MEASUREMENT AND FIELD OBSERVATION OF ATMOSPHERIC NANOPARTICLES

大気中ナノ粒子の測定とフィールド観測

Indra Chandra

Graduate School of Natural Science and Technology, Division of Natural System,
Kanazawa University

ABSTRACT

Field observation at Fukue Island was performed. A remarkable increase of new particles were identified as small as 3-4 nm under low concentration of pre-existing particles. We classified this event as type-A. In the case of type-B and -C, most of the days were identified under sulfur rich in the particle phase. It suggested that the nucleation might appeared in the upstream region and high altitude. Therefore, we conducted aerial observation to investigate the particle number concentration related to NPF events. We also tried to develop of nanoparticles detector that the minimum size of detection of particle is as small as 1 nm.

The gradually decreased SO_2 and $PM_{2.5}$ concentration were significantly affected the number of strong event in the last 5-year. In 2013, we observed the large-scale of air mass came to the site under high concentration of SO_2 and $PM_{2.5}$. However, in 2015, we only identified the weak event due to insufficient amount of SO_2 concentration. In the last 2-year (2016-2017), the strong events were re-appeared due to clean environmental (low concentration of $PM_{2.5}$). For that reason, we analyzed the 5-year data of field observation at Fukue site, particularly in the winter-to-spring season.

Recently, air pollutants in the East Asia released from various resources, for example, coal-fired power plant, industry, and anthropogenic emissions have influenced the environment. These emissions affected the air quality not only in the local area but also in the other region. They came from China, Korea, and Japan, transported in the long-distance, and changed the particle size distributions in the downstream region. This phenomenon also called as new particle formation (NPF). However, the mechanism of newly formed nanoparticles was incompletely understood. This is because those air pollutants consist of not only the gaseous pollutants (SO_2, NO_x, VOC, etc.) but also primary aerosols such as $PM_{2.5}$, PM_1, BC, and OC.

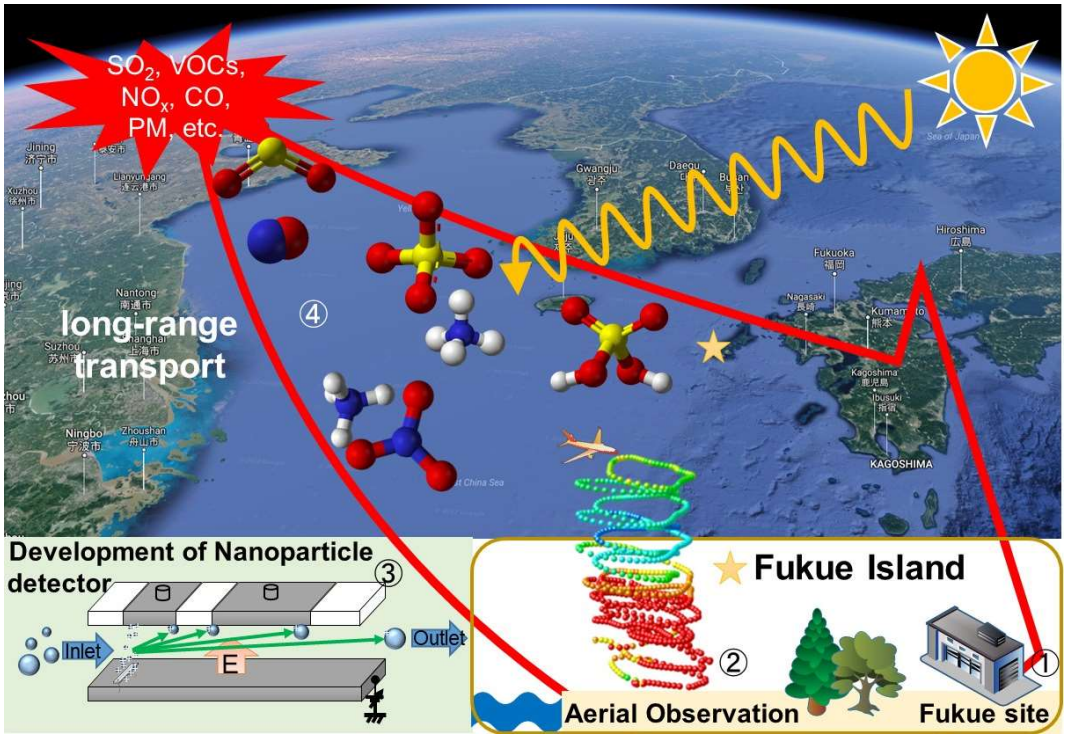

Figure 1. Objectives of the study.

Figure 1 shows the objectives of this study. In order to investigate the NPF events under long-range transport of polluted air, we conducted the field observation in Fukue Island (32.8ºN, 128.7ºE), Japan, a rural area located in the western coast of Kyushu, over certain period in 2013-2017. We investigated and analyzed the correlation between NPF and the long-range transport of air pollutants (①). For some case, we detected no clear initial particle formation process (>10

nm). It seems that the photochemical events might have taken place in the upstream, high-altitude region before entering the Fukue site. Therefore, in order to investigate the atmospheric layers of freshly-formed nanoparticles, we observed the concentration of atmospheric nanoparticles by the aircraft (~3.7 km from the ground based station) to describe how the polluted air might came to the site (②). The size, as well as its chemical composition, of the initial nucleating species in the sub-10 nm range was also considered as the main part to explain the NPF in the Fukue Island, Japan. We try to develop portable instrument which can detect atmospheric nanoparticles down to 1 nm in the laboratory (③). However, in the last 5-years (2013-2017), the level concentration of SO_2 and $PM_{2.5}$ tends to be decreased and it was influenced NPF in the downstream region (④).

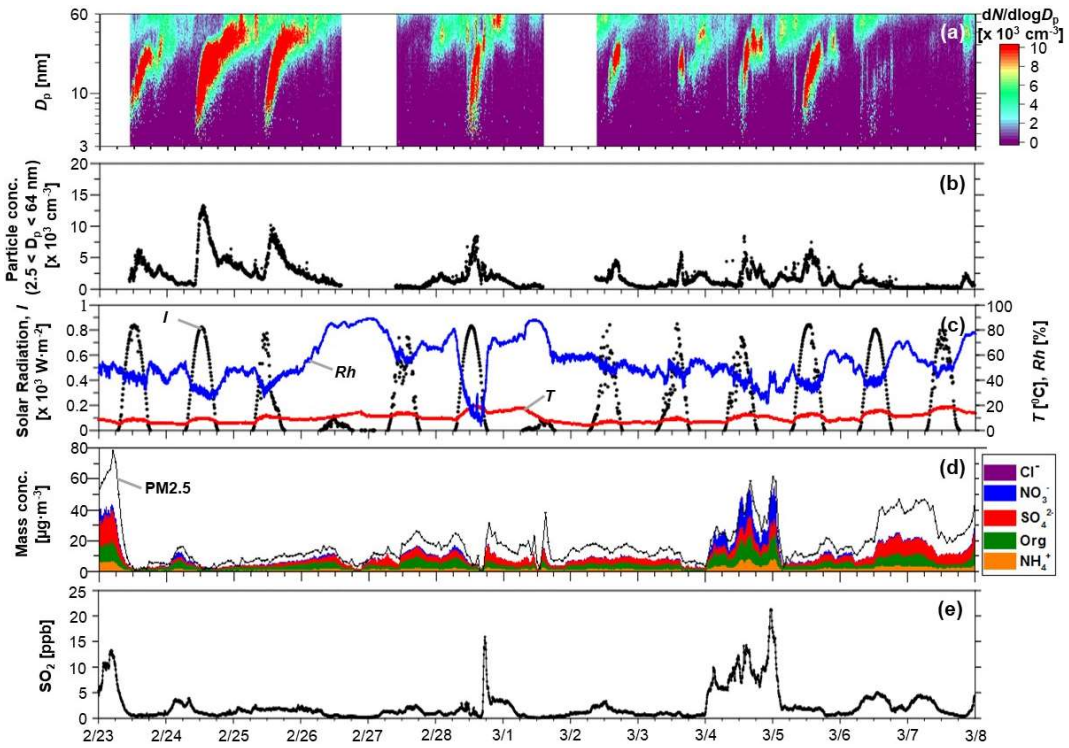

Figure 2. Overall data from Feb. 23 to Mar. 7, 2013.

Figure 2 shows the overall data from the first observation period (February 23 to March 7, 2013): (a) contour plot of the mobility size distribution, (b) total particle concentration ($2.5 < D_p < 64$ nm), (c) meteorological data (I, T, and RH), (d) the $PM_{2.5}$ concentrations (by TEOM) and mass concentrations of chemical

components (Cl^-, NO_3^-, SO_4^{2-}, Org, and NH_4^+ measured by ACSM), and (e) the SO_2 gas concentration. NPF and growth events were identified 8 times in 13 days. The NPF and growth were frequently observed on most of the sunny days, and the onsets of the NPF were identified mostly at times of peak solar radiation, or around noon As shown in Figure 2 (a), most of the NPF events started from 4-5 nm, which suggests that the particles were nucleated near the observation site. In some cases, however, the particle formation was detected only from mobility sizes larger than 10 nm. By comparing the mobility-based data with the PM2.5 concentrations and chemical composition (Figure 2 (d)), we can glean insight into the influence of the long-range air pollutants on the NPF. For example, we can identify remarkable increases in the concentration of air pollutants, i.e., transport events, at least three times: on February 23, March 4, and 6-7 (Figure 2 (d) and (e)). The data on aerosol chemical composition on these days indicated nitrate-rich particles on March 4, sulfate-rich particles on February 23 and March 6, and significant amounts of co-existing organic compounds on all three days.

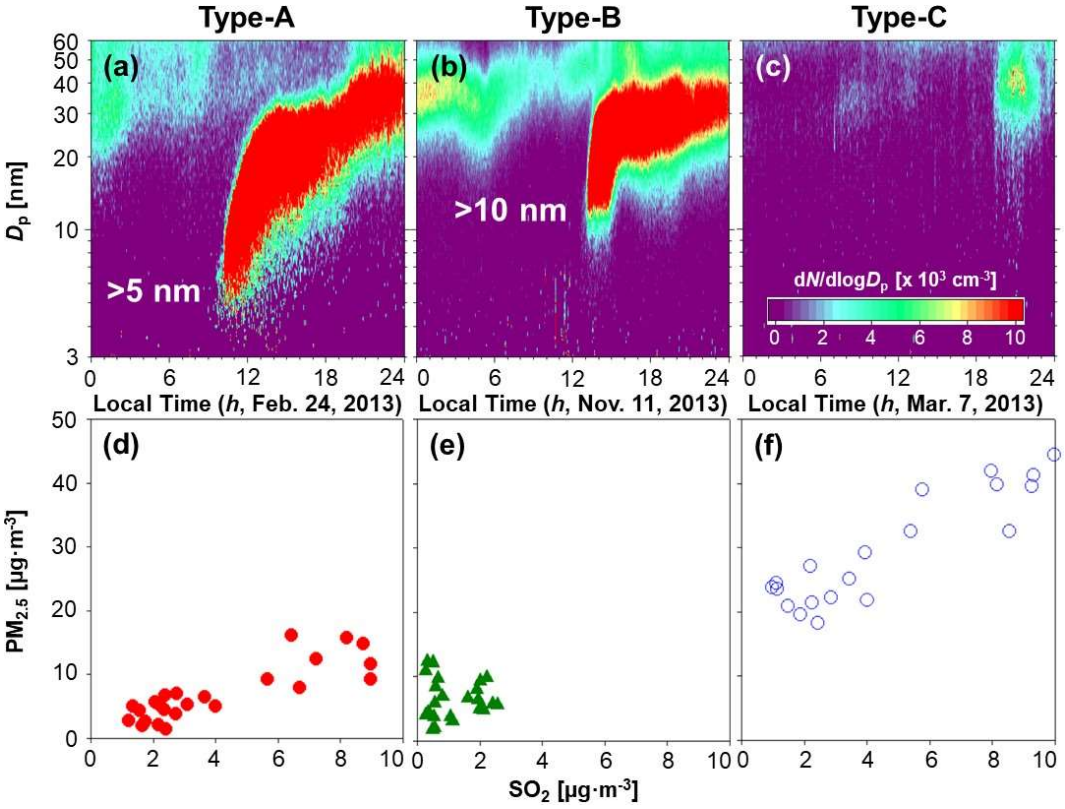

Figure 3. Classification of new particle formation (NPF).

We classified NPF into three types based on the initial size of nucleation. In general these types were influenced by solar radiation, pre-existing particles, precursor gas (SO_2), and the origin of air mass. Figure (a) to (c) are typical data for each type. Type-A is strong event when the NPF was observed in the morning (~10:00) starting from sub-10 nm and growth into several tens nanometer in few hours (Figure 3 (a)). As clearly seen in Figure 3 (d), type-A was identified under the high concentration of SO_2 (>1 ppb) and low concentration of $PM_{2.5}$ (<20 $\mu g \cdot m^{-3}$). Those initial size of nucleation cannot observed clearly in type-B (Figure 3 (b)). This type identified NPF starting from 10 nm around noon (~13:00) under low concentration of SO_2 and $PM_{2.5}$ (Figure 3 (e)). When the day is no detectable formation and growth of new particles, we classified as type-C (Figure 3 (c)). SO_2 concentrations was scattered from low to high concentration under high concentration of $PM_{2.5}$ (Figure 3 (f)).

In order to investigate the atmospheric layers of freshly-formed nanoparticles, we conducted aerial observation in Fukue Island, Japan, ~3.7 km from the ground based station. The intensive observation was carried out in 4-days (Apr. 13-16, 2017). In the early step, we observed the concentration of atmospheric nanoparticles starting from 6 nm with the altitude up to 1200 m.a.s.l. Noted that the altitude in the ground based station is 80 m. The particle number concentration (PNC) was measured by Water-CPC Model 3781 (TSI, Inc.) with time resolution of 2-sec. This low-cost WCPC uses water as condensing fluid to enlarge particles for easy detection by an optical detector. That instruments was carried out by kite-plane which is provided by Prof. M. Hayashi's group (Fukuoka Univ.). The kite-plane can be controlled manually and automatically. The kite-plane was also equipped by meteorological sonde (*T*, *RH*, *P*, W.D., and W.S.) as well as GPS (Latitude, Longitude).

Figure 4 shows the vertical distribution of atmospheric particle number concentration (PNC). Figure 4 (a) show the PNC (*N*, marked by color map) as a function of space (*x*, *y*, *z*) in the event day. The high concentration of particles (>10^4 cm^{-3}) was observed below 800 m in altitude. No significance number of particles in the high altitude (>800 m). However, insignificance number of particles was found in the other day (Figure 4 (b)). The PNC is around 2,000 cm^{-3} and it is similar with

the ambient number of particles in the clear day. It seems that abundant number of particle concentration (PNC) were identified in the layer between ~200 to ~600 m with the peak at the altitude of ~400 m before reaching the Fukue site.

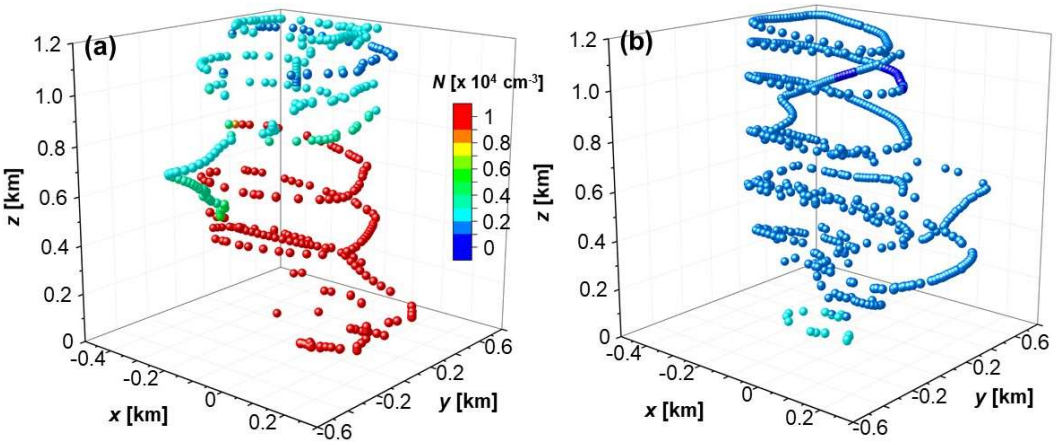

Figure 4. Vertical distribution of atmospheric particle number concentration: (a) event day and (b) non-event day.

We try to develop portable instrument which can detect atmospheric nanoparticles down to 1 nm in the laboratory. The schematic of the nanoparticle detector can be seen in Figure 5. There are three function of this device: (a) charging (②), (b) classifying (③), and (c) detecting (④ and⑤). The uncharged particles was introduced to the inlet (①). Then the particles were charged by the positive ions which is generated by the micro-plasma module. This micro-plasma could be controlled by the waveform of high voltage. Therefore, the particles are positively charged. Noted that there is an issue about the performance of this charger. The charged particles are subjected to electrostatic force by a uniform electric field formed between the parallel plates by the DC voltage (V). Only particles with a specific particle size will be collected by this metal plate. Ions with large mobility are immediately accelerated by the electric field and trapped by the metal plate (I_1). Meanwhile, the determined size of particles were detected by I_2. The large size of particles with a low electric mobility and uncharged particles are not captured and are discharged directly to the outlet. The electric charge of charged particles collected on a metal plate is detected as a current value by an ammeter. For example, if we know the concentration of atmospheric nanoparticles is around 10,000 cm^{-3}

and we used the flowrate of the system is 10 l/min, therefore, the current value of charged nanoparticles detector is 270 fA. Therefore, in principle, this portable instruments can be used to detect atmospheric nanoparticles with the size can be selected for sizes of the sub-5 nm.

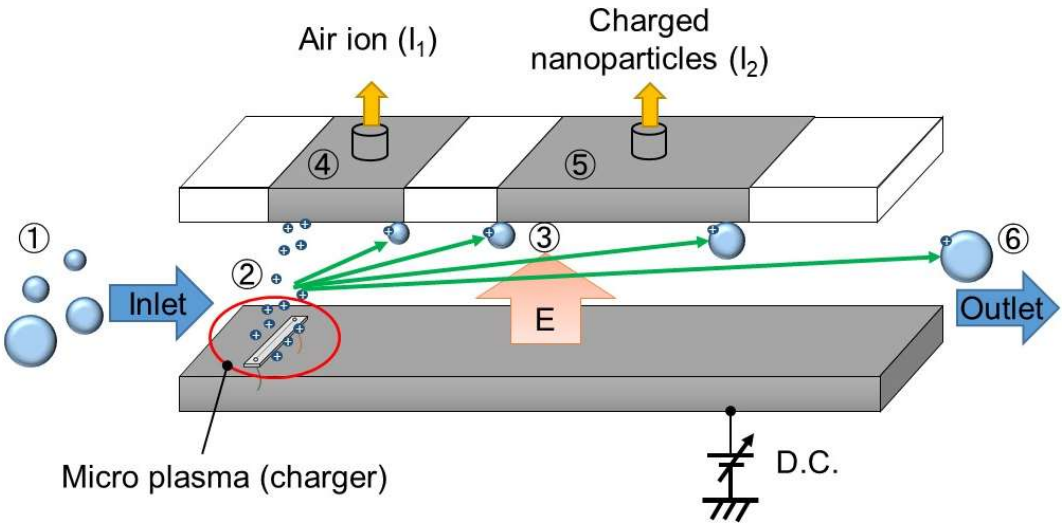

Figure 5. Schematic of nanoparticle detector.

The gradually decrease of $PM_{2.5}$ and SO_2 was affected the number of event in the Fukue site. Figure 6 (a) to (d) show the daily-averaged $PM_{2.5}$ concentration against SO_2 concentration over four period in 5-years. In 2013, we observed big events when the level concentration of SO_2 and $PM_{2.5}$ almost reached 10 ppb (unseen in this figure) and 35 $\mu g \cdot m^{-3}$ respectively. However, in the last 3-years (2015-2017), $PM_{2.5}$ concentration was relatively higher than SO_2 concentration. We could not observe the big events on these years. The strong event (type-A) on the last 2-years might reflected the clean environment. It suggested that the emission of SO_2 in upstream region was decreased due to local government have been controlling the emission gas, for instance, through desulphurization technologies in the large power plants. Therefore, the decline of SO_2 concentration might be influenced the NPF events and growth in Fukue Island, Japan.

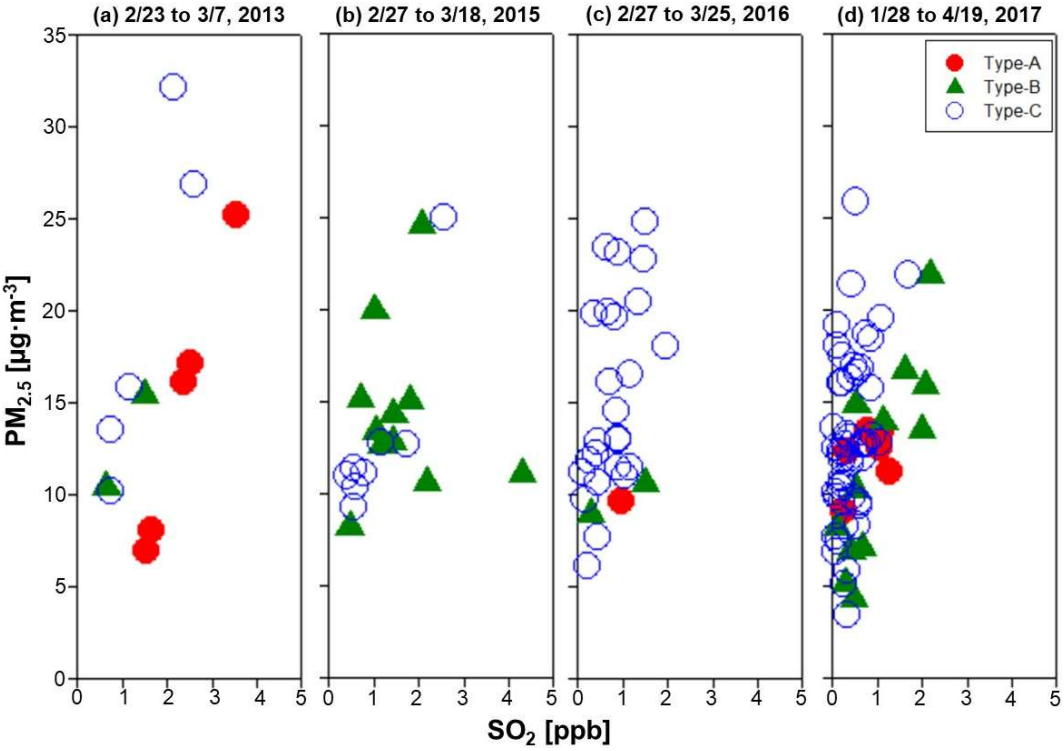

Figure 6. Daily-averaged $PM_{2.5}$ concentration against SO_2 concentration in: (a) Feb. 23 to Mar. 7, 2013; (b) Feb. 27 to Mar. 18, 2015; (c) Feb. 27 to Mar. 25, 2016; and (d) Jan. 28 to Apr. 19, 2017.

平成２９年　８月　１日

学位論文審査報告書（甲）

１．学位論文題目（外国語の場合は和訳を付けること。）

Measurement and field observation of atmospheric nanoparticles

（大気中ナノ粒子の測定とフィールド観測）

２．論文提出者　(1) 所　　属　自然システム学　　専攻

(2) 氏（ふり）　名（がな）　Indra Chandra（いんどら　ちゃんどら）

３．審査結果の要旨（600～650 字）

平成２９年７月１２日に学位論文予備審査会を開催して、提出された博士論文および研究業績を精査した。８月１日に口頭発表と質疑応答を行い、その後開催した論文審査委員会において、以下のように決定した。

大気中におけるナノ粒子生成過程は、新粒子生成と呼ばれ、大気エアロゾルの生成メカニズムと関連して重要な研究課題である。本論文は、長崎県・福江島においてナノ粒子の大気フィールド観測を長期間実施し、そのデータの統計的解析により、１）新粒子生成と長距離輸送された汚染物質との相関、２）新規開発した小型ナノ粒子センサによる飛行機観測、ならびに３）近年の大気汚染の変化と新粒子生成過程の関係について、主に実験的に系統的な検討を行ったものである。本論文の主要な研究成果は以下の通りである。１）大陸からの汚染源の長距離輸送により、新粒子生成には２つのパターンがあることを明らかにした。２）新規開発したナノ粒子計測装置により、ナノ粒子濃度の高度分布を計測できる。３）中国などからの汚染物質の輸送は、緩やかに減少しており、これに伴い下流域における新粒子生成が複雑な挙動を示すことを明らかにした。以上の通り、本論文は大気エアロゾルに含まれるナノ粒子の生成過程に新たな知見を与えるものであり、その学術的、工学的な価値は極めて高いと考えられ、博士（工学）の学位に相当すると判断する。

４．審査結果　(1) 判　　定（いずれかに○印）　○合　格　・　不合格

(2) 授与学位　博　士（工学）