

# An experimental assesment of changes to the size distribution of ammonium nitrate under isothermal conditioning.

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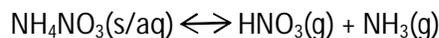
## SUMMARY

The volatility of ammonium nitrate was assessed under laboratory conditions in terms of size distribution changes once subjected to isothermal conditioning. Three temperature regimes were chosen to coincide with what is perceived to be representative of normal indoor temperatures, whilst three particle sizes in air and accumulation modes were investigated. The size distribution for each regime was then measured before and after transportation through an evaporator and these changes assessed.

Results show that for 50nm ammonium nitrate particles, 70-80% losses were recorded through the evaporation chamber. The least volatile was found to be 200nm particulate at 15°C. Generally, at 25°C the greatest reactions were found as was expected from prior research, however an overall increase in particulate concentration at 100nm for all temperature regimes was surprising. Possible multiple physiochemical transformations during transportation through the evaporator, along with activation of impurities within the water could explain these particle gains. The lack of humidity data, inter-transportation temperature profiling and lateral gas measurements limit the effectiveness of this study.

## INTRODUCTION

Secondary inorganic aerosol makes up a sizable fraction of total aerosol loading in the northern hemisphere, with ammonium nitrate (here-forth  $\text{NH}_4\text{NO}_3$ ) contributing upto 30% of this (Ansari and Pandis, 1998).  $\text{NH}_4\text{NO}_3$  is usually found in the accumulation mode of 100-300nm in diameter (Bergin et al., 1997), however they are volatile under normal atmospheric conditions and can deliquesce producing  $\text{NH}_3$  and  $\text{HNO}_3$  in the following reversible process



The balance of this process is known to be dependent on atmospheric pressure, temperature and relative humidity, factors that often differ from an outdoor to indoor environment. It is this volatility at what is considered normal ambient conditions which makes  $\text{NH}_4\text{NO}_3$  challenging yet important to understand.

$\text{NH}_4\text{NO}_3$  originates from outdoor sources, mixing anthropogenically formed  $\text{NO}$  and  $\text{NO}_2$ , predominantly from combustion sources which then oxidises to form nitric acid, which in the presence of ammonium is neutralised to form ammonium nitrate, (Lightstone et al, 2000).  $\text{NH}_4\text{NO}_3$  is a major constituent of atmospheric aerosol, usually found over continental landmasses and usually in the fine size range (Bergin et al 1997, lightstone et al, 2000, Nowak et al, 2010). Over the past decade there have been many attempts to model  $\text{NH}_4\text{NO}_3$  over larger continental land masses to help complete emission inventories and to aid understanding of visual and radiative forcing effects (Schaap et al 2004, Adams et al., 1999). However awareness of  $\text{NH}_4\text{NO}_3$  and its gas phase components of nitric acid and ammonia have been largely neglected as a contributing dynamic in indoor air pollution studies.

### MEASUREMENTS

Three sizes of ammonium nitrate aerosol were chosen for analysis, 50nm, 100nm, and 200nm. These were then subjected to three temperature profiles 15°C, 20°C, and 25°C as they passed through a 2m evaporator. The reduction of aerosol size is indicative of the rate and degree of dissociation.

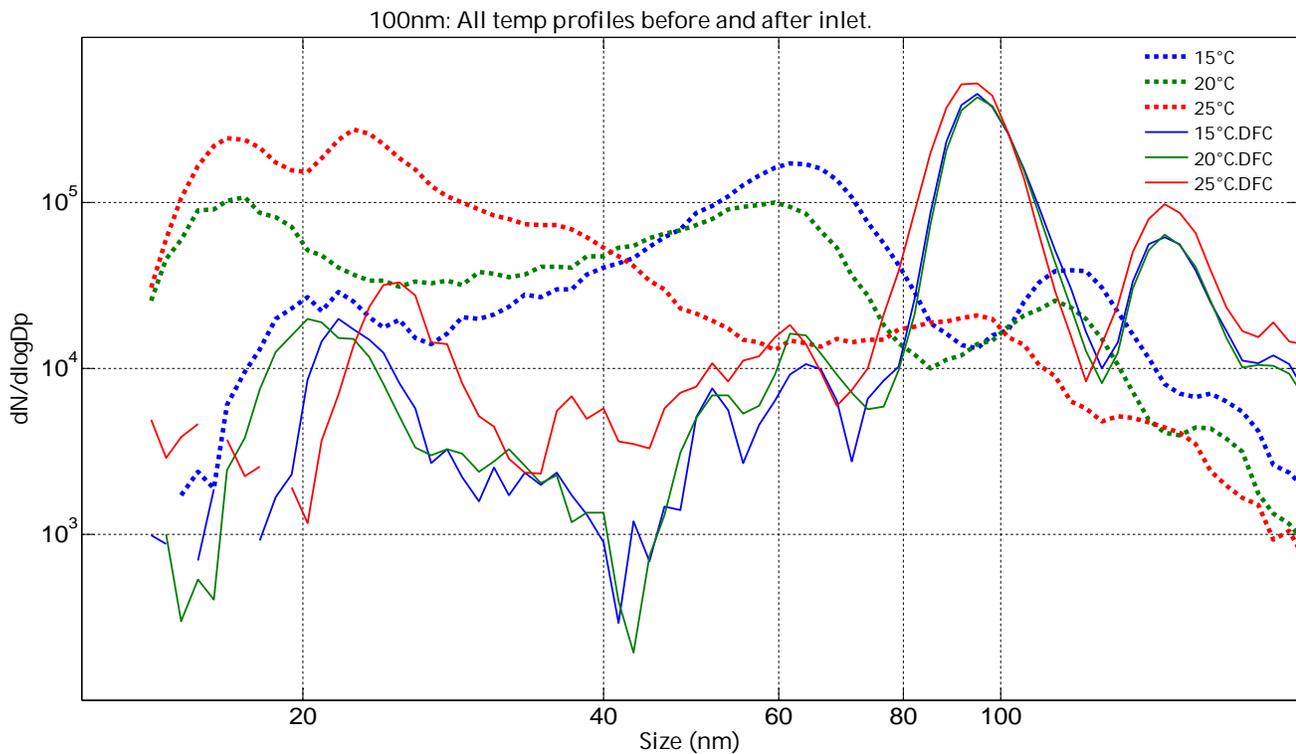


Fig. 1: Log Size distributions for monodisperse ammonium nitrate aerosol of 100nm is shown (hatched line) in relation to the original aerosol size distribution taken directly from the first DMA (DFC). Isothermal temperatures are represented by the red, green and blue lines.

The volatility of  $\text{NH}_4\text{NO}_3$  at 100nm is demonstrated in figure 1. The dissociation rate is seen to be similar for both 15°C and 20°C where-as for 25°C the rate and extent of the size distribution change is observed to be more significant. Small losses were found between the time the  $\text{NH}_4\text{NO}_3$  aerosol was created and the first DMA size selector (shown above labeled DFC).

## DISCUSSION

The changes in the size regime of  $\text{NH}_4\text{NO}_3$  are closely aligned to temperature. This is in accordance with prior research (Seinfeld and Pandis 1998, Dassios and Pandis 1999, Lunden et al., 2003). Between 70-80% of 50nm  $\text{NH}_4\text{NO}_3$  disappeared during transportation through the evaporation chamber. It is probable that due to residence time through the experimental set-up, most of the particles deliquesced into their gaseous precursors. It is theorized by Dassios and Pandis (1999) that  $\text{NH}_4\text{NO}_3$  particles smaller than 100nm can equilibrate between phases in just a few seconds under "typical" temperatures. This could explain the large losses seen here with transportation rate through the entire sampling set-up estimated to be between 3 and 4 minutes.

$\text{NH}_4\text{NO}_3$  volatility is evident once 100nm particles were produced. At 25°C reaction rates were at their greatest with a large transition of size distribution from 93nm measured directly from the first DMA down to 22nm after undergoing transportation through the evaporator.

For 200nm, the most volatility was again recorded at the highest temperature. The modal peak at 25°C was very similar to that of 20°C however much greater losses occurred at 25°C, whilst at 20°C a net gain in concentration was recorded during transportation through the evaporator. At 15°C the  $\text{NH}_4\text{NO}_3$  particles contracted by 28nm, thus displaying the least volatility of each size and temperature regime. This indicates that the larger the  $\text{NH}_4\text{NO}_3$  particle the less prone to volatility it becomes, even at temperatures where deliquescence is expected.

## CONCLUSION

Because of its volatility at ambient temperatures  $\text{NH}_4\text{NO}_3$  is challenging, yet of importance to indoor air research, Particle size changes and transitional changes from solid-liquid-gas phases in a reversible mechanism make  $\text{NH}_4\text{NO}_3$  and its component species ammonia and nitric acid a dynamic part of overall air mix within the indoor environment, both in terms of particulate residence time in the accumulation mode and the potential material damage caused by nitric acid sorption.

The evident overall reduction in particle sizes revealed here indicates either the removal or deliquescence of  $\text{NH}_4\text{NO}_3$  to its gas phase precursors, a stripping of the nitrate off the particulate, or aqueous phase particulate undergoing evaporation. It is shown here that the smaller the particle and the higher the temperature, the greater the reduction in size and thus indicating increased volatility. However it is wrong to presume that the reaction is greater for the smaller size fractions as it is possible that the larger particles undergo various physiochemical transitions during the transportation through the evaporator.

## REFERENCES

- Asif S. Ansari and Spyros N. Pandis, 1998, Response of Inorganic PM to Precursor Concentrations, *environmental science and technology*, 18, pp2706–2714.
- Bergin M H, Ogren J A, Schwartz S E, Mcinnis L M, 1997, Evaporation of Ammonium Nitrate Aerosol in a heated Nephelometer: Implications for Field Measurements. 31, 2878-2883.
- Fischer M L, Littlejohn D, Lunden M, and Brown L, 2003, Automated Measurements of Ammonia and Nitric Acid in Indoor and Outdoor Air, *Environment science and technology*, 37, 2114-2119.
- Konstandinos G. Dassios, Spyros N. Pandis, The mass accommodation coefficient of ammonium nitrate aerosol, 1999, *Atmospheric Environment* 33 pp2993–3003
- Lightstone J M, Onasch T B, Imre D, Oatis S, 2000, Deliquescence, Efflorescence and water activity in Ammonium Nitrate and Mixed Ammonium Nitrate/Succinic Acid Microparticles, *Journal of Physical Chemistry*, 104 pp9337-9346.
- Lunden M M, Revzan K L, Fischer M L, Thatcher T L, Littlejohn D, Hering S V, Brown N J, 2003, The transformation of outdoor ammonium nitrate aerosols in the indoor environment, *Atmospheric Environment*, 37, pp5633-5644.
- Seinfeld J H, Pandis S A, *Atmospheric Chemistry and physics: From air pollution to climate change*, 1998, John Wiley and sons, New York.
- Schaap M, van Loon M, ten Brink H M, Dentener F J, Builtes P J H, Secondary inorganic aerosol simulations for Europe with special attention to Nitrate, 2004, , *Atmospheric Chemistry and Physics*, 4, pp857-874.
- Sioutas C, Delfino RJ, Singh M. 2005, Exposure assessment for atmospheric ultrafine particles (UFP) and implications in epidemiological research. *Environ Health Perspect*, 8, pp947–955.