Determination of Real-Time Particulate Size Spectra and Emission Parameters with a Differential Mobility Spectrometer

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The Differential Mobility Spectrometer is designed to continuously measure the size spectra of aerosols, especially engine exhaust particulates. Measurement of the whole particle size spectrum without assumptions of the form of the size distribution allows identification of multimode spectra (such as simultaneous nucleation and accumulation modes) and calculation of total emissions with any desired size weighting. This paper largely concerns the modelling and performance of the instrument and the effect on alternative spectral weightings.

The Differential Mobility Spectrometer evolved from the Fast Aerosol Spectrometer described by Graskow and Collings [1],[2]. Size classification is by electrical mobility similar to a DMA or SMPS. As shown in slide 3, the classifier is similar to an 'inside out' DMA: the sample aerosol is charged and introduced to the centre of an annular column, surrounded by a clean sheath flow. An electric field generated by a central high voltage electrode causes the particles to drift radially and they are collected on an array of electrodes along the outer wall of the column. The currents due to the charged particles are measured by electrometers, indicating the particle size spectrum in real time. Compared with the earlier FAS, the DMS uses unipolar diffusion charging, a longer classifier and improved electronics to increase the maximum particle size from 60nm to 1000nm, eliminate sensitivity to particle surface composition, and improve sensitivity. With a lower limit of around 5nm this covers the full range of nucleation and accumulation mode exhaust particles. The prototype instrument is shown on slide 4: it also incorporates real time calculation of the particle size spectrum from the raw currents. Engine emissions measurements with this prototype will be presented in ref [3].

Slide 5 shows the classification principle of the DMS: the mean charge per particle (on the left hand log scale) and mobility and electrical mobility (on an arbitrary log scale) are plotted against a logarithmic scale of particle diameter, with grid lines at decades. The size range of interest, from around 5-1000nm, gives a mobility range of around 4½ orders of magnitude: instruments operating with predominantly singly charged particles (such as the FAS and the SMPS over most of its range), must cover such a range of electrical mobilities which is impractical for simultaneous classification in a single column.

Unipolar diffusion charging places a much greater charge on the larger particles, reducing the range of electrical mobility. The approximate mean diffusion charge is proportional to d^2 for smaller particles and close to d^1 for larger ones, but, because only charged particles are detected in the classifier, the charge is effectively constant at 1 for small particles. The charging characteristic combined with the change from free-molecular to continuum drift behaviour causes a flattening in the electrical mobility vs d_p which limits the maximum particle size: optimisation of the charging process and classification pressure extend this limit to beyond 1μm in the current prototype. For the largest particles, field charging is difficult to avoid and this causes an inversion in the mobility relationship, therefore these particles are excluded from the classifier with an upstream impactor stage.

Along with time response and sensitivity requirements, the size resolution of the instrument is important for measurement of exhaust particulates. This is most easily quantified as the closest separation in size between two monodispersed aerosols which are still resolved as distinct peaks by the instrument. Over the wide size range of this instrument a logarithmic metric is appropriate. A resolution of ¼ decade, equivalent to a ratio in diameter of approximately 1.8, allows discrimination of the nucleation and accumulation modes. To support this resolution, the output spectrum must be discretised in steps no more than half as far apart; over the 5-1000nm size range, this requires at least 20 elements, although more are preferred to reduce errors in classification caused by quantisation of the spectrum: the prototype outputs the spectral density at 32 sizes.

In the DMS, the response to a given particle size will be spread over a number of electrometer detectors by several factors listed in Slide 7. Amongst continuous measuring instruments, one of the advantages of the DMS concept is the relative ease of providing many detector stages to minimise this source of smearing: the prototype has 22 detectors. Diffusion of particles in the classification column is relatively less significant for a DMS compared with conventional DMAs as the most diffusive small particles are detected at the start of the column.

In order to optimise the design of the instrument, it is necessary to model the overall spectral broadening. This can be considered as the convolution of the various effects, but this calculation is not convenient as some of the factors are substantially non-gaussian in their distribution and classification is a non-linear function of particle size. Therefore, a Monte-Carlo model, implemented in Matlab, and shown schematically in Slide 8 is adopted. This model combines calculations of the processes of charging and classification with random assignment of the

factors responsible for response broadening. Calculation of the full particle charge distribution function (as opposed to just a correlation for mean charge) is required: this is similar to Adachi et al [4]. The classifier is modelled with established relations for particle mobility. The model incorporates random assignment of particle size (for non-monodispersed aerosols), charger Ni· t (ion density· residence time product), particle charge, classifier introduction radius, manufacturing tolerances, and diffusive displacements in axial and radial directions. Modelled electrometer currents are accumulated over approximately 1000 iterations of the model in a few seconds which yields a stable output.

When run over the whole range of particle sizes, the model yields a transfer function, shown in Slide 9 for the prototype, which relates the steady input particle spectrum to the output currents. This is possible because the behaviour of the instrument is stationary and linear to superposition of particle spectra. Experimental measurement of this function in such detail would not be practical but verification can be performed at a variety of particle diameters. The features visible in the transfer function around 50nm are associated with the transition from single to multiple charges per particle: the data processing algorithm is designed to avoid unwanted artefacts in the output caused by this effect.

The resolution is calculated from the instrument transfer function by considering the output produced by a monodispersed spectrum and producing an estimate of the spectrum with the intended data processing. The modelled response to such aerosols spaced at four / decade (5.6nm, 10nm....1um) are shown in Slide 10. The resolution, twice the standard deviation of the estimated distributions, is plotted below and is in the region of 0.15 to 0.2 decades over the size range except for the range affected by the transition to multiple charging.

Reweighting the number spectrum allows calculation of other total emissions metrics such as total length or surface area which may be relevant to health effects and future emissions standards, or mass which is valuable for correlation with current measurements. Slide 12 shows the effect of different weightings on cumulative mass emissions measured with the DMS from a 2.2l passenger car diesel engine over the NEDC cycle. The total number measurement clearly indicates a different relative significance of the urban (<800s) and extra-urban (>800s) phases compared with alternative mass weightings. The d_p^3 is based on a spherical assumption for the particles whereas $d_p^{2.4}$ is suggested by Kittelson et al [5] due to the fractal-like behaviour of accumulation mode particles. Over this test, the difference between these two is small as the particle diameter is quite stable.

The broadening of estimated particle size distributions due to finite size resolution of the instrument affects the accuracy of reweighted statistics as shown in Slide 13. For example, a 60nm aerosol with $\sigma_g = 1.2$ (mass median diameter = 66nm) may be resolved with the same diameter but $\sigma_g = 1.6$ which has a mass median diameter of 116nm and twice the total mass for the same total number. If the broadening is known, correction of the reweighted statistics would be possible.

Slide 14 shows the spectral broadening produced by the DMS prototype (modelled) with different data processing algorithms. For 60nm geometric mean diameter aerosols with σ_g (gsd) varying from 1.1 to 2.4, the solid lines (left axis) indicate σ_g of the corresponding output spectrum from the instrument after processing. The dashed lines (right axis) show the ratio of this estimated σ_g to the actual input spectrum. The simplest form of data processing, used by some instruments, is to associate the raw signal from each detector or measurement with a particle size range and to build the spectrum up from these 'bins'. The output produced by such a technique is shown by the raw output lines: the estimated spectrum is broadened, about as much as considered in the previous example, leading to significant errors in reweighted statistics without correction.

Estimation of the size spectrum by inverting the transfer function gives a better estimate of the spectrum. This technique is also preferred for the removal of artefacts due to multiple discrete charging of particles. In order for this inversion to be mathematically well-conditioned, some redundancy is required and a least squares technique is used to derive a pseudo-inverse. The results of using this technique are shown by the linear inversion lines: the broadening is substantially reduced, especially for the wider distributions. Further improvement beyond this is possible with the non-linear inversion algorithm shown.

References:

[1] Graskow B, 'Design and development of a fast aerosol size spectrometer'; PhD thesis, University of Cambridge Department of Engineering, 2001.

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[4] Adachi M, Kousake Y, Okuyama K, 'Unipolar and bipolar diffusion charging of ultrafine aerosol particles.'; J. Aerosol Sci. 16 (1985) 109-123

[5] Kittelson D, McMurry P, Park K, Sikurai H, Tobian H, Ziemann P, 'Chemical and Physical Characteristics of Diesel Aerosol'; Presentation to Cambridge Particle Meeting, Cambridge, 23 April 2002.

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Determination of Real-Time Particulate Size Spectra and Emission Parameters with a Differential Mobility Spectrometer

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1. Determination of Real-Time Particulate Size Spectra with a Differential Mobility Spectrometer.

The DMS is designed to continuously measure the size spectrum of particulate emissions from IC engines on transient cycles.

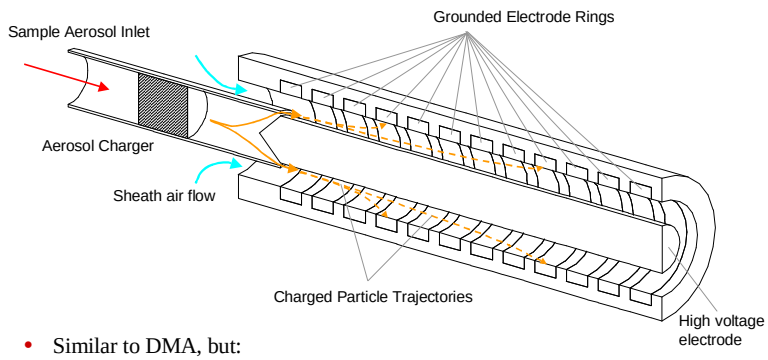
Contents

- Differential Mobility Spectrometer Development
- Prototype Instrument Performance
- Instrument Modelling
- Size Resolution and Spectral Weighting
- Conclusions

2. Contents.

This presentation will briefly discuss the DMS concept and performance of the prototype instrument, and will consider the use of the fully resolved number:size spectrum to estimate total emissions in other weightings, such as mass and surface area.

Differential Mobility Spectrometer.

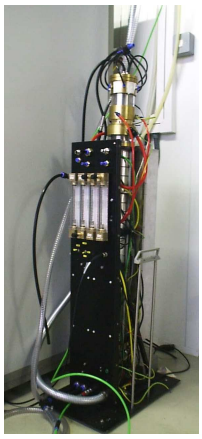


- Similar to DMA, but:
  - Aerosol inlet inside sheath flow
  - Single Monodisperse exit replaced by multiple collection electrodes.
  - Direct electrometer connection instead of aerosol particle counter.

3. DMS Concept.

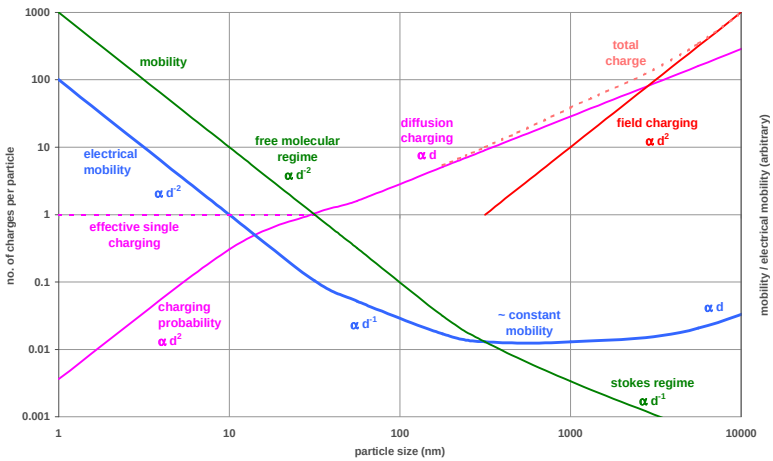
The DMS operates similarly to an 'inside out' DMA: charged particles are introduced into the centre of an annular classifier with a strong radial field, surrounded by a clean sheath flow. The particles drift outwards according to their electrical mobility, and are collected on an array of electrodes on the outer wall connected to electrometers, allowing real time measurement of the whole size spectrum.

DMS Research Progress



- Size range from 5nm to 1000nm
  - operation at 0.25bar
  - multiple charging on large particles to reduce mobility range
- Eliminate sensitivity dependence on particle composition
  - unipolar diffusion charger
- Elimination of transient artefacts
- Data processing to recover particle spectrum from electrometer measurements
  - capable of running in real-time (faster than 10x per second)
- Improved sensitivity
  - increased sample flow
  - improved electronics

Diffusion Charged Classification



Instrument Performance for Engine Exhaust Particulate Measurement

- Time response
  - Sub second response required for measurements on standard test cycles.
  - Prototype achieves sub 0.5s $T_{10\text{-}90}$
  - Target 200ms for future instruments.
- Sensitivity
  - Intended for CVS or raw measurements with Diesel and Gasoline engines and roadside applications.
  - Prototype noise floor ~ $4x10^4$ $dN/dlogd_p$ /cc for 60nm particles: corresponds to approximately $2.5x10^4$ /cc accumulation mode, $1x10^4$ /cc monodispersed
  - Tests show satisfactory measurement of:
    - Diesel (non-trap) and GDI accumulation mode particulates from CVS dilution tunnel
    - Nucleation mode particulates formed by Diesel with particulate trap, in CVS tunnel
    - Roadside measurement of Nucleation and Accumulation modes.
- Size resolution
  - For discrimination of nucleation from accumulation mode particulates.
  - Requires ~ ¼ decade resolution.

4. DMS Progress

The DMS prototype is shown here. Compared with previously reported work, this instrument offers a much wider size range and better sensitivity and transient performance.

The main changes to achieve this are the use of unipolar diffusion charging, improved electronics and a longer classifier.

This prototype also includes software to recreate the particle size spectrum from the electrometer readings in real time.

5. Diffusion Charged Classification

Unipolar diffusion charging applies a substantially multiple charge to larger particles. This reduces the electrical mobility range over the particle size range of interest compared with single or equilibrium charging. This is important for achieving simultaneous classification in a single column.

Beyond a maximum size limit, electrical mobility becomes a positive function of diameter, so these particles must be excluded from the column with an impactor.

6. Required Instrument Performance

The instrument is intended for measurement of engine exhaust particulates, particularly on transient emissions test cycles.

This requires sub-second time response. The sensitivity of the instrument is suitable for measurements either raw or in CVS dilution systems, or for roadside measurements.

Discrimination of the nucleation and accumulation modes requires good size resolution.

Size Resolution

The size resolution of a DMS is dependent on the 'blurring' of the spectrum as it passes through the system. Important mechanisms are:

- Width of diffusion charging pdf.
  - including any distribution in charging Ni.t
- Finite ratio of sample flow: sheath flow in classifier
- Manufacturing tolerances in classifier
- Finite size/number of detector rings
  - analogous to finite time response of DMA/CPC in SMPS
- Brownian diffusion / effect of turbulence in column
- Data processing algorithm

Effect of column transfer function on these distributions is non-linear, so simple convolution in deterministic model is not possible.

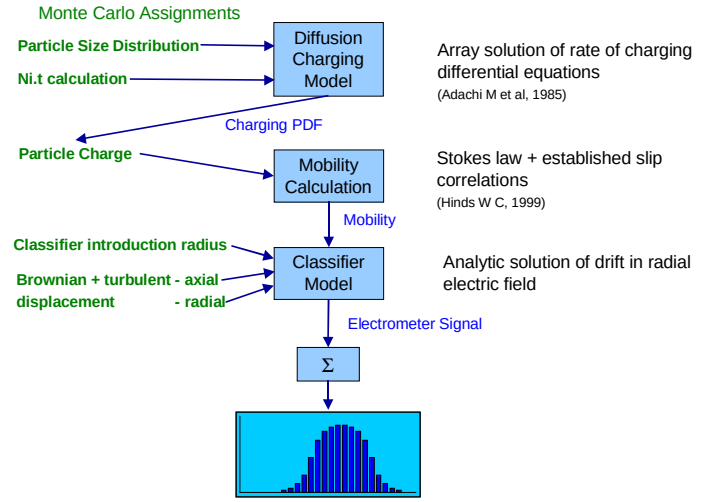
Therefore, Monte-Carlo modelling approach is adopted

7. Size Resolution.

The size resolution of the DMS is a function of a number of factors which blur the response, in terms of distribution of current over the various electrometers, and the processing of those data to recover the particle size spectrum.

In order to assess the blurring and derive the required data processing, all these factors are considered in a Monte-Carlo model of the instrument.

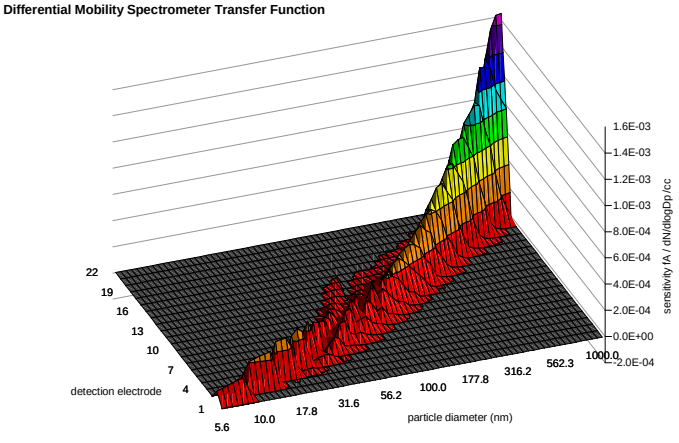
Monte-Carlo Modelling of DMS



8. Monte-Carlo DMS Model

Given a particular particle size, the Monte-Carlo model randomly assigns values to each of the blurring factors, and then predicts the current detected on each electrometer. The currents are accumulated over approximately 1000 runs with the same aerosol parameters but new random assignments to predict the overall response to a given particle size.

Instrument Transfer Function

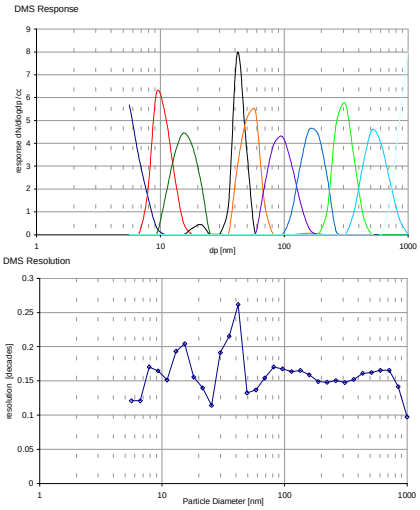


9. Instrument Transfer Function

Running the model over a range of particle sizes yields a matrix which expresses the output current vector as a function of the particle size spectrum discretised into a vector.

This is an instantaneous transfer function (not considering the time domain behaviour).

Differential Mobility Spectrometer Size Resolution



- The response of the whole instrument + inversion algorithm is a function relating elements of the estimated spectrum vector to given sizes in the sample aerosol.
- The response of ten sizes at ¼ decade is plotted here.
- The resolution of the instrument depends on the width of these responses and can be calculated from them.
- For the prototype instrument, this is below ¼ decade over almost the whole size range of interest.

10. DMS Size Resolution

Given the instrument transfer function and the data processing algorithm, the estimated spectrum for given input monodispersed aerosols can be predicted.

As the closest spaced gaussians which show distinct maxima are spaced at 2x standard deviation, this metric on the monodispersed responses is the resolution.

This is estimated between 0.15 and 0.2 decades over most of the size range of the DMS.

Spectral Measurement allows Reweighting

- Ability to reweight spectra allows correlation of different aerosol measurements: number, surface area, mass
- Use of a real-time number based instrument to identify most important phases of a transient cycle for total emissions.

Initial target:

- Develop a cumulative weighting of the number:size spectrum which correlates with total mass measurements

Final goal:

- Calculation of absolute emissions masses from spectral data
  - requires the above plus very accurate calibration of size classification.

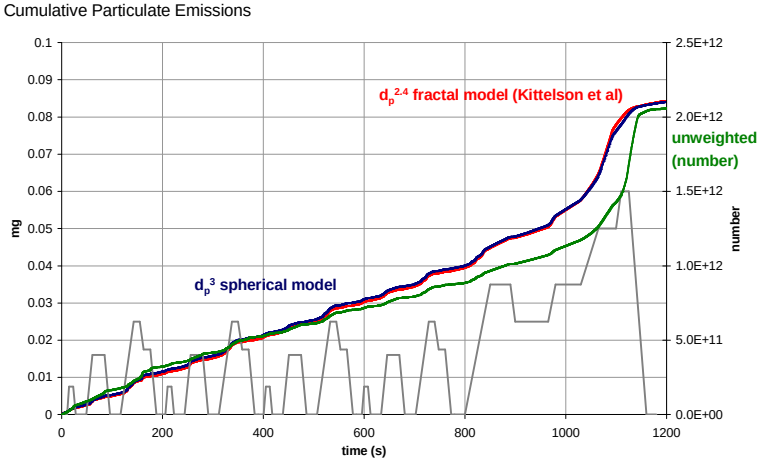
11. Spectral Measurement Allows Reweighting.

The resolution of the whole particle size spectrum rather than just a summary parameter allows the calculation of total emission statistics on any basis, eg. number or area.

Correlation with mass measurements is especially valuable, and work is going on to develop a spectral weighting that allows this.

The fast response instrument can then be used to identify phases of a transient cycle particularly significant for total emission production.

Alternative Spectral Weightings

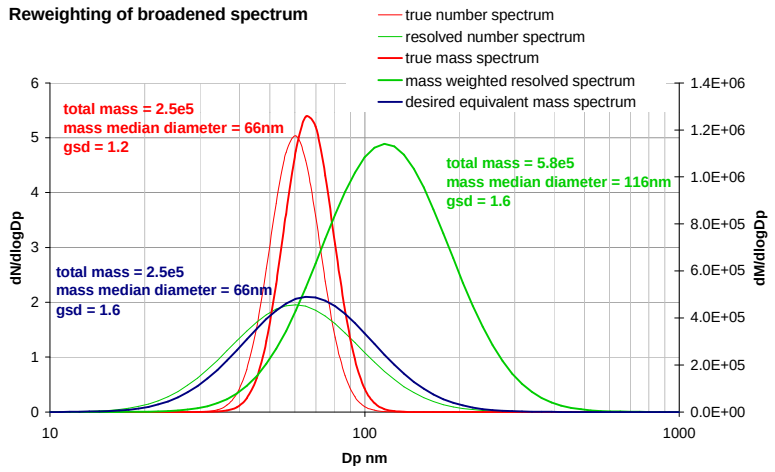


12. Alternative Spectral Weightings.

Plotting the cumulative emissions trajectory over an NEDC test cycle measured with the prototype DMS shows the difference between the total number and two alternatives for a total mass correlation.

The relative significance of the urban and extra-urban phases is substantially different for the alternative bases.

Effect of Spectral Broadening on Alternative Spectral Weightings

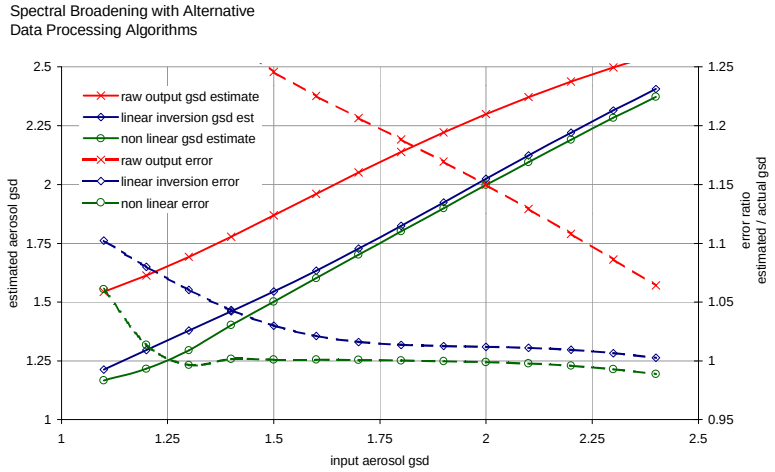


13. Effect of Spectral Broadening on Weightings

If blurring in the instrument broadens the estimated spectrum compared with the actual one, reweighted totals of the estimated spectrum will be in error even if the total number is correct.

The light green line shows a broadened estimate of the light red spectrum: the total number is correct, but when reweighted by mass (heavy lines) the total is more than 2x too high. If reweighting is applied, this effect should be corrected, yielding the blue mass weighted estimate.

Data Processing Effect on Spectral Broadening



14. Data Processing Effect on Spectral Broadening.

This graph shows the effect of alternative data processing algorithms on different widths of 60nm centred spectra resolved by a DMS.

The simplest 'raw output' approach where each electrometer is attributed to a given size range substantially broadens the response. It is better to 'invert' the transfer function to estimate the spectrum: linear and non-linear algorithms for this show substantially less broadening: virtually none on exhaust-like gsd around 1.8.

Conclusions

- A DMS instrument has been built to resolve engine spectra with sub-second response time.
- Modelling shows a resolution of better than 4/decade is possible over a size range from 5nm to 1000nm.
- In calculating alternative spectral weightings from the instrument output, any broadening of spectral features due to finite resolution must be considered if the moments of the size distribution are to be preserved.
- Use of an inversion algorithm as opposed to attributing each detector to a size bin is preferable in order to minimise spectral broadening
- Particulate diameters vary enough during the course of a vehicle emissions test cycle that mass and number emission trajectories differ significantly, however, d_p^3 and $d_p^{2.4}$ mass weightings produce similar results.

15. Conclusions.