



Particulate Mass Measurement with DMS Series Fast Spectrometers

This note describes how new software for the DMS500 & DMS50 fast particulate spectrometers can be used to measure particulate mass in real-time, with specific emphasis on Diesel engine emissions. Applications for the technique discussed include Diesel Particulate Filter (DPF) evaluation and real time engine calibration to meet emissions standards. Data validating the methods used is also presented.

Resolution of the full particle number:size spectrum allows the measurement to be weighted by any function of particle size, e.g. number, surface area, or mass (Figure 1). The new software fits lognormal functions to each individual aerosol mode and reduces many of the pitfalls associated with mass calculation. Practical advice on using a DMS instrument for mass calculation follows. For a more technical discussion of all the important factors, turn to the appendix on page 5.

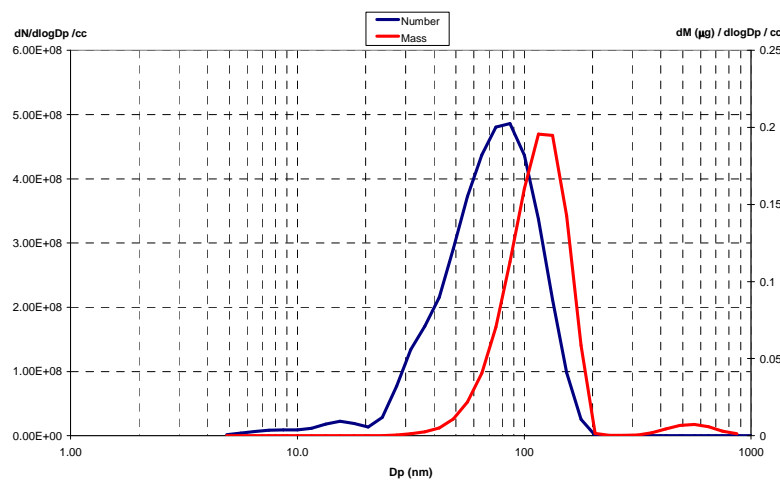


Figure 1: Diesel Engine Aerosol Studied with DMS500: Number Spectrum & Weighted by Mass

Practical Mass Measurement with the DMS500

The calibration is specific to a particular DMS instrument, and also contains a description of a specific type of aerosol to be examined in terms of the modes present and densities used to calculate mass. Upon selecting this in the DMS User Interface (v2.01 or above[†]), the instrument will now display lognormal fits for nucleation and accumulation modes along side the standard spectrum, and can write the mass of either/both modes to a datafile or analogue outputs.

For best results, the instrument must be completely warmed up, high gain (or medium for 3 range DMS500s) should be selected and the instrument must be autozeroed. For transient applications it is recommended to run at full 10 Hz (200 ms time response for DMS500) as sharp transient spikes in mass are often observed which contribute significantly to the cumulative mass in a test. 4:1 primary dilution should be used when directly sampling from an exhaust system with the heated sample line option (see app. note(s) DMS03; and/or DMS05 for DPF related applications), and sufficient dilution from the internal rotating disc diluter should be used to keep the dynamic range indicator in the green zone as much as possible throughout the test. Dilution correction can be enabled to compensate the concentration for both types of dilution if desired.

[†] provided with all new DMS instruments and available for free upgrade to existing customers. Note that a computer upgrade may be required for existing customers.

Post processing any DMS data file to give mass is also possible as part of the DMS Excel tools (v4 onwards, downloadable from the Cambustion website from mid-2006).

To calculate actual mass emission rather than mass concentration, exhaust volumetric flow needs to be taken into account. This can be done by taking exhaust volumetric flow values, converting to instantaneous mass per sample point, and summing over the period of interest in Excel:

$$\text{Total Exhaust Mass } (\mu\text{g}) = \sum \text{Mass Conc } (\mu\text{g} / \text{cc}) \times \text{Exhasust Vol Flow } (\text{cc} / \text{s}) \times \text{Sample Interval } (\text{s})$$

The sample interval can be obtained from the difference of any two consecutive values in column A of the DMS file.

It should be noted that the mass concentration (as with all DMS data) is strictly valid at Standard Temperature and Pressure (S.T.P., i.e. 0 °C and 1 atm. abs. pressure); therefore volumetric exhaust flow measurements should be converted to S.T.P.

Volumetric exhaust flow can be estimated from engine air inlet mass flow if available. The volumetric flow of the air inlet can be calculated from the intake mass flow correcting for the difference in density between ambient air and that at 0 °C. For diesel engines running at $\lambda > 2$ it can be assumed that the S.T.P. volumetric flow of intake air and exhaust gasses are roughly equal to within around 3–4 %. For conditions nearing stoichiometry, fuel flow and/or λ may have to be considered.

Data representing exhaust flow, intake flow, fuel flow and/or λ can be usefully logged in real-time via the DMS’s analogue inputs, and then used to get real-time exhaust volumetric flow when post-processing in Excel.

A comparison has been made^{1,2} between DMS mass concentration measurements and a) CVS tunnel concentration by filter paper and b) Raw exhaust concentration (direct DMS feedgas sampling) by hot weighing a Diesel Particulate Filter before and after soot loading. The CVS and DPF methods were attempted on a chassis dynamometer with a 2.2 litre 4-cylinder common rail diesel (Engine ‘A’), and the DPF method alone was also attempted on an engine dynamometer with a 2.0 litre 4-cyclinder common rail diesel (Engine ‘B’). The experimental setup for the DPF weighings is shown in Figure 2.

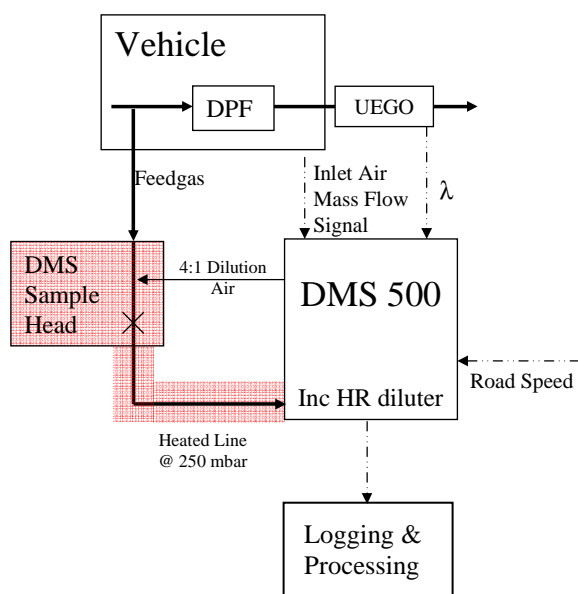


Figure 2: Experimental setup for DPF mass tests

Figure 3 shows the real time soot loading rate over an NEDC cycle, calculated from the accumulation mode mass concentration given by the new software (with nucleation mode discriminated out by software and ignored), and the exhaust volumetric flow taken from the engine air intake mass flow (see app. note DMS06 for a similar example showing particle number and size in each mode over such a cycle).

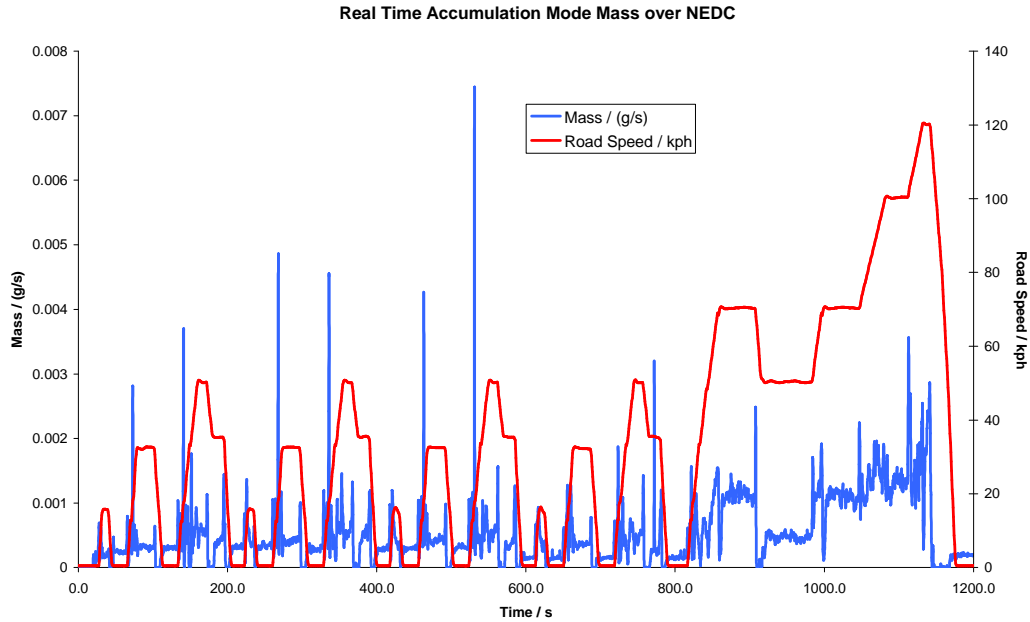


Figure 3: Real time soot mass loading rate over NEDC (engine 'A')

The transient spikes in mass in the trace are genuine and correspond to bursts of soot during acceleration where the concentration *and size* of particles increases somewhat, giving much more mass over a very brief period. Thus the use of a very fast response instrument, such as the DMS500, is both justified and indeed necessary to capture a significant proportion of the mass emitted over the cycle.

Filter Paper & DPF : DMS correlation : index = 3.19

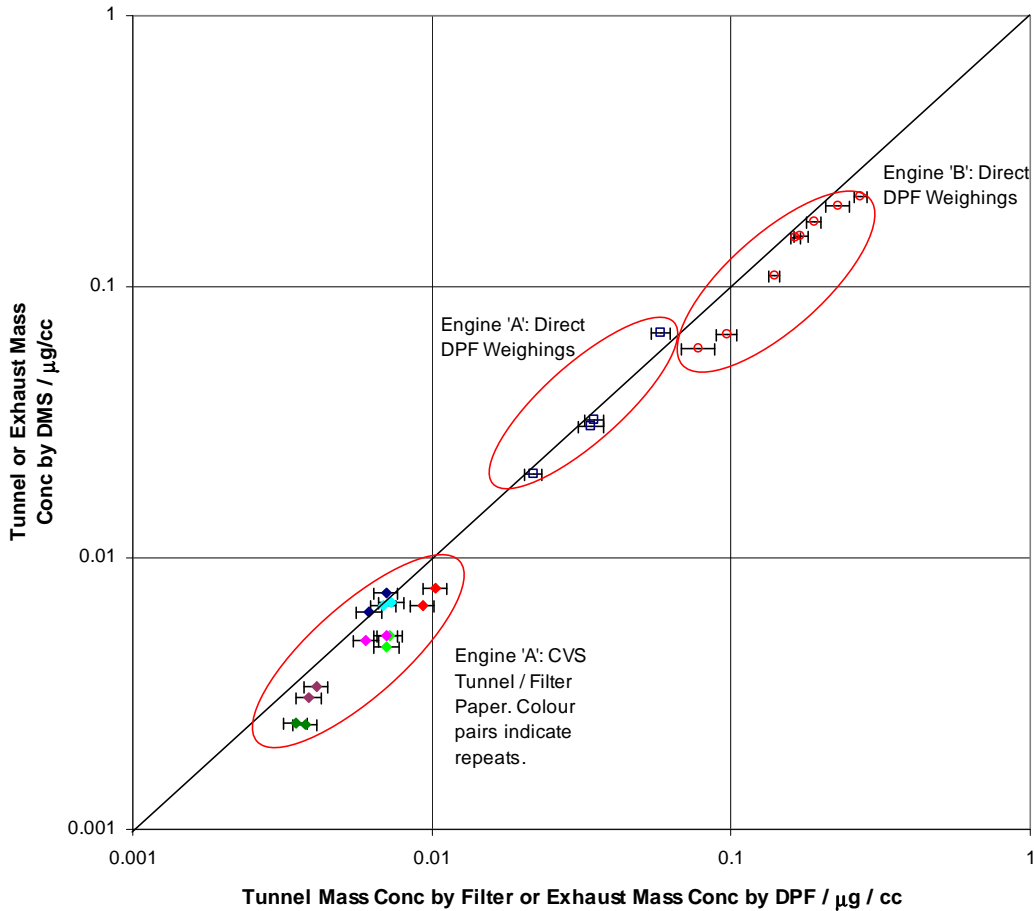


Figure 4: Comparison of mass concentration measured with DMS500 and by gravimetric methods. Line indicates 1:1 correlation and is not a line of best fit to the data. Error bars in DPF weighings are based on precision of balance used, those for filter papers are based upon repeatability figures quoted in ref³.

Figure 4 summarises all the mass concentration results from these tests. In attempting to achieve correlation with the filter paper mass measurements, one must be aware of some of the shortcomings of that technique. The material collected on the filter paper during the test forms a good site for condensation of some heavy hydrocarbon materials which are actually vapour phase in the exhaust. Thus these gas phase pollutants are included in a filter mass measurement, and are responsible for a degree of variability. Please note that these data assume a mass:size relationship best suited to DMS instruments without the new “agglomerate” calibration, please see the appendix for a fuller explanation.

DMS series fast particulate spectrometers are very useful tools for calculating both real-time particulate mass and total mass emission over a test. The new software ensures that data post-processing can be kept to the bare minimum of incorporating exhaust volumetric flow to achieve this.

Appendix

For non-spherical particles, diameter is not well defined, so particulate classification must be made on the basis of an equivalent diameter. For instruments based on a DMA (e.g. SMPS) where the particles are singly charged, classification is by mobility diameter which is the diameter of a sphere with the same aerodynamic drag as the particle. With multiple charging, which is significant for larger particles in the SMPS ($> \sim 100$ nm) and most combustion particles in DMS instruments ($> \sim 30$ nm), the mobility diameter can be measured if compensation is made for the number of charges per in the data processing (as it is in the DMS series). This is important for mass calculation because the volume of a non-spherical particle is generally not the same as that of the mobility equivalent sphere. Furthermore, for accumulation mode particles, the ratio of actual volume to equivalent sphere volume is not constant but varies with particle diameter. This is because these particles consist of an agglomeration of smaller spheres (~ 20 nm diameter), and the packing efficiency becomes lower as the cluster becomes bigger. This effect is described in the literature equivalently as either a variable effective density (assuming a spherical relationship of volume with mobility diameter), or a fractal dimension of the particles such that the volume is no longer proportional to d_p^3 .

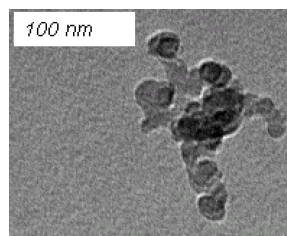


Figure 5: Typical Diesel Engine Accumulation Mode Fractal Agglomerate⁴

Mobility diameter measurement gives no information about the particle density, which must be assumed. The aerodynamic diameter, (measured by impaction instruments, e.g. ELPI), is the diameter of a sphere of unit density with the same mass:charge ratio as the particle. This depends on density, but more strongly than required to accurately predict the mass, so mass estimation from aerodynamic size measurements still requires knowledge of the density. Measurement of both the aerodynamic and mobility diameters provides one method of measuring the effective density.

In the literature, the effects of accumulation mode density and fractal structure are generally considered together in effective density measurements. Along with data based on aerodynamic & mobility diameters⁴ there are measurements comparing the classification of a DMA and Aerosol Particle Mass Analyser⁵ (APM), which selects an aerosol monodispersed in charge:mass ratio. Data^{4,5} obtained with the APM shows the relationship between mobility diameter and particle mass for diesel accumulation mode particles shown above from heavy duty engines, with regression to a mass = $\rho \cdot d_p^n$ model, with $\rho = 6.05 \times 10^{-24}$ and $n = 2.34$ on average (Figure 6). A recent study⁶ with the Centrifugal Particle Mass Analyser⁷ (CPMA; an improved type of APM) and SMPS has shown that a power law close to $d_p^{2.34}$ also holds for light duty diesels.

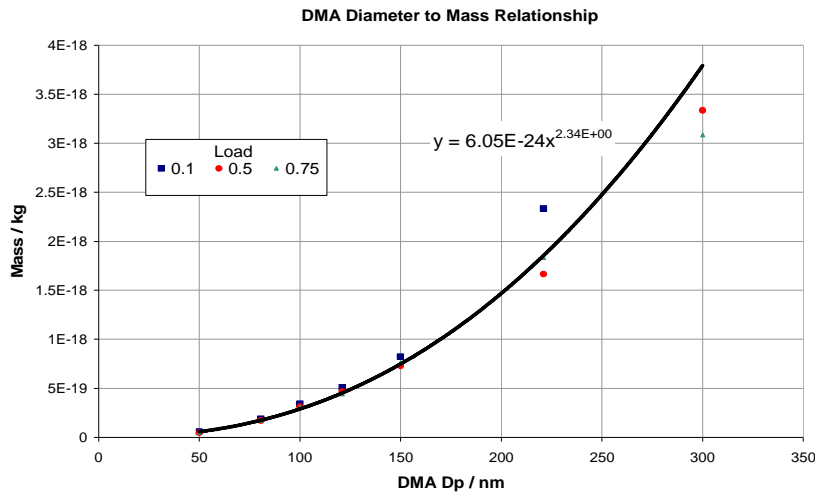


Figure 6: Relationship between Diesel Particle Size (as measured by an SMPS) and Mass⁵. Black line shows the average over all loads.

For the accumulation mode size range, this is considered the best relationship to use to predict mass. As stated above, given the difficulty in defining the diameter of fractal agglomerates it is important to note that instruments which measure size by particle drag alone (e.g. SMPS) will give subtly different diameter measurements of agglomerates than instruments which size on charge:drag ratio (e.g. DMS series and other similar instruments). This difference is only noticeable for particles > 100 nm in diameter (i.e. as multiple charging becomes prevalent), so does not really affect number based measurements for typical diesel particulates to any significance. However, when weighting by mass, the tail of the accumulation mode distribution will provide a significant contribution to the overall mass. To take this into account, a recent study¹ has compared DMS500 and SMPS and combined with data from Park *et al.*⁵ has concluded (Figure 7) that the correct relationship for the DMS500 between size and mass is best expressed as:

$$\text{Mass } (\mu\text{g}) = 1.53 \times 10^{-16} \cdot d_p^{3.19} \text{ (nm)}$$

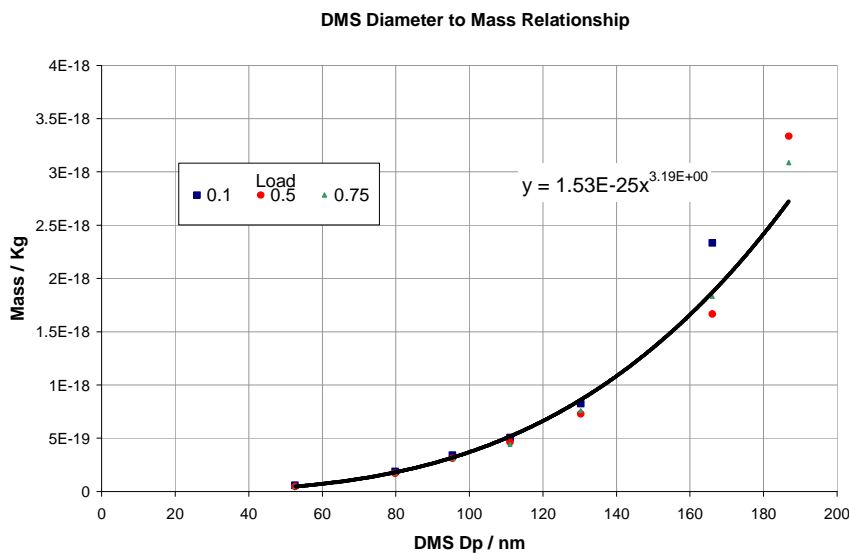


Figure 7: Relationship between Diesel Particle Size (as measured by a DMS500) and Mass¹

However, since 2008, Cambustion have been supplying an empirical soot (agglomerate) calibration with all new instruments (this is available as an upgrade to existing customers). This is described in more detail in the note *Calibration of the DMS Series* and application note DMS09, both available from

the Cambustion website. This involves calibrating the DMS with a DMA (to measure mobility equivalent diameter), and so instruments with such a calibration require less of a “correction”. Taking this into account, for instruments running a “Diesel_Agg....dmd” file the recommended mass to size relationship (which the .dmd file defaults to) is:

$$\text{Mass } (\mu\text{g}) = 2.20 \times 10^{-15} \cdot d_p^{2.65} \text{ (nm)}$$

For GDI mass, we recommend using the standard “spherical calibration” and assuming unit density, i.e.

$$\text{Mass } (\mu\text{g}) = 5.20 \times 10^{-16} \cdot d_p^3 \text{ (nm)}$$

(see application note DMS08 for further information about GDI sampling). Again, “GDI_....dmd” files will default to these settings.

The broadening of size distributions by some instruments can introduce a source of error into mass calculation. A number of physical effects (e.g. diffusion, probabilistic charging, finite sample flows, discretised detection) result in the raw output from particle spectrometers being spread over a wider size range than the actual spectrum. If this is not corrected, the centre of the size distribution when reweighted to reflect mass will shift further than is correct, leading to a significant error in the total mass estimation. The standard DMS data processing deconvolutes the raw output with the broadening function of the instrument such that this effect is minimised for distributions wider than $\sigma_g \approx 1.2^\dagger$. The new lognormal data processing algorithm (introduced below) allows resolution of aerosol modes as narrow as $\sigma_g \approx 1.05$.

Lognormal Data Processing

Cambustion have recently introduced unique data processing software^{1,8} which can parameterise aerosol size distributions from DMS instruments in terms of their fit to a number of lognormal size distributions. The software can operate in real-time or via a post-processing utility, and is described in more detail in application note DMS06. The principle advantages of this technique in terms of engine aerosol mass calculation are:

- Automatic discrimination of Nucleation and Accumulation modes; acts as “software thermodeuder” — even for overlapping modes.
- Up to 10 times greater mass sensitivity than re-weighting of the standard spectrum.
- Greatly increased spectral resolution — can resolve aerosols as narrow as $\sigma_g \approx 1.05$, previously unachieved of for a fast (i.e. non-scanning) aerosol mobility sizer (see app. note DMS06 for an example), as it works with the fundamental instrument response, not just fitting a line to a spectrum.
- Takes account of the instrument’s noise base (measured when automatically zeroing the instrument), only returning aerosol modes of true significance.
- Makes handling large unwieldy data files easier, and allows simple real-time output of required quantities as analogue outputs, making data from DMS instruments as easy to interpret and use as traditional fast response gas analysers.

The mass calculation from spectral data is in general, due to the weighting used, very sensitive to erroneous detection of large particles due to noise. Fitting a lognormal function suppresses noise far from the peak of the distribution. This can increase the sensitivity in mass measurements up to 10 times. The DMS500’s response to a “perfect”, steady 60nm nucleation mode aerosol was calculated and then added to the real instrumental noise base. This was processed with both the standard and lognormal DMS data processing algorithms, and the mass weighted results are shown in Figure 8.

[†] σ_g = GSD = Geometric Standard Deviation = measure of the width of a lognormal size distribution. Always > 1.

From Figure 8:

Mass Sensitivity of DMS500: 0.1% of reading + 2 $\mu\text{g m}^{-3}$

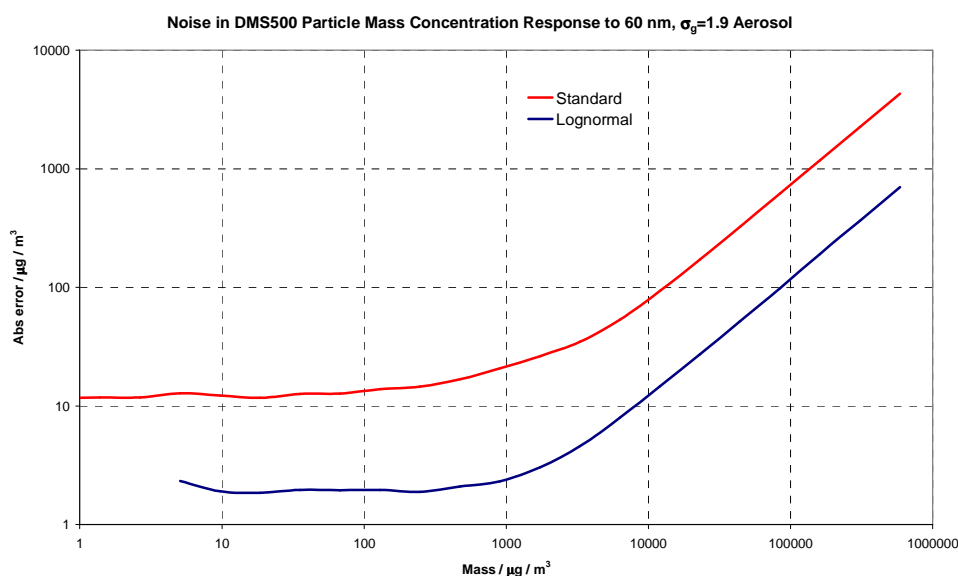


Figure 8: Sensitivity to Mass of Standard and Lognormal Data Processing Algorithms. Expressed as the RMS difference between “true” mass of computer synthesised aerosol response and that from processing by both methods, after the addition of real instrumental noise.

¹ Diesel soot mass calculation in real-time with a Differential Mobility Spectrometer. J.P.R. Symonds, K. St.J. Reavell, J.S. Olfert, B.W. Campbell, S.J. Swift. Submitted to *Journal of Aerosol Science* **2006**

² Real-Time Diesel Particulate Filter Efficiency and Mass Measurement From Spectral Data. T. Hands, C. Nickolaus, J. Symonds, *American Association of Aerosol Research*, Austin, USA **2005**

³ UN-ECE Particle Measurement Programme (PMP) Light Duty Inter-laboratory Correlation Exercise, Report on First Results. J. Andersson, P. Dilara, **2005**

⁴ Performance of SMPS and ELPI with Diesel Exhaust Particles. Imad Abul Khalek, paper 19 from 4th *ETH Conference on Nanoparticle Measurements*, Zurich **2000**

⁵ Relationship between particle mass and mobility, and between aerodynamic and mobility size distributions for diesel exhaust particles. K. Park, F. Cao, D.B. Kittelson, P.H. McMurry, *Environmental Science & Technology* **37** 577–583 **2003**

⁶ The effective density and fractal dimension of particles emitted from a light-duty diesel vehicle with a diesel oxidation catalyst. J.S. Olfert, J.P.R. Symonds, N. Collings. Submitted to *Journal of Aerosol Science* **2006**

⁷ New method for particle mass classification — the Couette centrifugal particle mass analyser. J.S. Olfert, N. Collings, *Journal of Aerosol Science* **36** 1338–1352 **2005**

⁸ Correlation of Particle Mass Measurements with Electrical Mobility Classified Spectra. K. Reavell, J. Symonds, 9th *ETH Conference on Combustion Generated Nanoparticles*, Zurich **2005**