

PA62) Investigation of Laboratory Generated Individual Aerosol Particles and Powdery and Aqueous Samples of $(\text{NH}_4)_2\text{SO}_4$ by ATR FT-IR Imaging Technique

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1. Introduction

A recent work demonstrated the practical applicability of ATR FT-IR imaging technique with the combined use of low- Z particle EPMA for the characterization of individual aerosol particles (Ro et al., 2009). In the present work, laboratory generated individual $(\text{NH}_4)_2\text{SO}_4$ aerosol particles were analyzed by the combined application of ATR FT-IR imaging and low- Z particle EPMA techniques. In addition, ATR FT-IR spectra were obtained from powdery and aqueous $(\text{NH}_4)_2\text{SO}_4$ samples. The objective of this work is to investigate qualitative and quantitative aspects of ATR FT-IR absorption spectra obtained from different physical states, concentrations, and particle sizes of $(\text{NH}_4)_2\text{SO}_4$ samples.

2. Materials and Methods

Analytical grade $(\text{NH}_4)_2\text{SO}_4$ powders (Aldrich, 99.99% purity) were used to prepare a saturated aqueous mother solution (denoted as an 100% solution), a saturated solution diluted by two (denoted as a 50% solution), by four (25%), by ten (10%), by fifty (2%), and by 100 (1%). Then artificial aerosols were generated from these solutions using a home-made nebulizer, and collected on Al foils using a 3-stage Dekati PM-10 cascade impactor. ATR-FT-IR imaging data for aerosols on stage 2 (2.5~10 μm size range), of the pure $(\text{NH}_4)_2\text{SO}_4$ compound were measured using Perkin Elmer Spectrum 100 FT-IR spectrometer interfaced to Spectrum Spotlight 400 FT-IR microscope. A Germanium hemispherical internal reflection element (IRE) crystal of 600 μm diameter was used. Individual aerosol particle sizes were measured from their secondary electron images obtained from SEM measurements prior to ATR FT-IR imaging.

3. Results and Discussion

Figure 1-A shows full ATR FT-IR absorption spectra of ammonium sulfate bulk powder (spectrum #1), 50% saturated solution (spectrum #2), and an individual aerosol particle generated from this solution (spectrum #3). Spectrum #1 shows sharp peaks of $\nu_4 \text{NH}_4^+$ and $\nu_3 \text{SO}_4^{2-}$ bands at 1,403 and 1,065 cm^{-1} , respectively. A broad absorption band, centering at around 3,100 cm^{-1} , exhibits shoulder peaks of ν_3 , ν_1 , and $2\nu_4$ bands of NH_4^+ at 3,180, 3,042, and 2,848 cm^{-1} , respectively (Boer et al., 2007; Downing et al., 1977). In spectrum #2, the presence of a sharp peak at 1,641 cm^{-1} ($\nu_2 \text{H}_2\text{O}$) and the shift of broad absorption band centre at around 3,400 cm^{-1} , where ν_1 , ν_3 and $2\nu_2$ bands of water occur, ensure the presence of water as it is the spectrum of an aqueous solution. It is noticeable that $\nu_4 \text{NH}_4^+$ and $\nu_3 \text{SO}_4^{2-}$ peaks in spectrum #2 are shifted to wavenumbers higher than those of the powder spectrum (1,403 to 1,446 and 1,065 to 1,079 cm^{-1} , respectively). This shift of peak positions is a clear indication of different physical states of the two samples. This capability of FT-IR to identify physical state of samples is very valuable because the phase of airborne particles is one of the most important physical properties of aerosols owing to their different contributions to radiative forcing of the aerosols with same chemical compositions but in different phases. Spectrum #3 almost resembles with the spectrum of the bulk powder. The absence of ν_2

H₂O peak at $\sim 1,640\text{cm}^{-1}$ indicates that the aerosol contains an insignificant amount of water although it was produced from an aqueous solution.

In Figure 1-B, absorbances of individual aerosol particles according to their particle size are shown. The absorbances of the aerosol particles generated from the mother solutions with different concentrations more or less show the same trend although their absorbances are linearly proportional to their areas. In other words, the generated particles are in the similar physical and chemical states irrespective of the concentrations of their mother solutions. For the aqueous solutions, ATR FT-IR absorbances are linearly proportional to the concentrations of the solutions (Beer's law) shown in Figure 1-D. After aerosol formation, the concentrations of individual particles become similar to each other regardless of the concentrations of their mother solutions. this kind of behaviour also occurs for real ambient aerosol particles.

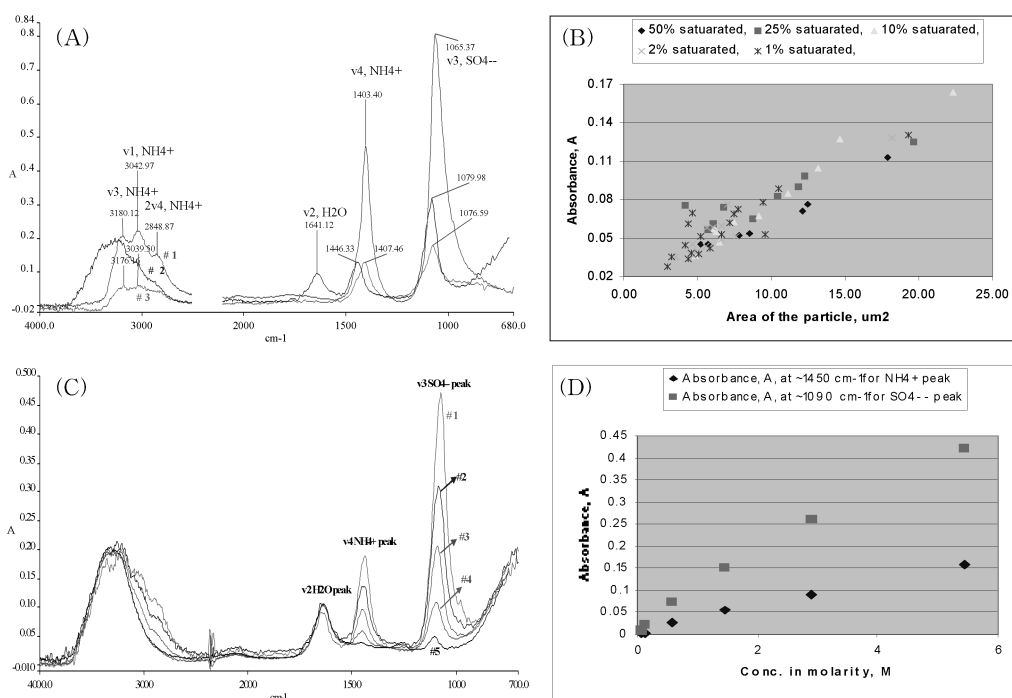


Fig. 1. (A) ATR FT-IR absorption spectra of ammonium sulfate powders (spectrum #1), 50% saturated solution (#2), and an individual particle generated from 50% saturated solution (#3) (B) Absorbance depending on size of individual particles generated from 50%, 25%, 10%, 2% and 1% saturated aqueous mother solutions. (C) ATR FT-IR absorption spectra of ammonium sulfate aqueous solutions: #1, #2, #3, #4, and #5 spectra are of 100%, 50%, 25%, 10% and 2% solutions respectively. (D) Absorbance depending on concentrations of aqueous solutions corresponding to those shown in Figure 1-C.

References

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