Environmental Aerosol Physics

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Assignment-paper:

Application of optical particle counting technique to environmental sampling and monitoring

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Introduction: Definition and effects of an Aerosol

Aerosol:

An aerosol is a multiphasic system in a gas in which dispersely distributed particles of solid or liquid nature are suspended.
Such airborne particles (or collection of particles) can be smoke, salt, fog, which includes even the products of spray cans.

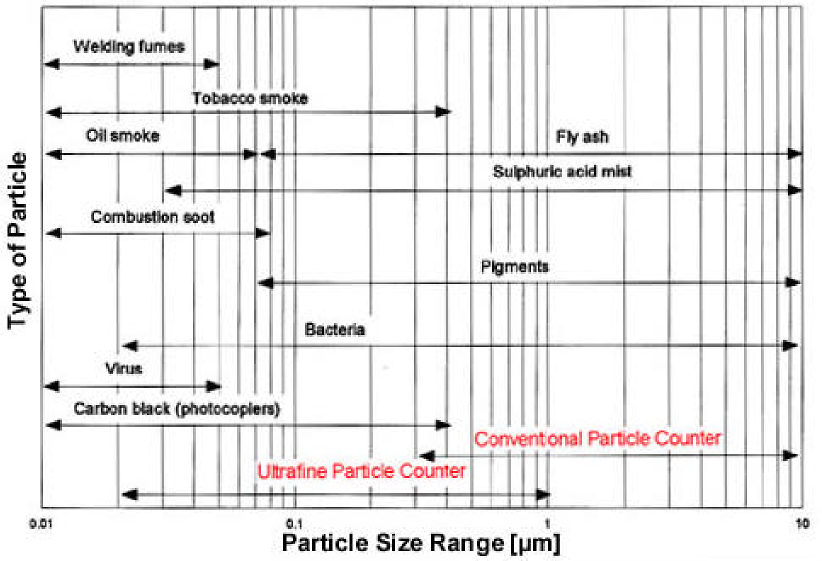

Fig.1: Examples of Particles and their size distribution

The health effects of an aerosol depends upon its inhalability; larger aerosols remain trapped in the naso-pharyngeal cavity, while the smallest ones are capable to penetrate the alveolar section of the lungs. Even though the exhalable fraction gradually increases with decreasing particle size, the " smaller " aerosols are considered the most dangerous.
Biological relevance have been assigned to particles in the sub-ultrafine region (<20nm), as they are capable to penetrate the interstitial cellular space of the alveolar lining by expressing their potentially toxic effect.
It is generally agreed upon that aerosols account for lung tumors, fibroses, allergies, and even for irritating or chemo-toxical effects. Accommodation, transportation (clearance, via the bronchial cilia and mucus or incorporation by phagocytes in the lymphatic tissue in alveoli), and deposition in the respiratory tract determine the potential effects of an inhaled particle.

Consequently, the effect of an aerosol depends on:

- on type and site of the deposit; this again is defined by the size, shape, and surface structure, the chemical composition, bio stability and hygroscopic properties of the particle (the more hydroscopic the particle, the deeper it can penetrate into the lungs);
- furthermore, in very small particles, the solubility and absorptive characteristics by the target cell, where it may then fully develop its toxicological effects, play a crucial role.

Definitions

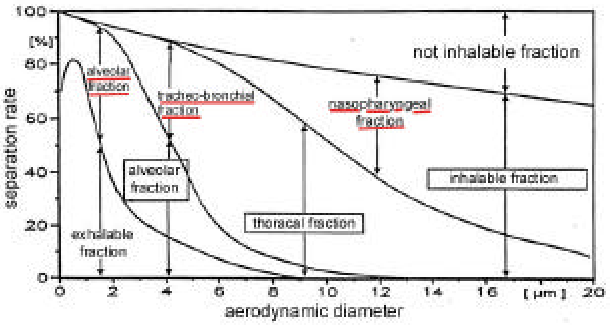

Fig.2: Aerosol fractions as a function of the aerodynamic diameter; medically relevant deposited aerosol fractions according to the industrial standards are underlined; the framed proportions relevant for the measuring techniques contain also their respective exhalable portions.

Separation Curves

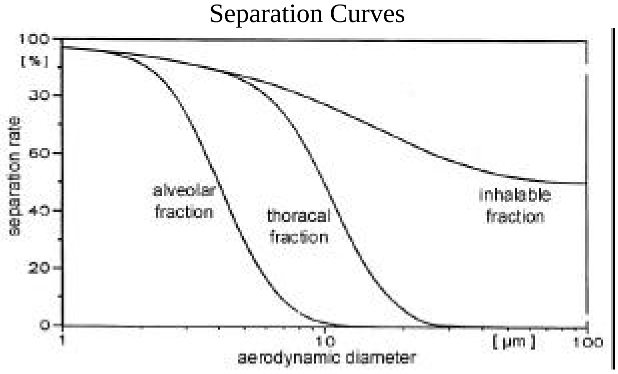

Fig.3: The separate fractions for the inhalable, thoracic and alveolar portions of airborne dust within the respiratory tract; because of the logarithmic representation an aerodynamic diameter " zero " is not representable; for which a separation rate of 100%.

The common instruments for atmospheric particle size classification include:

- optical particle counters
- electrostatic classifiers (not further described in this paper)
- diffusion batteries (not further described in this paper)

Optical Particle Counting Technique:
Optical particle counters (OPCs) can be used to determine the size-dependence of the aerosol light scattering coefficient in spite of uncertainties about particle shape and refractive index. These measurements are made in units of particles per cubic centimeter (pt/cm^3) versus traditional aerosol Measurements of milligrams per cubic meter (mg/m^3) made by photometers.

Advantages of optical direct-reading particle counting techniques:

- rapid response
- continuous (*in-situ*) measurements
- non-destructive detection

High resolution size distribution measurements over a size range typically from 0.5 to 30µm can be accomplished; since the instruments usually combine a PC for data processing, presentation of the results in graphical and tabular format is straightforward.

Disadvantage: the amount of light scattered may not be directly related to the property which needs to be investigated.
Solution: combination of optical detection techniques with the manipulation of other particle parameters (for example motion, mass, diameter, chemical properties, etc.)

Basic concept of a conventional OPC (refer also to fig.1):
A light source (typically a plasma laser or laser diode) is collimated to illuminate a sample volume of aerosol flowing out of a nozzle. As shown in fig.4, a photo-detector, rotatable and off-axis from the light beam, measures the amount of light scattered from single particles by refraction, reflection and diffraction. Both the size and the number of particles are measured simultaneously. The size of the particle is deduced from the intensity of the scattered light.
Typically, the wavelength of light used in OPCs ranges from about 0.6 to 0.8µm. As particles become smaller than a wavelength, the amount of light they scatter into the detector collection optics drops off rapidly. For example, to upgrade the sensitivity of a counter from 0.2 to 0.1µm requires about a 17-fold increase in light power focused into the view volume. To achieve a sensitivity approaching 0.1µm requires a well-designed laser/optical system with a narrow optical bandwidth in order to develop high light intensity in the view volume. Making the optical bandwidth too narrow in order to achieve high sensitivity can actually lead to calibration instability (in the presence of mild shock or vibration) with the attendant loss of sensitivity.

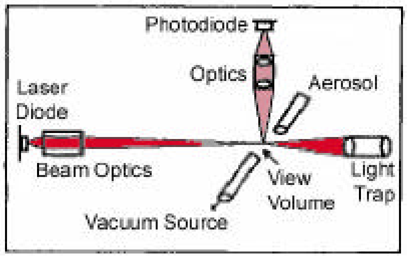

Fig.4: Basic design of an OPC

Basic concept of a Ultrafine OPC (refer also to fig.1):
An Ultrafine Optical Particle Counter (UOPC) measures ultrafine particle (0.05-1µm) concentrations in real-time.
Particles are drawn through the sampler using a built-in pump. Upon entering the instrument, particles pass through a saturator tube where they mix with an alcohol vapor. The particle/alcohol mixture then passes into a condenser tube where alcohol condenses onto the particles, causing them to grow into a larger droplet. The droplets then pass through a focused laser beam, producing flashes of light which are sensed by a photo-detector. The particle concentration is determined by counting the light flashes. If the particles were not "grown" into larger droplets, they would not produce enough light (scatter) to be detected.
The UOPC uses the same fundamental technology behind condensation particle counters (CPCs), that are used in research and industrial applications to track and record particle sources (for details regarding CPC's refer to lecture paper – Morawska).

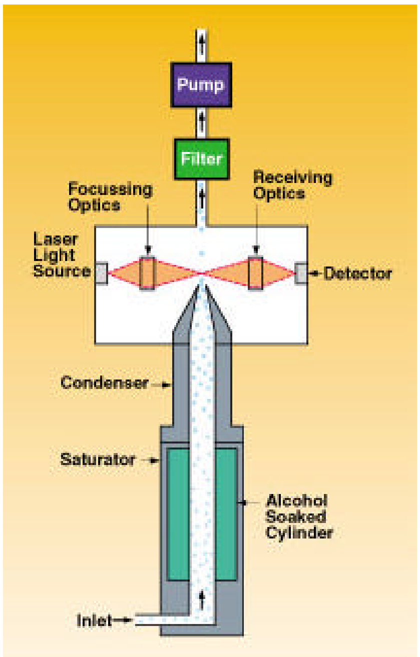

Fig.5: Sketch of an UOPC

Optical Physics and OPC:
As the exponential relationship changes inversely with particle size, some fundamental aspects should be briefly highlighted.

In the Rayleigh-region, where particles are smaller than the light wavelength, light is scattered equally in all directions (isotropically) from the particle. Its intensity varies as a function of the 6^{th} power of particle size in this region (exp = 6).

In the Mie-region, where particles are nearly the same size as the light wavelength, the light pattern surrounding the particle becomes "scalloped" (refracted). The forward lobe (pointing in the same direction as the laser beam) becomes larger as the particle size increases.

In the Geometric-region where particles are much larger than a wavelength, classical optical theory takes over. Light scattering from a particle can be calculated from the physical effects of diffraction, reflection, refraction, and absorption.

Coincidence Effect:
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 (see fig.6) 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. 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. This correction formula may be integrated into the analyzer's computer and the coincidence-corrected result reported.

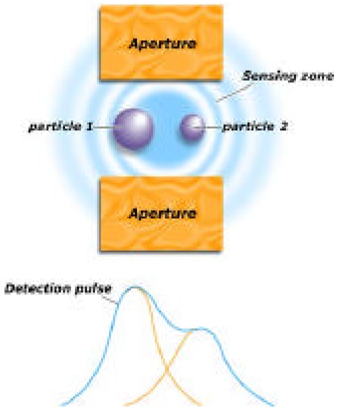

Fig.6: Coincidence Effect

Two simple models of coincidence are illustrated in fig.7 and help to analyze coincidence phenomena. In the case of horizontal interaction (a) one wide M-shaped pulse is produced; in the case of vertical interaction (b) one large pulse is observed (valid for electrostatic counters only); optical counters are not able to discriminate them as separate particles, once particle B hides behind particle A (in reference to the pathway of the laser light). Conversely, it is not always possible to identify the existence of two particles in the viewing window from the observed pulse.

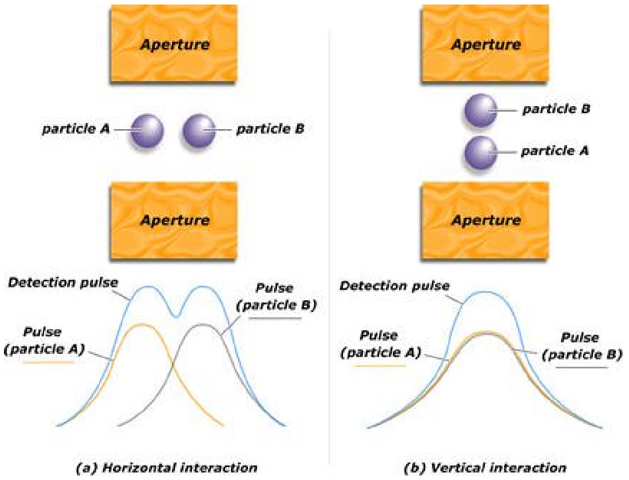

Fig.7: Variations of Coincidence

Selected Parameters: Counting Efficiency, Sensitivity and Resolution; referring to the Particle Size vs. Energy Curve illustrated in fig.8, the detected light energy falls off exponentially with decreasing particle size. In conventional OPCs the detected energy drops off at 0.3µm as a function of about the 4th power of particle size; at 0.1µm the detected light energy drops off as a function of about the 5^{th} to 6^{th} power of particle size.

- Accuracy - the "correctness" of the size measurement; expressed as a percentage (fig.8): $A = (D_m-D_t) \cdot 100 / D_t$ [%]
  where D_m, is the measured diameter and D_t, is the true diameter;
- Resolution - the smallest detectable particle size difference. It is the ratio of the standard deviation (s) to the diameter (D_m) expressed as a percentage (fig.8): $R = s \cdot 100 / D_m$. [%]
  Resolution is a function of the width of the bell-shaped curve. It is also referred to as "coefficient of variation, relative precision and relative standard deviation".
- Precision - the standard deviation (σ) of repeated measurements of the same size monodispersed spheres:
  $\sigma = \sqrt{[\sum(D_n-D)^2 / N-1]}$ [m]
  where: D_n = the n^{th} measurement of particle diameter (arithmetic mean of N measures)
  N = total number of measurement

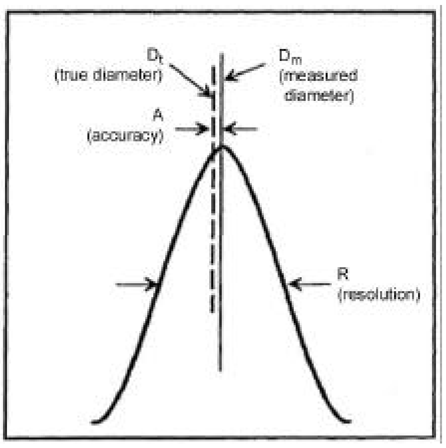

Fig.8: Particle Size vs. Energy Curve

- Reproducibility (also called repeatability and calibration stability) - the extent to which an OPC will give the same sizing and counting response to the same diameter PSL spheres over a long period of use.
- Sensitivity - the smallest size particle an OPC can detect at a specified counting efficiency, e.g. conventional OPCs detect 0.3µm particles at 50% counting efficiency.
- Counting efficiency - the detected particle concentration divided by the true concentration (as measured by a hypothetically perfect instrument); this curve provides useful information regarding the sensitivity and resolution of the instrument.
- False count rate - the counts per unit volume using perfectly filtered air at a specified flowrate.
- Signal - the magnitude of the sensed scattered light produced only by the passing of a particle through the view volume. Size is deduced from the signal magnitude. Noise is the opposite of signal in that it is produced by anything but a particle in the view volume. A high signal-to-noise ratio implies low false count rate.

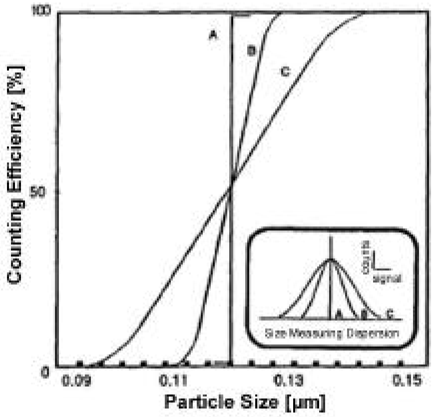

Fig.9: Counting Efficiency Curves

Selecting an optical particle counter (OPC) appears deceptively simple. Typically, the specification focuses on sensitivity, flow rate, size range and coincidence loss. Secondary requirements are number of channels, the sample/hold periods, and alarm limits. For example:

- Specifying sensitivity without considering the counting efficiency curve could mean good sensitivity (ability to sense small particles) but extremely poor resolution (ability to detect small differences in particle size). Poor resolution can cause large errors in the particle count.
- Relying exclusively on sensitivity or counting efficiency measurements based on ideal (transparent and spherical) test particles can result in wrong answers when counting particles in the real world. These particles occur in a wide variety of shapes and refractive indices, causing large errors in particle sizing.
- Failure to recognize the difference between a "highly tuned" lab instrument (which can easily slip out of calibration with normal handling) and a "ruggedized" field instrument (which holds its calibration month after month) can be costly. Poor calibration stability causes sizing drift, non-repeatability, random spikes and ultimately, loss of user confidence.

Calibration of an OPC: As an aid to arrive at a definition of counting efficiency, let us assume the presence of an ideal reference particle counter (fig.10). This counter can "see" every particle passing through the view volume to a diameter much lower than the lowest detection limit of the OPC under test. Typically, this instrument is a condensation nucleus counter (CNC or an OPC with a verified counting efficiency of 100% at the lower detection limit of the OPC under test). However, a CNC only counts particles above a given size corresponding to a preset threshold (e.g. 0.01µm); it cannot size particles. A reference CNC must be used with an electrostatic classifier to analyze particles by controlled deflection in an electrostatic field (see also lecture paper – Morawska).

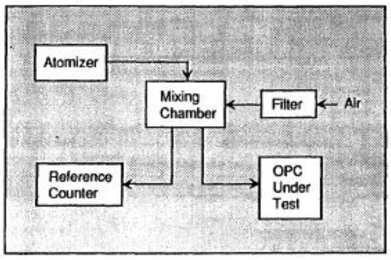

Fig.10: OPC-adjustment

An aerosol carrying mono-dispersed polystyrene latex (PSL) spheres is generated by the atomizer (fig.10). The aerosol is mixed with filtered air in the mixing chamber. The OPC under test and the reference counter simultaneously sample the mono-dispersed spheres at the same concentration. As smaller mono-dispersed spheres are introduced, there is a point where the OPC under test fails to detect all the particles that the reference instrument is sensing. Further reduction in particle size results in the eventual loss of particle detection.
Therefore, counting efficiency is expressed as follows:

$\eta_C = N_m/N_t \cdot 100$ [%]

where N_m is the measured concentration and N_t is the true concentration as measured by the reference instrument. Thus, measurements with ideal (PSL) spheres represent a powerful tool for assessing the sensitivity, accuracy, resolution and false count level of a counter. This calibration technique serves two purposes:

1) Gives comparative evaluations of a wide variety of counters,
2) provides a measure of how well a counter maintains its calibration (reproducibility).

Particles in the Real World versus the Lab World:
In the field of optical particle counting one generally specifies sensitivity and counting efficiency on the basis of ideal test particles that are transparent and spherical. Most often, PSL spheres are used for testing. In the particle counting industry, there is a tendency to emphasize PSL sphere sensitivity and skirt the issue of OPC sizing accuracy and sensitivity with particles found in the real world. Unfortunately, real world particles come in a wide variety of shapes and refractive indices, leading to a significant degradation of sensitivity, resolution and accuracy. For convenience, OPC measurements are based on the introduction of aerosol with suspended PSL particles of highly mono-dispersed sizes over the range of approximately 0.1 to 3µm. OPCs are calibrated with "ideal" particles having a refractive index between 1.5 and 1.6. The size measured by the OPC is then an "equivalent PSL diameter", depending on the calibrating aerosol used.
At particle diameters of 0.1µm, optical scattering is strongly dependent on the particle's shape, color and electromagnetic characteristics which reinforces the fact that significant error exists in sizing real world particles. Particle sizing errors due to changes in refractive index encountered with particles that are highly reflective while others absorb most of the incident light energy.

Current UOPC-Technology based on the TSI-model 3320:
The model described in fig.11 (Thermo-Systems Inc. - sketch depicted below) accelerates the aerosol sample flow through an accelerating orifice. The aerodynamic size of a particle determines its rate of acceleration, with larger particles accelerating more slowly due to increased inertia. As particles exit the nozzle, they cross through two partially overlapping laser beams in the detection area (fig.11 - lower left inlet). Light is scattered as each particle crosses through the overlapping beams. The optical arrangement that brings about the translation uses an elliptical mirror (fig.11 - lower right inlet). This gives much improved light collection. The elliptical mirror, placed at 90 degrees to the laser beam axis, collects the light and focuses it via an extra lens onto an avalanche photo-detector (APD). The APD then converts the light pulses into electrical pulses. The configuration of the detection area improves particle detection and minimizes Mie- scattering oscillations in the light-scattering-intensity measurements.
The use of two partially overlapping laser beams results in each particle generating a single two-crested signal. Peak-to-peak time-of-flight is measured with 4-nanosecond resolution for aerodynamic sizing. The amplitude of the signal is logged for light-scattering intensity. The smallest particles may have only one detectable crest and are binned separately. In uncorrelated mode, small particles are displayed in the smallest size channel (less than 0.5µm). Particles with more than two crests, indicative of coincidence, are also binned separately but are not used to build aerodynamic-size or light-scattering distributions.

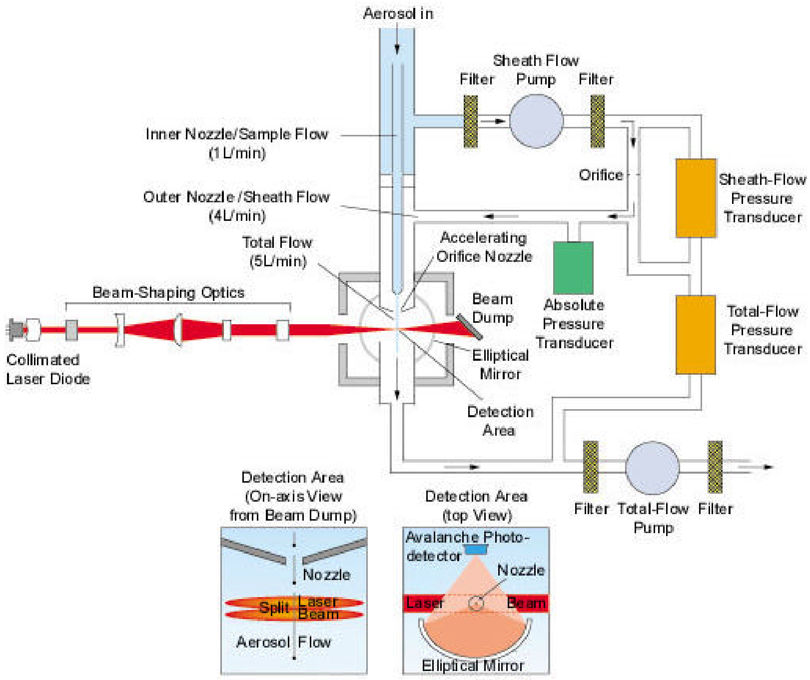

Fig.11: Sketch of the UOPC Model 3320 (TSI)

Field-applications of OPC:
Applications where optical particle counting and sizing would typically include those cases when only a small quantity of sample is available, identification of trace amounts of contamination, the analysis of mixed particle systems, and when an exact end point is required.
State authorities and industry's alike can use particle sizing techniques for the following applications:

Abrasives - Absorption and adsorption of heavy metal vapor; on the other hand, polishing and lapping compounds must be produced to very strict tolerances. Too many large particles can produce surface defects in the polishing process; e.g. in the reduction of corrosion and fouling of the gas turbine blades or the surfaces of the heat exchangers in the boiler furnaces.

Powder sizing - powder production and surface coating process (sintering); there is an optimum particle size for toners and powders, too large and image quality will degrade, too small will effect transfer properties and will clog equipment and degrade image quality or homogeneity of the coating layer respectively. Particle count data can identify excessive amounts of either large or small particles.

Biological application - counting of cells is a common task, sizing information enables checks to be made to ensure that the correct particles are counted. Applications would include evaluating effect of pesticides, food additives, drug development, cell cultures, yeast viability, etc.

Biohazard detection - in military applications, biological warfare relies heavily on particle counters to monitor the spread and effectiveness of the modified bacterial and viral strains.

Polymers - the production of materials to high tolerances for large scale industrial applications; e.g. chromatography column packing, electronic displays, etc. rely on particle counters whenever surfaces are coated.

Workplace monitoring - in a corn or grain mill, for example, the dust (flour) concentration requires strict monitoring. Likewise in the wood industry; processing and manipulation of wood products may lead to a substantial dust freight in the ambient air of the workplace. The field measurements show that the instrument enables a more comprehensive and more realistic characterization of the individual dust burden of workers exposed to health-endangering aerosol concentrations than was previously possible.

Spray technology - to boost combustion efficiencies in the motor industry, nebulization is crucial to optimize the allover efficiency in the turnover of the fuel input and the output obtained as work; other applications regard the performance evaluations i.e. not only are alternative means of aerosol generators studied but can also be referred to existing particle generators as used in measurement equipment (e.g. electrothermal AAS, nebulizers in ICPs, etc).

Filter and air-cleaner testing - contamination control and fluid clarification are key processes in a wide range of industries including the pharmaceutical, food and drink manufacture, biotechnological GM-production, semi-conductors, chemicals, hydraulics and aerospace applications where small particles and trace quantities of contamination must be removed from ultra-high purity process streams which rely on highly efficient filtration systems.

Indoor air-quality monitoring - cleanroom design and micro-contamination control in semiconductor and micro-machine industries, as well as optical and ceramic materials processing The OPC has two basic functions in the cleanroom. The first is to certify the cleanroom to meet standards. The second function is to support a quality maintenance program in the cleanroom. The goal is to eliminate "killer defect" particles which can destroy product yield.

Ambient air monitoring - examples of the applications in environmental protection and monitoring involves the control of generation and removal of particulate pollutants (PM_1, $PM_{2.5}$, PM_{10}, etc.) contained in the air. Especially soot sampling enables precise allocation, correlation, and removal of diesel emission. Gaseous pollutants like SO_X, NO_X, PAH, PCDD, PCDF, etc. readily adsorb on particulate matter by increasing the potential toxic effects of the aerosols in ambient air.

Atmospheric research - heterogeneous processes on stratospheric aerosols and polar stratospheric clouds (PSC) play an important role in the activation and passivation of reservoir gases such as $ClONO_2$, HCl, $BrONO_2$, HBr and N_2O_5. Knowledge of the growth of aerosol particles and their phase transitions upon cooling as well as their influence on the chemistry of the polar stratosphere are important for an improved understanding of these stratospheric processes.

Drug delivery studies - medical inhalation therapies often encounter restricted efficiency in supplying an aerosol to the target tissue in the lungs. Usually therapeutic aerosols are deposited far off the intended site; till now, medical staff just counteracted this problem by increasing the dose rather than the aerosol properties.

Inhalation toxicology - distribution studies of monodisperse aerosols within the respiratory tract, enhance the understanding and allow predictions to be made of the inhalation of toxic polydisperse particles.

Characterization of test aerosols used in particle instrument calibration - UOPCs are used for the calibration of conventional OPCs.

Basic research - in basic aerosol science UOPCs are used to study the generation, distribution, and deposition of suspended particulate matter.

Conclusion:
Simple OPCs are powerful tools to monitor aerosol concentrations in terms of particles per cubic meter [pt/m^3]. As their lower detection range is somewhat restricted by the wavelength of the laser source used, the more complex UOPCs are capable of detecting particles as small as 20 nm. As UOPCs employ condensation chambers to count particles, additional equipment is needed to size the particle according to its aerodynamic diameter.
Sensitivity is a problem in any OPC; sensitivity fluctuates considerably along the detection spectrum of each particle counter and are quite poor in the smaller particle size class (Rayleigh- and Mie-region) compared to the larger size class (Geometric region).
Vertical interaction of particles can not be discriminated when talking about coincidence in OPC, while electrostatic classifiers may easily detect them.
Stability must be considered at least as important as sensitivity. It is extremely important that the counter maintain its calibration over the long term, otherwise, particle concentration baselines become meaningless.
Instead of an absolute particle sizer and counter, the OPC can be used more effectively as an early warning trend indicator or burst detector. This will allow authorities and production quality supervisors to shut down or interfere with a process if the concentration level or parameters exceeds a preset threshold. Thus the OPC can function both as a process tool in quality assurance program and as an environmental tool in public health services.

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