E^{-9}$
1	$35\cdot E^{-9}$
5	$31\cdot E^{-9}$

The change in number concentration: N_0 and $N(t)$: initial and final (after time t) number of particles homogenously spread:

$$N(t)=\frac{N_0}{1+N_0\cdot K\cdot t}\qquad [1/m^3]$$

For spherical particles and for a contained system with no particle losses:

$$d(t)=d_0\cdot\sqrt[3]{\frac{N_0}{N(t)}}\qquad [m]$$

$$d(t)=d_0\cdot\sqrt[3]{1+N_0\cdot K\cdot t}\qquad [m]$$

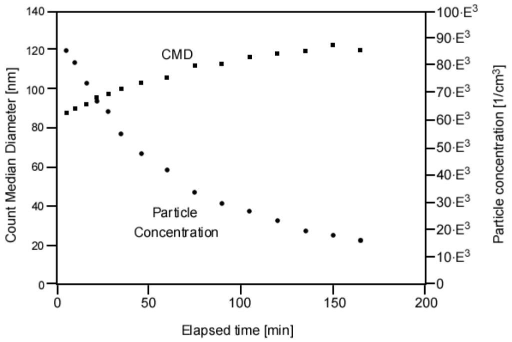


Fig. III-1.2: **Shift in particle spectra**; the higher the concentration, the faster coagulation takes place; ETS introduced into a test chamber typically displays such a behaviour.[xvii].

K, coagulation constant	[m³/s]
t, time	[s]
d_0, initial particle diameter	[m]
d(t), final particle diameter	[m]

initial number concentration [cm⁻³]	time for number concentration to halve [s]	time for particle size to double [s]
$1\cdot E^{12}$	0.002	0.014
$10\cdot E^{19}$	0.2	1.4
$100\cdot E^{6}$	20	140
$1\cdot E^{6}$	$2\cdot E^{3}$ (33 min)	$14\cdot E^{3}$ (4 h)
$10\cdot E^{3}$	$200\cdot E^{3}$ (55 h)	$1.4\cdot E^{6}$ (16 d)

Polydisperse coagulation: in an environmental setting aerosols are always polydisperse. Numerical methods required to calculate particle growth by coagulation for polydisperse aerosol. A useful estimation of average K for aerosol with a log-normal distribution of CMD and σ_g is:

$$\overline{K}=\frac{2\cdot k\cdot T}{3\cdot\eta}\cdot\left[1+e^{\ln^2\cdot\sigma_g}+\frac{2.49\cdot\lambda}{CMD}\cdot\left(e^{0.5\cdot\ln^2\cdot\sigma_g}+e^{2.5\cdot\ln^2\cdot\sigma_g}\right)\right]$$

σ_g, standard deviation		[-]
CMD, count median diameter		[m]
k, Boltzman constant	$1{,}381\cdot E^{-23}$	[J/K]
T, temperature		[K]
η, viscosity of medium		[g/(m·s)]
λ, mean free path		[m]

Kinematic coagulation: e.g.

- gradient coagulation.
- turbulent coagulation
- acoustic coagulation

In general:

- external force creates relative motion between particles;
- the greater the particle number the greater the rate of coagulation;
- there are no simple equations that describe these processes in a complete way;

Reactions: large surface area of aerosol leads to a range of reactions between gas and liquid or solid particles. The types of reactions occur between:

- compounds in a particle;
- particles of different chemical composition;
- the particle and one or more gas molecules;

Mass transfer steps for the gas to particle reactions:

- diffusion of specific gas molecule to the surface of the particle;
- transfer across the interface or reaction at the interface;
- diffusion into the particle;

Any one of these steps may control the reaction; e.g.

- **Absorption**: gas molecules become dissolved in a liquid droplet;
- **Adsorption** gas attaches to a surface layer via two different mechanisms:
  i) physical (physiosorption): gas molecules are held to particle surface by van der Waals forces
  i) chemical (chemisorption): chemical bonds are formed to hold the gas molecules on the particle surface

Surface deposition of aerosol particles: deposition mechanisms are based on sedimentation (coarse particles only), diffusional deposition (the smaller the particle, the higher diffusional deposition), and deposition by impaction or interception due to inertia (usually for coarse particles only).

NB: i) sedimentation is the deposition mechanism for larger particles, sub-micrometer particles deposit mainly by diffusion;
i) in ambient environment (no high flow rates), sedimentation and diffusional deposition are the main mechanisms;
i) resuspension does not affect sub-micrometer particles

The surface deposition process depends on the nature of aerosols (size, shape, electrical charge), condition of the surface (roughness, sticky, non-sticky), and air flow characteristics (flow rate, degree of turbulence).

NB: deposition velocities determined experimentally tend to be significantly higher than those determined by theory or from wind tunnel experiments.

Theoretical model of deposition process:

$$\vec{\phi} = -D \cdot \vec{\nabla} C \qquad [1/s]$$

The steady-state one dimensional particle flux towards the surface is:

$$\phi(d) = \left[D_t(z) + D_p(d)\right] \cdot \frac{dC(z,d)}{dz} + v_s(d) \cdot C(z,d)$$

The deposition velocity is the number of particles with diameter d deposited per unit surface in unit time:

$$v_d(d) = \frac{\phi(d)}{C(z,d)} \qquad [m/s]$$

D, diffusion coefficient	[m]
v, velocity	[m/s]
C, concentration	[1/m^3]
C(z,d), concentration of particles with a diameter d at a distance z from the surface	[1/m^3]
$D_t(z)$, turbulent diffusion coefficient	[m^2/s]
$D_p(d)$, Brownian diffusion coefficient	[m^2/s]
$v_s(d)$, sedimentation velocity	[m/s]
$\phi(d)$, flux due to Brownian diffusion	[1/s]

Aerosol formation and generation: contribution and significance of various processes for formation and generation of particles in different size ranges.

The nuclei mode ranging from about 0.005 to 0.05μm are also known as "Aitken nuclei"; particles in this mode:

- are formed from condensation of hot vapour during combustion processes, and nucleation of atmospheric species to form fresh particles
- constitute majority of atmospheric particles by number, but usually only a small fraction by mass
- move to accumulation mode by coagulating with accumulation mode particles
- contain most of the trace elements and toxic compounds

The accumulation mode ranging from about 0.05μm to 2μm are among the most stable particle size range; particles in this mode:

- are formed by gas to particle conversion, chemical reactions, condensation and coagulation
- remain airborne and in the mode for long periods of time as the removal mechanisms are least efficient in this regime; therefore, are the dominant fraction responsible for adverse health effects (particle size range of 0.1 to 1 μm are easily deposited in the lungs)

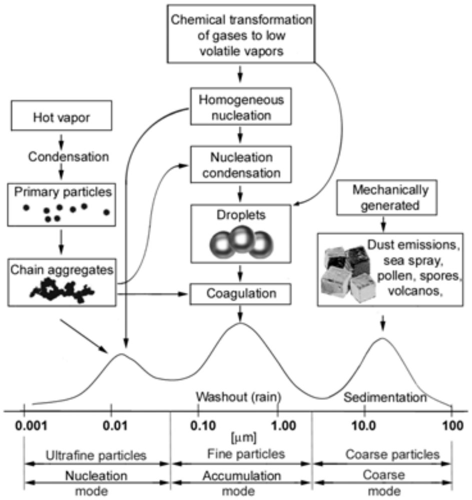


Fig. IV-3 Schematic of the 3 main size distributions; it shows the mass weighted formation mechanisms for atmospheric particles[xviii]

- **The larger particle mode** ranging from about 2μm to 100μm, the so-called coarse particles; particles in this mode are formed by mechanical processes and are removed by sedimentation and washout.

Source Category	Emissions [Tg/yr]	Source Category	Emissions [Tg/yr]
Fuel combustion & indust. processes	10	Soil and rock debris	50-250
Industrial process fugitive emissions	3.3	Forest fires	1-50
Nonindustrial fugitive emissions	110-370	Sea salt	300
Transportation	1.3	Volcanic debris	25-150
TOTAL (antropogenic)	125-385	from gases (H_2S, NH_3, NO_x, HC, etc.)	345-1100
		TOTAL (natural)	721-1850

Aerosol aging: time frames for aging processes are:

- short time scale (seconds to minutes) immediately after emission/generation;
- medium time scale (hours); indoor and ambient environment;
- long time scale (days); ambient environment/transport of air masses;

Important aspects in Modelling:

- modelling approach (indoor, outdoor, etc.)
- models available
- comparison of different modelling approaches

PART IV - INSTRUMENTATION AND MEASUREMENTS

1. Measurement techniques

What to measure?

- particle mass;
- particle number;
- mass or number size distribution;
- chemical composition;
- biological composition;
- radioactivity;
- combination of these;

How to measure? In general, each aerosol measurement technique covers a unique range of particle characteristics such as:

- concentration;
- size;
- shape;
- chemical or biological composition;

Choosing the proper instrument for a particular application is of critical importance. A thorough understanding of the principles and limitations of each measurement method is essential

Type of aerosol measurements

- sample collection and real time measurements (on site);
- active (e.g. pump) and passive sampling (exposure of collecting device);
- personal and area sampling (in either case should be representative);
- continuous measurements or grab sampling (e.g. once an hour);
- sampling from flows - isokinetic sampling;

The **degree of comprehensiveness** in air quality assessment is a function of the endpoint

- basic research;
- regulatory compliance (sampling procedure to achieve comparable results);
- remedial action;

Detection is a two stage process: i) measurement for the determination of the quantity;
i) data deconvolution for the determination of the quality

a) Mass measurement techniques

Sample collection methods (static):

- Filter collection;
- Inertial and gravitational collection;
- Diffusional deposition;
- Electrostatic deposition;

Dynamic methods

- Piezoelectric mass monitor;
- Tapered-Element Oscillating;
- Microbalance Method (TEOM);
- Optical techniques: light scattering;
- aerosol photometer – nephelometer;

b) Number concentration measurement techniques - concentration of atmospheric particles is most commonly performed using (both techniques provide no information about the size distribution):

- condensation nucleus counters;
- aerosol electrometers;

c) Size distribution measurement techniques: for atmospheric particle size classification it includes:

- optical particle counters (inlets determines which sort of particles may be measured);
- electrostatic classifiers;
- diffusion batteries;

d) Combination of physical measurement techniques: Information on particle size distribution is generally obtained by combining a dynamic aerosol detection technique with a size classification technique

2. Filter collection: Filter collection is conducted for further:

- gravimetric analysis (mass – standard filters do not allow microscopic analysis)
- microscopic analysis (shape, number, elemental composition, morphology)
- microchemical analysis (chemical composition; organic and inorganic; elements and compounds)
- radioactivity measurements

Filter holders can be:

- opened-faced
- in-line
- cassette variety

General consideration in setting up a filtration sampling system:

- selection of a filter (according to application must for example withstand elevated temperatures);
- ensuring a positive seal (leakages falsify results);
- flow rate stability and measurements; e.g. $[m^3/s]$;
- minimising particle losses in the system;
- filter performance testing;

Selection of a filter - Criteria for selecting a filter:

- collection efficiency of the filter for the aerosol size distribution to be tested;
- pressure drop across the filter;
- compatibility of filter with the sampling conditions (such as temperature, pressure, humidity, corrosiveness, etc);
- cost constrains relating to sampling effort and the number of filters required (filters may cost up to AU$ 100 a piece)

Filter classification - Filters used for aerosol sampling are:

- fibrous filters;
- porous-membrane filters;
- straight-through pore membrane filters;
- granular-bed filters.

Filtration mechanisms - Mechanisms causing particle deposition are:

- diffusion;
- inertial impaction;
- interception;
- gravitational settling.

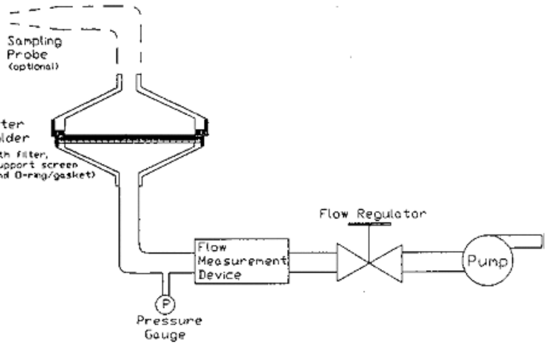


Fig. IV-2.1 Filter; simple filter sampling

Fibrous filters:

- mat/weave of fibres with diameter of 0.1 to 100μm. Cellulose or wood (paper), glass, quartz, and polymer fibre filters available;
- porosities of 60% to 99%, thickness of 0.15 to 0.5mm
- particle collection throughout the depth of filter from interception, impaction and diffusion onto filters;
- high collection efficiencies require low air velocities;
- pressure drops are the lowest among all filters under comparable conditions;

Porous-membrane filters:

- microporous membranes with torturous pores throughout the structure;
- polymer, sintered metal and ceramic microporous filters available;
- pore sizes (determined from liquid filtration) in the range 0.02 to 10μm;
- porosities of < 85% and thickness of 0.05 to 0.2mm;
- particle collection through attachment to microstructure elements;
- high collection efficiencies, but highest pressure drop among all filters.

Straight-through pore filters:

- thin polycarbonate films (10μm) with cylindrical pores perpendicular to film surface, with diameters in the range 0.1 - 8μm;
- porosities are low, in the range 5% to 10%;
- particle collection through impaction and interception near the pores and diffusion to tube walls of pores;
- collection efficiencies are intermediate between fibrous and micro-porous membrane;
- pressure drops are significantly higher than fibrous filters and comparable or higher than micro-porous membrane filters for equivalent collection efficiency.

Granular-bed filters:

- for special sampling, granules of speciality chemicals, sugar, naphthalene, sand, metal, glass beads are used;
- samples are recovered by washing or volatilisation;
- granular bead sizes range from 200 μm to a few mm;
- filtration is achieved by impaction, interception, diffusion and gravitation;
- filter porosities of 40% to 60% for stationary beds;
- low collection efficiency due to large granule size. To enhance diffusion low flow is used; bed depth is increased or smaller granules are used.

Filter efficiency and particle penetration characteristics - Filter penetration:

$$P = \frac{(C_d - C_b)}{(C_u \cdot D)} \qquad [-]$$

C_d, particle concentration downstream of the filter [1/m^3]
C_b, background particle concentration downstream [1/m^3]
i.e. blank measurement to establish background concentration
C_u, particle concentration upstream [1/m^3]
D, the dilution ratio (when applicable) [-]

Total penetration - penetration of particles over the whole size range. Fractional penetration - penetration within a defined size range. Filter efficiency (η):

$$\eta = (1 - P) \cdot 100 \qquad [\%]$$

Characterisation of filtration efficiency

- calculation from filtration theory;
- filter manufacturer's information (does not always provide the necessary filter efficiency for e.g. the 100 nm particle size);
- testing;

Flow rate measurements

- rate-meters;
- pressure drop across orifices ($\Delta p = p_{before} - p_{after}$ orifice);
- linear velocity meters;

To keep in mind:

- Filter loading changes filter performance (i.e. vacuum cleaner effect);
- Filtration efficiency is flow dependent;
- Before sampling, filters often have to be pre-conditioned (exposing the filter for 24h in order match with the conditions at the measurement site, i.e. to be equal in temperature and humidity);

3. Inertial collection techniques - Inertial particle collection is inefficient for very small particles but used for:

- determination of aerosol mass size distribution;
- determination of chemical, biological, radioactive size distribution.

Inertial classifiers are:

- impactors (body, conventional, multistage & virtual)
- cyclones

Stokes number: it formula is the governing relationship as to whether or not a particle will strike a body:

$$Stk = \frac{s}{d} \qquad [-]$$

$$s = V_0 \cdot \tau \qquad [m]$$

$$\tau = \frac{\rho_p \cdot d_p^2 \cdot C_c}{18 \cdot \eta} \qquad [s]$$

For body deposition:

$$Stk = \frac{\rho_p \cdot C_c \cdot d_p^2 \cdot U}{18 \cdot \eta \cdot d_b} \qquad [-]$$

If *Stk* > about 1, the particle will impact on the body; for deposition on an impactor, Stk can be calculates as:

$$Stk = \frac{\rho_p \cdot C_c . d_p^2 \cdot U}{9 \cdot \eta \cdot W} \qquad [-]$$

For body impactors:

$$d_{50} = \sqrt{\frac{18 \cdot \eta \cdot d_b}{\rho_p \cdot C_c \cdot U}} \cdot \sqrt{Stk_{50}} \qquad [m]$$

For conventional impactors:

$$d_{50} = \sqrt{\frac{9 \cdot \eta \cdot W}{\rho_p \cdot C_c \cdot U}} \cdot \sqrt{Stk_{50}} \qquad [m]$$

In general inertial impactors can be used for:

- cut-sizes in the range from 0.1 to 50µm;
- flow rates from a few cm^3/min to 1000s of m^3/min;
- sampling times from minutes to hours.

Major areas of consideration in impactor use:

- particle bounce from the collection surface; solution: sticky surface (takes care of mass stability, chemical composition, purity, and choice of the surface coating in relation to the measurement purpose);
- overloading of collected deposits; solution: shorter collection time;
- interstage particle losses; solution: determine experimentally for sampled particles;

Virtual impactors: impaction plate replaced by a collection probe; advantage: both size fractions remain suspended in the air; disadvantage: "contamination" of the minor flow containing larger particles, with smaller particle.

- **Cyclones**: particles larger than the cut-off size are deposited on the walls of the cyclone cylinder; theoretical analysis of a cyclone is more complex than of an impactor; most cyclones are used as single stage cyclones.

Principle of inertial classification:

- rapid change of direction of gas flow
- particles with sufficient inertia cross gas streamline and escape from the flow (particles with less inertia remain in the flow); e.g. cascade impactor
- escaped particles are captured for further analysis

s, particle stopping distance	[m]
d_p, physical particle diameter	[m]
V_0, particle initial velocity	[m/s]
τ, particle relaxation time (the time a particle takes to reach 1/e of its final velocity when subjected to a gravitational field):	[s]
ρ_p, particle density	[g/m^3]
C_c, Cunningham slip correction factor	[-]
η, viscosity of medium	[g/(m·s)]
U, average air velocity at the nozzle exit	[m/s]
d_b, body diameter	[m]
W, nozzle diameter	[m]

Commonly used parameters:

$\sqrt{Stk}$ - dimensionless particle size

$\sqrt{Stk_{50}}$ - the value corresponding to d_p collected with 50% efficiency (d_{50})

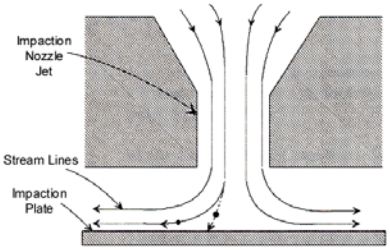


Fig. IV-3.1 Impactor; Cross-sectional view of an inertial impactor[xix]

For smaller particle sizes where inertial deposition is becoming less efficient, improvements can be achieved by:

- increasing the value of the slip correction factor or by lowering pressures (low-pressure impactors);
- decreasing the nozzle diameter: micro-orifice impactors.

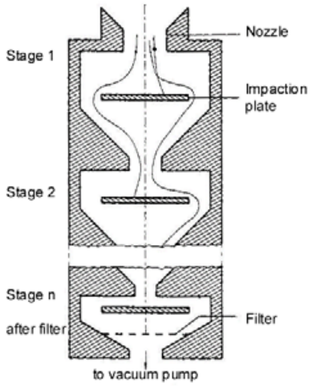


Fig. IV-3.2 Multistage Impactor

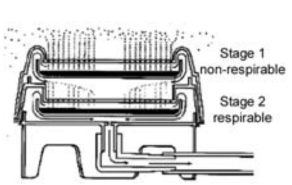


Fig. IV-3.3 Anderson Impactor used to sample bioaerosols

Dynamic mass measurement techniques:

- **Beta gauge**: measurement principle is based on near exponential decrease in the number of beta particles transmitted through a thin sample as the area density is increased; depends on the type of particles - different types of material will result in different results; therefore, instrumental calibration is essential.
  Advantages: instrumental simplicity and ease of automation for large-scale application.
  Limitations: potential biases: particle size effects, substrate inhomogeneity, atomic number dependence, etc.
- **Piezoelectric crystal** (vibration of crystal + electrically applied voltage)
  Piezoelectric crystal measurement method: Measurement principle is based on oscillation of a piezoelectric crystal produced by rapidly alternating field or voltage. The vibration frequency depends (among other factors) on the thickness and density of the crystal, or material collected on the crystal.
  Advantages: Mass sensitivity and short response time;
  Limitations: Potential biases (calibration, particle size effects, adherence effects, overloading, particle losses);
  Application: Quartz crystal microbalances (QCM), are used in inhalation hazard assessment at workplace.
- **Tapered-element oscillating microbalance** (TEOM): measurement principle is based on the change of vibration frequency of an oscillating element due to mass collected on it; using different impactors in the

  $$\Delta m = K_o \cdot \left(\frac{1}{f_b^2} - \frac{1}{f_a^2} \right) \quad [g]$$

  K_0, instrumental constant [g·Hz]
  f, oscillation frequency [Hz]

  Stages will provide information about the particle size.
  Advantage: near real time readings (after a minimum measurement interval of 10mins);
  Limitations: potential biases (calibration, particle size effects, overloading, damping, temperature effects);
  Applications: ambient and indoor air monitoring, particulate emission measurements;

4. Optical techniques for particle measurements

Real-time measurements of particle concentration and size distribution of light scattering (e.g. laser) and extinction by single particles or assembly of particles;

Types of measurements available:

- in situ, a beam of laser-light sent through the atmosphere and detection at the end of the path e.g; **L**ight **D**etection **a**nd **R**anging (**LIDAR**);
- extractive

Applications range from ambient and indoor monitoring, occupational and industrial hygiene, emission testing, research, etc

Single particle techniques cover size range from about 0.07 (0.1-0.2 with higher efficiencies) to over 100µm with concentration ranges from <1 to about $1 \cdot E^5$ particles per litre; scattering could also provide information about the particle mass. NB: requires knowledge of density!

Ensemble scattering techniques: are applicable to concentration measurements in the volume range7 (recalculated to mass) from a few µg/m^3 to several hundreds µg/m^3; instruments used for ensemble scattering measurements are called photometers.

a) Light scattering and extinction by a single particle

a) Light scattering and extinction by a single particle - rigorous electromagnetic theory was developed by **Mie** (1908).

Light Scattering: it assumes that spherical particle of diameter d_p; particle material has refractive index m; as the particle is situated at the origin of a system of spherical coordinates it is illuminated in one plane, with a linearly polarised, monochromatic wave (electric vector perpendicular to light propagation). The power of light scattered by a particle per unit solid angle in direction θ is then:

$$S_\lambda(\theta,\phi,d_p,\lambda,m) = I_o \cdot \frac{\lambda^2}{4\pi^2} i(\theta,\phi,\alpha,m)$$

$$\alpha = \frac{\pi \cdot d_p}{\lambda} \qquad [-]$$

The power of light collected by a certain optical arrangement is:

$$P_\lambda(d_p,\theta_0,\Delta\Omega,\lambda,m) = I_0 \cdot \frac{\lambda^2}{4 \cdot \pi^2} \cdot \iint_{(\Delta\Omega)} i(\theta,\phi,\alpha,m) \cdot \sin\theta \cdot d\theta \cdot d\phi$$

I_0, illumination intensity	[W/m^2]
I, scattering function	[-]
ϕ, polarisation angle	[°]
λ, wavelength	[m]
θ_O is mean scattering angle	[°]
ΔΩ is the receiver aperture	[m]

Scattering coefficient:

$$Q_s = \frac{S_\lambda}{I_0 \cdot d_p^2 \cdot \pi / 4} \qquad [-]$$

Light Extinction is the attenuation of a parallel beam of light due to absorption and scattering by particles. The power of light which is removed by a particle from a parallel beam of light is:

$$-\Delta P_\lambda = I_0 \cdot \frac{\pi}{4} \cdot d_p^2 \cdot E_x(\alpha,m) \qquad [W]$$

$E_x(\alpha, m)$, extinction coefficient	[W/m^2]
P_λ, power of light collected	[W]

Rayleigh (dipol) approximation: when the particle size is much smaller than the wavelength: α << 1,

- the particle is subjected to an almost uniform field which induces an oscillating dipole in the particle;
- the particle oscillates like a dipole with a polarisation proportional to the electric field of the incident wave (in the forwards and backwards direction);
- the scattering properties of the particle are then expressed by its polarisability;

The power of light scattered by a spherical particle per unit solid angle is:

$$S_\lambda(\theta,d,\lambda,m) = I_0 \cdot \frac{\pi^2}{2 \cdot \lambda^4} \cdot p_s^2 \cdot \left(1+\cos^2\theta\right) \qquad [-]$$

p_s is the polarisability of a spherical particle which is a function of particle volume [-]

Lorenz-Mie theory: when the particle size is of the same order as the incident light: α ≈ 1. It assumes that there is a strong interaction between the particle and the incident beam, and simple relation between scattered intensity and particle diameter. This range is treated by the more complex Lorenz-Mie theory of light scattering for homogenous spheres illuminated by a plane wave. When the particle size is much larger than the wavelength: α >> 1, classical optics is used and the scattered light is considered as consisting of three parts which are due to diffraction, reflection and refraction. The scattering coefficient is:

$$Q_s(\theta,\alpha,m) = Q_0(\theta,\alpha) + Q_1(\theta,m) + Q_2(\theta,m)$$

Q_0, relates to diffraction	[-]
Q_1, relates to reflection	[-]
Q_2, relates to refraction	[-]

The diffracted part of scattered light (Q_0) is independent of the optical constants of the material, but is dependent on the size parameter (α). The reflected and refracted parts of scattered light (Q_1 and Q_2) are independent of particle size, but dependent on optical constants. Light extinction in Rayleigh approximation

$$E_x(\vartheta,\alpha,m) = 2 - 2 \cdot \pi \cdot \int_0^{\vartheta} Q_s(\theta,\alpha,m) \cdot \sin\theta \cdot d\theta \qquad [-]$$

Commercially viable optical systems are divided into instruments using low angle scattering (diffraction lobe), collecting light in the forward direction (θ < 90°), and employing right angle scattering.

b) Light scattering and extinction by an assembly of particles

Light Scattering

$$R = c_n \cdot \int_0^\infty f\left(d_p\right) \cdot P_\lambda\left(d_p, \lambda, m\right) \cdot dd_p \qquad [-]$$

Light Extinction - transmission of the light beam traversing a homogenous mixture of particles is (Lambert-Beer law):

$$T = \frac{I}{I_0} \qquad [-]$$

$$= exp\left\{ -c_n \cdot s \cdot \frac{\pi}{4} \cdot \int d_p^2 \cdot E_x(\alpha, m) \cdot f\left(d_p dd_p\right) \right\} = e^{-K_s}$$

P_λ, strength of light scattered by a single particle	[W]
$f(d_p)$, probability density function of the particle size distribution	[-]
c_n, number concentration of the particles	$[1/m^3]$
R = constant · c_m (only if P_λ is a function of the particle volume)	
note: if R varies, one cannot distinguish whether this is due to variation in particle concentration, or in optical properties	
I, intensities before traversing the particles	$[W/m^2]$
I_o, intensities after traversing the particles	$[W/m^2]$
S, extinction length	[m]
K, turbidity	[-]

Gravimetry and photometry: the mass concentration of a polydisperse aerosol is:

$$c_m = c_n \cdot \rho_p \cdot \int_0^\infty f\left(d_p\right) \cdot \frac{\pi}{6} \cdot d_p^3 \cdot dd_p \qquad [g/m^3]$$

Specific scattering function is:

$$P_{\lambda s}\left(d_p, m, \lambda\right) = \frac{P_\lambda\left(d_p, m, \lambda\right)}{\rho_p \cdot d_p^3 \cdot \pi / 6} \qquad [W]$$

Note 1: Specific scattering function runs through a maximum at about: $d_p \approx \lambda$. For atmospheric aerosols and visible light (λ from about 400 nm to 800 nm), particles within the accumulation mode coincide with the maximum of the specific scattering function.
Note 2: Light scattering by gas molecules should also be taken into account (dipole theory applies in this range).

Main aspects of design and operation of single particle optical counters (OPC):

- optical systems (nowadays mainly laser);
- formation of sensing volume;
- pulse processing;
- calibration -size (latex spheres with a known diameter; e.g. 102nm), and concentration (currently only via inter-comparison among various instruments);
- range of number concentrations;
- sensitivity and sample flow rate;
- size accuracy and resolving power;

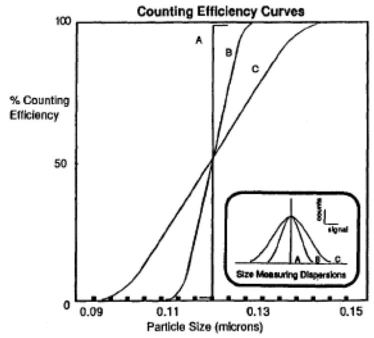


Fig. IV-4.1 Cut of Point; the optical detection limit is determined by the wavelength employed by the laser system.

Range of Number Concentrations: counting rate when each particle produces a single count:

$$\frac{dN}{dt} = c_o \cdot Q \qquad [1/s]$$

A less than 10% loss in particle count is due to coincidence effects:

$$\frac{c}{c_0} = exp\left\{-c_{max} Q t_r\right\} \qquad \geq 0.9\ [-]$$

The lower limit of the detectable number concentration depends on the background noise:

$$c_{min} > c_{ns} = \frac{(dN/dt)_{ns}}{Q} \qquad [1/m^3]$$

c_0, number concentration	$[1/m^3]$
Q, low rate	$[m^3/s]$
t_r, recovery time of the electronics	[s]
c_{max}, maximum permissible number concentration	$[1/m^3]$
c_{ns}, an apparent number concentration from noise concentration measurement should start at the level; $c_{min} \geq 10 c_{ns}$	$[1/m^3]$

Sensitivity and sample flow rate: in the submicrometer size range the counting efficiency decreases with decreasing particle size; lower detection limit is a gradual transition rather than a sharp step; this often has to be taken into account in data analysis. Furthermore, the composition of aerosol during the experimental run has to be constant; instruments have to be operated in their linear range; the range of linearity is limited:

- at high concentrations by multiple scattering;
- at low concentration by the stray-light background;

In situ sensing - is a non-invasive technique, where aerosol characterisation takes place outside the measuring instrument. In situ testing is applied for:

- characterising clouds and fogs;
- visibility measurements;
- air quality measurements;
- measurements of particle characteristics in industrial processes;
- measurements of particle velocity;
- characterisation of droplet sprays;
- colloidal suspensions;

5. Advanced techniques using optical particle detection

Advantages of optical direct-reading particle counting techniques feature rapid response, continuous measurements, non-destructive detection. Disadvantage of optical direct-reading particle counting techniques regard the amount of light scattered may not be directly related to the property which needs to be investigated; often, we do not measure what we want to measure; a solution can involve the combination of optical detection techniques with the manipulation of other particle parameters (for example motion).

Aerodynamic particle sizer (APS 3310, is a portable device manufactured by, TSI, Inc. St. Paul, MN - USA)
The instrument is used for size classification of particles in size range from 0.5 to 30µm. It measures aerodynamic diameter of particles accelerated in flowing air and detected by scattered light of two laser beams. External tubing is necessary for sampling; super-isokinetic at the measured flow inlet - oversampling of larger particles (to compensate for losses in the inner nozzle); sample dilution (optional) when particle concentration exceeds recommended limits.

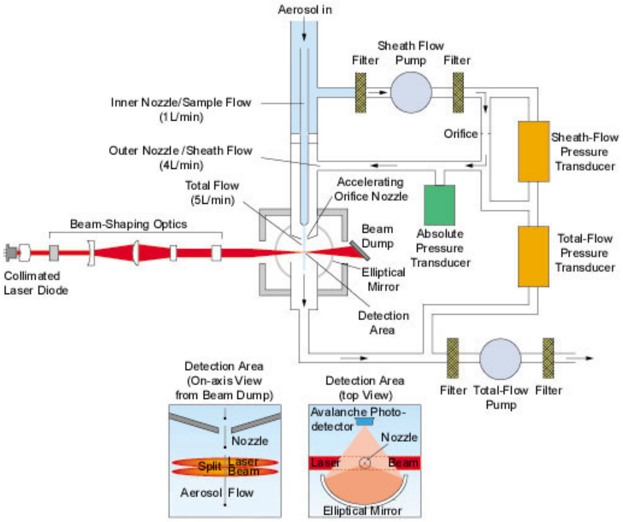


Fig. IV-5.1 Block diagram of an APS; sheath and aerosol flow are controlled by an complex network of interacting filters, pumps and pressure sensors.

Laser Velocimeter Sensor

Factors affecting velocity measurements:

- nozzle dimensions;
- spacing between the nozzles;
- distance of the beams from the acceleration nozzle;

These dimensions are difficult to control during instrument manufacture, and thus each instrument has slightly different calibration parameters. In particle detection a high speed data accumulator systems used in the detector module by using:

- small-particle processor versus larger particle processor;
- short scanning times versus longer scanning times.

Droplet deformation is more important for droplets of low surface tension (such as oils) than of high surface tension (such as water).

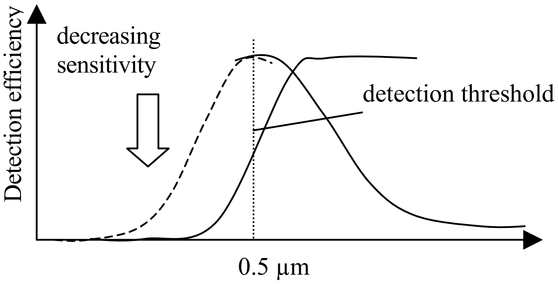


Fig. IV-5.2 OPC; detection efficiency versus particle size; superimposed the detection efficiency of the system

Coincidence Effects: ideally, if the particles go through the sensing zone one by one, it is possible to count the total number detected in the sensing zone. However, simultaneous occupancy of the sensing zone by more than one particle often occurs. This phenomenon is called "coincidence" and the resulting count error is known as the coincidence error. When more than 2 particles are located in the view window (aperture or sensing zone), coincidence phenomena are observed particle 1 and particle 2 are detected as a single, somewhat distorted, large pulse; therefore, one of the cells is not counted (coincidence loss).
The degree of coincidence loss depends on the concentration. Thus, the magnitude of the coincidence error increases with the concentration of particles. By using measurements from samples of different concentrations, the coincidence correction formula can be established.

- result in detection of phantom particle coincidence;
- affect the tail of a spectrum at the larger particle sizes;
- result in serious overestimation of mass recalculated from particle number;
- important when a large number of small particles is present;
  solution: anti-coincidence logic and corrections.

6. Electrical techniques

- most aerosol particles carry some electric charge;
- electrical force acting on charged particles in an external electric field can be very large compared to other forces.

Undesirable aspects of the electrical force on particles:

- enhances particle deposition on surfaces;
- modifies particle movement;
- makes particle behaviour difficult to analyse.

Under controlled conditions electrical force can be used in:

- aerosol control equipment;
- aerosol sampling;
- aerosol measuring.

Charge distribution of atmospheric particles

- bipolar ions are produced by cosmic rays and radioactive elements in the atmosphere. Average concentration: 500 to 1000 ion pairs/cm^3 of air;
- aerosol particles are charged by interactions with the ions;
- after a sufficiently long time of exposure, Boltzman equilibrium charge state is achieved, in the free atmosphere it takes about 30 minutes.

Charge distribution:

$$f_n = \frac{exp\left(-n^2 \big/ 2\cdot\sigma^2\right)}{\sum exp\left(-n^2 \big/ 2\cdot\sigma^2\right)} \qquad [\%]$$

Gaussian distribution approximation for particles larger than 0.05µm:

$$\sigma^2 = \frac{d_p \cdot k \cdot T}{2 \cdot e^2} \qquad [-]$$

$$f_n = \frac{exp\left(-n^2 \big/ 2\cdot\sigma^2\right)}{\sqrt{2\cdot\pi\cdot\sigma^2}} \qquad [-]$$

f_n, fraction of particles of size d_p having n elementary units of charge		
d_p, particle diameter		[m]
k, Boltzman constant	1,381·E^{-23}	[J/K]
T, temperature		[K]

Behaviour of charged particles - In the absence of external electric fields Coulomb's law. In the presence of external electric fields^{xx}:

$$V_{elec} = n \cdot e \cdot E \cdot B \qquad [-]$$

The electrical mobility of particles:

$$Z_p = \frac{V_{elec}}{E} = \frac{n \cdot e \cdot C_c}{3 \cdot \pi \cdot \eta \cdot d_p} = n \cdot e \cdot B \qquad [\mathrm{m}^2/(\mathrm{V}\cdot\mathrm{s})]$$

N, number concentration		[1/m^3]
e, elementary charge	1.6·E^{-19}	[C]
E, electrical field intensity·		[V/m]
B, mechanical particle mobility·		[s/g]
C_c Cunningham slip correction factor		[-]
η, viscosity of medium		[Pa·s]

Particle charging mechanisms can occur in several ways;

- static electrification;
- charging by small ions (diffusion charging and field charging);
- thermionic charging;
- self charging (for radioactive aerosols).

Charge can be also imposed externally by exposing it to a radiation source like a **^{85}Kr Aerosol discharger** (β-source that emits fast electrons). Particle charging is achieved by bombarding it with those electrons; i.e. increasing the ion concentration can shorten the time of establishing charge equilibrium. This is done using a radioactive source or a bipolar ion generator. Most common aerosol dischargers (other names: neutraliser or deioniser) use ^{85}Kr.

a) Aerosol size classification

The Electrostatic Classifier (EC) - TSI Model 3071A is used for size classification of particles in the size range from 0.005 to 1μm, based on particle electrical mobility. The built-in ^{85}Kr emitter does not charge the passing aerosol but rather gives them an electrical equilibrium (according to the Boltzmann Charge distribution – see below). For a given voltage, charged particles with mobilities greater than a certain amount will migrate to the oppositely charged cylinders as the aerosol gas stream pushes them through. Uncharged particles pass through unaffected. A sheath of particle free air surrounds the central rod. Special focus should be laid on the sheath-air humidity, which should be equal to aerosol humidity. At the beginning of a scan, the inner cylinder is maintained at the same potential as the outer cylinder; i.e. grounded. Once the scanning process is started, the centre rod voltage gradually decreases in voltage. The relation between particle size and electrical mobility in EC:

$$Z_p = \frac{Q_t - (Q_s + Q_a)/2 \cdot ln\left({}^{r_2}\!/_{r_1} \right)}{2 \cdot \pi \cdot V \cdot L} \qquad [\mathrm{m}^3/(\mathrm{V \cdot s})]$$

Z_p, mean electrical mobility of particles extracted through the slit	[1/m^3]
Q_t, total, flow rates	[m^3/s]
Q_s, sample flow rates	[m^3/s]
Q_a aerosol flow rates	[m^3/s]
L, length of the inner electrode	[m]
V, voltage on the collector rod	[V]

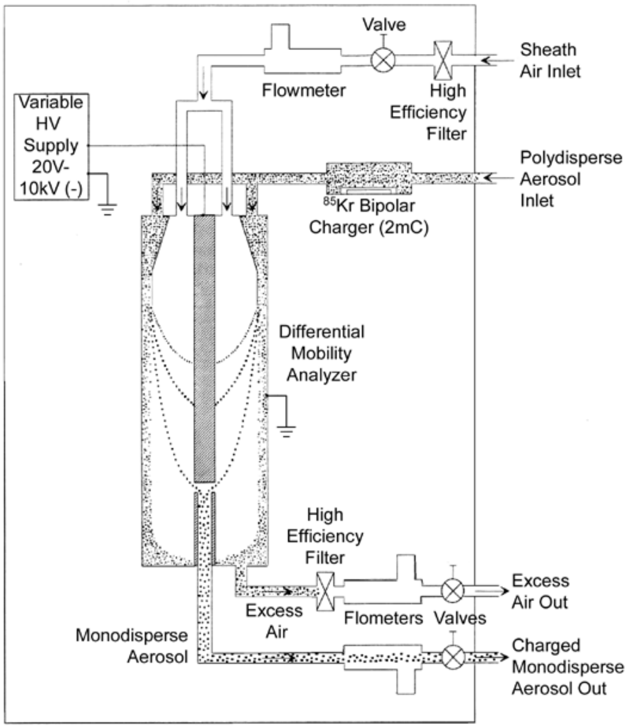


Fig. IV-6.1 Electrostatic Classifier; schematic of an EC Model 3071, it shows the key elements (^{85}Kr discharger, sheath flow, high DC voltage source amongst others).

Aerosol collection by electrostatic precipitation. Steps in electrostatic precipitation involve charging the particles (usually by field charging using a corona discharge), and subjecting them to a strong electric field, causing them to deposit on a collection surface. Such tricks are often applied in particle morphology examination by electron microscopy and in cleaning techniques (such as electrofilters).

Boltzmann charge distribution: It predicts that a significant fraction of particles larger than 100nm carry more than one charge. One must use a more complex data reduction scheme for multiple-charged particles. A dry passed over an 85Kr bipolar β-emitter, (discharger or neutralizer) exposes the aerosol particles to high concentrations of bipolar ions which alters the charge distribution to Boltzmann's equilibrium. In that process, the particles and ions undergo frequent collisions due to the random thermal motion of the ions. Within milliseconds, the particles reach a state of equilibrium, in which the particles carry a bipolar charge distribution; whereas in the free atmosphere, cosmic radiation would take as much as 30mins to achieve that. The Boltzmann charge distribution assumes that the fraction of particles with *n* positive charges equals the fraction with *n*-negative charges. Thus, in time, an equilibrium state is attained in which the particles carry a bipolar charge distribution, as shown by the table below.

d_p	Charges on aerosol particles [%]								
[μm]	-4	-3	-2	-1	0	+1	+2	+3	+4
0.01				0.340	99.32	0.340			
0.02				5.230	89.53	5.230			
0.04			0.230	16.22	67.10	16.22	0.230		
0.08		0.01	1.250	21.30	54.88	21.30	1.250	0.01	
0.10		0.08	2.780	23.37	47.53	23.37	2.780	0.08	
0.20	0.32	2.33	9.660	22.63	30.06	22.63	9.660	2.33	0.32
0.40	2.19	5.92	12.05	18.44	21.26	18.44	12.05	5.92	2.19
0.60	3.82	7.41	11.89	15.79	17.36	15.79	11.89	7.41	3.82
0.80	4.83	7.94	11.32	14.00	15.03	14.00	11.32	7.94	4.83
1.00	5.42	8.06	10.71	12.70	13.45	12.70	10.71	8.06	5.42

Tab. IV-6.1 Charge distribution of aerosol particles according to Boltzmann's law

Condensation detection techniques - Condensation detection techniques are used in condensation nuclei counters (CNC, called also Condensation Particle Counters) for detection of ultrafine particles down to about 3 nm. It is usually used in combination with other devices (size classifier like model 3071A) in order to measure a particular size class (monodisperse) of an aerosol. The SMPS system (scanning mobility particle counter) is such a system employing both an EC and a CPC. It is described in more detail in part VI-3. The principle of operation employ condensation at supersaturation of a working fluid (Butyl alcohol), followed by growth of particle due to condensation, and ultimately detection of these enlarged particles.

Condensation nuclei counters (CNC or CPC). The techniques used to activate condensation and growth are adiabatic expansion (Wilson chamber), followed by conductive cooling (e.g. mixing of hot and cold air streams utilizing butanol). The techniques used for aerosol detection involve either photography, light extinction, and/or light scattering.

Modern CNC most commonly use conductive cooling and light scattering.

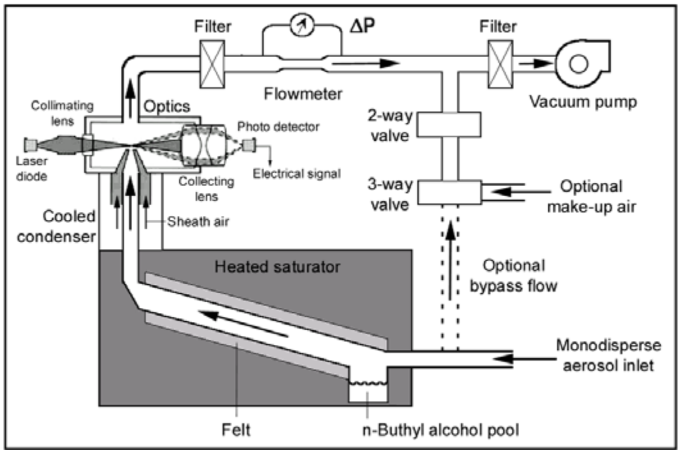


Fig. IV-6.2 Condensation Particle Counter; schematic of an CPC Model 3022; it shows the key elements (condensation chamber, OPC, and pump among others).

7. **Diffusion size separation techniques** - diffusion technique is used to collect ultrafine particles and vapours and to determine size distribution of ultrafine particles down to about 1nm (atomic diameters; e.g. $\varnothing_{Pb} = 0.5$nm). Diffusion samplers separate particles by differential diffusion mobilities. Main types of diffusion samplers:
   - diffusion battery;
   - diffusion denuder.

Theory of the diffusion technique. Convective diffusion equation for particle concentration (c) profile:

$$\frac{D_p}{r} \cdot \frac{\partial}{\partial r} \cdot \left(r \cdot \frac{\partial c}{\partial r} \right) = v(r) \frac{\partial c}{\partial z} \qquad [1/m^4]$$

D_p is particle diffusion coefficient	[m^2/s]
v(r) is the velocity profile	[m/s]

Assumptions:
- the concentration is in a steady-state condition;
- the flow field is laminar;
- no diffusion in the direction of flow;
- no production or reaction of aerosol in the device;
- the sticking coefficient is 100% (no bouncing back effects).

Diffusion devices Tube Type (channel type):
- cylindrical tubes;
- rectangular channels;
- parallel circular plates;
- annular tubes;

Screen Type: Diffusion batteries consist of a number of tubes or screens

Aerosol penetration through a screen. The theoretical penetration through a fine mesh screen can be calculated as follows[xxi]:

$$P = exp\left[- B_f \cdot n \left(2.7 \cdot Pe^{-2/3} + \frac{1}{\kappa} \cdot R^2 + \frac{1.24}{\kappa^{1/2}} \cdot Pe^{-1/2} \cdot R^{2/3} \right) \right]$$

$$B_f = \frac{4 \cdot \alpha \cdot h}{\pi \cdot (1 - \alpha) \cdot d_f} \qquad [-]$$

$$Pe = \frac{v \cdot d_f}{D} \qquad [-]$$

n, number of screens	[-]
d_f, fibre diameter	[m]
h, thickness of a single screen	[m]
α, solid volume fraction of the screen	[m^3]
κ, hydrodynamic factor of the screen	[-]
R, interception parameter (d_p/d_f)	[-]
Pe, Peclet number	[-]
v, velocity entering the screen	[m/s]

Wire screen diffusion battery

Developed in the International Laboratory for Air Quality and Health for size classification of radon progeny. It consists of five stainless steel wire screen batteries, 47 mm in diameter, and a reference filter (0.8μm Millipore). It is operated at a flow rate of 5L/min. Concentration detection per size class occurs with a standard CPC scanning each channel separately.

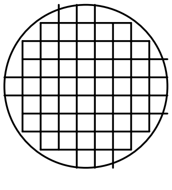


Fig. IV-7.1 Wire Screen Diffusion Battery; basically consists of parallel aligned pipes with ever decreasing diameter.

Deconvolution technique (qualitative analysis) requires calculation of transmission values from time interval counts. Furthermore, the reconstruction of active particle size spectrum from transmission values, tracing down particles to atomic size can be likewise achieved.

8. Aerosol laboratory - equipment

Instrumentation used in aerosol studies, testing and monitoring:

- instrumentation for aerosol detection and characterisation;
- aerosol generators;
- experimental/calibration chambers;
- exposure chambers;
- wind tunnels (big facility);
- filter testing rigs (big facility);

Minor equipment:

- Pumps;
- flow meters and flow calibration devices;
- temperature and humidity probes, pressure sensing devices, etc.;

Aerosol laboratory - general comments

Safety precautions should consider the potential for inhalation of the study aerosol, the exposure to radioactive aerosol and radioactive sources, the physical danger related to the presence of connecting tubing and cables, and comfort issues, as well as noise aspect.

Aerosol generation

Purposes for aerosol generation:

- test aerosol for instrument calibration;
- aerosol for studying physical or chemical interactions;
- aerosol for inhalation studies.

Good laboratory practice

- general cleanliness of the laboratory;
- routine cleaning of the instrumentation;
- log books for instrument usage.

An ideal generator should:

- have constant and reproducible output;
- output characteristics should be easy to control.

Characteristics of a generated aerosol

- For most applications aerosol should be monodisperse (spread of particle sizes as small as possible with $\sigma_g < 1.2$);
- Polydisperse aerosol is used for specific applications;
- Particle diameter (number or volume);
- Particle concentration;
- Other specific characteristics regard chemical composition, charge, shape, radioactivity content, etc.

Aerosol generation methods (see lecturing script Hofmann *Aerosolfysik*):

- atomisation of suspension of monodisperse particles;
- atomisation of a solution;
- atomisers;
- nebulisers;
- vibrating orifice atomisers;
- spinning disc atomisers;
- controlled condensation techniques;
- dry dispersion;
- fluidised beds;
- size classification instruments (cascade impactor, differential mobility analyser);
- combustion aerosol generators (environmental tobacco smoke);
- vibrating-Orifice Generators.

The initial droplet diameter and the dried particle diameters can be calculated as[xxii]:

$$d_d = \sqrt[3]{\frac{6 \cdot Q}{\pi \cdot f}} \quad \text{[m]}$$

$$d_p = d_d \cdot \sqrt[3]{C} \quad \text{[m]}$$

Q is the liquid flow rate	[m^3/s]
f is the vibrating frequency	[1/s]
C, solvent concentration in the liquid	[1/m^3]
d_d, droplet diameter	[m]
d_d, particle diameter	[m]

Problems and issues in aerosol generation by atomisation:

- liquid evaporation;
- aerosol drying;
- formation of aggregates;
- difficulties in particle concentration control;
- contamination;

9. Environmental tobacco smoke generator designed in the ILAQ:

The generator was designed to both simulate the frequency, period and volume of inhalations, and the deposition of mainstream smoke in the lung of a smoker. The generator does not simulate the chemical and physical changes that occur in the lung.

Experimental chambers: issues to consider regard:

- control parameters (temperature, humidity, air exchange rate);
- air circulation in the chamber;
- mixing of aerosol within the chamber;
- leakages from and to the chamber;
- chamber surface material;
- chamber cleaning;

Calibration of flow, pressure and velocity

Flow rate measurements: • variable-pressure head meters; orifice or venturi meter; • variable-area meter; • rotameter.	**Flow meter calibration**: • spirometer; • soap bubble meter; • mercury sealed, piston meter;
Pressure measurements: • manometers; • pressure gauge (magnehelic); • pressure transducer.	**Velocity measurement**: • Pitot tube; • hot-wire anemometer; • laser Doppler anemometer.

10. Aerosol sampling and transport

- Sample Environment (try to understand it; indoor ≠ outdoor, homogeneity of environment).
- Sampling Inlet (often does affect sampling).
- Sample Transport System - loss of particles due to diffusion (< particles) and impaction (> particles).
- Sample Diluter (optional).
- Sample Storage Volume (optional).
- Measuring Instrument (compatible with instrumentation).

Representative sampling - A sample is representative of an aerosol in its original environment if the sampling process does not affect particle characteristics such as number and mass distributions and concentrations.

Factors affecting aerosol characteristics during sampling

1. Aspiration efficiency and deposition in the sampling inlet.
2. Deposition during transport.
3. Extremes or inhomogeneity in the ambient aerosol concentration.
4. Agglomeration of particles during transport.
5. Evaporation and/or condensation of aerosol material during transport.
6. Retainment of deposited aerosol back into the sample flow.
7. High local deposition causing flow restriction or plugging.

Types of aerosol sampling

Sampling of particles from a quiescent environment (calm, non-moving, static environment).
Sampling from a gas flow (dynamic), which carries aerosol particles.

Desirable sampling conditions

- Constant free stream flow rate during sampling.
- Stable aerosol condition during sampling.
- The sampling gas velocity must be low enough so that the sampled particle can accommodate itself to the sampling gas flow within a distance comparable to the inlet diameter (inertial condition).
- The sampling gas velocity must be high enough so that the sampled particle does not settle appreciably (gravitational-settling condition).
- Application of larger inlet diameters (of the order of a centimetre) as they are less susceptible to deposition caused by free-stream turbulence (the larger the better, but this implies an increased pumping rate, requires heavier equipment).

a) Isokinetic and isoaxial sampling - isoaxial sampling: direction of the sample flow is aligned with that of the gas flow. Sampling is isokinetic when it is isoaxial and the mean sample flow velocity through the face of the inlet is equal to the gas flow velocity.

For isokinetic sampling aspiration efficiency is 1 (100%) for all size particles. For sub-isokinetic sampling aspiration efficiency increases from 1 to a limit of U_0/U for larger particles. For super-isokinetic sampling aspiration efficiency decreases from 1 to a limit of U_0/U for larger particles

Isokinetic or non isokinetic sampling (does not relate to sub-micrometer particles, in such cases can be neglected):

- in general it is recommended that sampling conditions are isokinetic;
- it is possible to correct for non isokinetic (or anisoaxial) effects, but correction factors are not always reliable;
- for sampling of sub-micrometer particles, isokinetic conditions are not required.

Sampling in calm air - conditions for representative sampling from calm air involve inertial conditions $Stk \le 0.016$. Where Stokes number is based on the average inlet sampling velocity U and the inlet diameter d.

Particle settling velocity condition (so the orientation of the nozzle has no influence) $v_{ts} / U \le 0.04$.

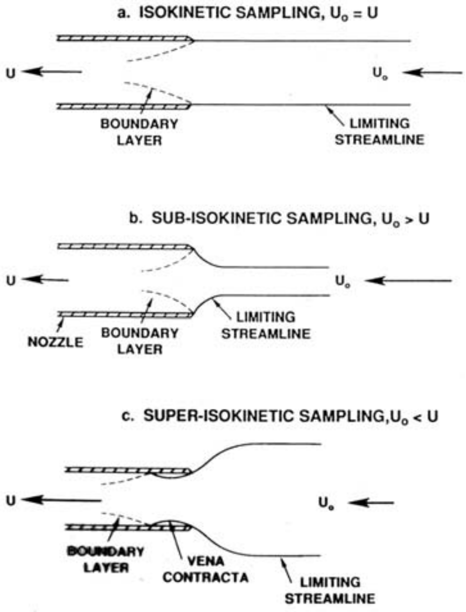


Fig. IV-10.1 Isoaxial sampling; schematic diagram of isoaxial sampling with a thin-walled nozzle.[xxiii]

b) Sample Transport - the losses in the sampling line are caused by the following mechanisms:

- gravitational settling;
- diffusional deposition;
- turbulent inertial deposition;
- inertial deposition at flow constrictions;
- electrostatic deposition;
- thermophoretic deposition;
- diffusiophoretic deposition.

Particle losses during transport

Assessment of the losses:

- Semi-empirical formulae to correct for the losses.
- Experimental measurement of the losses (a more advised option).

To minimize the losses it is necessary to both minimize the distance particles travel and to minimize the time particles spend in the sampling system.

c) Instrument and system calibration - instrument and system calibration are of principal importance for successful measurement of aerosol properties in a sampling environment. While there are theoretical means for assessment of instrument or system performance, calibration provides information which is more reliable and more applicable for the particular sampling conditions. Calibration can be conducted via direct measurement or using primary standards; e.g. latex spheres size calibration; currently no concentration standards are available; gravimetric techniques are applicable for larger particles only. Reliable and accurate calibration requires:

1. A proper selection of a desired test aerosol.
2. A complete understanding of the principles and procedures of operation.
3. A thorough investigation of the relevant parameters.
4. A sufficient knowledge of the capabilities and limitations of the instrument.

General comments - before undertaking setting up of a sampling system, it should be checked whether there are standard procedures for this type of sampling. There are prescribed standard sampling procedures for certain types of measurements, such as:

- duct sampling (American National Standards Institute - ANSI - standard N13.1, 1996);
- testing of PM10 monitors (US EPA procedure).

Calibrate, calibrate, calibrate

- A newly acquired instrument.
- After repair, maintenance, transport or intensive use.
- On a routine basis.

11. Factors affecting aerosol measurement quality - if "... measurement processes are to serve both the practical needs of humankind and excellence in the pursuit of new scientific knowledge, they must be endowed with an adequate level of accuracy.."

Nomenclature used to indicate correctness of the data:

- accuracy: is the degree of agreement of a measured value with the true or expected value of the quality of concern;
- precision: is the degree of mutual agreement among individual measurements as the result of repeated application under the same condition. Precision measures the variation among the measurements and may be expressed in different terms;bias: The tendency to skew estimates in the direction that favours the anticipated result (also used to describe the effect of a systematic error on a set of measurements);
- variability: the innate characteristic in which measurements deviate from preset values;
- sensitivity: A method that provides reliable data even though operation was close to the limits of detection;
- limits of detection and quantification: The minimum amount of particulate that a system or method is capable of measuring; in order to quantify the results, the signal should be at least 3 times the SNR (signal to noise ratio).

Detection limits: the instrumental detection limit (IDL): the lowest instrumental signal, which can be reliably distinguished from instrument noise. The method detection limit (MDL): the smallest atmospheric concentration of a species, which can be reliably distinguished from the sampling medium's concentration.

$$MDL = {t \cdot \sigma}/{v} \qquad [s/m]$$

t, Student's t value for an appropriate confidence level with n-1degrees of freedom,	[-]
σ, standard deviation of replicate analyses of blanks or samples with low concentrations of the analyte	[-]
v, air flow rate	[m/s]

Outliers: the evaluation of an "outlier" must have unbiased and statistically based criterion. The removal of an "outliers" (bad data points) can only be done after thorough analysis: e.g. the Q-Test could be used:

$$Q_{exp} = \frac{x_? \cdot x_n}{range} \qquad [1/cm^3]$$

$x_?$, the questionable value	$[1/cm^3]$
x_n, the neighbouring value	$[1/cm^3]$

Aerosol measurement errors

Example	AEROSOL MEASUREMENT ERRORS
1	The combined effect of sensor response and inlet losses for the Aerodynamic Particle Sizer
2	Variation in responses from different instrument
3	Particle statistics
4	Artefacts
5	Presentation of data
6	Corrections for density and other properties
7	Change in measurement conditions
8	Comparing data from different particle instruments

Quality Control (QC) is a mechanism established to control errors. It is a set of measures within a sample collection providing an analysis methodology to assure that the process is in control and it helps to provide quality that is satisfactory, adequate dependable and economical. QC involves calibration, standardization, instrument maintenance, facilities maintenance, education and training, and inspection and validation.

Quality Assurance (QA) it is a definite plan of operation that specifies standard procedures that help to produce data with defensible quality, and the reported results with a high level of confidence. QA is a necessary plan of data production and it serves as a guide of the air monitoring program for production of quality data.

Basic requirements in QA are:

- to recognize possible errors
- to understand the measurement system used
- to develop techniques and plans to minimize errors

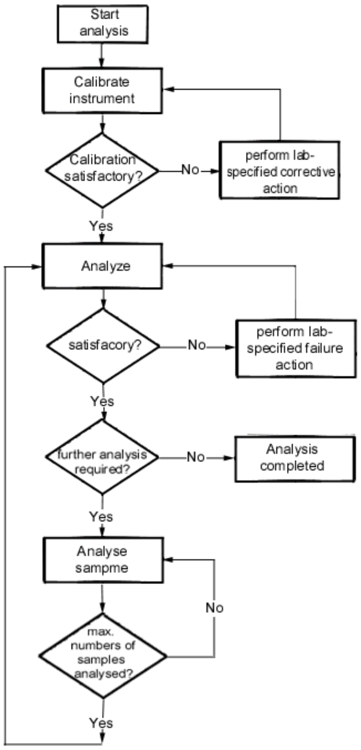


Fig. IV-11.1 QA; flowchart for quality assurance.[xxiv]

The program also includes:

- Evaluating what was done
- Reporting evaluated data which are technically sound and legally defensible

12. Particle data analysis and presentation

The most common measures regard (i) particle count and (i) particle mass. Created from these are (i) particle count distribution, (i) particle mass distribution, and (i) particle surface distribution. Other types of distribution (i) radioactivity distribution and (i) chemical property distribution.

Particle size distribution can be presented as:

- frequency distribution;
- histogram;
- cumulative distribution;

Ideal size distributions are:

- Normal distributions tend to arise when a multitude of small additive (+ or -) factors influence a variable that would otherwise have a single value.
- Log-normal distributions arise when multiplicative factors (both greater and less than 1) act upon a variable that would otherwise have a single value (example: particle break-up or agglomeration).
- A power-law distribution can be created by a process that subdivides material, with breakage rates proportional to the size of the material.

The power-law distribution is given by:

$$f(d) = a \cdot d^{b} \qquad [-]$$

The cumulative power-law distribution:

$$F(d) = \left(\frac{a}{b+1}\right) \cdot d^{(b+1)} \qquad [-]$$

a and b are constants and $b < 0$ [-]

Concentration distributions - measurements are conducted:

- at one location for many times, or
- at many locations for one time, or
- at many locations for many times, distribution of concentration values are usually found

The distributions are:

- constant and uniform;
- normal;
- log-normal;

Poisson: the Poisson distribution deals with particle count data obtain from sampling an aerosol that has a constant number concentration, but even if the concentration is constant, particles entrance into the sampler is probabilistic: $\sigma = \sqrt{\mu}$

$$P(n|\mu) = \mu^{n} \cdot \frac{e^{-\mu}}{n!} \qquad [-]$$

n, number of successes interested in [-]
μ, mean n umber of successes in a given time [-]

Summarising data with a few parameters

- Count or mass mean diameter.
- Count or mass median diameter (CMD or MMD).
- Number-weighted or mass-weighted average.
- Range.

Relations for log-normal distributions:

$$MMD = CMD \cdot e^{3\cdot(\ln\sigma_g)^2}$$

$$SMD = CMD \cdot e^{2\cdot(\ln\sigma_g)^2}$$

σ_g, standard deviation of size distribution [-]
CMD, count median diameter [m]

Confidence intervals and error analysis - usual statistical procedures apply for confidence intervals for single readings; confidence intervals for mean (sample mean and standard deviation, standard deviation of the mean); and error analysis: propagation of error. Testing hypothesis with size distribution data must be done to compare one's measured aerosol size distribution against another or against a theoretical distribution to identify whether:

- the aerosols are from the same or from different sources?
- something has changed during the period between the measurements?
- different conditions produce different size distribution?

Statistical ways of testing hypotheses with size distribution data:

- Data from a normal distribution (Student's *t* test); Correlation and regression; Analysis of variance (ANOVA); Distinguishing among count distributions (Chi-Square); Distinguishing count or mass distributions (Kolmogorov-Smirnov test);
- Other statistical techniques for particle data analysis can be done via Multiple regression analysis (to determine if one variable is dependent on two or more others) or via time series analysis (to identify time related trends in the data);

Some advice: if undertaking statistical analysis of a more complex set of data, talk to a statistician!

Data inversion (deconvolution) - Data inversion: if exact measurements of a parameter (for example particle diameter) cannot be obtained, it may be possible to calculate it using the knowledge of the instrument behaviour.

Problems:

- solutions becoming unstable when the number of data is large;
- solutions are not unique;
- exact solutions often do not exist;

13. Analytical techniques for determination of the concentration of atmospheric aerosol

Non-destructive techniques:

- X-ray fluorescence analysis (XRFA)
- Proton induced X-ray emission analysis (PIXI)
- Instrumental neutron activation analysis (INAA)

Advantages:

- simultaneous quantitative analyses for elements with atomic numbers of about 12 and higher
- only small amounts of material required - usually rapid response (PIXI)

Limitations:

- self absorption (XRFA)
- overlap of emission spectra (XRFA) - variability of blank levels

Destructive techniques:

- Inductively Coupled Plasma Emission Spectroscopy
- Atomic absorption spectroscopy

Advantages:

- simultaneous quantitative analyses of a large number of elements
- only small amounts of material required - rapid response

Disadvantage: need for sample dissolution

Limitations: Matrix and interelement interferences

Atmospheric carbon TC = OC + EC + CARBC

NB: Common atmospheric carbonates are: Na_3CO_3, K_2CO_3

TC; Total carbon
OC, Organic carbon
EC, Elemental carbon; is typically in the range from 15 to 25%
CARBC, Carbonates; usually contributes < 5% to TC

Carbon determination

Total carbon (TC): combustion of all carbon in a sample to form CO_2 followed by quantisation of C.

Elemental carbon (EC): optical methods based on absorption of visible light (EC is the only significant visible light absorbing species).

Organic carbon (OC): pyrolysis-combustion techniques (pyrolysis of OC in an inert stream gas stream at relatively low gas stream, followed by combustion of EC).

Sulphate and nitrate analysis

Step 1: Water extraction of anions and cations (NO_3^-, SO_4^-, NH_4^+, Cl^-) from a filter
Step 2: Ion chromatography for analyte separation and detection, or
Selective ion electrode (for NH_4^+), or
Determination of pH (strong acid - NO_3).

Limitation of analytical techniques

- Sample storage.
- Sample handling.
- Artefacts (errors in concentration determination).
- negative artefacts (loss of semi-volatile materials, loss of nitrates, etc).
- positive artefacts (retention of gaseous HNO_3, SO_2, sorption of OC).

14. Microanalysis - Microscopes and microprobes are used for analysis of individual particles:

- chemical constituents;
- morphology (size and shape);
- physical and optical properties.

Basic principles of microanalysis:

- a beam of excitation radiation (photons, electrons, protons, neutrons, ions) bombards the sample;
- the interaction of the beam with the sample results in emitted radiation;
- emitted radiation is separated by a spectrometer and collected by a detector.

Instruments used for microanalysis

- Light microscopy (LM).
- Transmission electron microscopy (TEM).
- Scanning electron microscopy (SEM).
- Electron probe microanalysis (EPMA).
- Laser microprobe mass spectrometry (LMMS).
- Secondary ion mass spectrometry (SIMS).
- Fourier transform infra-red spectroscopy (FTIR).

Bioaerosol sampling and analysis

1. Collection of bioaerosols from the ambient air
   - Impactors (Anderson Impactor);
   - Impingers (liquid impingement);
   - other (settle plates, combination of techniques).
2. Sample analysis
   - direct counting of bioaerosol particles (light microscope, epifluorescence microscope);
   - culturing of micro-organisms into countable colonies, followed by identification and counting.

Size classification of viable submicrometer bioaerosols: a combined method developed at QUT, based on interfacing the Scanning Mobility Particle Sizer to a liquid impinger. Advantage: high efficiency, about 16 times higher than that achieved using a centrifugal air sampler. Even better is the **UV-APS**: Particle time of flight between two laser beams is recorded and, using a calibration curve, converted to aerodynamic diameter – APS. No information can be given on the viability of the particle – measures the total concentration (viable + nonviable) of particles. Live bacteria contain a variety of intracellular biomolecules associated with energy yielding reactions. These molecules are associated to fluorescence characteristics; e.g. Nicotinamide Adenine Dinucleotide Phosphate NAD(P)H (presence of NAD(P)H is an indicator of bacterial viability), or Riboflavin. Excitation at 349/355 nm and Emission at 400 to 540 nm.

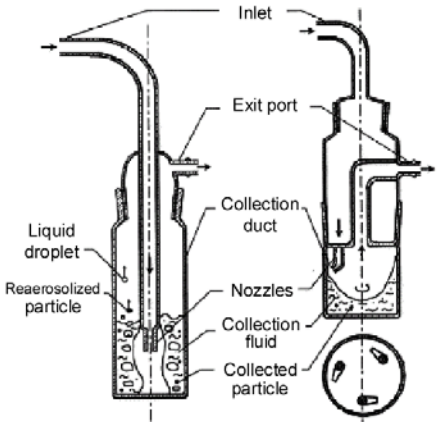


Fig. IV-14.1 Impinger

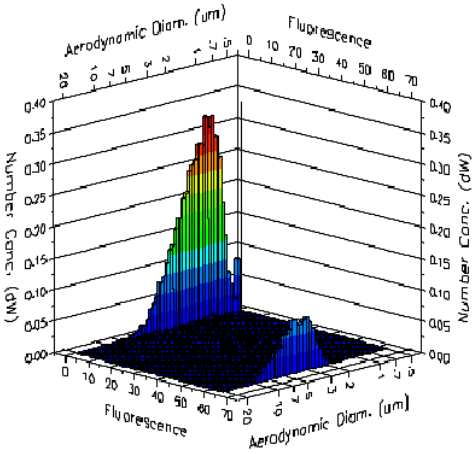


Fig. IV-14.3 UV-APS spectrum of viable bio-aerosols; no information can be given on the viability of the particle – measures the total concentration (viable + nonviable) of particles.

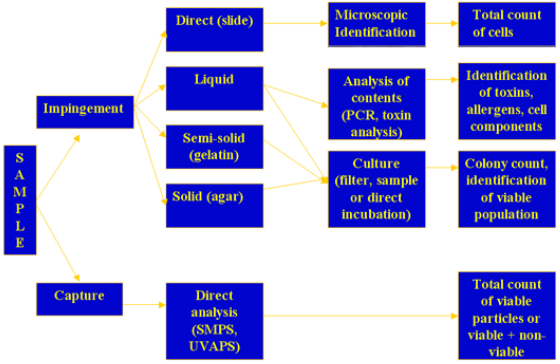


Fig. IV-14.2 Bio-sampling procedures

PART V - HEALTH EFFECTS OF PARTICLES

Effects of airborne particles

- health effects (epidemiology as the main trigger);
- effects on atmospheric properties;
- visibility reduction;
- fog formation and precipitation;
- solar radiation reduction;
- temperature and wind distribution alteration (e.g. climate change);
- effects on materials;
- effects on vegetation.

1. Health effects of particles – seldom with direct proofs about the mechanism. In general, inhalation of airborne particles contributes to excess mortality and morbidity (not all adverse effects result in death). Specific health "end points" include:

- declines in lung function;
- increased respiratory symptoms such as cough, shortness of breath, wheezing and asthma attacks;
- chronic obstructive pulmonary disease;
- cardiovascular diseases (diffusion across the epithelium of alveoli, changes coagulation of blood);
- lung cancer.

a) Syndromes, illnesses and sensitivities exhibited or acquired as a result of indoor environment exposures - The indoor exposures causing these responses are believed to be a function of the synergistic effects of two or more pollutants (or even among particles):

- Sick Building Syndrome (goes away once building is avoided).
- Building Related Illness (acquisition due to exposure to that building).
- Multiple Chemical Sensitivity (synergistic effects to a number of chemicals).

b) Factors influencing particle deposition in the respiratory tract

- The physio-chemistry of aerosol (particle size/size distribution; density; shape; hygroscopic/hydrophobic character; chemical reactions).
- The anatomy of the respiratory tract (diameter; length; breathing angles of airway segments).
- The physiology of the respiratory tract (airflow pattern; breathing pattern).

c) Particle deposition in respiratory tract; can be either total or fractional deposition (extrathoracic in nose or mouth; bronchial; bronchiolar; or alveolar).

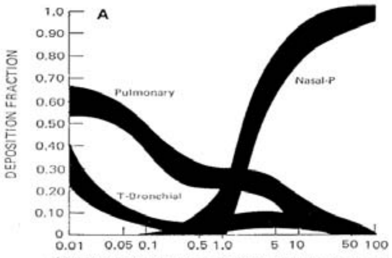


Fig. V-1.2 Particle deposition;

d) Determination of particle deposition in respiratory tract can only be determined via experimental studies involving human or animal experiments; lung cast experiments in post mortem.

Alternatively, computational modelling: NB: Experimental studies show significantly higher deposition rates than predicted by modelling.

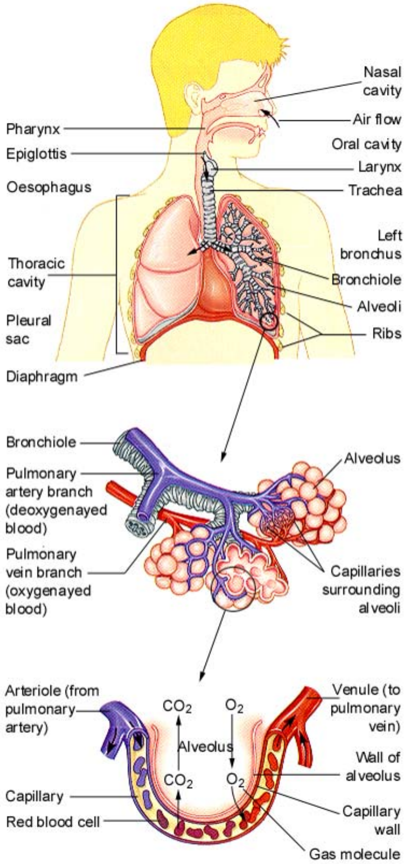


Fig. V-1.1 Respiratory Tract; schematic diagram of the human respiratory tract and its compartments

2. Elements of Predictive Risk Equation (Risk Assessment)

a) **Exposure - response assessment** (how to find it). Epidemiological studies on humans (generally, there is no threshold level between non-damaging and damaging effects, the change among these is rather gradual):

- observational (epidemiological);
- experimental (clinical studies);
- case studies, surveys (asthmatic people).

Animal studies to evaluate the length of time (acute, chronic, sub-chronic) and the end point (morbidity, mortality, carcinogenicity, irritation, etc). In vitro studies to investigate the effects of pollutants on cell or organ cultures.

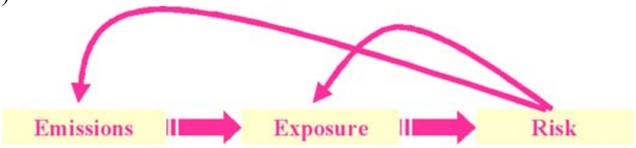


Fig. V-2.1 Exposure and Risk;

b) **Risk assessment to air pollutants**: state of the art (still, too little is known, more needs to be done in this field):

1. General agreement on <u>quantitative</u> assessment. There are very few situations where this level of understanding of health risk is established
2. General agreement on definite <u>qualitative</u> established risk. This category is more common
3. Conflicting data. This is a very common outcome of the comparison of different <u>epidemiological studies</u> or of results obtained using different risk assessment methods.
4. Established lack of risk. This situation is equally rare as agreement on quantitative risk assessments
5. Lack of data - risk suggested

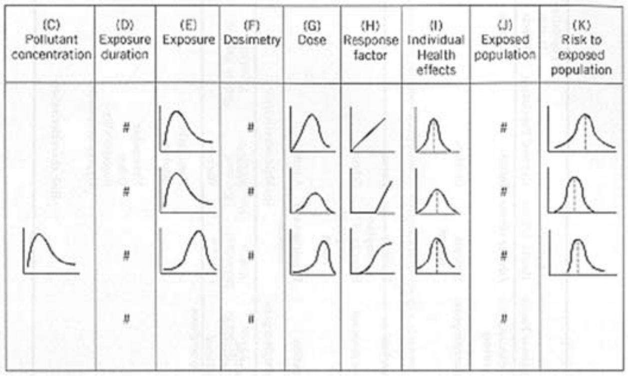


Fig. V-2.2 Concentration, Dose, Exposure and Risk;

c) **Criticisms** as to the current state of air pollution risk assessments

- <u>existing scientific knowledge</u> and understanding are <u>insufficient</u> or inappropriate to allow for meaningful quantitative estimates of risk (if quantification is not possible, there is no health standard to be set up)
- risk estimates are based on <u>faulty</u> or <u>incomplete</u> models
- scientific uncertainties are not adequately identified, characterised or communicated: e.g. an association between air pollution and mortality in six US cities.

d) **Exposure & Risk Analysis** - Current epidemiological and clinical evidence and hypotheses:

"Ultra-fine particles are able to provoke alveolar inflammation, with release of mediators capable, in susceptible individuals, of causing exacerbations of lung disease and of increasing blood coagulability, thus also explaining the observed increases in cardiovascular death associated with urban pollution episodes."

Seaton et al, 1995, The Lancet

"Increased daily mortality is specifically associated with particle mass constituents found in the aerodynamic diameter size range under 2.5 μm, that is, with combustion-related particles." and also: "these results indicate that research and control strategies should focus on the smaller particles".

Schwartz et al, 1996, Journal of Air & Waste Management Association

"Since ultrafine particles are always present in the urban atmosphere, they play a role in causing acute lung injury in sensitive parts of the population."

Obersdörster et al, 1995, Inhalation Toxicology

e) **Epidemiological approach** - Inability of epidemiology to provide conclusive answers without comprehensive scientific characterisation: e.g. link between exposure to radon and lung cancer:

- Canadian study based on a review of over 700 people who died of lung cancer did not detect an association between residential exposure to radon and lung cancer risk.
- Swedish study based on a review of over 1300 lung cancer victims found that exposure to radon significantly increased risk.

PART VI - APPLICATIONS, Standards and guidelines, Indoor and outdoor, Motor vehicle emissions, Other

VI - 1. Standards and Guidelines

Ambient Air - mass concentration standards with a trend towards smaller particles (total, regardless of size, thus is becoming more and more obsolete):

- Total Suspended Particulate (TSP)
  US Environmental Protection Agency (old) - 75 μg/m^3
  National Health and Medical Research Council (Australia) 90 μg/m^3
- Particulate matter < 10 μm aerodynamic diameter (instead of TSP: PM_{10});
  US Environmental Protection Agency standards (announced on July 17, 1997)
  Annual PM_{10} standard - 50 μg/m^3
  24-hour PM_{10} standard - 150 μg/m^3
- Particulate matter < 2.5 μm aerodynamic diameter ($PM_{2.5}$) rather than the PM_{10} standard (the 1μm particles are situated at the cross-point of particles originating from combustion processes and the tail of mechanically abrasive origin)
  Annual $PM_{2.5}$ standard - 15 μg/m^3
  24-hour $PM_{2.5}$ standard - 65 μg/m^3

Indoor Air – non-industrial: no standards whatsoever.

Clean room standards (e.g. class 100 = <100 particles/ft^3 = 3531 particles/m^3) - number concentration standards. Maximum concentrations for ambient air within a clean room are defined as the number of particles larger than a given size per unit volume of air.

Motor vehicle emissions: mass emission standards - total mass (total emission should not exceed ambient air level; is very costly to measure)

a) **Emission standards** - The 1996 US Heavy Duty Diesel Engine Urban Bus PM standard - 0.05g/BHp-hr (break horsepower per hour = 67.05mg/kWh). The US EPA standard for in-use particulate exhaust emissions from gasoline light duty vehicles - 80 mg/mi (49.7mg/km) for the intermediate useful life or 100 mg/mi (62mg/km) for the full useful life.

Outdoor particles - Important aspects:

- concentration levels and characteristics;
- short and long term trends of concentration levels and other characteristics;
- monitoring networks;
- source characterisation and emission inventories;
- dynamics of reactions and interactions;
- modelling;
- standards and guidelines.

Some of the current issues

- focus on fine and ultra fine particles;
- emission inventories;
- relation between different sets of particulate data;
- links between exposure and health;
- towards new standards.

The main particle sources in the urban environment

- motor vehicle emissions;
- particles from photochemical processes;
- biogenic emissions;
- marine aerosols;
- forest fires;
- dust.

Fine and ultra fine particles - what do we know about them?

- $PM_{2.5}$ monitoring data;
- nephelometry monitoring data;
- various sets of data for different particle characteristics.

Ranges of $PM_{2.5}$ concentrations Santiago: 40 - 65 μg/m^3
US cities: 10 - 30 μg/m^3

Trends in fine particle concentration and sub-micrometer particle concentration levels.

b) Air monitoring and research station (AMRS) - Queensland University of Technology/Queensland Department of Environment.

AMRS **Instrumentation**:

- NO_x analyser;
- SO_2 analyser;
- Nephelometer;
- ANSTO fine particle sampler;
- O_3 analyser;
- TEOM (PM_{10}) ambient particulate monitor;
- CO analyzer;
- Wind speed and direction monitor

Monitoring procedures:

- continuous monitoring of and PM_{10} concentrations and meteorological conditions;
- grab sampling of particle spectra twice a day, everyday;
- grab sampling at regular intervals during notable atmospheric or meteorological conditions;
- triplicate samples.

Parameters employed for **characterisation of particle size distribution**

- number median diameter (NMD);
- total SMPS range (0.016 to 0.626µm);
- total APS range (0.7 to 0.30µm);
- subdivisions of SMPS and APS ranges.

Correlation analysis: Correlation coefficient - Pearson-product moment correlation

$$r_{x,y} = \frac{Cov(x,y)}{\sigma_x \cdot \sigma_y}$$,[?]

n, number of datum points [-]

$$Cov(x,y) = \frac{1}{n}\sum^{n}\left(x_j - \mu_x\right)\cdot\left(y_j - \mu_y\right)$$

A two-tailed test used to test the null hypothesis (H_0), that there is no linear relationship between the two data sets:

$$t = |r| \cdot \sqrt{\frac{n-2}{1-r^2}}$$ [s] reject H_0 if $t > t_{crit}$

Correlation analyses

- particles/gases;
- SMPS/APS;
- SMPS/TEOM (PM_{10});
- APS/TEOM;

VI - 2. CASE STUDY: Assessment of a contribution of a major arterial road to particulte concentration in its vicinity

Boundary conditions:
- City environment.
- Short time frame for assessment.

Aspects to consider or to take into account:
- what is "background level"?
- changeability of meteorological conditions;
- horizontal and vertical distribution.

a) Indoor particles

Important aspects:
- indoor particle sources;
- outdoor particle sources;
- air filtration and ventilation;
- sampling considerations.

Importance of indoor air quality (IAQ)
- We spend up to 90% of time indoors.
- Buildings are tighter as a measure to conserve energy.
- Change in people's lifestyles have introduced new contaminants.

Indoor particles
- hair and skin detritus;
- dust;
- tobacco smoke;
- combustion products from: wood, stoves, fireplaces, kerosene heaters, gas heaters and stoves;
- residues from personal care products;
- residues from household cleaning products;
- sprays (pesticides, paints);
- asbestos and other fibres;
- radon decay products;
- biological aerosols.

Ventilation
- Ventilation rate units: air changes per unit time.
- Ventilation is governed by: use of windows and doors.
- HVAC system's design and operation.

Tightness of the building - Ventilation parameters are important for:
- the mixing and dilution of aerosol sources;
- the transportation from sources to receptors.

Filtration - Important factors:
- filter type;
- filter efficiency;
- filter mounting and integrity.

Types of commonly used filters
- Metal viscous oil filters.
- Dry arrestance filters.
- Electrostatic filters.

Sources of indoor pollution
- Occupants;
- outdoor air;
- soil, water;
- furnishings;
- building materials;
- tobacco combustion;
- consumer products;
- combustion appliances;
- maintenance products;
- heating, Ventilation and Air Conditioning (HVAC) systems;
- cooking, vacuuming, dusting.

Factors affecting concentration of indoor pollutants
- the type, nature and number of sources;
- source use characteristics;
- building characteristics;
- infiltration or ventilation rates;
- removal rates by surfaces, chemical transformation or radioactive decay;
- air mixing;
- existence and effectiveness of air contaminant removal system;
- outdoor concentration of pollutants;
- meteorological conditions.

Filter testing
1. Laboratory testing: testing rigs.
2. In situ testing.

Some challenges in filter testing:
- for high efficiency filters: extremely low particle concentration downstream.
- for in situ testing: inhomogeneous particle concentration across the filter face.

Filtration and ventilation in air conditioned buildings

Components of an HVAC system:

$$S_A = a \cdot Q_A + (1 - a) \cdot R_A \qquad [m^3/s]$$

a is a constant	[-]
O_A, Outdoor air	[m^3/s]
R_A, Return air	[m^3/s]
S_A, Supply air	[m^3/s]

- Mixing plenum
- Fans
- Filters
- Cooling fans

Modeling of indoor particle concentration and exposure - Complexity of processes and parameters involved requires significant simplifications in model assumptions. The majority of available models are based on particle mass balance. A simple particle mass balance model (Salvigni, 1996). Assumption: in order to apply the particle balance equation, a uniform particle concentration must be present:

$$V\,\frac{dC(t)}{dt} = \left[G + Inf + (1-\varepsilon)\cdot Q_{OA}\cdot C_e\right] - \left(Q_{OA} + \varepsilon\cdot Q_{RA}\right)\cdot C(t)$$

A general solution:

$$C(t) = \frac{G + Inf + (1-\varepsilon)\cdot C_e}{Q_{OA} + \varepsilon\cdot Q_{RA}}\cdot\left[1 - e^{-\frac{Q_{OA}+\varepsilon\cdot Q_{RA}}{V}\cdot t}\right] + C_o\cdot e^{-\frac{Q_{OA}+\varepsilon\cdot Q_{RA}}{V}\cdot t}$$

$$= C_1(t) + C_2(t)$$

C(t), indoor particle concentrations	[1/m^3]
C_e, outdoor particle concentrations	[1/m^3]
G, particle generation rate fr/ indoor sources [1/s]	
Inf, particle infiltration from outdoor	[1/s]
Q_{OA}, flow rates of O/A	[1/m^3]
Q_{RA}, flow rates of R/A	[1/m^3]
V, effective volume of the indoor space	[m^3]
ε, efficiency of the air handling unit	[-]

Environmental tobacco smoke (ETS)

- One of the most important indoor pollutants.
- Contains over 4000 compounds in gaseous, vapour and particle form.
- Particulate phase contains all of the tar and a significant amount of toxins (for example – nicotine).
- Markers used for ETS characteristics.

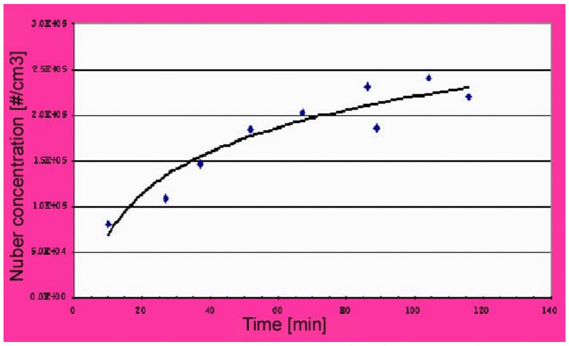


Fig. VI-2.1 ETS; environmental tobacco smoke concentration in a QUT-bar increases with time.

b) Particle measurements from combustion processes

- engine emissions;
- motor vehicle emissions;
- stack emissions;
- waste incinerators;

Measurement challenges

- Difficult testing conditions: high temperatures, noise, corrosive gases;
- Wide range in particle concentrations;
- Variation in particle concentration across the duct cross section;
- Entrained water;
- Air infiltration;
- Chemical reactions (acid gases);

Planning combustion emission measurements

- Check for existing sampling procedures; e.g.: US EPA Method 5 or 17 for stack emission testing;
- Chose the method most appropriate and economic for your application;
- Adapt the method if necessary;
- Remember about safety considerations;

MOTOR VEHICLE EMISSION TESTING -

Sampling characteristics

Flow rates (exhaust flow rate; sample flow rate; dilution flow rate);

Temperatures (exhaust flow; sample flow);

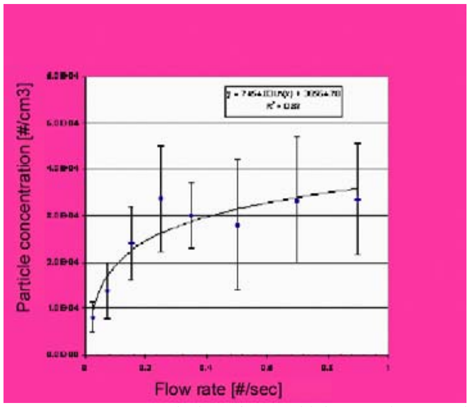


Fig. VI-2.2 MVE; emissions from vehicles on a busy road.

c) Other areas of aerosol studies and applications

Industrial hygiene testing is performed to:

- determine if a risk to worker health exists;
- comply with the regulatory requirements;
- monitor continued performance of good work practices and engineering controls;
- gather data for use in epidemiological studies;
- identify high hazard jobs;

Examples of industrial environments

- mining industry;
- mineral sand processing;
- fibrous material processing (asbestos);
- raw material processing;
- manufacturing industry;

Material synthesis

- optical fibres for telecommunication;
- pimentary titania;
- fumed silica;
- ceramics;
- metallic fuels;
- diamonds;

Specifics of aerosol characterisation in industrial processes

- high concentrations;
- aerosols tend to be non-spherical aggregate structures;
- short time scale in which particle formation, growth and transport takes place;
- removing of aerosol sample can dramatically change its characteristics;

Industrial and occupational hygiene

- aerosol contaminant almost always known;
- sampling performed using portable monitors (personal breathing zone sampling);
- concentrations higher than in ambient air but lower than in process testing;

Clean rooms - The main characteristics: extremely low aerosol concentrations

- pharmaceutical industry;
- hospitals;
- microelectronic industry;

Radioactive aerosols - Sources of radioactive aerosols:

- ambient air and soil;
- tobacco smoke and fossil fuel effluence;
- nuclear industry;

Pharmaceutical aerosols

- generation of aerosol;
- the use of aerosol in therapy;
- the use of aerosol in diagnostic procedures;

Large scale atmospheric processes - Tropospheric aerosols and cloud studies are conducted to:

- determine earth's radiative budget;
- investigate climate change;
- explain meteorological processes;

VI - 3. CLOSING SUMMARY

The decrease in concentration of environmental tobacco smoke (ETS) particles introduced to an enclosed space can be represented as:

$$C(t) = C_o \cdot e^{-\lambda \cdot t\ t} \qquad [1/m^3]$$

C_o, ETS concentration at the beginning of the experiment	[1/m^3]
C(t) is the concentration at time t	[1/m^3]
λ, constant	[-]

Dusttrak - measures the extinction and converts it into concentration over time via an conversion factor δ:
- portable instrument that measures aerosol mass concentration in the particle size range 0.1 - 15µm;
- mass determined from light intensity scattered by the aerosol within a fixed sensing volume;
- measurements time averaged over 1 s or more in the 0.001 - 100mg/m^3 mass range;

Nephelometer - measures the "visibility" which is related to a range of particle mixtures:
- measures the light scattering extinction coefficient - a parameter;
- related to visual range and aerosol particle mass per volume air;
- utilises green light (λ = 530nm); time averaged over 120s;

SMPS - Scanning Mobility Particle Sizer
- measures the particle size distribution in the range of 5 to 1000 nm
- measurement cycle time - 60 to 500 s
- concentration range - 20 to 1·E^7 particles/cm^3.
- aerosol flow rate - 0.2 to 2.0L min^{-1}.
- sheath air flow rate - 10 times aerosol flow aerosol temperature range - 10 to 35°C.

SMPS Basic components
- **IMPACTION:** removes particles larger than a known aerodynamic size.
- **ELECTROSTATIC CLASSIFIER:** aerosol enters a Kr-85 Bipolar Charger and particles with a narrow range of electrical mobilities exit for counting.
- **CONDENSATION PARTICLE COUNTER:** particles grow to an optically detectable size by heterogeneous condensation and pass through a light beam to scatter light onto a photodector.

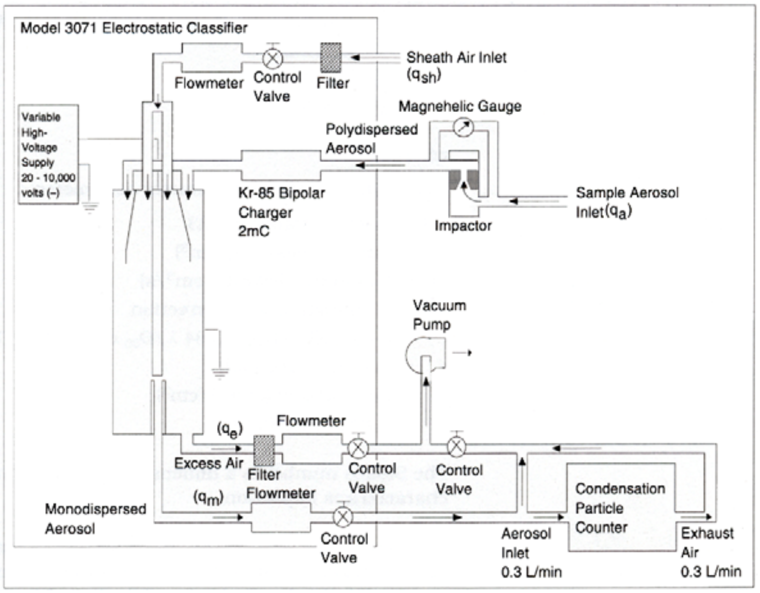


Fig. VI-3.1 SMPS system; schematic diagram of the scanning mobility particle sizer consisting of an EC and a CPC

APS-Aerodynamic Particle Sizer
- in real time, the sensor measures particle aerodynamic diameter in the size range 0.5 to 30µm;
- particle type - airborne solids or non-volatile liquids;
- sampling time - 1s to 18 hrs;
- ambient temp. range - 10 to 40°C;
- ambient rel. hum. - 20 to 80%;

APS Basic Components

Accelerating Orifice - consists of an outer orifice and inner nozzle: particles are accelerated by clean sheath air at velocities related to their aerodynamic diameter;

Laser Velocimeter - a 2mW polarised HeNe laser is split; as the particle crosses between the 2 beams 2 pulses are generated and measured by the PMT; the time between the pulses is related to the particle's velocity and thus diameter.

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