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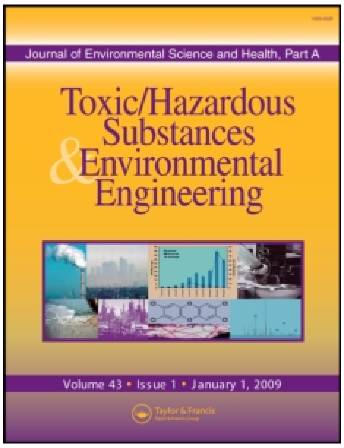

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THE INFLUENCE OF RELATIVE HUMIDITY ON THE SIZE OF ATMOSPHERIC AEROSOL

Keywords : relative humidity, aerosol, hygroscopic, deliquescence

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ABSTRACT

The relative humidity of ambient air is very often over 75% throughout the year in Taiwan. Thus, the influence of relative humidity on the growth of hygroscopic aerosols in the atmosphere is particularly important. In this study, a TDMA system (Tandem Differential Mobility Analyzer) equipped with newly developed a SMPS (Scanning Mobility Particle Sizer) was used to observe the sizes of submicron ammonium sulfate aerosols, from 63.8nm to 224.7nm, at five controlled relative humidities, 50%, 75%, 81%, 85% and 89%. It is the first time that the hygroscopic growths and deliquescence points of submicron aerosols of ammonium sulfate have ever been closely observed by use of the SMPS. The expermental results showed that the abrupt size changes of aerosols at their deliquescence points can be more precisely observed than in previous studies. It was also shown that there was no apparent growth in an ammonium sulfate aerosol until the relative humidities was over 75%. At relative humidities between 81% and 89% , the growth ratio of size was about a factor of 1.3 to 1.6 and the water content of ammonium sulfate aerosols by mass was about 47% to 66% .

INTRODUCTION

Humidity is one of the pertinent environmental factors in atmosphere. It has strong influence on the chemical and physical properties of atmospheric aerosols because some of aerosols inorganic components are hygroscopic, such as sulfates, nitrates, chloride and etc.. When humidity reaches the deliquescence point, these inorganic salts aerosols grow abruptly due to the phase change from solid to liquid. These inorganic salts aerosols do not grow until humidity reaches deliquescence point. At deliquescence point, aerosols grow abruptly due to the phase change from solid to liquid, which plays a important role on the physical and chemical reactions of atmospheric aerosols. For instance, sulfur dioxide can be absorbed in aqueous phase of atmospheric aerosols and oxidized to sulfate which can be inhaled through respiratory tracts to cause adverse health effects. On the other hand, the hygroscopic growth of aerosols also has influence on visibility. The scattering of light by aerosols will be enhanced because of the water absorbed and condensed on aerosols and the size growth of aerosols. Visibility will thus be deteriorated. Taiwan is a subtropical island so that it is very humid. Because humidity is usually greater than 75%, the influence of humidity on the size of atmospheric aerosols is important. In this study, hygroscopic aerosols investigated, ammonium sulfate, is the most abundant and representative inorganic salts in urban atmosphere. The experimental system is the Tandem Differential Mobility Analyzer (TDMA) equipped with newly developed SMPS (Scanning Mobility Particle Sizer). The size change of aerosols under controlled humidity was measured by TDMA and SMPS to understand the growth of aerosols and the influence of humidity on the size of aerosols.

THEORETICAL BACKGROUND

The hygroscopic phenomenon of inorganic salts was first presented by Kohler [1]. At low humidity, the size change of aerosols is not significant. Hygroscopic salt particles begin to dissolve and form liquid particle at deliquescence point. At humidity greater than deliquescence point, aerosols continue growing with humidity.

In general, deliquescence point is decreased with temperature. In other words, lower deliquescence point is found when temperature is increased. Tang and Munkelwitz [2] presented the relationship between deliquescence point and temperature based on thermodynamics, which is expressed in the following,

$$\ln \frac{H_d(T)}{H_d(T^*)} = \frac{\Delta H_s}{R} [A(\frac{1}{T} - \frac{1}{T^*}) - B \ln\frac{T}{T^*} - C(T - T^*)] \tag{1}$$

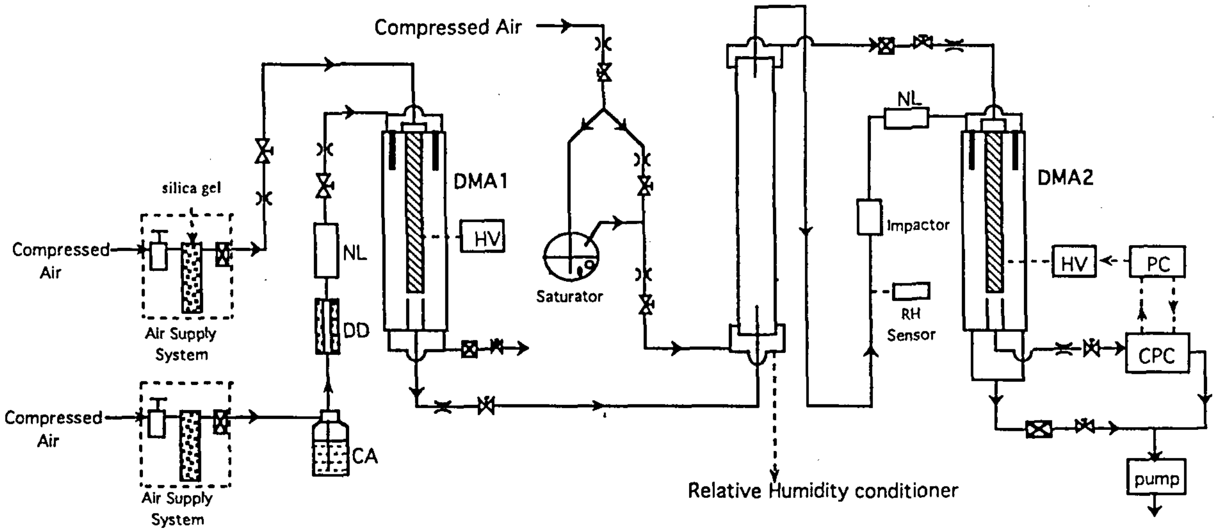
Where T is absolute temperature, and T* is reference temperature, 298^0K. Hd(T*) and Hd(T) represent the deliquescence point at T* and T, respectively. ΔHs is the integral heat of condensation and R is the universal gas constant. A, B, and C are constants. As for ammonium sulfate, Hd(T*) is 79.9%, ΔHs is 1510 cal/mole, A is 0.1149, B is -4.489×10^{-4}, and C is 1.385×10^{-6} ·[2] According to equation (1), the deliquescence point of ammonium sulfate at 20^0C, 80.3%, can be calculated. The relationship between size of liquid droplets and vapor pressure is described by the kelvin effect equation. As for hygroscopic inorganic salt aerosols, Raoult's law is also applied to account for the effect of solute in solution on the vapor pressure. The relationship between diameter of aerosols and humidity can be derived as expressed in equation (2) [3, 4]

$$H = \frac{P}{P_s} \times 100\% = (1 + \frac{6\, i\, m_s M_w}{M_s \rho \pi D_p^3})^{-1} \exp(\frac{4 \sigma M_w}{\rho R T D_p}) \tag{2}$$

Where H is the relative humidity and Dp is the diameter of aerosol at equilibrium. P and Ps represent the vapor pressure and saturation vapor pressure at temperature T. i is the van't Hoff factor. ms and Ms represent the dry mass and molecular weight of solute, respectively. Mw, r and s stand for molecular weight, density, and surface tension of water, respectively. Thus, the diameter of hygroscopic aerosols at equilibrium can be obtained based on equation (2).

EXPERIMENTAL METHODS

A Tandem Differential Mobility analyzer system (TDMA) equipped with a newly developed Scanning Mobility Particle Sizer (SMPS) was established to observe the growth of ammonium sulfate aerosols with humidity. The TDMA system has been used by Liu et al. [5], MuMurry et al. [6] and Juozaitis et al. [7]. But none of these studies has ever incorporated the SMPS. This experimental system shown in figure 1 includes the following four major experimental methods ; Collison atomizer (CA). differential mobility analyzer (DMA), relative humidity conditioner, and condensation particle counter (CPC). The relative humidity conditioner was a 120 cm long with inside diameter of 2.209 cm stainless steel column. Air from clean air supply system was saturated by a saturator and mixed with dry air to generate the humidified air with designated relative humidity, 50%, 75%, 81%, 85%, and 89%. The water vapor of humid air flowing in the outer layer of relative humidity conditioner diffused and contact with the monodispersed aerosols generated from the first DMA flowing in the center of relative humidity conditioner. Thus, the aerosols grew due to the condensed water vapor. The relative



CA	Collison Atomizer
CPC	Condensation Particle Counter
DMA	Differential Mobility Analyzer
NL	Neutralizer
DD	Diffusion Dryer
HV	High Voltage Supply
PC	IBM Personal Computer

⋈ valve

)(flow meter

☒ Absolute Particle Filter

Pressure Regulator

valve

flow meter

FIG. 1. Schematic Diagram of Experimental System.

humidity of aerosol flowing from conditioner was measured. The humidified air from conditioner was filtered to be the sheath air of the second DMA so that the relative humidity of conditioner and DMA were the same. Four different size of monodispersed aerosols of ammonium sulfate, 63.8nm, 117.6nm, 174.7nm, and 224.7nm, from the first DMA were generated.

RESULTS AND DISCUSSION

Size Distribution of Ammonium Sulfate Aerosol

The size distributions of ammonium sulfate of dry aerosol diameter at 63.8nm which were humidified at relative humidity of 50% and 75% are shown in figure 2. In contrast, the size distributions at relative humidity of 81%, 85%, and 89% are given in figure 3. It is also noteworthy that bimode is observed for size distribution shown in figure 2 and 3. Although most of the aerosols carry single charge after they flow through neutralizer of the first DMA, some aerosols may carry double or more charge to cause the bimode distribution of aerosols from the first DMA.

As for the deliquescence growth, it is clearly indicated that ammonium sulfate aerosol does not grow until 75%. And the size distribution is shifted to larger size with higher relative humidity. The deliquescence point is must between relative humidity of 75 and 81%. Similar size distribution of ammonium sulfate at three other initial diameter were observed. The size distribution and number concentration of ammonium aerosols at five different relative humidity for four dry aerosol diameter investigated are summarized in table 1. The comparison of aerosol diameters observed and the aerosol diameters calculated from equation

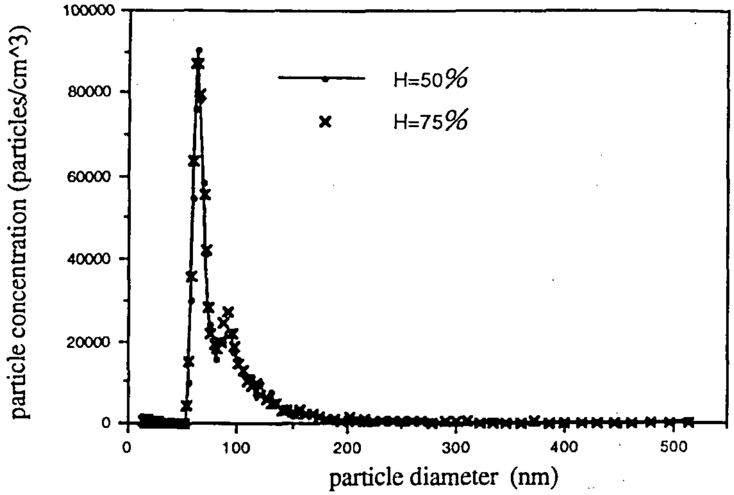


FIG. 2 Distribution of Aerosol With Dry Diameter of 63.8nm at Relative Humidities, 50% and 75%.

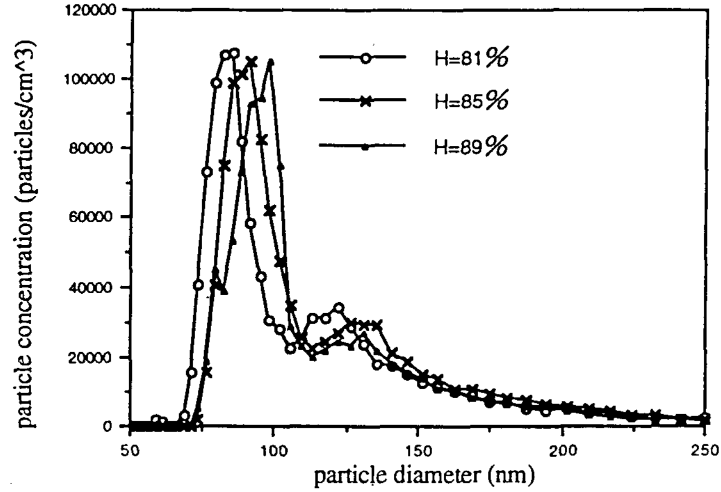


FIG. 3 Distributrion of Aerosol With Dry Diameter of 63.8nm at Relative Humidities,81, 85, and 89%.

TABLE 1. The size distributions of ammonium sulfate aerosols at five different relative humidities

initial aerosol (nm)		H=50%	H=75%	H=81%	H=85%	H=89%
63.8	mode(nm)	63.8	63.8	85.1	91.4	98.2
	σg	1.36	1.36	1.39	1.38	1.41
	concentration (10^4 particles/cm^3)	1.22	1.23	1.64	1.60	1.06
117.6	mode(nm)	117.6	117.6	168.5	174.7	194.6
	σg	1.45	1.43	1.40	1.42	1.38
	concentration (10^4 particles/cm^3)	1.25	1.40	1.25	1.30	1.24
174.7	mode(nm)	174.7	174.7	241.4	259.5	289.0
	σg	1.38	1.36	1.37	1.33	1.33
	concentration (10^4 particles/cm^3)	0.576	0.469	0.594	0.601	0.555
224.7	mode(nm)	224.7	224.7	322.0	333.8	289.0
	σg	1.50	1.45	1.50	1.41	1.49
	concentration (10^4 particles/cm^3)	0.729	0.842	0.782	0.757	0.722

Note : mode is the peak concentration of aerosols

(2) is shown in figure 4. The difference between them is estimated to be less than 10% so that they are in good agreement with each other.

Growth Ratio and Water Content of Ammonium Sulfate Aerosol

The growth ratio defined as the ratio of aerosol size measured to the initial aerosol size is described in table 2.

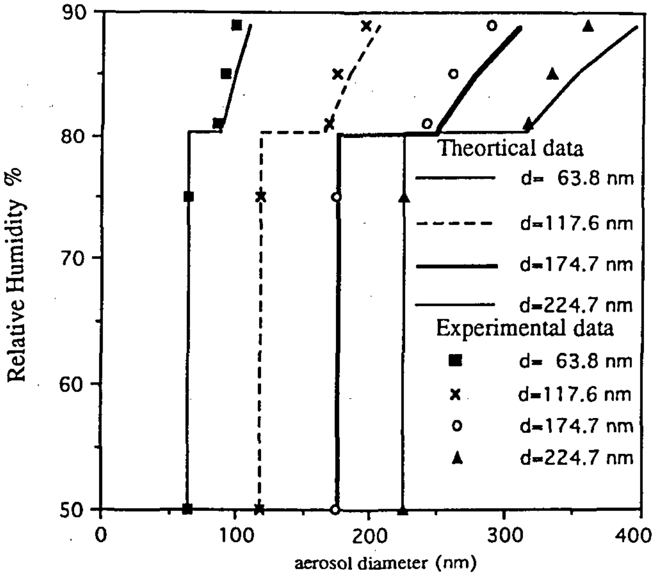


FIG. 4 Experimental and Theoretical Results on the Hygroscopic Growths of Ammonium Sulfate Aerosols Particle.

The results indicates that ammonium sulfate aerosol grow to about 1.3 and 1.6 times larger in size at relative humidity between 81 to 89%. On the other hand, the relationship between growth ratio of hygroscopic aerosols in mass and relative humidity derived by Ferron [8] is expressed in the following equation.

$$G = \frac{m_w + m_s}{m_s} = 1 + \frac{M_w}{M_s}\frac{i\,H - R'}{R' - H} \qquad (3)$$

Where

$$R' = \exp\left(\frac{4\,\sigma\,M_w}{\rho\,R\,T\,D_p}\right)$$

TABLE 2. The size growth ratios of ammonium sulfate aerosols

initial size, nm	H=81%	H=85%	H=89%
63.8	1.33	1.43	1.54
117.6	1.43	1.49	1.65
174.7	1.38	1.49	1.65
224.7	1.43	1.49	1.60

ms and Ms stand for the dry mass and molecular weight of initial aerosols respectively. ms and Ms represent the mass and molecular weight of water. i is the van't Hoff factor and H is the relative humidity. According to equation (3), growth of aerosol mass can be calculated and the water content can be further obtained. As shown in table 3, the water content reaches 50% for ammonium sulfate at relative humidity of 81%. When relative humidity is at 89%, the water content is as high as 60%.

Errors on the aerosol diameter in equilibrium calculated from equation (2) come from two aspects [9]. One is the application of Raoult's law to the real solution. For instance, the error is about 8 to 14% for 50nm aerosol and 7% for aerosol greater than 50nm. The other is the ignorance of density and surface tension of droplet and the estimated error is about 0.004 to 1%.

The fluctuation of temperature and relative humidity are two major factors to cause the error on the aerosol diameter observed in this study. The effect of

TABLE 3. The water content values of ammonium sulfate aerosols at different relative humidities

initial size, nm	H=81%	H=85%	H=89%
63.8	49.44	54.55	62.96
117.6	48.72	56.33	65.16
174.7	49.24	57.08	65.87
224.7	49.75	57.45	66.22

temperature fluctuation on the aerosol diameter reported by Li et al. [9] is shown in the following equation.

$$\frac{\delta R'}{R'} = \frac{4\,M_w}{R\,\rho\,D_p}\left(\frac{\sigma}{T} + \frac{\delta\sigma}{T} + \frac{\sigma}{\rho}\frac{\delta\rho}{\delta T}\right)\left|\frac{\delta T}{T}\right|$$
$$\approx \frac{4\,M_w\sigma}{R\,\rho\,D_p T}\left|\frac{\delta T}{T}\right| \qquad (4)$$

According to this equation, the estimated error at temperature 20^0 C , dR'/R, is less than 0.01%. Thus, the error on the aerosol diameter observed for hygroscopic growth caused by temperature fluctuation is very small. The estimated error on aerosol diameter from the relative humidity fluctuation based

$$\frac{\delta R'}{R'} = \frac{4\,M_w}{R\,\rho\,D_p}\left(\frac{\sigma}{T} + \frac{\delta\sigma}{T} + \frac{\sigma}{\rho}\frac{\delta\rho}{\delta T}\right)\left|\frac{\delta T}{T}\right|$$
$$\approx \frac{4\,M_w\sigma}{R\,\rho\,D_p T}\left|\frac{\delta T}{T}\right| \qquad (4)$$

According to this equation, the estimated error at temperature 20^0 C, dR'/R, is less than 0.01%. Thus, the error on the aerosol diameter observed for hygroscopic growth caused by temperature fluctuation is very small. The estimated error on aerosol diameter from the relative humidity fluctuation based on equation (2) is within 1% for 0.3% change of relative humidity fluctuation, that is the relative humidity fluctuation in this experimental study. Thus, the estimated errors from temperature and relative humidity fluctuation is small and would not cause any significant error on the aerosol diameter observed in the hygroscopic growth experiments in this study.

CONCLUSIONS

The deliquescence point of ammonium sulfate aerosol was first observed by TDMA with Scanning Mobility Particle Sizer. It was the first time that the abrupt growth of aerosol diameter for hygroscopic growth of inorganic salt was observed in detail by use of TDMA incorporated with Scanning Mobility Particle Sizer. The results indicates that the deliquescence point of ammonium sulfate aerosol can be better determined. The deliquescence point determined is 81%. The growth of aerosol diameter of ammonium sulfate at the range of relative humidity from 81 to 89% was by the factor of 1.3 to 1.6 larger than the initial diameter. Furthermore, the estimated water content of mass of ammonium sulfate aerosol was about 47% to 66% at the same range of relative humidity.

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