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創成研究Ⅲ

所属専攻・学年	物質工学専攻 2年
学生氏名	伊藤絵里香 
課題名	シングルナノ粒子用 PSM の開発
コーディネータ教員	大谷 吉生 (物質工学専攻)
課題担当教員	瀬戸 章文 (物質工学専攻)
創成研究Ⅱ 派遣先企業	独立行政法人 産業技術総合研究所
創成研究Ⅱ 研修期間	平成20年10月1日～平成21年1月22日
創成研究Ⅱ 研修先	茨城県つくば市

## 平成21年度 創成研究Ⅲ 研究成果報告書

専攻・学年	物質工学専攻 2年
氏名	伊藤絵里香
創成研究Ⅱ派遣先名	独立行政法人 産業技術総合研究所
創成研究Ⅱテーマ名	シングルナノ粒子用 PSM の開発

### 【1. 創成研究Ⅱ終了後の研究課題の進捗】

創成研究Ⅱでは産業技術総合研究所において測定機器のトレーサビリティについて学び、シングルナノ粒子用 PSM の開発の基準器となる計測装置の校正を行った。創成研究Ⅲでは校正した装置を用いて、粒径10nm 以下のシングルナノ粒子を計測するために PSM の操作条件の検討を行っている。修士論文では、研修で行った校正結果を基に、PSM の開発および、そのトレーサビリティについて記述する予定である。

### 【2. 創成研究に関連した研究活動・研究発表】

18th International Conference on Nucleation & Atmospheric Aerosols  
“Nucleation and growth of nanoparticles and ions in mixing-type CPC”  
(要旨を別途添付)

### 【3. 総括】

私たちの身の回りには計測機器がたくさんあり、当たり前のようにそれらの測定値を信頼しているのではないかと思います。しかし、その信頼性を保証するということの難しさや、その重要性をこの創成研究で学ぶことができました。そして、その信頼性の証であるトレーサブルな計測機器を開発することで、今後のナノテクノロジーの発展に少しでも貢献できればいいと考えています。

# Nucleation and growth of nanoparticles and ions in mixing-type CPC

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**Abstract.** Mixing-type condensation nucleus counter (MT-CNC) was developed and used to study the nucleation and growth of nanoparticles and ions by varying the particle size and chemical species. Supersaturation ratio was precisely controlled by the improved evaporator and mixing part of a particle size magnifier (PSM; originally developed by Okuyama et al., 1984 [1]). Size-classified silver and NaCl nanoparticles less than 10 nm in diameter were used as nuclei for heterogeneous condensation of ethylene glycol vapor. Activation of atmospheric ions generated by  $^{241}\text{Am}$  alpha-ray source was also studied. The growth rate of activated nuclei was determined by the pulse height analysis using an optical particle counter (OPC) and CPC as a detector. We achieved the activation of 8 % of 2nm-NaCl particles with subsequent growth up to two micrometer droplets.

*Key Words:* Nanoparticle, Condensation nucleus counter, Particle size magnifier, Ion induced nucleation

## Introduction

Condensation particle counter (CPC) has been widely used to measure the number concentration of aerosol [2]. In CPC, particles smaller than the optical detection limit (<100 nm) grow to detectable size droplets by the condensation of supersaturated vapor. However, due to the Kelvin effect, it is difficult to activate ultrafine particles, especially smaller than 10 nm in diameter. It is a key to control the supersaturation ratio in the CPC while minimizing the diffusional losses and preventing homogeneous nucleation [3]. Particle size magnifier (PSM) is one of the candidates to detect ultrafine aerosol particles. PSM is a mixing-type CPC, which is capable of generating uniform supersaturation by turbulent mixing between cooled aerosol and hot vapor [1]. Recently Kim et al. used T-shaped tube as a mixing part of PSM [4] and successfully activated 1.6-nm silver nanoparticles. However, since they used a conventional saturator (liquid soaked felt or silica gel) to generate vapor laden gas, it was difficult to control the supersaturation independently from the experimental parameters (aerosol and vapor flow rates, and temperatures). In this study, we developed an improved version of PSM equipped with a newly designed evaporator system and mixing part to observe nucleation and growth of nanoparticles and ions.

## Basic design of improved version of particle size magnifier

PSM consists of three parts, *i. e.*, an evaporator, a mixing part and a condenser. Figure 1 shows the schematic diagram of PSM used in this study. The working fluid (ethylene glycol) was fed to the evaporator by a syringe pump for controlling the flow rate. The tip of the syringe needle was touched on a stainless steel porous filter. The working fluid fed to the filter was immediately vaporized by heating the filter. Thus the vapor concentration of ethylene glycol was controlled by the flow rate of syringe pump, not by the evaporation temperature. The vapor is then mixed with cooled aerosol turbulently in the mixing part. In order to maintain the temperatures of the vapor and the mixture, ceramic heaters were installed around the transfer tubes in the mixing part. The chamber of mixing part was quenched by a pair of Pertier coolers to keep the mixed aerosol temperature at about 10 degree C. The temperatures of mixing part were monitored at five locations by thermocouples and controlled individually to ensure well-defined supersaturation.

Supersaturation ratio,  $S$ , is defined by  $S=P_i/P_e$  (where  $P_i$  is the vapor pressure of mixture and  $P_e$  is the equilibrium vapor pressure at a given temperature). Here,  $P_i$  was tuned by liquid flow rate to generate a given value of  $S$  without changing the temperatures. Figure 2 shows an example of the relation between supersaturation ratio  $S$  and mixing ratio  $R_h=Q_c/(Q_c+Q_a)$ , where  $Q_c$  and  $Q_a$  are the flow rates of vapor and aerosol, respectively. The solid line in Fig. 2 shows the supersaturation ratio when saturated vapor was mixed with aerosol (in the case of liquid saturator). As shown by dotted and broken lines in Fig. 2, the supersaturation ratio can be easily controlled using unsaturated vapor from the syringe pump system.

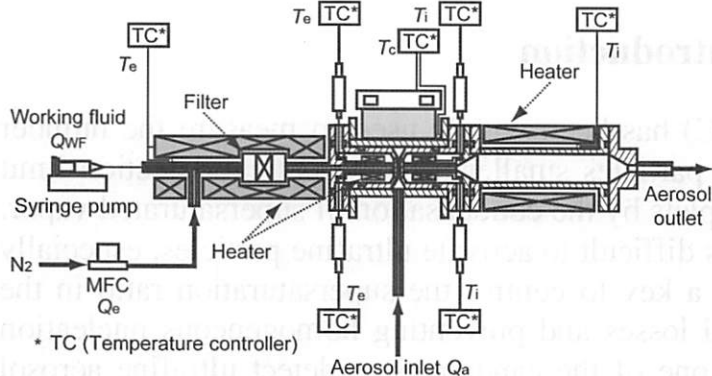


Figure 1. The schematic of the PSM.

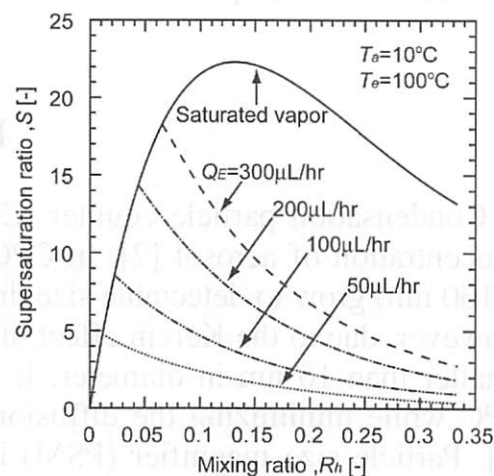


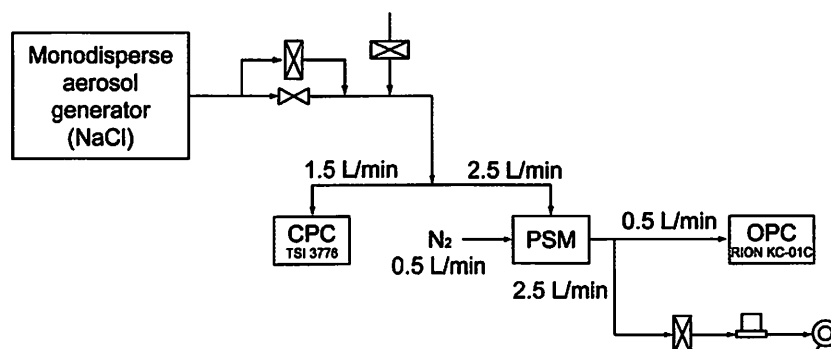
Figure 2. Supersaturation ratio of ethylene glycol vapor in the PSM as a function of mixing ratio of gas flow.

## Experiments

Figure 3 shows the experimental setup for evaluating the counting efficiency of MT-CPC (= PSM + OPC). The test particles of sodium chloride were generated by an evaporation-condensation method. The generated particles are charged to be in equilibrium state as they pass through the  $^{241}\text{Am}$  bipolar charger. The size of the test

particles was controlled by classification with a differential mobility analyzer (DMA). These monodispersed particles were split into two flows. Part of the flow was introduced to an aerosol electrometer (AE: TSI 3076) or CPC (TSI 3776, 50% detectable size of 2.5 nm) to measure the reference particle number concentration of test aerosol. The other flow was introduced to the newly-developed PSM of various supersaturations. An optical particle counter (OPC; Rion KC-01C, detection range of larger than 0.3  $\mu\text{m}$ ) was used as a detector of the number concentration of grown droplets. The aerosol flow rate was set at 2.5 L/min, which was higher than the commercial CPC for reducing diffusional losses. The vapor flow rate and temperature were fixed at 0.5 L/min and 100 degree C, respectively. The aerosol temperature was tuned to be at 10 degree C by Peltier cooler. The supersaturation ratio was controlled by changing ethylene glycol liquid flow rate from 300  $\mu\text{L/h}$  ( $S=4.34$ ), 350  $\mu\text{L/h}$  ( $S=5.07$ ) and 400  $\mu\text{L/h}$  ( $S=5.79$ ).

In order to evaluate ion-induced nucleation, the atmospheric ions generated by  $^{241}\text{Am}$  alpha ray source were also introduced into PSM. In this setup, the monodisperse aerosol generator was replaced by an aerosol neutralizer chamber for generating bipolar ions. In order to ensure that no particles are generated by homogeneous nucleation, an aerosol electrical precipitator (EP) was placed upstream of PSM to measure the background level when EP was switched-on and the activated droplets when EP was switched-off alternately every 60 seconds. In this experiment, a CPC (TSI 3776; 50% detectable size of 4 nm) was used as the detector of activated droplets.



**Figure 3.** Experimental setup for measuring counting efficiency.

## Results and discussion

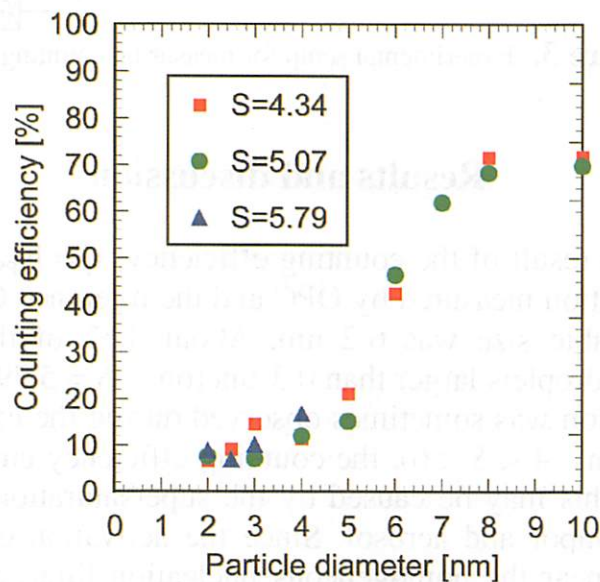
Figure 4 shows the result of the counting efficiency,  $\eta = N_{\text{PSM/OPC}}/N_{\text{CPC}}$  ( $N_{\text{PSM/OPC}}$  and  $N_{\text{CPC}}$  are the concentration measured by OPC and the reference CPC, respectively). At  $S = 5.07$ , 50 % detectable size was 6.2 nm. About 8 % of the 2-nm particles were activated and grew to droplets larger than 0.3-micron at  $S = 5.79$ . It should be noted that homogeneous nucleation was sometimes observed during the experimental runs. In our experimental conditions ( $4 < S < 6$ ), the counting efficiency curve did not change with the supersaturation. This may be caused by the supersaturation non-uniformity during the mixing between vapor and aerosol. Since the activation of nuclei by the present PSM was conducted near the homogeneous nucleation limit, a fraction of introduced aerosol passed through a region of a higher supersaturation in the mixing chamber. The present PSM changes the supersaturation only by liquid flow rate so that the temperature and velocity profile in the mixing chamber remain the same, leading to the

activated fraction ( $\approx$  percentage of aerosol passing through a higher supersaturation region) invariant

Figure 5 shows the electrical mobility distribution of the atmospheric ions generated by alpha ray irradiation by  $^{241}\text{Am}$ . The peak of positive ion lies at around electrical mobility of  $8.38 \times 10^{-5} \text{ m}^2\text{V}^{-1}\text{s}^{-1}$  which corresponds to 1.55 nm of electrical mobility diameter. Those of negative ion are  $1.94 \times 10^{-4} \text{ m}^2\text{V}^{-1}\text{s}^{-1}$  and 1.02 nm. The concentrations of positive and negative ions measured by an ion counter (including losses during transfer line) were  $1.07 \times 10^6$  and  $6.95 \times 10^4$  ions/cc, respectively. Figure 6 shows the time dependent change in the concentration of droplets growing from ions at  $S = 6.84$ . At this supersaturation, the activated droplets were clearly distinguished from the background ( $0 < t < 50 \text{ s}$  and  $120 < t < 180 \text{ s}$ ) however the activation efficiency was rather low at around 0.002%. This result is similar to those obtained by Adachi et al. (1992) [6]. They used a PSM with DBP as working fluid and detected very small fraction of activated ions. Now we consider the relation between the critical supersaturation ratio and Kelvin diameter for singly charged particles which was obtained from Kelvin-Thomson's equation as,

$$S^* = \exp \left[ \frac{M}{\rho RT} \left\{ \frac{4\gamma}{d_p} - \frac{q^2 \left(1 - \frac{1}{\epsilon}\right)}{2\pi\epsilon_0 d_p^4} \right\} \right]$$

where  $M$  is the molecular weight,  $\rho$  is the density,  $R$  is the gas constant,  $T$  is the absolute temperature,  $\gamma$  is the surface tension,  $d_p$  is the particle diameter,  $\epsilon$  is the dielectric constant and  $\epsilon_0$  is the space permittivity. In the case that working fluid is ethylene glycol, the critical supersaturation calculated by the above equation is 10 at Kelvin diameter of 1.5 nm, but  $S^* > 10000$  is required at the same Kelvin diameter in the case of DBP vapor, which might be above the homogeneous nucleation limit. Therefore it was concluded that the newly-developed PSM system with ethylene glycol has a potential to activate nanoparticles ( $< 2 \text{ nm}$ ) and ions.



**Figure 4.** Size dependence of counting efficiency of MT-CNC at various supersaturation ratio.

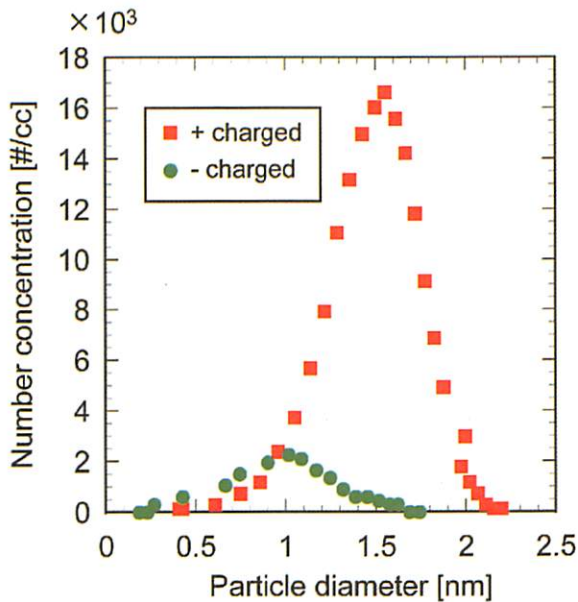


Figure 5. Electrical mobility distribution of the atmospheric ions generated by  $^{241}\text{Am}$ .

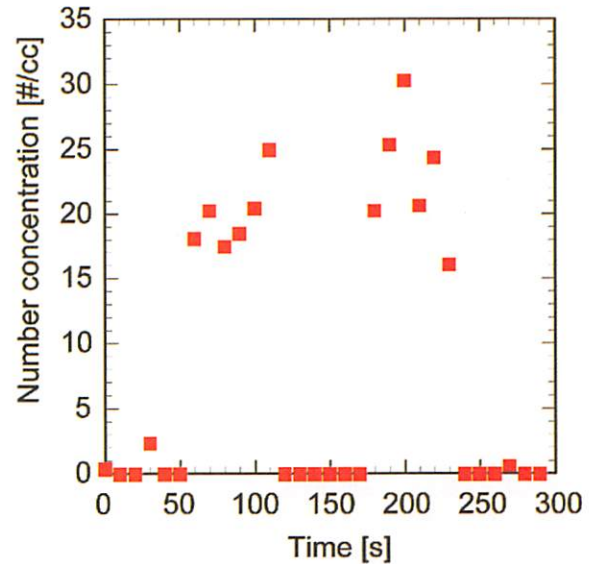


Figure 6. Time dependent changes in of particle number concentrations at  $S = 6.84$ .

Fig

## Acknowledgments

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