Feature Article

A New Instrument to Measure the Mass of Nano-Particles from Internal Combustion Engines

Olfert Jason

Particles from internal combustion engines are known to reduce visibility, harm human health, and affect climate. A new instrument called the Couette centrifugal particle mass analyzer (Couette CPMA) has been developed to measure the mass of nano-particles. A unique system of forces allows for particle mass measurements over a wide range with high resolution. The Couette CPMA was used to measure the effective density, fractal dimension, and mass concentration of particles emitted from a light-duty diesel vehicle.

Introduction

Particles in the environment are known to affect climate change and reduce visibility[1, 2]. There is also evidence that suggests that particles can have a negative effect on human health[3]. Particles can be generated by a variety of sources, both natural and anthropogenic; however, particulate emissions from internal combustion engines are a major source of ultra-fine particles in the atmosphere. Particles and aerosols can be characterized by many different properties such as number concentration, mass concentration, particle size, mass, density, volume, fractal dimension etc., and each of these properties, in some degree, are important in understanding how particles affect climate, health, and visibility.

A new instrument has been developed called the Couette centrifugal particle mass analyzer (Couette CPMA). The Couette CPMA can be used to measure the mass of nano-particles, including those from internal combustion engines. Furthermore, by measuring the mass of particles and the size of particles, other important particle properties can be determined such as effective density and fractal dimension[4, 5]. The particle effective density is an important parameter because it can be used to convert aerosol size distributions to mass distributions from which the total mass concentration can be calculated[6]. Also, the morphology of an agglomerate particle is characterized by its fractal dimension. The fractal dimension is a measure of the 'stringiness' of a particle, where a fractal dimension of 3 indicates a spherical particle and a fractal dimension of ~2 is a long chain-like agglomerate structure. The morphology affects the behaviour of particles in the atmosphere[7] and possibly impacts upon the effect particles have on human health.

Couette Centrifugal Particle Mass Analyzer

The Couette CPMA is a new instrument that classifies particles by their mass[8, 9]. The Couette CPMA consists of two rotating coaxial cylindrical electrodes rotating at different angular velocities (see Figure 1). Electrically

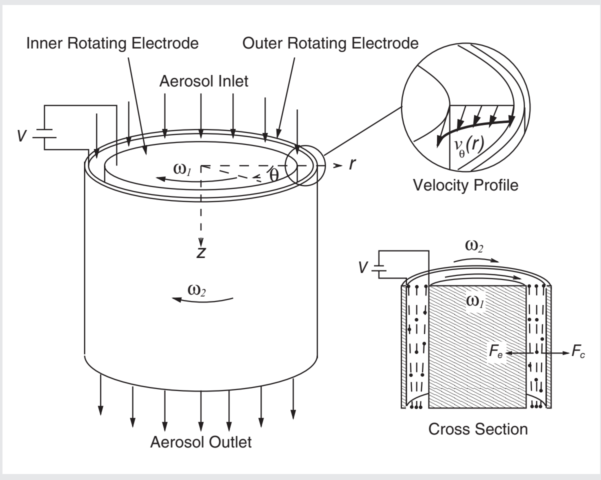

Figure 1 Schematic of the Couette centrifugal particle mass analyzer.

charged particles pass between the electrodes where they experience electrostatic and centrifugal forces (*Fe* and *Fc*, respectively) acting in opposite directions. Particles also experience a drag force which opposes the direction of motion. Particles of a particular mass-to-charge ratio will pass through the Couette CPMA, depending on the rotational speed and voltage difference between the electrodes. Other particles will either be forced to the outer electrode if the centrifugal force is stronger than the electrostatic force or they will be forced to the inner electrode if the electrostatic force is dominant. Particles that impact the inner or outer electrode adhere to the surface and will not pass through the Couette CPMA. Since the charge on the particles is known then the mass of the classified particles is known. The voltage and rotational speed can be stepped to classify particles of different mass-to-charge ratios.

The Couette CPMA design represents a significant improvement over the aerosol particle mass (APM) analyzer. The APM, developed by Ehara et al.[10], operates in a similar manner to that of the Couette CPMA; however, unlike the Couette CPMA, the APM's inner and outer electrodes rotate at the same angular velocity. One major problem with the APM is that the instrument suffers from particle losses in the classifier due to unstable forces. The external forces in the APM are the centrifugal force, which is proportional to r and the electrostatic force, which is proportional to $1/r$ (where r is the distance from the centre of rotation). A particle of the correct mass-to-charge ratio will be balanced at the 'equilibrium radius', r^*. If the particle is positioned so that $r>r^*$ the centrifugal force will be greater than the electrostatic force and the particle will move toward the outer electrode. Depending on the force imbalance, the axial flow velocity, length of classifier, and drag on the particle, the particle may impact on the outer electrode. Similarly, particles may impact on the inner electrode if they are positioned at $r<r^*$. This unstable system of forces in the APM causes many particles to be lost in the instrument, which greatly reduces the transfer function of the instrument. In the Couette CPMA the inner electrode rotates slightly faster than the outer electrode. This creates a concave velocity profile between the electrodes (known as Couette flow; see Figure 1) such that the centrifugal force on the particle will decrease as the radius increases. With this system, particles of the correct mass-to-charge ratio move toward the equilibrium radius[*1] and the transfer function of the Couette CPMA is greatly improved compared to the APM. Figure 2(a) and (b) show the trajectory of particles of the same mass-to-charge ratio in the APM and Couette CPMA (from the model described in[8]), where the equilibrium radius is centred between the two cylinders (r_c). The figure shows that the particles move toward the equilibrium radius in the Couette CPMA, but they move away from the equilibrium radius in the APM, resulting in particle losses. This improvement in transfer function in the Couette CPMA allows for higher resolution measurements and increased measurement range.

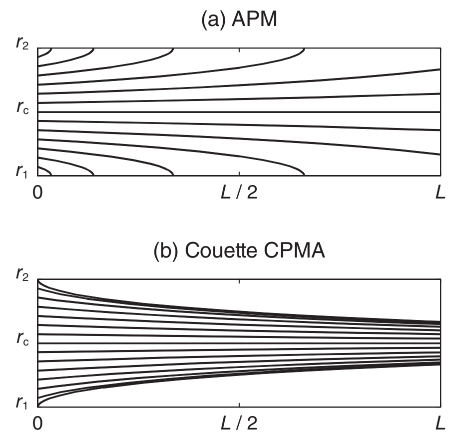

Figure 2 Trajectory of particles of the same mass-to-charge ratio in the (a) APM and (b) Couette CPMA. The *x*-axis represents the distance the particles travelled down the length, *L*, of the instruments. The *y*-axis represents the radial distance, *r*, from the centre of rotation, where r_1 and r_2 are the radius of the inner and outer cylinders, respectively. The electrostatic and centrifugal forces are balanced at the centre between the two cylinders (i.e. $r^*=r_c$).

*1: A stable system of forces can also be created in this type of instrument by manipulating the electrostatic field by changing the instrument geometry[11], with an instrument called the Fluted CPMA. However, the improvement in the transfer function is not as great as seen in the Couette CPMA.

Application to Internal Combustion Engines

By measuring the mass of particles with the Couette CPMA and the size of particles with another instrument called the differential mobility analyzer (DMA), the effective density and fractal dimension of the particles can be found. The Couette CPMA and the DMA were used to measure the effective density and fractal dimension of particles emitted from a light-duty diesel vehicle fitted with a diesel oxidation catalyst (DOC) over a range of engine loads[12]. It was found that at high engine loads, the DOC increased in temperature and sulphate levels in the particulate matter increased (as measured from filter samples), presumably due to the increased production of sulphate and/or release of sulphate from the DOC at high temperatures. Figure 3 shows the measured effective density of the particles at a low (8%) and high

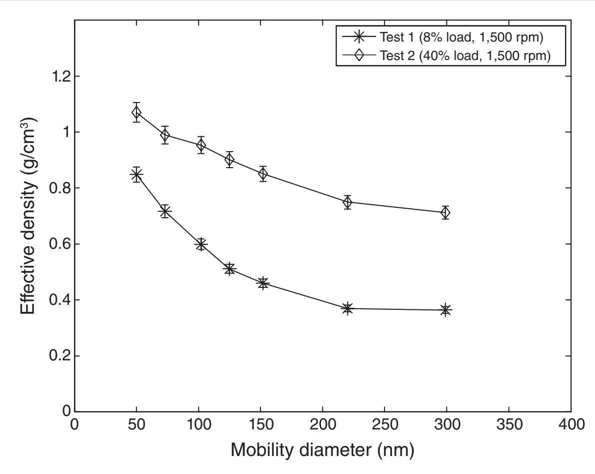

Figure 3 The effective densities of diesel particles measured at high and low load.

engine load (40%). At low engine loads (8%), sulphate levels were low, which corresponded to lower effective densities. However, at higher engine loads (40%) there was an increase in sulphate levels, which resulted in a drastic increase in the effective density of the particles since the sulphate condensed on the particles. Figure 4 shows the relationship between the size and mass of the particles for a low load and high load test. The fractal dimension of the particles for each test can be determined by fitting the mass-size curve with a power-law relationship[5]. The fractal dimension of particles for all the low load tests (8-15%) ranged from 2.22-2.48, which is in good agreement with previous studies[4, 13]. At high engine load (40%), sulphate levels were much higher and the fractal dimension was 2.76 indicating that the particles were much more spherical.

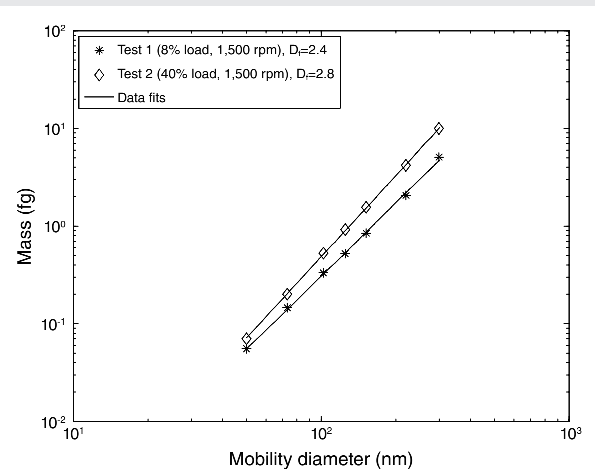

Figure 4 The size-dependent mass of particles from a light-duty diesel vehicle.

The effective density, derived from the Couette CPMA measurements, can be used to convert an aerosol size distribution to an aerosol mass distribution, which can be integrated to give the total aerosol mass concentration. Current particulate air quality regulations and diesel particulate matter regulations from the US Environmental Protection Agency (EPA) and the European Union are based on total aerosol mass concentration, measured with a gravimetric filter method. However, it is well documented that gravimetric filter measurements can be affected by a variety of artifacts. These artifacts include adsorption of vapour onto the filter, volatilization of semi-volatile compounds from filtered particles, and an array of chemical reactions between filtered particles, the gas, and filter substrate. Furthermore gravimetric filter measurements often require long sampling times and cannot make transient measurements. The mass concentration of diesel exhaust was measured in real-time using a differential mobility particle spectrometer (DMS) to measure the aerosol size distribution in real-time and by measuring the size-dependent effective density function with the Couette CPMA[6]. This system allows for a real-time measurement of the mass concentration without the measurement artifacts of filter-based methods. The mass concentration of particulate emissions was measured from two diesel vehicles (engine 'A' and 'B') by using the DMS-CPMA system and by weighing the particulate emissions collected on filter paper and the vehicle's diesel particulate filter (DPF). Figure 5 shows the comparison of the results and the DMS-CPMA measurements are generally within 20% of the filter-based measurements over a wide range of mass concentrations.

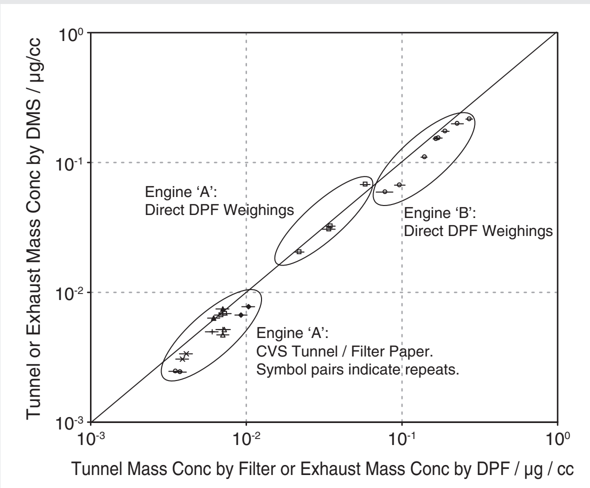

Figure 5 Comparison of DMS-CPMA and filter-based mass concentration measurements of particulate emissions from two light-duty diesel vehicles

Conclusions

The Couette CPMA is a new instrument used to measure the mass of particles. A stable system of forces is created by using Couette flow between the rotating cylindrical electrodes. This improves the transfer function of the instrument, which allows the instrument to operate at higher resolutions and a wider measurement range. The Couette CPMA has been used to measure the effective density and fractal dimension of particles emitted from a light-duty diesel vehicle. It was found that increased levels of condensable sulphate led to increases in the effective density and fractal dimension of the particles. The Couette CPMA was also used with a DMS to measure the mass concentration of diesel vehicle exhaust. These results were generally within 20% of filter-based gravimetric measurements.

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Olfert Jason

University of Alberta