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Environmental Nanoparticles – Exploring the links between Vehicle Emissions and Ambient Air

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NANOPARTICLES IN THE ATMOSPHERE: SOURCES, COMPOSITION, LIFETIMES AND HEALTH EFFECTS

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ABSTRACT

Current air quality policies for particulate matter are focussed on the PM_{10} size fraction covering all particles smaller than 10 µm aerodynamic diameter. The United States has introduced an additional air quality standard for $PM_{2.5}$ (the so-called fine particle fraction) and the European Union is considering setting a limit value and population exposure reduction targets for $PM_{2.5}$. Much recent attention has focussed on even smaller size fractions of particles: the ultrafine fraction (normally taken as less than 0.1 µm diameter), and the nanoparticle fraction widely considered as particles less than 0.05 µm diameter, although there is no universally agreed definition. This talk will consider the sources of atmospheric nanoparticles including both primary emissions and formation of secondary particles. Primary emissions are dominated by emissions from road traffic and these are likely to dominate the particle number count, although not necessarily the particle mass, within urban areas. It is demonstrated that a large proportion of nanoparticles in engine exhaust form by condensation of semi-volatile vapours during the dilution of the exhaust gases with colder ambient air. Such processes were initially observed in the laboratory but have been shown to occur within the atmosphere. Subsequent evolution of nanoparticle size distributions is considered. *In vitro* toxicological testing and work with some animal models has tended to suggest that particles become more toxic per unit mass as they become smaller. However, the ultrafine and nanoparticle fractions of airborne particle matter represent only a very small proportion of the mass of particles, and their contribution to the adverse effects of PM_{10} exposure is currently not clearly known.

PROSPECTS FOR VEHICLE LEGISLATION AND THE PMP PROGRAMME

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ABSTRACT

Within the UN-ECE forum, the Governments of France, Germany, Japan, the Netherlands, Sweden, Switzerland plus the United Kingdom as Chairman, agreed to a collaborative programme aimed at developing measurement systems by which ultrafine particles could be controlled in a regulatory framework. The eventual outcome would be a system, or systems, that would replace or complement the existing gravimetric method of particulate filter mass measurement. The Particle Measurement Programme (PMP) workgroup developed a tri-phased approach to complete this work.

In Phases 1 and 2 of the programme, a wide range of measurement instruments and sampling systems were assessed over standard regulatory tests: in Phase 1, measurement systems addressing particle properties including mass, number, active surface and chemistry were evaluated along with dilution methods, sample conditioning and cost and logistical aspects. Phase 2 subjected the best performing systems to more rigorous evaluations, and as an outcome recommended two measurement systems:

- A gravimetric method based broadly upon that proposed for the US for 2007 type approvals. This offers significant improvements in repeatability compared to the current European filter method
- A particle number method using a Condensation Particle Counter and sample pre-conditioning to eliminate the volatile particles which may contribute significantly to variability. This system proved to be robust to different engines and exhaust chemistries and in Phase 2 showed better repeatability than the modified gravimetric method on two heavy-duty Diesel engines.

In PMP Phase 3: the inter-laboratory correlation exercise managed by JRC, a repeated set of measurements is underway across several European laboratories, with a ‘Golden Particle Number Measurement System’, and a ‘Golden Vehicle’ transported from laboratory to laboratory. The ‘Golden Vehicle’ is a Euro IV compliant, DPF equipped Diesel vehicle. Strict calibration and validation exercises are included to ensure the optimal performance of the Golden Measurement System and determine the real requirements for these exercises in a regulatory environment. The modified particulate mass measurement system is also being evaluated. Preliminary results show that the number method is approximately 20 times more sensitive than the revised mass method, but that both are capable of enabling discrimination between Diesel vehicles equipped with particle filters and those without.

UK AMBIENT NANOPARTICLE MEASUREMENTS

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ABSTRACT

Particle number concentration data are reported from a total of eight urban site locations in the United Kingdom. Of these, six are central urban background sites, whilst one is an urban street canyon (Marylebone Road), and another is influenced by both a motorway and a steelworks (Port Talbot). Highest concentrations are at the Marylebone Road site with lowest at the Port Talbot site, with the central urban background locations lying somewhere between with concentrations typically around 20,000 cm^{-3}, with a seasonal pattern affecting all sites with highest concentrations in the winter months and lowest in the summer. Data from all sites show a diurnal variation with a morning rush hour peak typical of an anthropogenic pollutant. Hourly particle number concentrations are generally only weakly correlated to NO_x and PM_{10}, the former showing a slightly closer relationship. At the Port Talbot site different diurnal patterns are seen for particle number count and PM_{10} influenced by emissions from road traffic (particle number count) and the steelworks (PM_{10}) and local meteorological factors. At the Birmingham Centre site the directionality of particle number concentrations can be associated with local transport sources. At the London Marylebone Road site there is high directionality driven by the air circulation in the street canyon which is similar across the range of nanoparticle sizes.

NANOPARTICLE MEASUREMENTS AND INTERCOMPARISONS IN EUROPE

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ABSTRACT

This presentation will first summarise the existing measurement techniques for nanoparticles (1 nm < Dp < 100 nm). Then, particular attention will be directed towards electromobility measurements as a technique suitable for monitoring particle number concentration and size distributions (< 1 µm) under field conditions. Results from a recent intercomparison workshop illustrate how particle size spectrometers of different design perform for a variety of laboratory-generated and environmental test aerosols. A further section of the presentation will be dedicated to the statistical and meteorological evaluation of long-term particle size distribution data sets obtained from ambient aerosols in Europe. Very recent results from a multiple site study in Leipzig using a number of up to 8 concurrent measurements demonstrate the usefulness of electromobility measurements to determine spatio-temporal characteristics of ambient aerosols (3-900 nm) within a city. Finally more specialised techniques building upon electromobility analysis will be briefly outlined, notably hygroscopicity and volatility analysis and their first applications in environmental monitoring.

COMPOSITION AND BEHAVIOUR OF NANOPARTICLES

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ABSTRACT

The composition of atmospheric nanoparticles is poorly known. Whilst sizing of particles below 100 nm presents few difficulties, ambient composition determination is more challenging.

Current methods of direct composition determination are pushed to their limits by both sampling and detection considerations. Offline collection techniques include impaction / filtration and thermophoretic or electrophoretic collection. The usefulness of such techniques is limited due to the very low masses of material and the resulting requirement to sample for extended periods.

Recent development of online techniques has shown promise for particles larger than around 40 nm diameter, with quantitative component mass loadings, particle density and shape becoming accessible. Such techniques have not been widely deployed for nanoparticle investigation. Furthermore, for particles much smaller than this, particle focussing and detection is currently difficult.

There are several techniques which have been used to probe physical properties of particles which are directly dependent on their composition. Use of such derived properties may be used to infer the behaviour of the ultrafine and nanoscale particle behaviour.

The relatively few measurements of ambient nanoparticle composition will be presented from a range of locations alongside derived property measurements. A tentative description of the composition of the ambient combustion-derived particle population as it dilutes into the background air will be attempted from this composite picture.

Finally, a brief survey of promising selected techniques from the laboratory will be presented to help identify candidates for future compositional analysis of atmospheric nanoparticles.

CALIBRATION ISSUES

Ian Marshall
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ABSTRACT

Not Received

RECENT DEVELOPMENTS IN THE PHYSICAL CHARACTERISATION OF ULTRA FINE PARTICLES

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ABSTRACT

The importance of ultra fine particles has been driven by the development of materials with novel physico-chemical properties engendered by their very small particle size. Developments in internal engine combustion efficiency actually increased the number of particle emitted from engines, whilst more recent after treatments have been developed to reduce such emissions. Concerns about the potential health effects, both local and systemic, potentiated by the inhalation of ultra fine particles in environmental has significantly increased our need for instrumentation capable of reliably measuring (or monitoring) the physical properties of particles with sizes ranging down from, say, 800 nm to; “Well, as small as you can” is often the criterion we are given, but certainly below 10 nm.

This presentation will describe the measurement techniques that have been developed to characterize various ultra fine aerosol (and particle) parameters, including number concentration, and particle size distribution and how to monitor both these parameters as they vary with time. The physical behaviour of particles that are smaller than say 500 nm begins to be dominated by their diffusional rather than their inertial properties which mitigates against traditional techniques such as cascade impaction. The amount of light scattered by such small particles also reduces precipitously, again limiting the viability of basic optical techniques. This presentation will describe condensation particle counting (CPC) techniques as well as diffusional mobility analysis of particle size using Scanning Mobility Particle Sizing (SMPS®), in both time weighted and real time modes. Examples of practical applications of these techniques will be described, together with their relevance to the most recent pressures and concerns associated with ultra fine particles.

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WORLD’S FASTEST AEROSOL SPECTROMETER APPLIED TO AUTOMOTIVE AND ENVIRONMENTAL PM

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ABSTRACT

A new technique for transient aerosol measurement is described. The technique is based on the electrical mobility classification of a diffusion charged aerosol – giving size classification for particles from 5 to 1000nm.

A technique for sampling aerosol directly from an internal combustion engine exhaust without using a CVS dilution tunnel is described and data is presented showing transient measurements of the exhaust aerosol from a modern light duty Diesel engine – both upstream and downstream of a Diesel Particulate Filter (DPF). A technique is described for evaluating the transient efficiency of the filter. Extension of the technique for estimating particulate mass is discussed.

Transient roadside aerosols from Diesel and gasoline traffic are also presented. A steady road side aerosol is used to compare the output of the DMS500 fast aerosol spectrometer to other spectral aerosol instrumentation (SMPS and ELPI).

Transient aerosol spectra from other environmental sources are presented including:

- Gas turbine aero engine exhaust
- Medical Inhaler
- Emissions from welding and grinding
- Cigarette aerosol

FROM A FEW ANGSTROM UPWARDS – A NEW TYPE OF SMPS+E

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ABSTRACT

In the recent years small particles and nucleation of new particles (Aitken mode) became more into the focus of atmospheric aerosol research. Therefore also the development of new techniques and instrumentation has been increased.

Up to now mainly sensitive Condensation Particle Counters (CPC) are used for the range down to a few nanometre. The main disadvantages of CPCs are:

1. limitation to a d50 cut-off as 2 to 5 nm
2. a relatively slow response time
3. due to the operation principle of nucleus condensation a defined temperature difference and a condensation liquid and supply is required

An alternative to the condensation particle counting is the direct counting of charged particles (or ions) by electrometers. Faraday Cup Electrometer (FCE), require no liquids and supply, no optical and laser parts and are theoretical not limited in the particle size. The only limitation is given by the number of charged particles and the necessity to combine it with a Differential Mobility Analyser (DMA) to cut out adequate charged particles.

The presented new GRIMM FCE 5.700 is highly sensitive to low concentration but on the other side robust enough to mechanical shocks and pressure fluctuations.

The FCE in combination with the GRIMM Nano S-DMA (a Vienna type DMA), which is able to measure even below 1 nm, is the proper solution for nucleation measurements. With this system it is possible to measure already bigger ion clusters around 0.8 nm and up to about 50 nm [1].

There are three important advantages of this system:

1. The DMA has an active length of just 15 mm, short inlet distances and avoids electrical fields at the isolator section. This leads to comparatively low losses of fine particles.
2. The FCE has a sensitivity down to ~ 0.1 fA (1 Hz, ~ 7 charged particles/ccm at 5 lpm), an automatic zero point adjustment, changeable concentration ranges and sheath airflow to reduce the humidity.
3. The connection of both devices is very simple. The DMA outlet is directly connected with the FCE inlet. The DMA is directly screwed into the FCE inlet section, so that the classified particles are directly introduced to the FCE. The distance to the FCE filter is less than 20 mm, which also leads to a reduced particle loss.

The nano-DMA is a short version of the new Vienna Type DMA 5.500 of GRIMM, which allows flexible length combinations by an easy alteration [2].

Both units are controlled and supplied by a separate DMA-controller. This controller supplies the system with sheath air (5 to 20 l/min) and sample air (1 to 5 l/min), controls the high-voltage power supply for the DMA and has a data acquisition system and interface integrated.

LITERATURE

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[2] Reischl, G. P., Mäkelä, J. M. and Necid, J. *"Performance of Vienna Type DMA at 1.2 - 20 Nanometer" Aerosol Sci. and Technol., Vol. 27, pp. 651 - 672 (1997).*

GENERATION OF CHARACTERISED SOOT PARTICLES

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ABSTRACT

Soot particles are considered as an air pollutant with adverse health effects. The controlling of the particulate pollution is of great importance in regard of the varying characteristics of soot particles in dependence of combustion techniques and the exhaust subsequent treatment techniques.

A combustion aerosol standard (CAST) has been developed to generate submicron soot particle with adjustable and reproducible characteristics. The CAST is designed for following applications: 1) research of soot characteristics, 2) calibration of particle measuring instruments, 3) investigation of soot emissions with regard to the fuel type (gaseous and liquid fuel), 4) improvement of soot reduction techniques with e.g. additives, and 5) filter testing.

Using the CAST techniques, defined soot particles are formed within a well controlled flame. After leaving the combustion chamber, soot particles are subsequently mixed with a quenching gas in order to prevent further combustion processes in the particle stream and to stabilize the soot particles. The quenching inhibits the condensation of water in the particle stream at ambient air condition. To dilute the particle stream, compressed air is supplied to the quenched particle stream. The characteristics of soot particles from CAST can be adjusted and reproduced using corresponding reproducible operation parameters. The particle size can be varied within a range from 20 – 300 nm. The particle concentration reaches the level of 10^7particle/cm^3 and can be diluted using particle dilutor. The ratio of the elementary to organic carbon (EC/OC) of the soot can be varied as well in order to produce soot standard with defined EC/OC-ratio. The CAST burner can be designed with different size in order to produce exhaust gases from 2 up to over 2000 L/min.

Beside the CAST burner for gaseous fuel, a further burner has been developed for liquid fuel (diesel, gasoline, kerosene etc.). This one gives the possibility to investigate soot emissions and soot reduction (e.g. using additive) directly with the fuel concerned and with small operation expenditure. The experiments have been performed with propane and diesel. The evaluation of the performance of the CAST burner has been focused on the following targets: characterization of the particle size and number concentration using SMPS, coulometric analysis of the chemical composition of soot to learn the content of elementary and organic carbon, and overall stability and reproducibility of operation.