Analysis of the Volatile and Hygroscopic Properties of Diesel Exhaust using the VH-TDMA

N.K. Meyer and Z.D. Ristovski.

International Laboratory for Air Quality and Health, Queensland University of Technology, Brisbane, Australia.

Diesel nanoparticles (diameter <50 nm), are of concern as they may pose special health risks because of their small size and high number concentrations (Utell and Frampton, 2000). Predominant theories on the production of these particles involve the binary nucleation of sulphuric acid and water. However, more recent results have implicated the ternary nucleation of ammonia, sulphuric acid and water in the process. To date, resolution of this question has not been possible even though modelling studies have predicted that binary nucleation could not be completely responsible for the large number of particles produced. Alternate theories involve the condensation of volatile organic compounds onto smaller non-volatile cores.

At present, the structure of these particles is still a matter of debate. The analysis of Diesel nanoparticles has thus far been limited to separate analyses of their volatile and hygroscopic properties. Recently Mathis et al. (2004), using TEM analysis, showed that several types of volatile nanoparticles exist that contain at least two compounds with different volatility. They concluded that some particles are coated by the more volatile, hydrophilic component, whilst other particles are surrounded by a hydrophobic component

As such, the Volatilisation and Humidification Tandem Differential Mobility Analyser (VH-TDMA) (Johnson, 2004) is an ideal candidate for determining the structure and physical properties of diesel nanoparticles. The method measures the change in diameter of size classified nanoparticles as they are first heated and then exposed to high humidity. Aerosol particles composed of multiple chemical species exhibit complex volatilisation curves. The resulting volatilisation curve displays distinct features associated with the removal of various components. This allows the volume fraction of each component to be calculated. The humidification curve provides additional information concerning the solubility of the remaining un-volatilised particle before and after each species is removed.

The experiments presented here utilise the combined analytical power of the VH-TDMA to provide simultaneous analysis of the particles volatile and hygroscopic properties.

The formation of these particles is influenced by a number of sampling parameters such as: dilution ratio, residence time, temperature and humidity (Abdul-Khalek et al 1999; Abdul-Khalek et al 2000). As such, these factors were heavily considered when re-creating natural dilution conditions that would stimulate formation of the nuclei mode particles. Furthermore the fuel sulphur level has been shown to play an important role in particle formation (Vaaraslahti et. al 2004). The fuel used in these experiments was 500ppm sulphur.
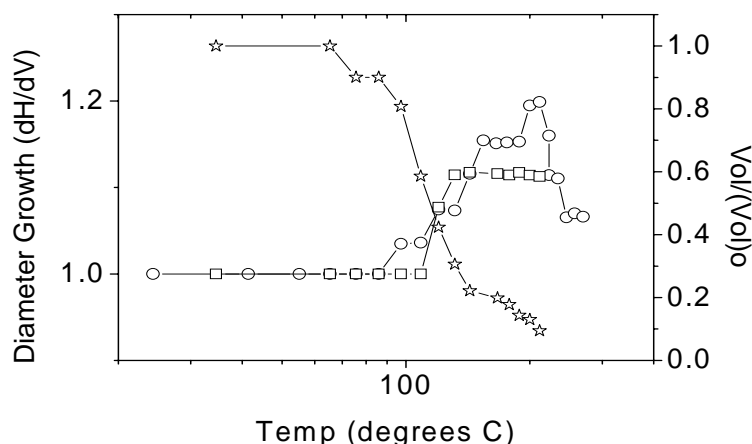

Fig 1. The VH-TDMA curve of diesel nanoparticle from an engine running at 1750RPM @ 180Nm.The dotted and square markers indicate the hygroscopic growth of the 23.3nm and 41.4nm diesel nanoparticles. The star marker represents a standard volatilisation curve for these particles.

A VH-TDMA volatilisation curve for diesel nanoparticles of two initial size ranges (23.3nm and 38.5 through 42.9nm) is shown in figure 1. The left and right *y*-axis show the hygroscopic growth (d_V/d_H) and non-volatilised particle volume fraction ($V(T)/V(T_0)$) respectively, versus temperature. The volatility curves show that the particles contain at least two compounds with different volatility.

The first fraction evaporates in the temperature range between 80-170°C, while the second evaporates between 170-250°C. Hygroscopic growth first appears at temperatures above 110°C with the evaporation of the first fraction. This fraction is hydrophobic in nature and is most likely derived from unburned lubricating oil or fuel. The remaining fraction is shown to be hydrophilic with two separate growth phases clearly shown for larger and smaller particles. Both size fractions exhibit the hygroscopic growth and volatilisation properties expected of a mixed fraction of ammonium sulphate and a hydrophobic, non-volatile component.

This indicates the possibility of ternary nucleation of sulphuric acid, water and ammonia. Similar behaviour was observed for different particle sizes and different engine loads.

Figure 2 shows the decrease in volume of heated diesel nanoparticles formed at high loads. We see a clear distinction between the nuclei mode and accumulation mode particles. The nucleation mode particles reduce to <10% of their original volume while the accumulation mode particles exhibit non-volatile behaviour. Later analysis of the hygroscopic properties of the high load accumulation mode particles shows that they are coated with a layer of hydrophobic material which evaporates by 60°C. Once this coating is removed the particles exhibit hygroscopic growth up until 200°C after which the particle exhibits non-volatile behaviour. The hydrophilic coating clearly mimics the behaviour of a sulphate condensate which, due to its high volatilisation temperature, is thought to be ammonium sulphate
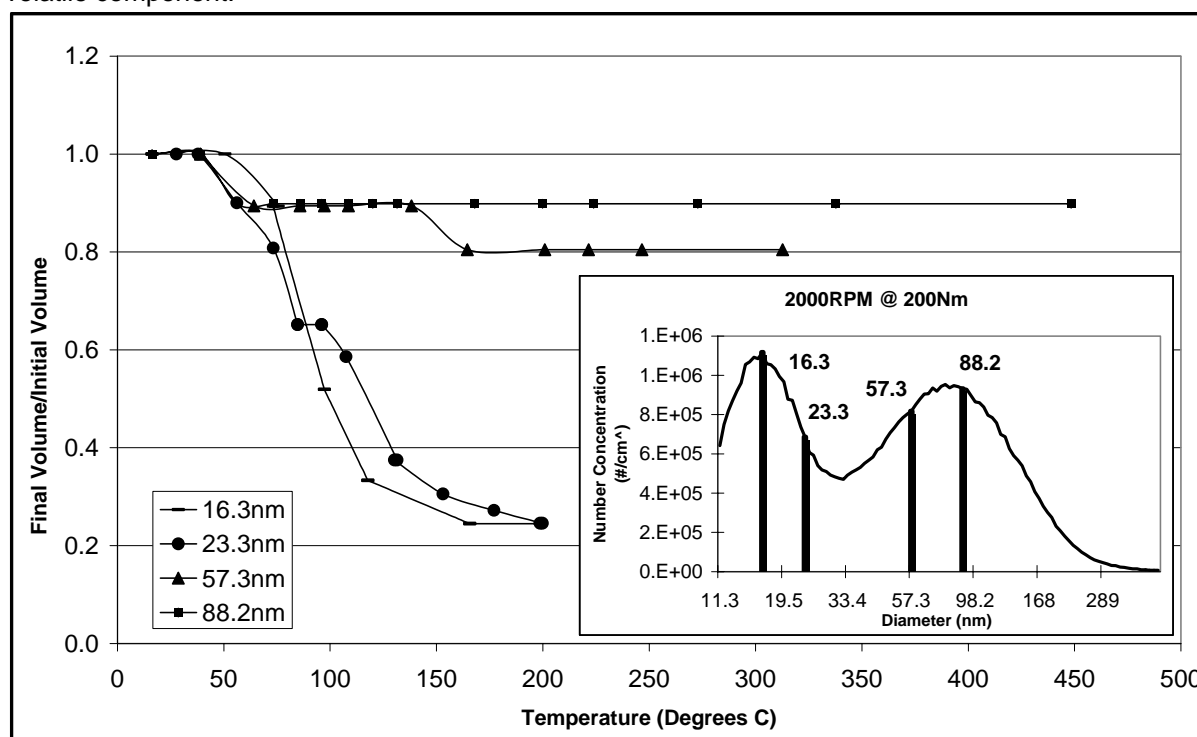

Fig.2 Analysis of the volatile properties of diesel nanoparticles produced at high load. The volatilisation curves of the diesel nanoparticle produced at high loads are represented. The insert shows the size distribution from which the mono-disperse samples were taken.

Abdul-Khalek, I., Kittelson, & D., Brear, F. (1999) SAE Technical Paper Series 1999-01-1142

Abdul-Khalek, I., Kittelson, & D., Brear, F. (1999) SAE Technical Paper Series 2000-01-0515

Johnson, G. R., Z. Ristovski & Morawska L. (2004) *J. Aerosol Science*, **35**(4):443-455.

Mathis, U., Kaegi, R., Mohr, M. & Zenobi, R. (2004) *Atmos. Environ.* **38**, 4347-4355.

Utell MJ & Frampton MW (2000) *J Aerosol Med.* 13(4):355-360

Vaaraslahti, K., Virtanen, A., Ristimaki, J., & Keskinen, J. (2004) Environ. Sci.Technol. **38**, 4884-4890