博　士　論　文　要　旨

Direct Measurement of Physical Properties of Individual Particles by Atomic Force Microscopy and its Application to Atmospheric Aerosols

原子間力顕微鏡を用いた個別粒子の物性評価法の開発と実大気エアロゾルへの応用

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Abstract

The physical properties and phase state of aerosol particles have significant implications on global climate and public health. However, the properties of individual aerosol particles can be diverse. Detailed measurements and analyses on a particle-by-particle basis are required to fully understand the physical properties of ambient aerosols in complex mixing states. This thesis utilized atomic force microscopy (AFM) to evaluate the physical properties of individual aerosol particles, with particular emphasis on the adhesion force, Young's modulus, and viscosity related to the aerosol phase state. Firstly, the possible artifacts and bias on the adhesion force measurement due to the use of various types of AFM systems and probes are evaluated. The result indicated that it is recommended to measure the adhesion force of a standard sample, such as Si wafer, prior to conducting AFM adhesion force measurements in order to obtain a more precise evaluation of aerosol particle adhesion force. Secondly, the adhesion force measurement was applied on sea spray aerosols (SSA) of atmospheric relevance. It was suggested that the adhesion force of SSA particles is influenced by the organic shell coating surrounding the inorganic core. Finally, optimal measurement conditions for the viscoelasticity of atmospheric aerosols were investigated. It was found that these properties are highly sensitive to relative humidity and vertical AFM tip velocity. In conclusion, this study successfully demonstrated that AFM can be a novel tool to quantitatively characterize the physical properties of aerosol particles on an individual basis.

1. General Introduction

Atmospheric aerosols emitted from various sources vary in chemical composition, size, and physical properties. Their mixing states is also not uniform. So far, discussions on the mixing states of aerosols mainly involved how different chemical components are mixed within the particles. However, associated physical properties and the phase states of aerosol particles can also be diverse. The physical properties and phase state of such particles have a significant impact on global climate and public health. Therefore, more accurate analysis reflecting the mixing state of aerosol particles on the individual particle basis is required.

More recently, new methods using atomic force microscopy (AFM) and scanning probe microscopy (SPM) are attracting more attention for characterizing physical properties of individual aerosol particles. A force-distance curve can be obtained by plotting the cantilever deflection as a function of the physical distance between the tip and the sample in nano-meter horizontal resolution. The force-distance curve reflects the forces acting between the AFM tip and the sample surface, which can be used to directly and quantitatively infer various types of physical properties. Such sensitivity and spatial resolution of nanometric scale could also be applied to evaluate the physical properties of individual aerosol particles in complex mixing states.

The focus of this thesis is the development of a novel method for characterizing the physical properties of individual aerosol particles using AFM and its application to samples of atmospheric relevance. In Chapter 2, to improve the accuracy of the adhesion force measurement of individual particles, the state of the AFM probe and how it affects the adhesion force of the particles was evaluated by measuring the adhesion force of a Si wafer. In Chapter 3, the adhesion force measurement was applied on atmospherically relevant sea spray aerosols (SSA) with various organic contents. In Chapter 4, the phase state and related viscoelasticity of individual organic particles were measured using AFM and potential application of the method to ambient aerosols was evaluated. Chapter 5 presents the general conclusions of this thesis.

2. Improving the Accuracy of Aerosol Adhesion Force Measurements Using Atomic Force Microscopy

2.1 Introduction

Aerosol particles interact with surfaces through adhesion forces after deposition. Solid particles readily bounce off from the impaction surface while liquid particles tend to stick and stay attached. Therefore, this force determines whether the particles continue to remain in contact with the deposition surface or re-suspend into the atmosphere. Thus, the adhesion force is closely related to the generation and removal of atmospheric aerosols.

Adhesion forces of individual aerosol particles are obtained from force-distance curve mapping obtained using AFM. The force-distance curve mapping method is capable of directly and quantitatively measure the adhesion force of individual aerosol particles, by considering the spatial variation and topographic effects within the surface of a single particle. However, it may be influenced by factors other than particle topography, such as the condition of the AFM probe which slightly differ from one tip to the other. In this Chapter, measurements with multiple probes of the same type were performed to assess the impact of probe conditions on aerosol particle adhesion. Furthermore, we verified whether a Si wafer commonly used as substrate for aerosol particles can serve as a standard for achieving more precise adhesion measurements by AFM.

2.2 Materials and methods

In this study, NaCl, $MgSO_4$, artificial sea salt (ASS), ammonium sulfate (AS) and glucose (Glu) were used as representative model particles for inorganic and organic particles, respectively. These aqueous solutions were aerosolized by an atomizer and collected on a Si wafer using a single jet impactor.

The adhesion force of laboratory generated particles was measured using two AFM instruments, a Nanofinder HE (NF; Tokyo Instruments, Japan). Vertical velocities of AFM probes were 1.0 μm/s for NF. Advanced TEC^{TM} AFM probes (ATEC; Nanosensors^{TM}, Neuchatel, Switzerland), whose sprint constant is 0.33-0.36, were used for adhesion measurements. To minimize the influence of humidity on the measurement results, measurements were performed at a relative humidity of 18-35%.

Two types of force-distance curve method were performed in this study. Firstly, the AFM probe was approached to the sample until the maximum loading force applied to the sample for NaCl, $MgSO_4$, and Glu particles, and then pulled away to measure the force curve one point at a time (method 1). The particle and Si wafer areas were extracted based on the force curve mapping data obtained by Igor Pro software. The adhesion forces of Si wafer were defined as the average value of the entire Si wafer area. Another method operates the probe in the pre-defined Z-axis range to acquire a force-distance curve mapping (method 2). The adhesion forces of the Si wafer were defined as the average values of several force-distance curves on the Si wafer, each of which was collected prior to measuring the force-distance curve mapping on a single particle. The force-distance curve mappings were obtained with horizontal resolutions of 50 nm. These results were analyzed using R.

Additionally, to consider the impact of surface slopes on adhesion force, the approximate slopes of the sample surface were obtained by calculating the least squares of the heights collected from force-distance curve in the data point and the adjacent four points. In both methods, adhesion force values for particle surfaces with slopes less than 15 degrees relative to the perpendicular plane were extracted and their median value was defined as the typical adhesion force representing individual particles.

2.3 Result and Discussion

Figure 1 shows comparison of adhesion force of Si wafer and aerosol particles. The results are illustrated with the horizontal axis representing the adhesion force of the Si wafer, and the vertical axis representing the particle adhesion force. This figure demonstrates that the adhesion force of particles increases with that of the Si wafer for both glucose and inorganic salt particle (NaCl and $MgSO_4$). This most likely reflects the variation in the tip's curvature radius, such that the contact area between particles/Si wafer and the tip increases as the radius of curvature increases.

When comparing the slopes of adhesion forces between Si wafers and inorganic particles by method 1, it was found that the adhesion forces of inorganic salt particles (NaCl and MgSO4) and that of Si wafers scale with a linear relationship (Figure 1). This result suggests that the inorganic salt particles have similar adhesion forces. Comparison of these results with data measured for ASS and AS by method 2 showed that these particles have comparable adhesion. The adhesion forces of glucose particles obtained by both methods show similar range and increase with that of Si wafer in the similar manner as the inorganic salt particles. When comparing the adhesion forces of particles, it was found that glucose had a higher adhesion force than inorganic salts. This suggests that glucose particles have a stronger adhesion force than inorganic salt particles when measured with an AFM probe having the same radius of curvature at the tip. These results warrant the direct comparison of adhesion forces as long as the tips record similar range of adhesion forces on a Si wafer.

3. Characterization of adhesivity of organic enriched sea spray aerosols by atomic force microscopy

3.1 Introduction

Sea spray aerosols (SSA) can deposit on the surfaces of infrastructure, such as buildings made of concrete or steel, leading to corrosion, particularly in coastal regions. Simulation studies have been made to estimate the deposition of SSA on infrastructure. However, it should be pointed out that these studies are made based on the simplified assumption that every particle would adhere upon contact with the surface, which may not always be the case in the real world situation. To date, few studies have evaluated the potential variability of adhesion forces resulting from complex mixing of inorganic and organic compounds present in SSA particles. Despite its significance in environmental problems associated with the sea-atmosphere-land interface, adhesion behavior of various types of SSA's remains poorly understood. Here, we characterized the adhesion forces of laboratory-generated SSA and ambient aerosols on an individual particle basis using atomic force microscopy (AFM).

In this study, artificial sea salt (ASS) and two standard monosaccharide samples, glucose (Glu) and fucose (Fu), were used as pure components representing inorganic and organic compounds in the ocean, respectively. Additionally, mixtures of ASS and glucose (ASS/Glu) in various mass ratios were studied to determine how the adhesive behavior of SSA is affected by the different degrees of organic mixing. In addition, the adhesion forces of aerosols derived from the bulk sea foam (SF) were measured to represent the adhesivity of SSA particles naturally enriched in a variety of marine organic matters. Furthermore, adhesion behavior of these laboratory generated particles were compared to that of ambient sea salt particles. Therefore, the objectives of this chapter were to (i) demonstrate the applicability of AFM-based methods to a wide variety of atmospherically relevant SSA particles with complex chemical compositions and mixing states, and (ii) quantitatively evaluate their adhesion on an individual particle basis.

3.2 Materials and methods

ASS, Glu, and Fu were dissolved in ultra-pure water at 0.2–0.5 wt%. In addition, mixed solutions of ASS and Glu were also prepared at 3 different mass ratios (4:1, 1:1, 1:4). These solutions were aerosolized by an atomizer and dried through silica-gel-filled diffusion driers. SF particles were generated from frozen samples of sea foam collected on the northern coast of the Noto Peninsula, Japan. The sample was diluted 10 times with ultrapure water after thawing, aerosolized by bubbling filtered air through a gas washing bottle, and dried using silica gel-filled diffusion driers. Collection of ambient aerosol particles were performed at the Kanazawa University campus, along the western coast of central Japan. These samples were deposited on Si wafers.

The method 2 described in the second chapter was performed for the measuremet of the adhesion force. During measurements, filtered and dried air was constantly supplied around the AFM head and the relative humidity (RH) was maintained at 20%. Our results indicate that the adhesion force values on Si wafer fall within the 35-65 nN range.

Chemical analyses were conducted on the selection of particles after physical characterization by AFM. The micro-Raman spectroscopy was used on the individual SF particles to examine their chemical composition. The ambient aerosol particles were subjected to identification and grouping utilizing either micro-Raman spectroscopy or scanning electron microscopy (SEM-EDX, S3000N, Hitachi, Tokyo, Japan) combined with energy dispersive X-ray spectrometry (EDX, EMAX-500, Horiba, Kyoto, Japan).

3.3 Results and discussion

A comparison of ASS with the monosaccharides Glu and Fu revealed that organic particles had consistently greater adhesion forces than purely inorganic particles (Figure 2). The monosaccharides in this study exhibited larger adhesion forces, which could be attributed to their phase state (semi-solid) caused by the presence of water within the particles. Furthermore, a comparison of pure ASS and Glu particles and their mixtures shows that the degree of mixing is closely correlated with the adhesion forces. The adhesion force of pure ASS is the smallest, but it increases with the increasing fraction of Glu. These results suggest that the extent of particle coating by the organic matter is likely to influence their adhesion forces, considering the gradual change of particle shapes corresponding to the organic mass ratio found.

Regarding natural origin particles, specifically those with more atmospheric relevance, the shell-rich (SFSp) particles displayed greater adhesion than SS and SFSS particles (Figure 2). This is in line with previous research using standard materials that found organic-rich particles tend to have higher adhesion forces than inorganic-rich particles. The adhesion forces of SFSp particles are comparable to those of ASS/Glu (1:1) particles, while the adhesion forces of SFSS and SS are comparable to those of ASS and ASS/Glu (4:1) particles. Notably, standard and natural particles with similar adhesion forces exhibited common morphological characteristics. The potential factors causing the fluctuations in adhesion forces of SFSp particles can be attributed in part to the fact that the SFSp particles are not a pure saccharide, but also comprised of many polysaccharides and lipids present in the SML. The organic compounds within the SF particles were not directly identified in this study. Further investigation into the nature of highly adhesive particles is necessary through adhesion force measurements of various organic compounds such as polysaccharides, dicarboxylic acids, and fatty acids, as well as their mixtures with ASS.

4. Improving the Accuracy of Aerosol Viscoelasticity Measurements Using Atomic Force Microscopy

4.1 Introduction

The phase state of aerosols has an impact on global climate and various atmospheric processes, and is heavily influenced by the water uptake behavior of aerosol particles. It is known to be influenced by the surrounding environment, such as relative humidity. Additionally, the viscoelasticity of aerosols, which includes viscosity and elasticity, is also closely related to the phase state of the aerosol (hence RH).

Recently, methods have been developed to directly measure the phase state, elasticity, and viscosity of individual submicron-sized particles using force-distance curve collected by AFM measurement. In previous studies, physical properties such as Young's modulus and viscosity were measured for individual aerosol particles. However, the previous study only reported the case of a constant vertical tip velocity of the AFM probe approaching the sample despite tip velocity effects were focused as reported in papers on living cells and rubber. Therefore, the purpose of this chapter is to investigate the extent to which the viscosity or elasticity (Young's modulus) values calculated from the model are affected by RH and the tip velocity (or indentation/deformation rate calculated from the tip velocity) of AFM measurement condition. The viscosities of individual particles were calculated by the linear three-dimensional Kelvin-Voigt (KV) viscoelastic model, and the Young's modulus values were also be obtained by the viscoelasticity model and compared with those obtained by the Johnson-Kendall-Roberts (JKR) elastic model using AFM. The applicability of these models in evaluating the viscoelasticity of aerosols will be discussed. In this study, glucose was used as a standard particle. The values for each property were obtained from the data collected through force curve mapping. The method's applicability to a wider range of atmospheric aerosols was also discussed for future consideration.

4.2 Materials and methods

Glucose were dissolved in ultra-pure water at 0.2 wt%. This solution was aerosolized by an atomizer and dried through silica-gel-filled diffusion driers. The particles were deposited onto a Si wafer substrate with a hydrophobic coating. The impactor used for the particle collection has a 50% aerodynamic cutoff diameter of 1.1 μm at a flowrate of 1.0 LPM.

A SPM-Nanoa with Nano 3D Mapping^{TM} Fast system (Shimadzu, Kyoto, Japan) was used for force-distance curve mapping measurements at ambient temperature (18–33 °C) and varying RH ranging from 20% to 45% by three types of saturated inorganic salts (CH3COOK; ≅25%, K_2CO_3; ≅37%, $MgNO_3$; ≅45%) using a custom-made humidity cell. Silicon AFM probes (ATEC-CONT, NANOSENSORS^{TM}, Neuchatel, Switzerland) with a nominal spring constant of 0.2 N/m and a tip radius of curvature of 10 nm were used for force-distance curve mapping measurements. Each force-distance curve mappings covered 3×3 μm (32×32 pixels). The AFM probe was approached to the sample until the maximum loading force applied to the sample was approximately 20 nN (method 1 described in second chapter). Vertical tip velocity of AFM probe was 1-50 μm/s for measurements. Five force-distance curves on individual particles that can be used for the estimation of Young's modulus and viscosity by KV model were extracted per mapping data.

4.3 Results and Discussion

Figure 3 shows the comparison between tip velocity and viscosity at different humidity levels. The data indicates a decrease in glucose viscosity with increasing humidity. This suggests that as humidity increases, glucose transitions towards a liquid phase due to water absorption. The results indicate that viscosity decreases as indentation rate increase at all humidity levels.

The results indicate that there is a noticeable tendency for Young's modulus to increase with increasing tip velocity or indentation rate under RH > 37%, which is opposite to the trend observed for viscosity. This suggests that glucose exhibits more elastic behavior at higher tip or indentation speeds. When comparing the JKR and KV results, there is no significant difference in magnitude at RH ≈ 25. However, the JKR results are lower at RH > 37%. This discrepancy may be due to the viscoelasticity of glucose in the RH>37% range, which cannot be accurately predicted by the JKR theory because the JKR theory is a theory about elastic bodies and cannot account for viscoelastic behavior of sample.

The varying trends in viscosity and Young's modulus response at different tip velocity and indentation rate indicate the significance of these physical properties in understanding the characteristics of aerosol particles. Thus, it is crucial to measure the physical properties of aerosol particles using AFM under diverse velocity conditions, not just RH. Future research should investigate the appropriate scale of tip velocity or deformation (indentation) rate and calculate viscosity accordingly for various atmospheric aerosol phenomena, such as morphological change, diffusion time, and deposition velocity.

5. General Conclusion

Atomic force microscopy can directly measure physical properties of aerosols, reproducing real atmospheric conditions with nanometer-scale resolution. By utilizing this feature, it is possible to measure the physical properties of aerosols under different humidity, temperature, and atmospheric pressure conditions and help to explore previously unknown characteristics.

Detailed measurements and analyses on a particle-by-particle basis are required to understand the physical properties of different aerosols. This thesis utilized atomic force microscopy (AFM) to evaluate the physical properties of individual aerosol particles in complex mixing states, with particular emphasis on the adhesion force, Young's modulus, and viscosity of aerosols related to the aerosol phase state. This study demonstrated that AFM can be used as an effective tool to quantitatively characterize the physical properties of aerosol particles on an individual basis.

These results suggest that measuring the physical properties of individual aerosols using AFM can provide a more detailed understanding of the phase state of atmospheric aerosols and their related properties. The particle adhesive properties obtained in this study will help to explain adhesion phenomena of aerosols occurring on the interface of the atmosphere, including corrosion of infrastructures and particle resuspension. Additionally, these measurements of aerosol viscoelasticity, including Young's modulus and viscosity, will provide a better understanding of new particle formation, atmospheric aerosol growth, cloud condensation and ice nucleation abilities, and atmospheric aging of aerosols. Such knowledge will eventually be incorporated into models to better predict the impacts aerosols have on the climate change and public health.

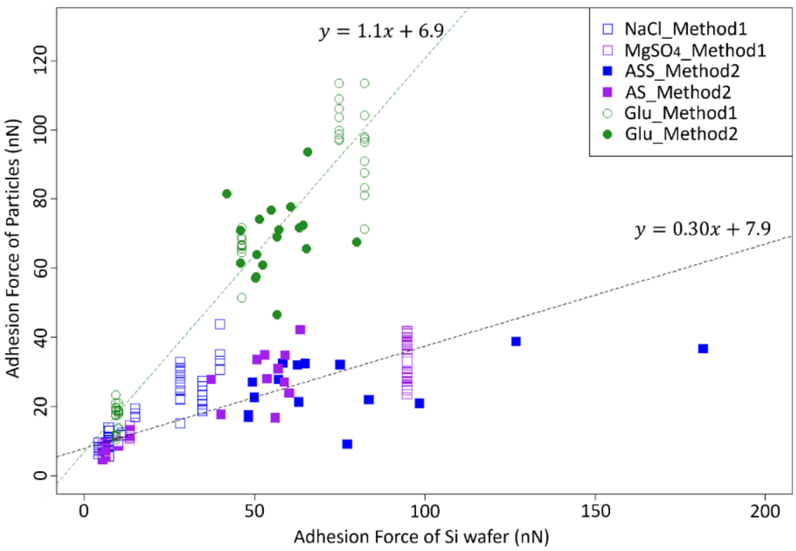

Figure 1 The plot of adhesion forces of Si wafer and aerosol particles using Nanofinder HE. The hollow shapes represent the results for the particles measured by method1, and the solid shapes represent the results obtained by method 2. Green and black dashed lines show fitting lines of glucose and inorganic particles, respectively.

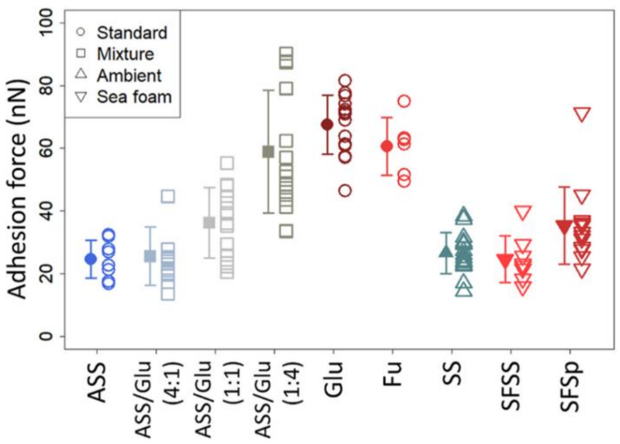

Figure 2 Comparison of adhesion force of ASS, ASS/Glu (4:1, 1:1, 4:1), two monosaccharides, SS and the two types of sea foam particles measured in this study. Hollow marks indicate the adhesion force values of individual particles, whereas solid marks and whiskers indicate the mean and standard deviation, respectively.

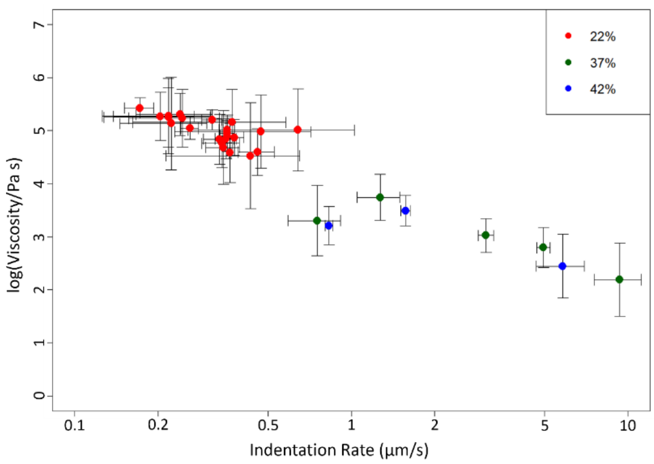

Figure 2 Log (η) versus indentation rate plot of glucose particles at each RH conditions.

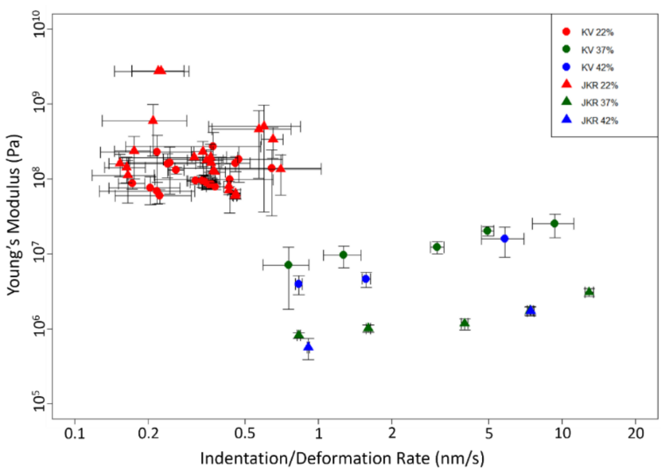

Figure 3 Young's modulus versus indentation rate plot of glucose particles.

令和　6年　1月31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。）

原子間力顕微鏡を用いた個別粒子の物性評価法の開発と実大気エアロゾルへの応用

Direct measurement of physical properties of individual particles by atomic force microscopy and its application to atmospheric aerosols

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3．審査結果の要旨（600～650字）

本学位論文では、原子間力顕微鏡を用いた単一粒子の物性評価手法を新規開発し、実環境中の大気エアロゾルに適用することで、沈着プロセスに関わる付着力の直接的な評価を可能にした。従来のエアロゾル研究では、大気中に浮遊している状態での挙動を左右する粒子の物理特性（粒子サイズ、空気動力学、光散乱特性、吸湿性など）に主眼が置かれたものが多く、付着力など沈着挙動に関連する物性は研究上の空白地帯となっていた。本学位論文では原子間力顕微鏡による独自の評価手法を確立したのみならず、測定結果の再現性を担保し、同手法が広く一般化できることを示した。また、能登半島の曽々木海岸で採集された「波の花」を利用し、より天然の環境に近い海洋起源エアロゾルを忠実に再現することで、糖類などの有機物を含む粒子が特に高い付着性を示すことをはじめて明らかにした。さらに、個別粒子レベルでの測定が可能な利点を最大限に生かし、多種多様な実大気エアロゾルの中に極めて付着性の高い粒子がわずかに存在することを発見した。こうした知見は、従来見過ごされていたエアロゾルが大気から取り除かれる過程と、腐食性や放射性エアロゾルの沈着、再飛散に伴う人体、環境への正確な影響評価につながる。同手法は、発展的に粘性や弾性など、大気化学にとっても重要な物性評価への展開が可能であり、当該分野において益々重要な役割を果たすものと期待される。以上を専攻の審査基準に照らし、博士（理学）の学位に相応しいと認め、合格とする。

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（　理学　）