INVESTIGATION OF THE HETEROGENEOUS REACTION OF AMMONIA ON DELIQUESCENT SEASALT USING FTIR SPECTROSCOPY.

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Introduction

- **Ammonia has mainly agricultural sources (live stock, fertiliser). It is expected to represent a significant atmospheric pollutant in Ireland (mixing ratio >50ppb)**
- **Adsorbed ammonia enhances the rate of oxidation of SO_2 to yield stable NH_4HSO_4 or $(NH_4)_2SO_4$ aerosols.**

NH3

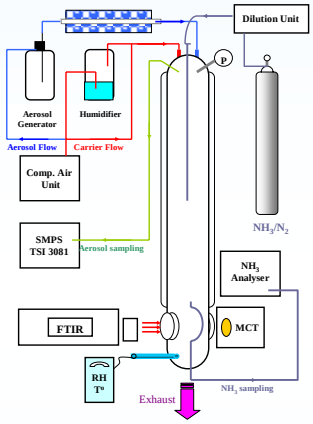
- Reduces environmental acidification
- Key role in nitrate/sulphate partitioning
- Enhances particle formation

- **Hygroscopic behaviour of $(NH_4)_2SO_4$ displays a much stronger hysteresis than that of H_2SO_4.**

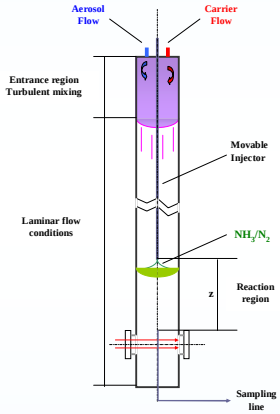
➢ **Uptake of ammonia into acidic aerosol can affect:**
- **growth pattern and ability to act as cloud nuclei**
- **alter optical properties (light absorption and scattering by particulate matter) .**

- **Ammonia uptake rate on deliquescent aerosol is controlled by diffusion towards counter ions in the bulk as well as the kinetics of surface regeneration.**
- **Spectroscopic technique can provide a more complete picture of the mechanism, as it probes bulk phase processes.**

Experimental Setup



The **aerosol** suspension in nitrogen is generated by a TSI 3076 atomizer from a 1%wt seasalt solution. A diffusion dryer allows for complete re-crystallization of the salt dissolved in the droplets.
The aerosol fraction is monitored downstream by a particle sizer (SMPS TSI 3081).
The **relative humidity** (RH) in the reactor can be tuned between 1% and 90%.

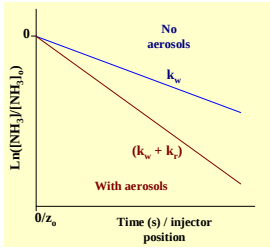


- **Laminar flow conditions**
(Reynolds Number R_e=60 at 5L/min.)

$$t = \frac{z}{f}$$ f: flow velocity ($cm \cdot s^{-1}$)

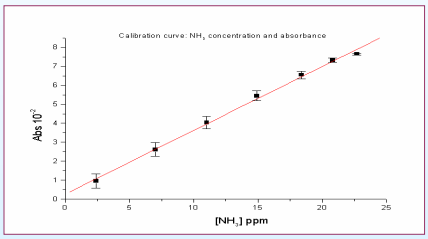
- **First- order reaction rate k:**

$$f\left(\frac{d[NH_3]}{dz}\right) = -k[NH_3]$$

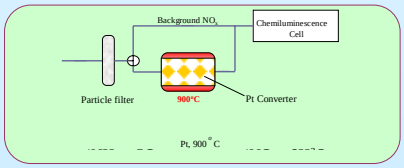


The **flow-tube** is made of glass and has an inner diameter of 10cm and a maximal reactive length of 80cm. This reactive length - i.e. the fraction of the reactor located between the tip of the injector and the sampling inlet - can be tuned up stepwise to this maximal value using a movable injector (6mm outer diameter).
It operates at atmospheric pressure and its temperature can be regulated.
It is fitted with spectroscopic windows (BaF_2) to allow for FTIR monitoring of both gas- and condensed phase (Digilab FTS 3000 coupled with external MCT detector).
The geometry of the reactor ensures that laminar flow conditions are always achieved, so that reaction time t is directly proportional to reaction length z.

NH3 Monitoring

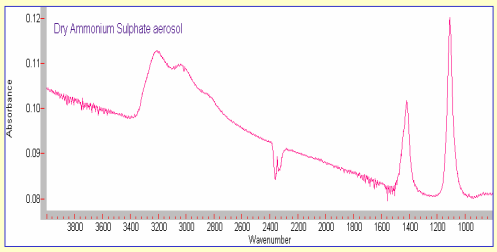


Ammonia calibration curve obtained using FTIR monitoring at 966cm^{-1}. Good linearity is observed down to the low ppm range. The short detection pathlength given by the flow-tube geometry (16cm), however, makes it difficult to measure below 1ppm with confidence.

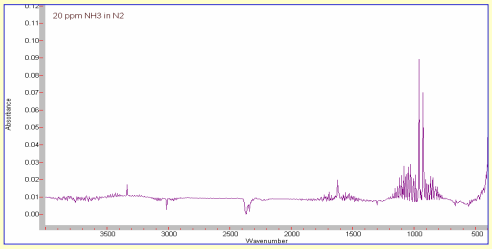


An improved detection limit for our apparatus can be achieved by converting ammonia into NO on a high temperature catalyst, and measuring the resulting change in background NO_x concentration using a conventional NO_x analyzer. This will allow us to work at more relevant ammonia concentrations.

Observations



Reference spectrum of ammonium sulphate aerosol suspension.
Total particle concentration: 2x10^5#·cm^{-3}
Mode: 150nm



Reference spectrum of ammonia
Ammonia partial pressure $[NH_3]$: 20ppm.

Results & Outlook

- Preliminary validation experiments show that our system can monitor both gas- and condensed phase composition.
- Good linearity is observed in gas-phase concentration changes.
- Ancillary deliquescence/efflorescence experiments show good reproducibility in terms of aerosol number density and composition.

Next proposed experimental steps include:

➢ **Kinetic measurement of NH_3 uptake rate against aqueous sea-salt aerosols of different ionic composition.**
➢ **Heterogeneous reaction of NH_3 on sulfuric acid aerosols.**
➢ **Spectroscopic investigation of ammonium nitrate nucleation.**

$$HNO_3 + NH_3 \longrightarrow NH_4NO_3$$

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