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学位授与の日付 平成 28 年 9 月 25 日

論文名 「Development of Simultaneous Measurement Method of Gaseous Ammonia and Fine Particulate Ammonium and Study on Their Behaviors in Urban Atmosphere
(ガス状アンモニアと微小粒子状アンモニウムの同時測定法の開発とそれらの都市大気中における濃度変動調査)」

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論文要旨

In atmospheric chemistry, ammonia gas (NH_3) is a dominant alkaline gas. It can readily react with atmospheric acids mainly sulfuric and nitric acids to form the corresponding ammonium particles that contribute to a significant fraction of total fine particulate matters ($\text{PM}_{2.5}$, particle size less than $2.5 \mu\text{m}$). Recently, the presence of ammonia has been found to elevate a yield of secondary organic aerosols through atmospheric aqueous chemistry. Atmospheric aerosol has negatively impacts on human health, climate change and environmental degradation process. In addition, an excess of total ammonia species (ammonia gas + ammonium particles) deposited to ecosystem can cause many environmental issues such as eutrophication of aqua, acidification of soil (by nitrification process) and biodiversity loss in sensitive ecosystem.

Because of its importance, a number of studies have attended to evaluate emission sources, to investigate its role in atmospheric chemistry and to estimate impacts on the ecosystem in recent years. On a global scale, the largest emission source of ammonia is

agriculture with two major sub-sectors including livestock wastes and application of synthetic nitrogen fertilizers. Whereas numerous researches have investigated on this source, only a limited number of studies on ammonia sources within the urban environment have been reported. Due to the introduction of three-way catalytic converters in gasoline-engine vehicles to reduce the nitrogen oxides emission, urban ammonia levels have been increasing. Moreover, other sources such as human emission (breath, sweat and smoking), garbage collection and pet excreta are also significant contributors. In our opinion, urban ammonia levels and its emission sources may vary city to city. Importantly, in urban area, the fine particles levels could be increased due to a close relationship between ammonia and acidic gases (e.g., sulfur dioxide (SO_2) and nitrogen oxides (NO_x)) emission, which consequently affects to public health. From these reasons, study on atmospheric ammonia in urban environment should be encouraged.

Recent studies have investigated the interactions between the surface-atmosphere exchanges with gas-particle partitioning of ammonia, and the results showed that the timescale of surface fluxes is similar to that of ammonium nitrate gas-particle partitioning. Therefore, low time resolution and only ammonia gas measurements are unable to fully characterize the dynamic behavior of ammonia. Finally, we have two purposes for our thesis. The first purpose is to develop a high time resolution and simultaneous measurement method for both gaseous ammonia and particulate ammonium at sub-ppb levels. The second is to investigate behavior of ammonia species at two distinct urban areas: Osaka, Japan and Ho Chi Minh City, Vietnam. In order to address these purposes, the work is divided as follows.

Chapter 1 is a brief description on ammonia issues with respect to emission sources, atmospheric chemistry and its impacts on human health and environment. In addition, overview on several NH_3 species measurement techniques and challenges in measuring NH_3 concentrations were pointed out. Finally, the purpose of this thesis was stated.

Chapter 2 describes a new continuous measurement method for gaseous ammonia. First, ammonia gas in ambient air was collected in an aqueous solution using a counter-current flow tube (CCFT) sampler. Then, ammonium formed in the aqueous solution was detected by the indophenol method using a continuous flow analysis system. Several parameters were optimized to achieve a good sensitivity. Based on a CCFT length of 50 cm

and air flow rate of $1 \text{ dm}^3 \text{ min}^{-1}$, the collection efficiency exceeded 98.5 % at an ammonia mixing ratio of up to 120 ppbv. The detection limit of this method was 62 pptv. Interferences from several gases were investigated, and the results showed that the present method was not affected by NO_x , O_3 , SO_2 , HONO, methylamine, formaldehyde, hydrogen sulfide or a mixture of these gases. The most important result was that only gaseous ammonia was detected in the present method without any interference from the particulate ammonium in ambient air. In addition, the present method showed good agreement with the dry denuder method.

In Chapter 3, a high time resolution and simultaneous measurement method for gaseous ammonia and fine particulate ammonium ($\text{PM}_{2.5}\text{NH}_4^+$) was developed. It is very important to completely separate ammonium particles from gas-aerosol mixture in ambient air. As described in Chapter 2, the CCFT sampler could collect only ammonia gas with the collection efficiency of 98.5 %, whereas almost all particles passed through it. Therefore, a wetted frit sampler connected at downstream of the CCFT sampler was adopted for measuring ammonium particles. An air sample was drawn through the samplers at a flow rate of $1 \text{ dm}^3 \text{ min}^{-1}$ and an absorption water flow rate of $120 \text{ mm}^3 \text{ min}^{-1}$. Then, the ammonium that formed in the absorption solutions were detected by the indophenol method using a continuous flow analysis system. Two approaches using generated ammonium particles under a laboratory condition and atmospheric particles in ambient air were used to evaluate particle collection efficiency (CE) of the wetted frit sampler. The results showed that particle CE was approximately 100 %. The estimated detection limits were 62 pptv (43 ng m^{-3}) and 49 ng m^{-3} for ammonia gas and $\text{PM}_{2.5}\text{NH}_4^+$, respectively. The present method was validated against the annular denuder method, with the results showing a good agreement between both techniques.

Chapter 4 presents the results from continuous and simultaneous measurements of NH_3 gas and $\text{PM}_{2.5}\text{NH}_4^+$ at two distinct urban areas: Osaka, Japan and Ho Chi Minh City (HCMC), Vietnam. Measurements were performed using the instrument as described in Chapter 3. Two selected urban sites in this study represent for two different urban environments. Two period measurements were carried out during 11 February – 12 March, 2015 (cold period) and 1 July – 14 September, 2015 (warm period) at the urban site in Osaka, while seventeen day

measurements from 21 May – 8 June, 2015 were conducted at the urban site in HCMC.

At the Osaka urban site, the average concentrations for NH_3 in cold and warm periods were 1.98 ± 0.93 and 4.21 ± 2.30 ppbv, respectively. Both of them were lower than those measured at the HCMC site with mean value of 8.34 ± 2.47 ppbv. Differences in NH_3 levels between two cities are as a result of their different emission sources. The diurnal profiles of NH_3 at the Osaka site showed a bimodal cycle but unclear with two peaks in the early morning and the late afternoon. Traffic emission was estimated to be a significant contributor to elevate NH_3 levels. In addition, a shift in the thermo equilibrium of ammonium nitrate aerosols at the high temperature in the late afternoon contributes to evolution of NH_3 during that time. In contrary, the diurnal profile of NH_3 in the HCMC site showed a pronounced bimodal cycle, with a sharp peak in the early morning and a broad peak in the evening. The contribution of traffic emission to NH_3 levels should be negligible. The diurnal pattern of NH_3 could be driven by the human activities and the evolution of the planet boundary layer and wind speed. High NH_3 level in the HCMC site are considered to be human sources and poor waste management systems, especially under high temperature and highly population density.

Whereas the NH_3 concentration in the HCMC site was much higher than those measured at the Osaka site, the $\text{PM}_{2.5}\text{NH}_4^+$ levels showed a different trend. The highest average level was observed during cold period with mean of $1.45 \pm 1.18 \mu\text{g m}^{-3}$, followed by warm period with mean of $0.93 \pm 0.61 \mu\text{g m}^{-3}$ at the Osaka site, and the lowest average level was observed at the HCMC site with mean of $0.74 \pm 0.30 \mu\text{g m}^{-3}$. The diurnal profile of $\text{PM}_{2.5}\text{NH}_4^+$ observed at the Osaka site showed a single but broad peak at noontime, suggesting the common formation pathway of sulfate aerosols which occurred strongly during the mid-day. Conversely, the diurnal profile of $\text{PM}_{2.5}\text{NH}_4^+$ at the HCMC site showed a single peak in the early morning, consistent with the $\text{PM}_{2.5}$ diurnal pattern. This peak occurred can be explained due to NH_3 absorption onto existing particles at very high $\text{PM}_{2.5}$ levels and humid condition in the early morning. However, it is noted that the average $\text{PM}_{2.5}\text{NH}_4^+$ concentration is still low at the HCMC site.

Ammonium particle formation and its contribution to aerosol pollution are further

examined. Availability of atmospheric acids mainly sulfates and nitrates as well as low temperature and high humidity are the factors facilitating the ammonium formation. Our results highlight that NH_3 plays key role in secondary inorganic aerosol formation; in consequence, it contributes to significant amount of $\text{PM}_{2.5}$ at the Osaka site. In contrast, high $\text{PM}_{2.5}$ levels observed at the HCMC site are from other sources (e.g. primary emission from vehicles) rather than secondary inorganic aerosol formation.

In Chapter 5, the main conclusions from the research were drawn.

審査結果の要旨

本論文は、悪臭物質として知られるアンモニアガスおよび近年問題となっている $\text{PM}_{2.5}$ の主要構成成分であるアンモニウムイオンの同時測定法の開発と、開発した装置を用いた大阪およびベトナムホーチミンにおける野外測定から、アンモニアの発生源解明を試みたものであり、次のような成果を得ている。

1) 向流管を用いたアンモニアガスの連続測定法を開発し、優れた感度と迅速な応答性を示し、他法との相関のよい測定法であることを確認した。また、共存する他の気体の影響を受けないこと、粒子として存在するアンモニウムの影響を受けない選択性の高い測定法であることを示した。

2) 向流管の後段にT字管を設置し、吸収液を導入、テフロン製の細管を通して、焼結ガラスフィルターに導き、気液分離管により吸収液だけを測定系に導くことで、粒子状のアンモニアをほぼ100%回収、分析する方法を開発した。他の測定法である管状デニューダー法との相関もよく、アンモニアガスと $\text{PM}_{2.5}$ 中の粒子状アンモニウムそれぞれを短時間で正確に測定できることを示した。

3) 開発したガス状アンモニアおよび微小粒子状アンモニウムの連続同時測定装置を用いて、大阪府立大学構内およびベトナムホーチミン市で測定を行い、大阪では自動車からの排出がアンモニアの主発生源であるのに対し、ベトナムでは、劣悪な家庭排液処理によるアンモニア放出が主発生源であることを明らかにした。また、ベトナムでは粒子状として存在しているアンモニウム濃度がガス状に比べて極めて低く、ベトナムの高い $\text{PM}_{2.5}$ 成分は、ほとんどがススまたは多環芳香族などである可能性を示唆した。

以上の諸成果は、環境データの少ないアンモニアガスおよび粒子状アンモニウムの測定データを示すと共に、今後のベトナムの環境改善のために必要な施策に示唆を与え、 $\text{PM}_{2.5}$ の主要成分であるアンモニウム塩の生成過程の解明、および発展途上国が経済発展する中で起こりうる問題解決に貢献するところ大である。また、申請者が自立して研究活動を行うのに十分な能力と学識を示したものである。