

FAST RESPONSE CLASSIFICATION OF FINE AEROSOLS WITH A DIFFERENTIAL MOBILITY SPECTROMETER.

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Summary

The development of a Differential Mobility Spectrometer for measurement of fast changing fine aerosol spectra, and application of it to automotive diesel engine particulate emissions during a drive cycle are presented. The instrument simultaneously measures in 26 size ranges classified on the basis of electrical mobility following unipolar diffusion charging, which limits anomalies due to particle composition and density. Optimisation of the design and operating conditions allows resolution of the particle size spectrum from approximately ten nanometres to several hundred nanometres with a time response of less than 200ms. This allows clear distinction of the nucleation and accumulation modes in the engine exhaust measurements, and detection of aerosol emission events of less than 500ms associated with transient events in the engine operation.

Introduction

The measurement of particulate emissions from internal combustion engines has predominantly been by gravimetric filter methods. Modern engine technology and concern about their health implications makes information about the instantaneous size spectrum of sub-micron particulate valuable. These aerosols range up to a few hundred microns in size and may vary with the engine conditions on a substantially sub-second timescale.

The size distribution of sub-micron aerosols is commonly measured with the Scanning Mobility Particle Sizer (SMPS). This instrument, comprising a bipolar diffusion charger, Differential Mobility Analyser (DMA) and Condensation Particle Counter (CPC) scans the particle size range: measuring the full spectrum in the order of a minute. This makes it inapplicable to transient engine conditions. The Electrostatic Low Pressure Impactor covers the size range of interest with a time response of the order of one second, but because it classifies on the basis of inertial impaction, requires significant density corrections to be made in order to correlate with the SMPS. Furthermore, inherent small particle losses restrict the minimum particle size to around 30nm.

Other concepts to deliver real time fine particle spectrum measurement have been reported. Lenz demonstrated multiple parallel DMA + CPCs but this is expensive for many size classes. Tammet (1998) describes the Electrical Aerosol Spectrometer, consisting of two classifiers similar to that of the DMS described below, the sample flow in one being unipolar diffusion charged and in the other field charged. This covers a wide size range with a faster time response than scanning instruments. Graskow (2001) demonstrated a Fast Aerosol Spectrometer which comprised a short DMS type classifier with photo-electric charging. This instrument showed a time response better than 100ms, but was restricted to a narrow size range of very small particles, below approximately 50nm. The photoelectric charging is very sensitive to the composition of the aerosol particles.

The aim of this development is particle spectrum resolution from 10nm to several hundred nm, covering the nucleation and accumulation modes in an internal combustion engine exhaust. Time response of approximately 200ms is desired. Insensitivity to particle composition is required, but the sensitivity is not as critical as for instruments aimed at atmospheric measurements.

Design of the Differential Mobility Spectrometer (DMS).

The classifier of the DMS is similar in concept to the well known cylindrical DMA, and is shown in Figure 1. A flow of charged sample aerosol is introduced in the centre of one end of a long

annular channel with a several times larger flow of clean sheath air at a matched velocity flowing outside it: the reverse of the standard DMA arrangement. A strong electric field, created between a high voltage on an electrode mounted on the inner wall of the channel and a number of electrodes mounted all along the outer walls, causes the charged particles in the sample aerosol to drift across the flow with a radial velocity component dependent on their electrical mobility. The outer electrodes collect the charged particles at an axial location depending on their radial velocity and hence mobility. Electrometers connected to these electrodes measure currents corresponding to the concentration of particles of a given mobility which is related to the particle size.

The differences in the operation of this instrument and the bipolar charged SMPS are explained with reference to Figure 2. The mobility of particles as a function of their diameter, d_p , follows Stokes' law, $\propto d_p^{-1}$ at diameters greater than the mean free path, λ , of the gas ($\eta = \text{viscosity}$):

$$\text{mobility} = \frac{1}{3\pi\eta \cdot d_p} \cdot C_c \qquad C_c = 1 + \frac{\lambda}{d_p} \left[2.34 + 1.05 \exp\left(-0.39 \frac{d_p}{\lambda}\right) \right]$$

For smaller particles the empirical correction factor, C_c , must be applied (Hinds, 1999) which approaches a d_p^{-2} dependence for small particles. Therefore the overall mobility range covering the required range of particle diameters is approximately three orders of magnitude, which would be very difficult to usefully resolve in a single column if all particles were singly charged (as predominates in bipolar diffusion charging). Unipolar diffusion charging can apply much higher levels of charge to large particles: the dotted line shows the approximate dependence of the mean charge, according to the correlation from Hinds (1999). This leads to a smaller range of electrical mobility, Z_p , the heavy line, on which the column classification is based. For small particles, the mean charge is fractional, corresponding to various proportions of singly charged and uncharged particles, but only those charged are detected, so the relevant electrical mobility is based on single charging in this range. Above $d_p \sim \lambda$, the dependence on d_p of mobility and mean charge tend to cancel out and size classification on this basis is no longer possible; for the largest particles, in a practical charger field charging will tend to dominate, and the electrical mobility dependence on d_p is reversed. In order to increase the maximum size limit of the instrument, it is necessary to delay these effects by increasing the mean free path, ie. reducing the column operating pressure below ambient.

The required gradient in the $d_p:Z_p$ relationship for size classification depends on the other factors which blur the instrument response. For large particles, the dominant factor is the probabilistic distribution of charging. With this distribution modelled by a similar method to Adachi et al (1985), and the correlations for particle mobility above, the mobility distributions for particles of sizes spaced at 4/decade, can be plotted: Figure 3. The area of the points is proportional to the probability of a number of charges and corresponding Z_p . At 1 bar, and a relatively low charger ion density \cdot residence time product, $N_i \cdot t$, different particle sizes above 200nm can clearly not be resolved. By reducing the pressure, the flattening of this graph is delayed, and by increasing charger $N_i \cdot t$ the relative spread in the distributions is reduced, to achieve good resolution as far as 1 μm .

Time response vs Sensitivity Trade-offs.

The operating pressure is thus set by the size resolution requirement. Increased $N_i \cdot t$ improves both size resolution and sensitivity, as it leads to an increase in the mean charge on the particles and hence current measured per particle collected. The charger should therefore clearly be designed to maximise the ion density, N_i , but the residence time is limited by the desired time response. Both to reduce this and to limit the variability in $N_i \cdot t$, the charger should be designed for close to plug flow for the sample gas. The maximum attainable $N_i \cdot t$ and required operating pressure fix the

electrical mobility range which the instrument must classify.

For all similar columns which classify this range, the non-dimensional group:

$$\frac{Z_p \cdot E \cdot \text{classifier diameter} \cdot \text{classifier length}}{\text{volumetric flow rate}} = \text{constant} \quad \Rightarrow \quad \text{transit time} \propto \frac{Z_p \cdot E}{\text{classifier diameter}}$$

The ratio of length to the diameter of the column is unlikely to have a strong effect on the performance provided it remains large. The sensitivity of the instrument is proportional to the flow of aerosol: it is clear that a strong classifier electric field, E , and long column is optimal for sensitivity: these are limited by electrical breakdown and practical considerations. Since time response can be assumed to scale with transit time, selection of column diameter trades off between time response and sensitivity.

For a practical charger, a column length of 660mm, operating at 10kV gives a transit time of approximately 1s (the transit can be corrected for), and this is then expected to be consistent with the desired time response of 200ms.

Diesel Engine Exhaust Spectrum Measurements.

The DMS described here has been constructed and tested on a number of automotive exhaust aerosols. These results are from a 1.8l direct injection diesel engine, with the sample drawn from the Constant Volume Sampling (CVS) dilution tunnel.

Figure 4 shows the aerosol spectrum resolved by the instrument the size range covered is up to 400nm. At this cold deceleration condition, nucleation and accumulation modes are clearly visible. Figure 5 shows the variation of two size classes, the peaks of these two modes, over time during the first 200s of a standard emissions drivecycle. Transients on the timescale of approximately 500ms are clearly distinguished: this response is limited by the CVS system: the time response of the instrument itself is measured at approximately 200ms.

Conclusions and Further Work.

The Differential Mobility Spectrometer concept based on a unipolar diffusion charger and a column similar to a DMA but containing a number of detection electrodes and operating at sub-ambient pressure is described.

A number of modelling techniques have been used to optimise the parameters of the instrument giving a size range covering approximately 10nm to 400nm and time response of 200ms.

Further optimisation of the charging process is likely to extend the size range from 5nm to 1000nm.

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References

- M.Adachi, Y.Kousake, K. Okuyama, 'Unipolar and bipolar diffusion charging of ultrafine aerosol particles.' J. Aerosol Sci. 16 (1985) 109-123
- B.Graskow, 'Design and development of a fast aerosol size spectrometer' PhD thesis, University of Cambridge Department of Engineering, 2001.
- W.C.Hinds, 'Aerosol Technology' 2nd Ed, J Wiley 1999.
- H.Tammet, A.Mirme, E.Tamm 'Electrical aerosol spectrometer of Tartu University.' J. Aerosol Sci. 29 (1998), S427-S428.

