



Introduction

In general it is well known in the macroscopic world that evaporation of liquids is promoted under low pressure conditions. One might therefore expect a particle sizing instrument operating at reduced pressure to lose or reduce in size many of the smaller (nucleation mode) particles by evaporation. This document sets out, both in theory and with experimental evidence, why this is not the case.

In Theory...

- Small particles have highly curved surfaces which could lead to weakening of surface bonds and increased evaporation (the Kelvin effect).
- The increased ratio of surface area to volume of small particles means that they are more likely to evaporate than larger particles.

However:

- As a particle evaporates it cools. In order to cool, heat must be transferred, and at low pressure there are simply fewer particles around to transfer this heat.
- A short sample residence time in an instrument will minimise any effect. The Cambustion DMS500 has a residence time of less than 2 seconds.

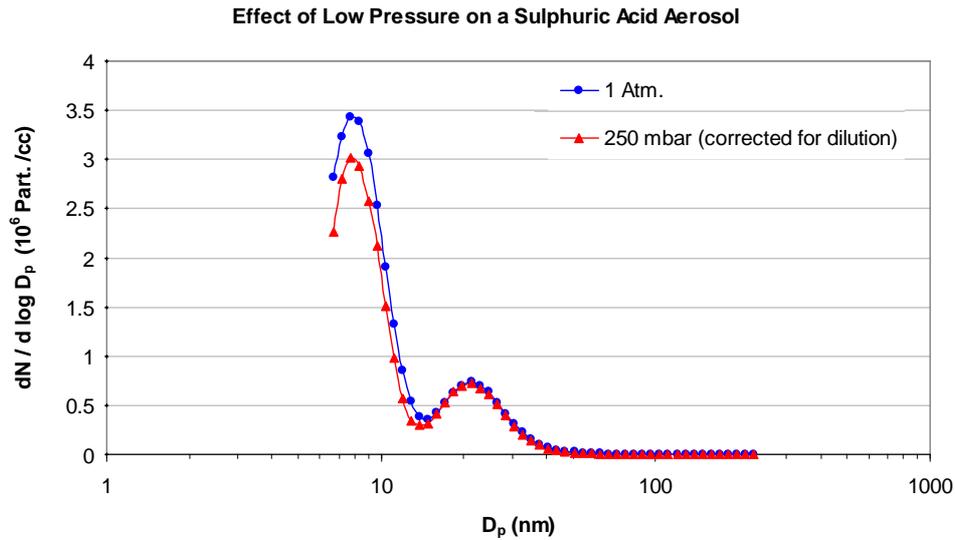
In Practice...

Sulphuric acid is a significant constituent of diesel emissions, and having a boiling point of 340 °C (pure) at atmospheric pressure, is one of the most volatile constituents. Nucleation mode aerosols of sulphuric acid were prepared by passing nitrogen through sulphuric acid in an atomiser, drying the water off, and heating the aerosol to evaporate it. The vapour is then diluted with cool air and re-nucleation occurs. This aerosol was analysed using a Scanning Mobility Particle Sizer (SMPS) under two conditions:

- Resident at atmospheric pressure for 2 seconds
- Resident at 250 mbar for 2 seconds

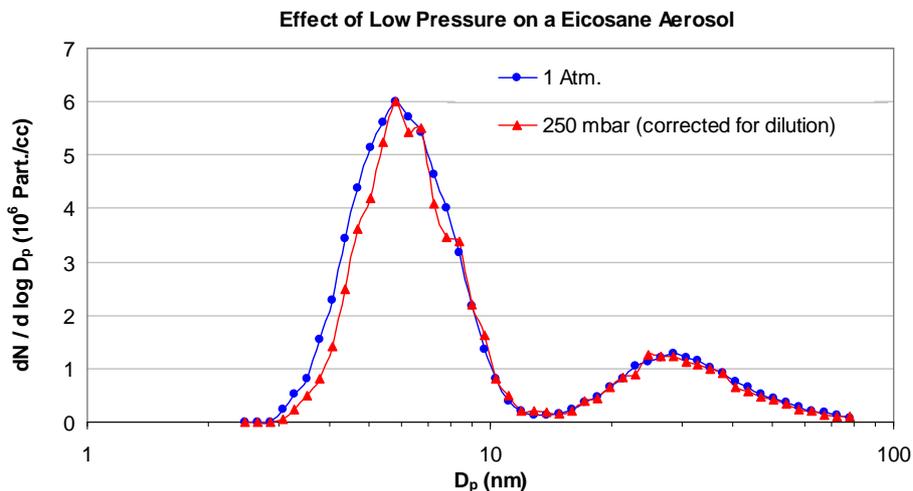
The 250 mbar condition was achieved by using an ejector pump to draw the sample through a choked orifice. The ejector pump dilutes the sample by a factor of 10 before measurement (it should be borne in mind that dilution would actually make worse any potential particle evaporation by reducing the partial pressure of sulphuric acid vapour).

The first figure overleaf shows the average SMPS spectra for the two conditions:



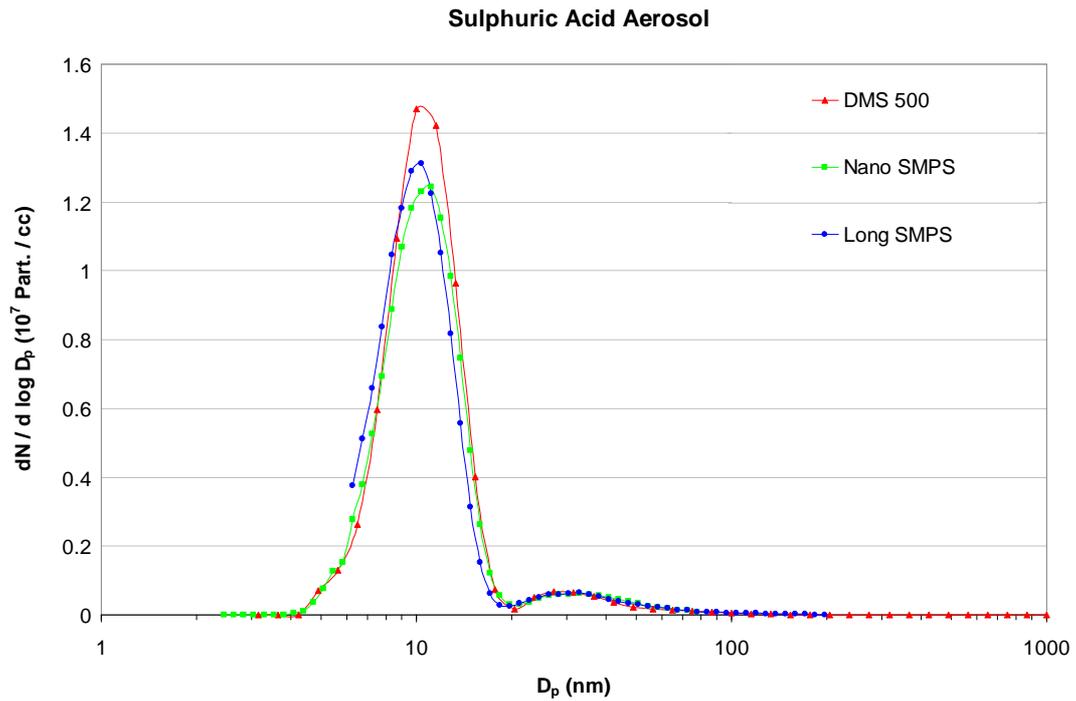
The two peaks in this figure correspond to the nucleation mode at 8 nm from the re-heating system, and the original atomised aerosol at 21 nm. The 250 mbar trace has been scaled by the ejector pump dilution factor. For the nucleation mode, only a small change in particle number between the two conditions is seen and no change in particle size. Note that a reduction in number caused by evaporation would always be accompanied by a reduction in size, and the number change seen is consistent with losses in the sampling / dilution system. No change is seen in the original aerosol mode at 21 nm.

The experiment was then repeated by atomising a solution of Eicosane ($C_{20}H_{42}$) in Hexane, and using activated charcoal in the diffusion dryer to remove the solvent. The use of a hydrocarbon removes any question of the ambient humidity causing a positive size change after the low pressure condition as could be argued to be the case for H_2SO_4 (although very unlikely as the dilution air supply has a relative humidity of just 3%). For this experiment a Nano- Differential Mobility Analyser (DMA) was used in the SMPS, to give a size range down to 2.5 nm. The results for the two conditions are shown below:



Again no real change is seen in size or number in either the nucleation mode at 5.8 nm or the original atomised aerosol at 28 nm.

Finally a direct comparison is made between the simultaneous measurement of a re-nucleated sulphuric acid aerosol as measured under normal operating conditions by a DMS500 and both a Nano- and a Long-SMPS.



Conclusions

It has been shown that any loss or reduction in size of volatile aerosols (typical of diesel emissions) is negligible at 250 mbar. In fact, for a sample in which much vapour is co-present, operating at low pressure would prevent particle growth from the vapour phase, and in this way can be seen as beneficial to particle stability.