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Introduction

Various researchers (HEI, 1997 and ETH, 1997) have investigated the number concentration and size distribution of particles emitted from diesel engines. It is widely accepted that the volume and mass concentration of particles in the exhaust of diesel engine has reduced steadily over the past twenty years due to the application of new technologies. However, knowledge of particle number concentrations is very limited.

Shi et al. (1998) and Abdul-Khalek (1998) have found that at specific dilution conditions, a large amount of ultrafine particles (< 50 nm) were formed during dilution of exhausts emitted from a modern diesel engine with a fuel of sulphur content between 0.03-0.05 wt %. The mechanism of the effect of dilution conditions is not clear, but one implication is that comparison of data between different researchers is problematic. Nuclei mode particles were believed to form by homogenous nucleation of sulphuric acid and water during dilution when the sulphur content of the fuel was higher (Baumgard and Johnson,1996). This paper describes the investigation of ultrafine particle formation from both an experimental and a theoretical perspective.

Experimental section

Experimental

A Perkins diesel engine was tested in this study. It is a vehicle specification model year 1995, turbocharged intercooled engine, emission certified at that time for the US market. Fuel sulphur content was between 0.03-0.05% in mass. A schematic diagram of the sampling system is shown in Figure 1. Details of the engine, dilution tunnel and fuel are reported elsewhere (Shi et al., 1998).

A TSI scanning mobility particle sizer (SMPS*, measuring range 9.6-352 nm) and an electrical low pressure impactor (ELPI, Dekati, measuring range (50% cut size) 30-10000 nm) were used in the

* It has been found that there could be a significant difference in particle size distribution between version 2.1 and 2.4 at size range smaller than 15 nm. All SMPS data in this paper were analysed under software version 2.4.

measurement and collection of particles. Commercial PTFE filters (47 mm and 70 mm) were used in Positions 1, 3 and 2.

Results and Discussion

In our engine test bed measurements, we found that measured particle size distribution and number concentration would change with dilution conditions (Shi et al., 1998). Kittelson and co-workers have reported a similar effect of dilution conditions.

In order to understand the mechanism, an attempt was made to determine the particle chemical component distribution. ELPI was used as a cascade impactor (electricity was off). Particles were collected on the aluminium foil placed on each stage of the ELPI. Anions were analysed with ion chromatography (Dionex LC20).

Sulphate and nitrate distributions collected on the ELPI stages are shown in Figure 2, where engine speed was 1600 rpm and engine load was 50% of full load. X-axis is the ELPI stage size range (50% cut size) and the y-axis is sulphate (SO_4^{2-}) and nitrate (NO_3^-) mass collected on each ELPI stage when 1 m^3 of raw exhaust is passed through the ELPI. Dry dilution air was compressed air with a filter and water trap in the line; its humidity was 5.4% at 22°C. Humid air was room air passing through a high efficiency filter; its humidity was 40-50% at 22°C. The humid air was just used for the dilution tunnel and the dry air was used for all other dilution. Samples from at dry dilution air runs were collected at Position 3 and at humid dilution air runs collected at Position 1.

Figure 3 shows the particle surface area distribution (converted from simultaneous SMPS measurements assuming spherical particles) and the ratios of sulphate (nitrate) mass to particle surface. Figure 4 the shows particle volume distribution (converted from simultaneous SMPS measurement assuming spherical particle) and ratios of sulphate (nitrate) mass to particle volume.

With dry air dilution, the highest sulphate concentration and the highest ratio of sulphate mass to corresponding particle surface area were found in the size range 116-185 nm, whilst the highest ratio of sulphate mass to corresponding particle volume were found in the size range 73-116 nm. However, with humid dilution air , there was an extra peak in the smallest ELPI size range, 30-73 nm where particle number (surface area and volume) concentration were also higher. The ratios of sulphate mass to corresponding particle surface area and volume would be even higher in the size range below 30 nm extrapolating the trend in Figures 3 and 4. The ratio distribution of nitrate mass

to corresponding particle surface area and volume was much flatter. These data clearly indicate that sulphate (sulphuric acid) was involved in ultrafine particle formation.

Theoretical Section

Theory of Sulphuric acid and water nucleation

There are two versions of nucleation theory available in the literature, Doyle (1961) and Wilemski (1984), one of which (Doyle, 1961) is thermodynamically incorrect.

Baumgard and Johnson (1996) used Doyle's version theory to predict H_2SO_4-H_2O particle formation in diesel exhaust during dilution. In this paper, the correct nucleation theory outlined by Viisanen et al. (1997) and Kulmala et al. (1998) is applied.

The H_2SO_4 hydrate (embryo) formation rate is predicted by the equation

$$I = C \exp(-\Delta G^*/kT) \qquad (1)$$

Where C is a frequency factor, k is Boltzmann's constant, T is the temperature and ΔG^* is the free energy required to form an embryo. The free energy of formation of an embryo of arbitrary size and composition is

$$\Delta G = n_1 (\mu_{1l} - \mu_{1g}) + n_2 (\mu_{2l} - \mu_{2g}) + 4\pi r^2 \sigma \qquad (2)$$

where n_1 and n_2 are the number of molecules of components water and H_2SO_4 in the embryo, μ_{1l} and μ_{2l} are the chemical potentials of water and H_2SO_4 taken for a macroscopic amount of a liquid phase of the same composition, μ_{1g} and μ_{2g} are the chemical potentials of components water and H_2SO_4 in the gas phase, σ is the surface tension of the binary mixture.

ΔG^* can be found by solving the two equations

$$\left(\frac{\partial \Delta G}{\partial n_1}\right)_{n_2} = 0, \left(\frac{\partial \Delta G}{\partial n_2}\right)_{n_1} = 0 \qquad (3)$$

Solving Equations (3), one obtains

$$\Delta \mu_i + \frac{2\sigma v_i}{r^*} = 0 \qquad (i = 1,2) \qquad (4a)$$

$$v_2 \Delta\mu_1 = v_1 \Delta\mu_2 \qquad (4b)$$

where v_1 and v_2 are the partial molar volumes . r* is the radius of the droplet, and $4\pi r^{*3}/3 = n_1 v_1 + n_2 v_2$.

The frequency factor C in equation (1) is described by Kulmala et al. (1998), where sulphuric acid hydration is considered. It should be noted that there is an error in equation (9) of Kulmala et al. (1998) and in equation (8) of Viisanen et al. (1997) where the power of n_a should be taken away.

Results and Discussion

Limited by the preparatory time for this Workshop, only preliminary results are available to be introduced here. Here, a primary dilution ratio of 18 and relative humidity of 20% were assumed. Baumgard and Johnson (1996) assumed that 4% of the sulphur in the diesel fuel (sulphur content 0.03-0.05 wt % in this study) would be converted to H_2SO_4 and half of this would be in the particle phase. This assumption is consistent with our filter measurement, and therefore is used in the model calculation.

Figure 5 shows the calculated H_2SO_4-H_2O particle nucleation rate. The dependence of the nucleation rate upon temperature and relative humidity are shown in Figures 6 and 7 respectively. Generally, higher relative humidity and lower temperature lead to a higher nucleation rate, which is consistent with the findings of the measurements. Temperature and relative humidity are two key factors affecting the measured particle size distribution and concentration. Dilution ratio changes temperature and gas phase H_2SO_4 partial pressure.

In the real situation, the processes of nucleation, coagulation and condensation will occur simultaneously (which will be modelled later). However, these results support at least qualitatively the hypothesis that H_2SO_4-H_2O nucleation is a major cause of nanoparticle formation during dilution.

Conclusion

The formation mechanism of nanoparticles during diesel exhaust dilution was studied. It is found that H_2SO_4-H_2O nucleation may play an important role in nanoparticle formation even in a modern diesel engine exhaust with a low sulphur fuel. This finding should be useful in comparing particle number emissions between different engines and in formulating emission testing strategies for regulatory applications.

Acknowledgement
This work was supported financially by Perkins Technology Limited.

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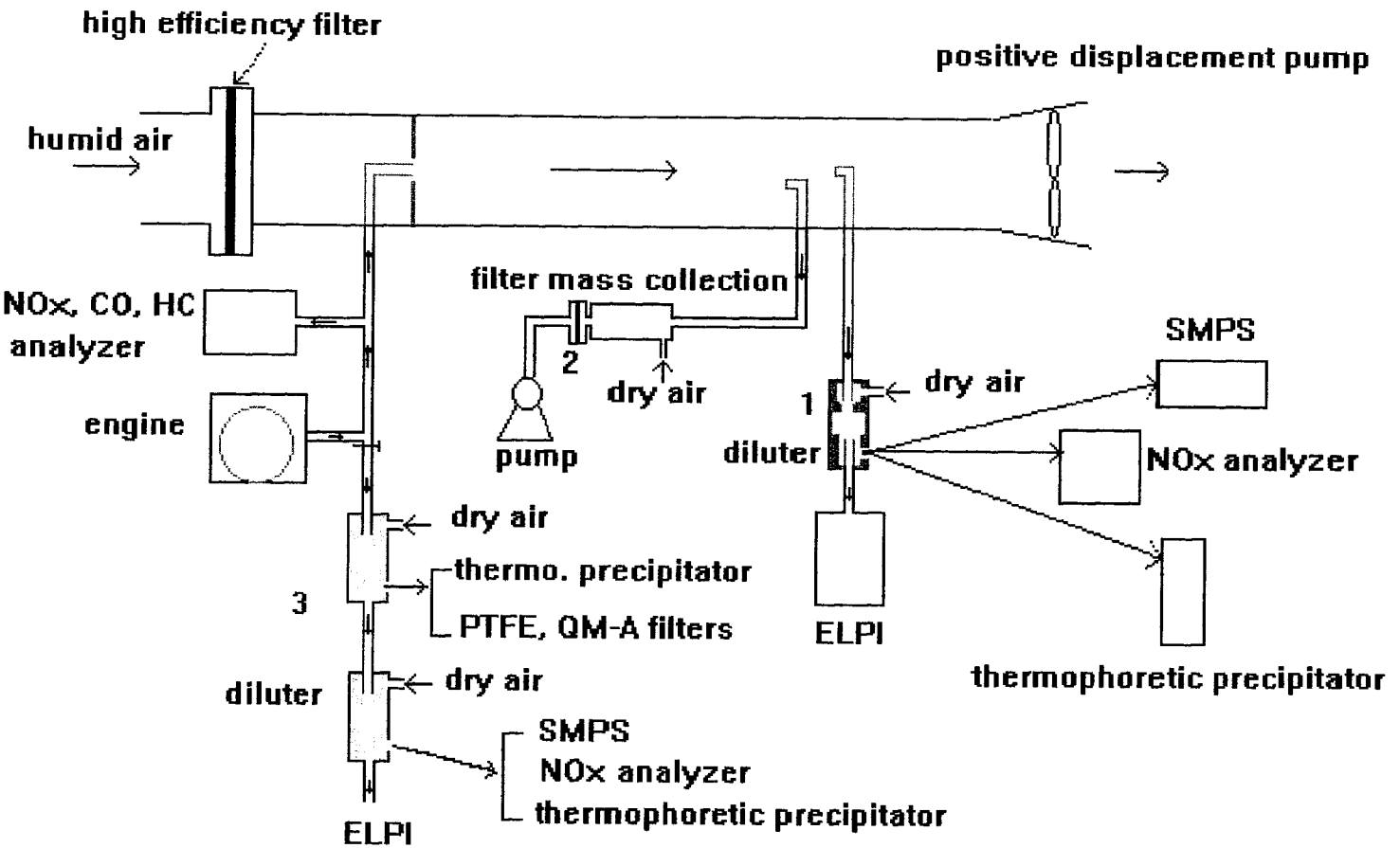
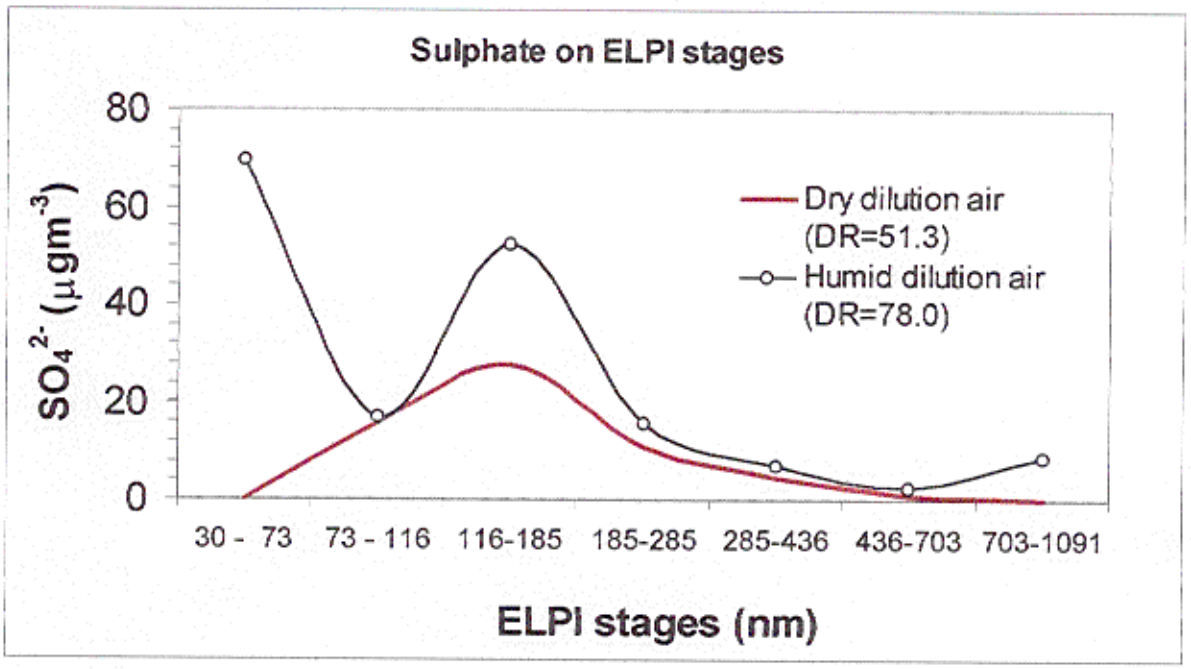


Figure 1. Sampling system at Perkins engine test bed.



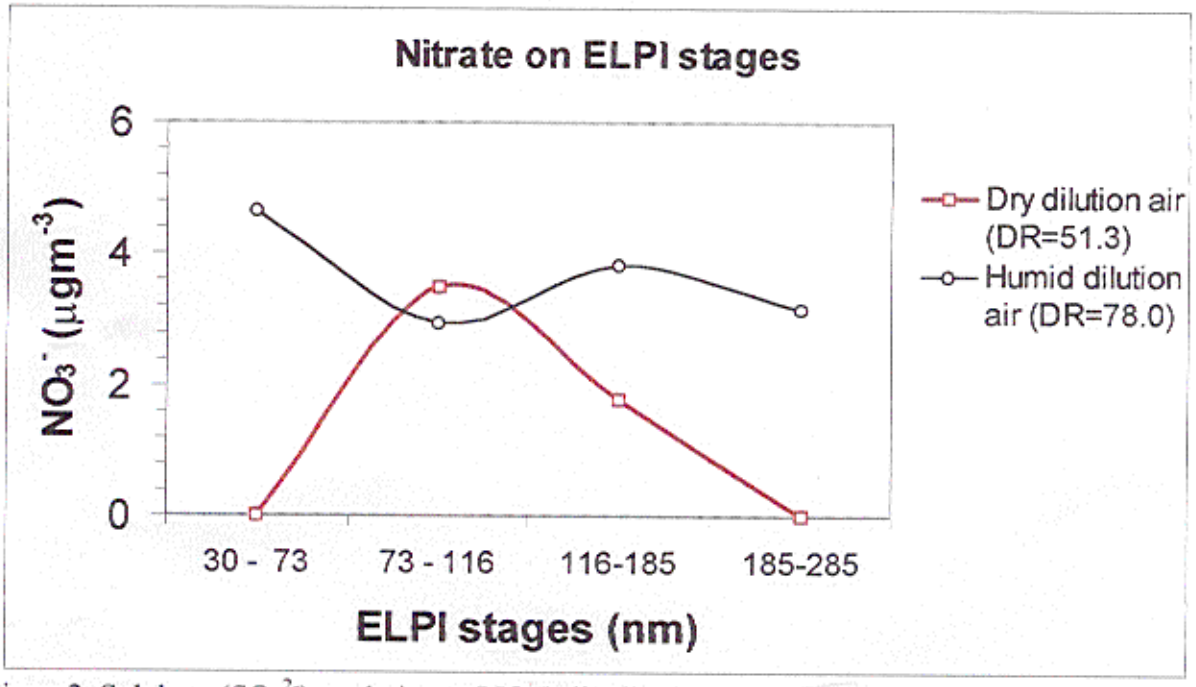
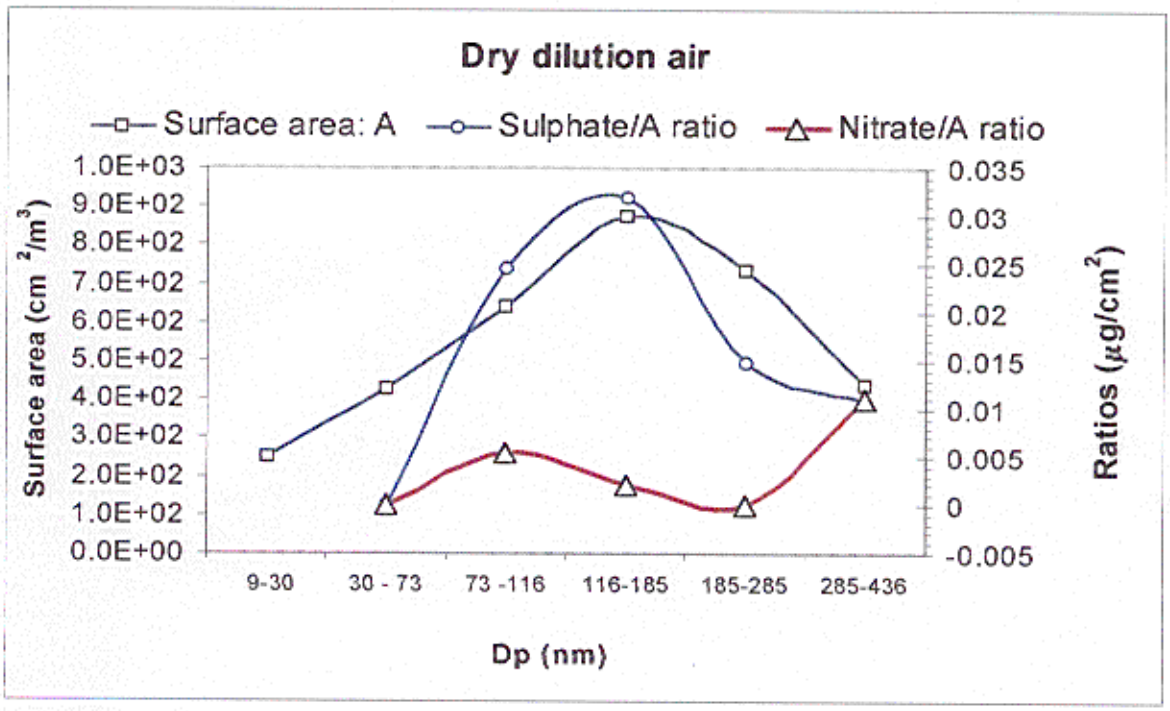


Figure2. Sulphate (SO_4^{2-}) and nitrate (NO_3^-) distributions collected on ELPI stages where engine speed was 1600 rpm and engine load was 50% of full load. X-axis is ELPI stage size range (50% cut size) and y-axis is the sulphate and nitrate mass collected on each ELPI stage when 1 m^3 raw exhaust was passed through the ELPI.



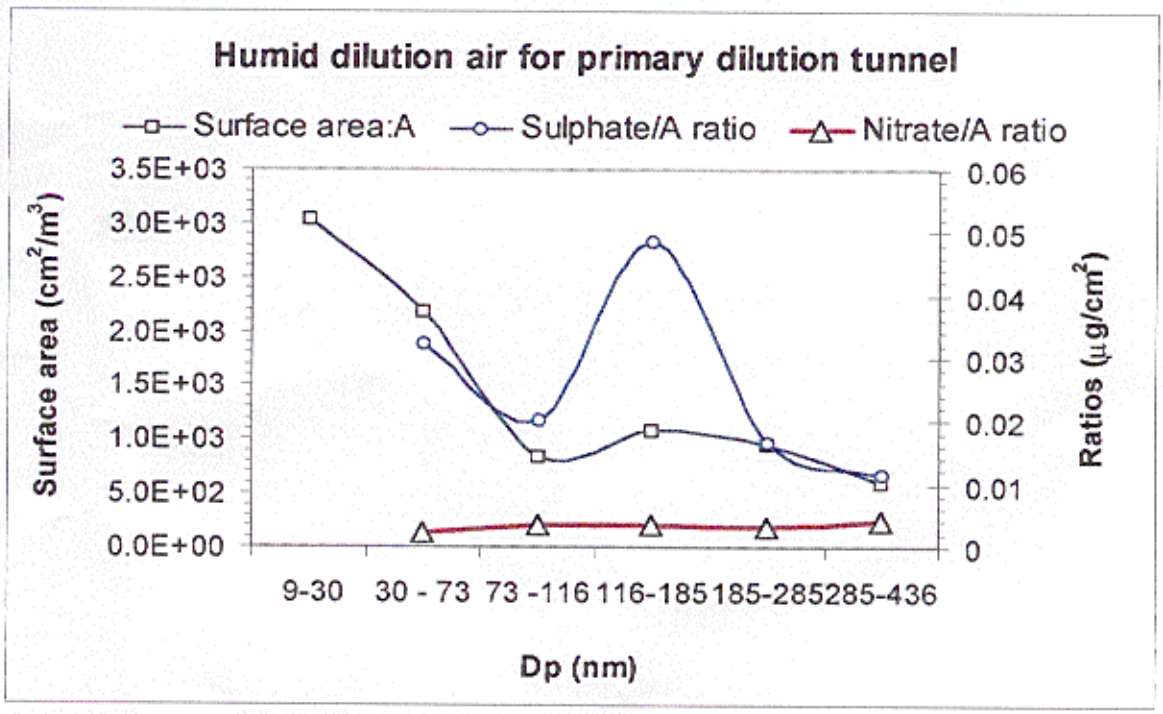


Figure 3. Particle surface area distribution (converted from simultaneous SMPS measurement assuming spherical particles) and the ratios of sulphate (nitrate) mass to particle surface area collected on the corresponding ELPI stage.

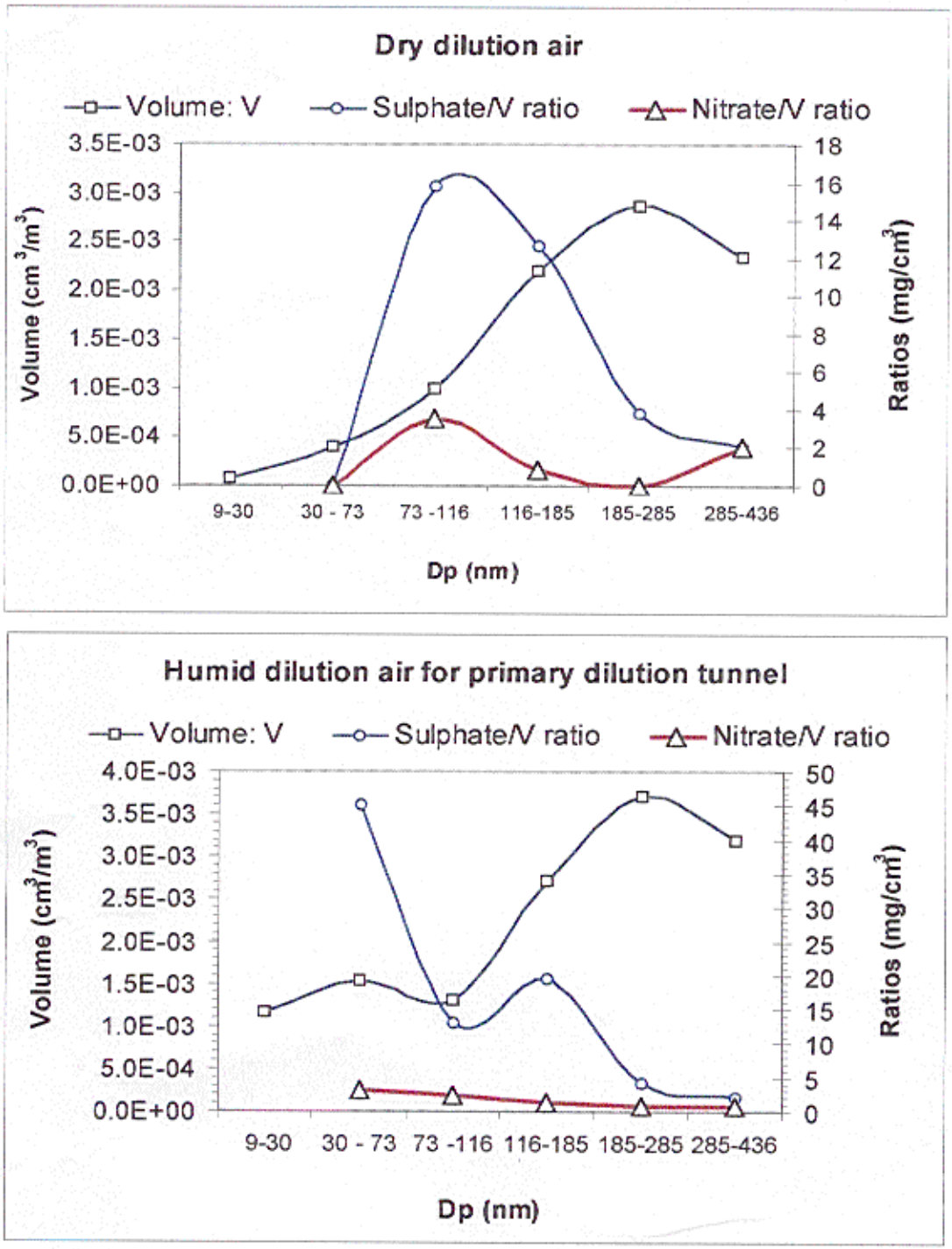


Figure 4 Particle volume distribution (converted from simultaneous SMPS measurement assuming spherical particles) and ratios of sulphate (nitrate) mass to particle volume collected on the corresponding ELPI stage.

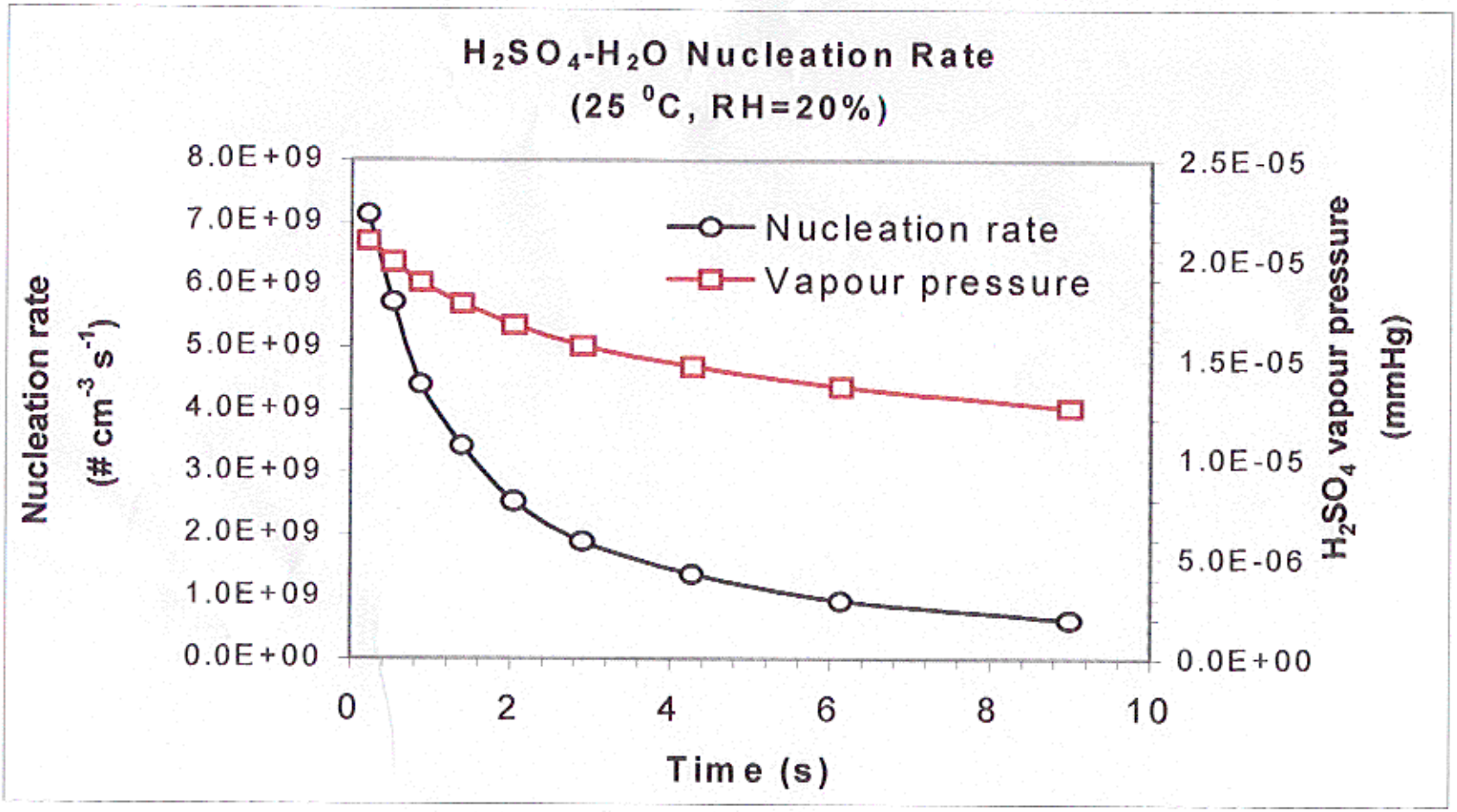


Figure 5. Calculated H_2SO_4-H_2O nucleation rate against time. The size of newly formed particles is just over 1nm.

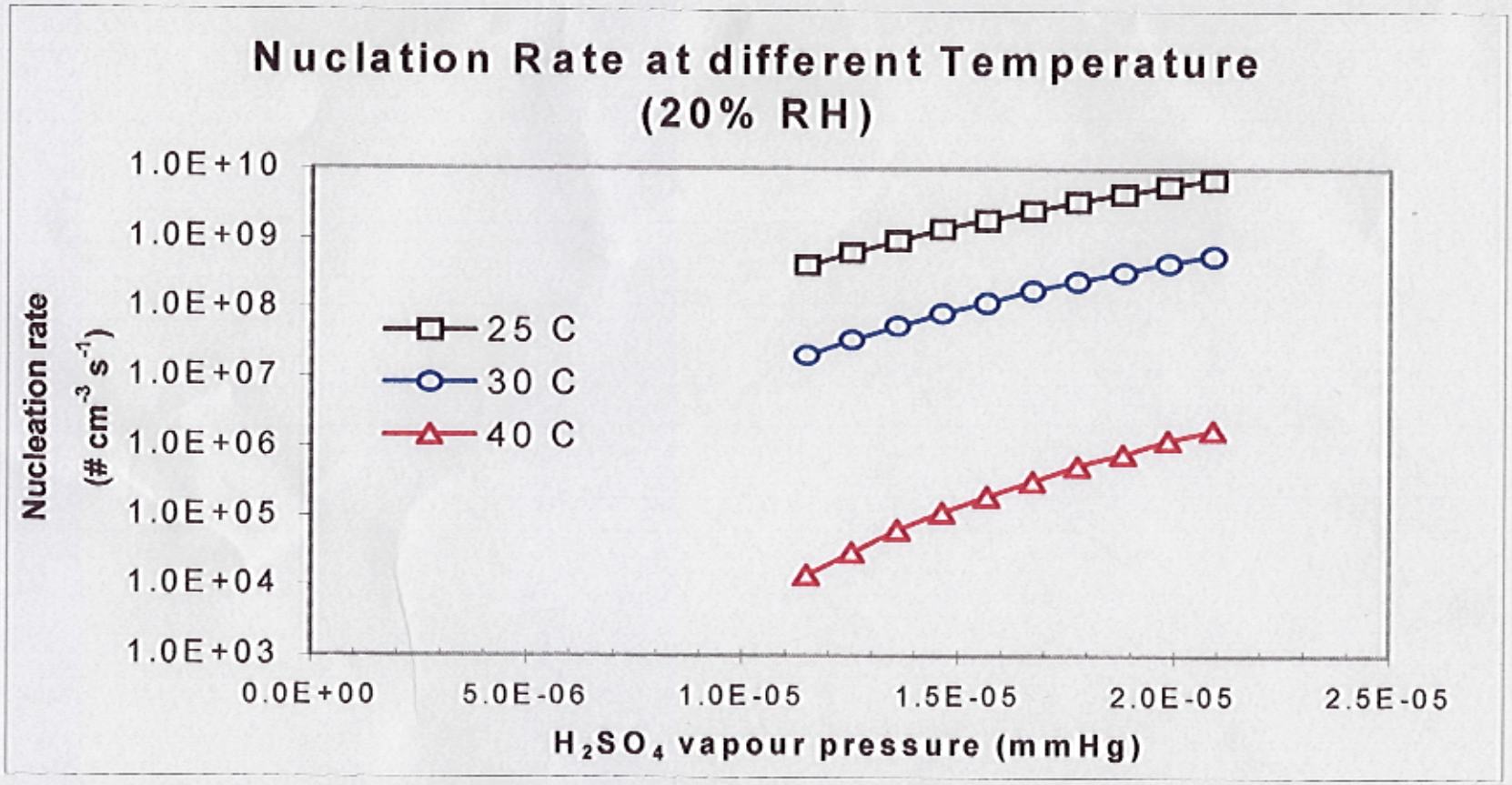


Figure 6. Calculated H_2SO_4-H_2O nucleation rate at different temperatures at a relative humidity of 20%.

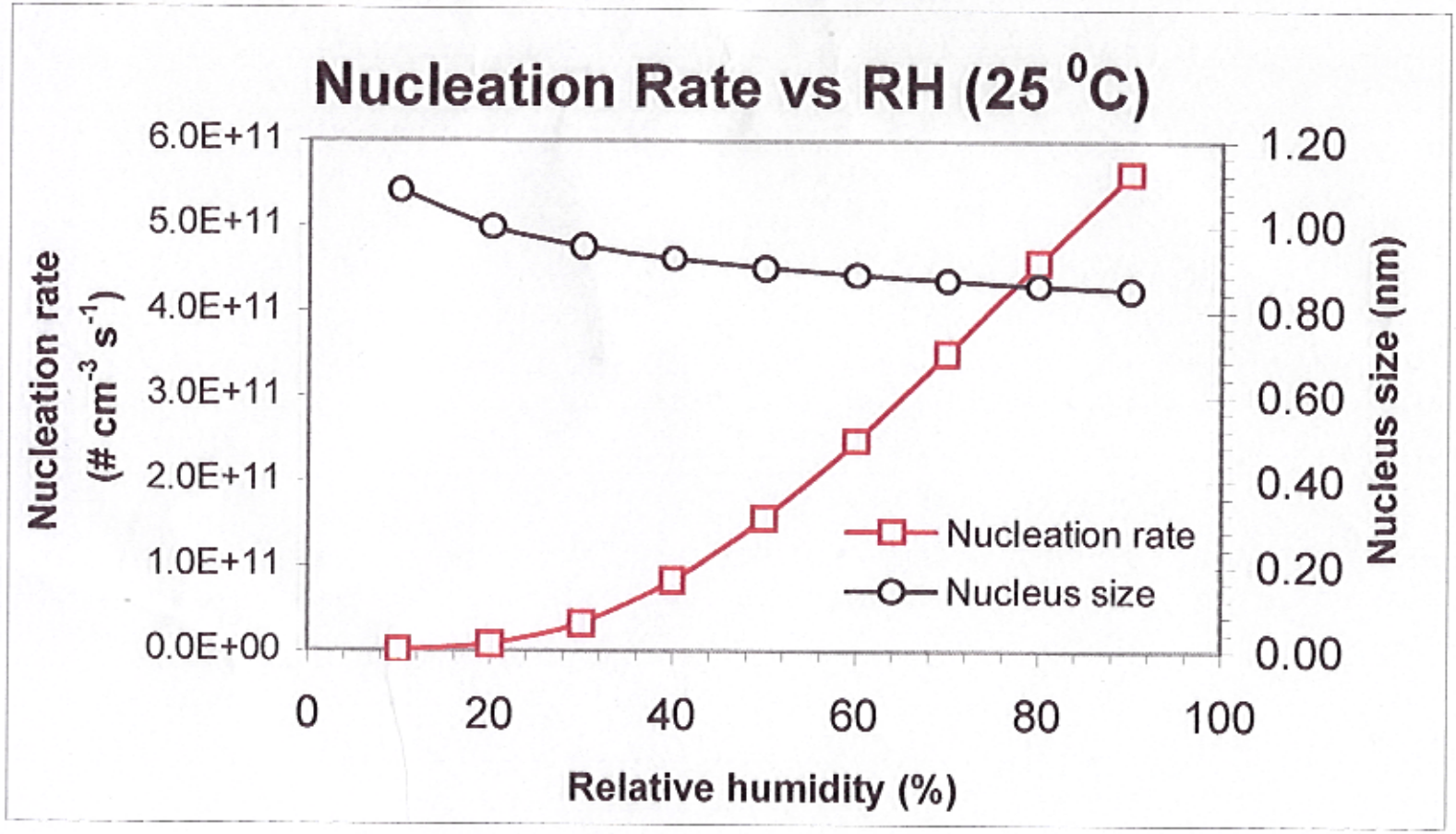


Figure 7. Calculated H_2SO_4-H_2O nucleation rate as a function of relative humidity at 25 °C.