Notes

Preliminary Study of Quantitative Analysis of Ammonium Ions in a Raindrop Following Liesegang Ring Formation

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NH_4^+ concentration in an individual droplet was determined by forming a Liesegang ring on a gelatin film containing $NaB(C_6H_5)_4$. The NH_4^+ concentration (mol L^{-1} abbreviated to M) was calculated from the NH_4^+ amount (mol) ascertained in a droplet using pixel count measurements. The droplet volume (L) was calculated by measurement of the diameter of a droplet print on the gelatin film. For rainwater, the NH_4^+ concentration estimated using this method corresponded with results obtained using ion chromatography.

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Introduction

Generally, the chemical components of raindrops are analyzed using rainwater that has been collected using sampling equipment. These results are interpreted as temporally and spatially averaged values, causing a loss of detailed information because the chemical components and the concentrations contained in each droplet depend on the droplet size and the heterogeneity of the droplets' distribution.[1,2] Componential analysis of raindrops is therefore important to investigate the physicochemical reactions taking place in rain and clouds. Although several studies have been conducted using analyses of individual raindrops, no consistently useful method has been reported. Kasahara *et al.* fixed individual raindrops by exposure to cyanoacrylate vapor after a breeze.[3] They conducted droplet size measurements and elemental analyses. Ma *et al.* used a combination of the collodion replication method and the synchrotron radiation X-ray fluorescence microprobe technique to elucidate the properties of individual raindrops.[4] Bächmann and his research group analyzed individual and size-classified raindrops using capillary zone electrophoresis.[1,5-8] Our group sought to determine the SO_4^{2-} concentration in individual raindrops by application of Liesegang ring formation.[9]

The Liesegang ring phenomenon was first noted by Liesegang in 1896: a periodic banded precipitate is formed from the reaction between two compounds in a gelatin solution.[10] Although some studies have undertaken qualitative analyses of ionic species,[11-13] the first quantitative determination of SO_4^{2-} concentration by applying Liesegang ring formation was achieved in an earlier study.[9] Liesegang rings were formed from the reaction between Ba^{2+} (barium chloride) in a gelatin film and SO_4^{2-} in a sample droplet. In this study, we applied this analytical method and improved it to determine the NH_4^+ concentration in an individual droplet. A predominant cation in the rain and fog water, NH_4^+ has a neutralizing effect on acid rain. Therefore, the determination of NH_4^+ concentration in raindrops is important to elucidate the physicochemistry of cloud, rain, and fog processes. Liesegang rings have been formed from a reaction between $B(C_6H_5)_4^-$ (sodium tetraphenylborate) in the gelatin film and NH_4^+ in the sample droplet.[14] To apply this method to films with no ring or with a distorted ring proved to be difficult, because the SO_4^{2-} concentration was determined from the relation with the Liesegang ring diameter. By improving this method, one can determine the NH_4^+ concentration from picture elements (pixels) of the crystalline products that constitute the Liesegang rings. In digital imaging, a pixel is the smallest representable element of an image. The pixel count increases concomitantly with the increasing spread of white crystalline formation in the gelatin film because of the increased NH_4^+ concentration. In this study, pixels in a digital microscope image were counted using a graphics editing program.

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Experimental

Sodium tetraphenylborate, ammonium chloride, and gelatin powder were supplied by Kanto Chemical Co. Inc. All were used without additional purification. A gelatin solution (5 wt%) containing 10 mM $NaB(C_6H_5)_4$ was coated onto a glass slide (25 × 75 × 1 mm) using a dip coater (MD-0408; SDI Co. Ltd.) at the sweep rate of 0.5 mm s^{-1}. Then the solution was dried rapidly in a current of hot air because natural drying gave the gelatin film an uneven thickness. Sample aqueous solutions containing NH_4Cl with concentrations between 5 μM and 10 mM were prepared using Milli-Q pure water. These concentrations resemble the actual NH_4^+ concentrations in rain and fog water. A certain amount of sample solution was dropped on the gelatin film; then each such film was stored in the glass desiccator at constant humidity of 80% for 4 days. These conditions were optimized based on results of preliminary experiments. The resultant Liesegang rings were observed using a digital microscope (BS-D8000II; Sonic Co. Ltd.). The pixel count of microscope images was obtained using a graphics

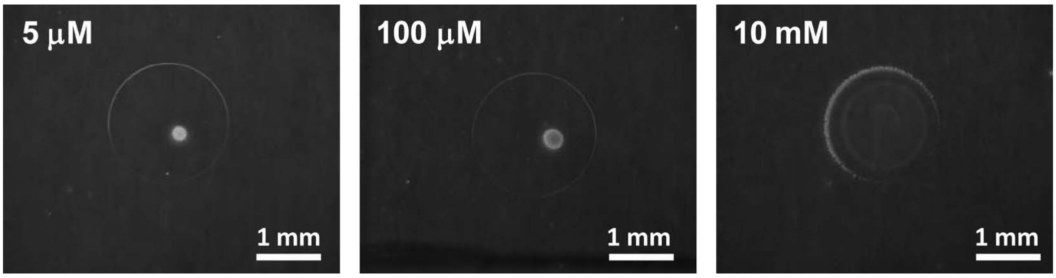

Fig. 1 Different crystalline formations were produced depending on the NH_4Cl concentration of the dropped sample solution. Each scale bar shows 1 mm. The outer cyclic shape is a droplet print of the dropped sample solution.

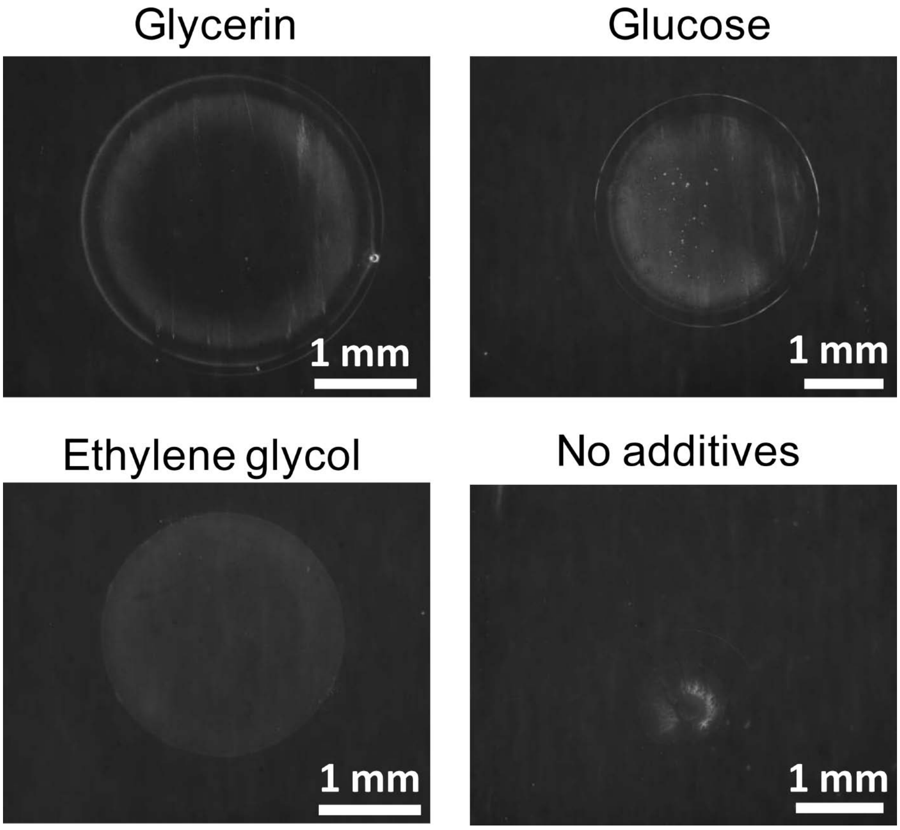

Fig. 2 Crystalline formation in each gelatin film containing an additive reagent such as glycerin, glucose, or ethylene glycol. The dropped sample solution is 5 mM NH_4Cl. Each scale bar shows 1 mm.

editing program (Photoshop CS2; Adobe Systems Inc.). For comparison, NH_4^+ concentrations in the rain and fog water collected using sampling equipment were also measured using an ion chromatograph (DX-120; Dionex Corp.) with a conductivity detector.

Results and Discussion

Formation of Liesegang rings

Liesegang rings of $NH_4B(C_6H_5)_4$ were formed from the reaction between $NaB(C_6H_5)_4$ and NH_4Cl. As representative examples, Fig. 1 presents results of crystalline formation when the concentrations of the dropped NH_4Cl sample solution were 5 μM, 100 μM, and 10 mM. An outer cyclic shape observed in all cases is not a Liesegang ring but a droplet print, which is the trace of the sample droplet on the gelatin film after drying. At low NH_4Cl concentrations, the crystalline product was generated clearly and was concentrated intensely around the center of the droplet print. However, the Liesegang rings were not observed. At high NH_4Cl concentrations, the crystalline product was generated thinly and broadly in the droplet print. The Liesegang rings were readily visible, especially at 10 mM. In an earlier study of SO_4^{2-} determination, however, the Liesegang rings were observed even at low concentrations. From these results, we inferred that NH_4Cl sample solution diffuses into the gelatin film only slightly at low concentrations. Actually, the high hydrophobicity of $NaB(C_6H_5)_4$ leads the gelatin solution to be hydrophobic, thereby inhibiting diffusion of the NH_4Cl sample solution. Therefore, the gelatin film was prepared by adding a hydrophilic reagent such as glycerin, glucose, or ethylene glycol.

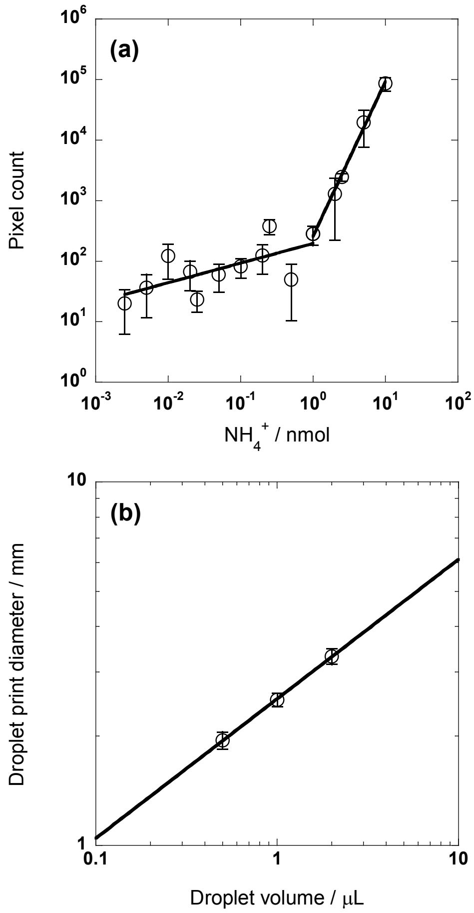

Fig. 3 (a) Relation between the amount of NH_4^+ in the sample solution and the pixel count of the crystalline product. Each value is the average of at least three trials. The error bar shows the standard deviation. (b) Relation between the droplet volume of the sample solution and the diameter of the droplet print on the gelatin film. Each value is the average of 40 trials. The error bar shows the standard deviation.

Hydrophilic gelatin film production

Gelatin solutions with 5 wt% of each additive reagent were prepared and coated onto the glass slides. Figure 2 portrays gelatin films with the hydrophilic additives after dropping 5 mM of the NH_4Cl sample solution. Adding these reagents rendered the gelatin film hydrophilic, which broadly diffused the NH_4Cl sample solution. We measured the pixel count of crystalline products generated in each gelatin film at various concentrations between 5 µM and 10 mM. The background value was defined as the pixel count when NH_4^+-free water was dropped on the film. Results for the glycerin-containing film showed that the pixel count increased concomitantly with increasing NH_4^+ concentration in the dropped sample solution. Furthermore, the reproducibility was high and the background pixel count was low. For glucose, the reproducibility was low and the pixel count variation was slight. Meanwhile, for ethylene glycol, the background pixel count was high; little pixel count variation was found to occur along with the variation of the NH_4^+ concentration. Based on these results, we adopted glycerin-containing film for determination of the NH_4^+ concentration.

Calibration curve for quantitative analysis

In the present study, the NH_4^+ concentration was determined according to the following procedure. (1) The NH_4^+ amount (mol) in the sample solution was estimated from the relation between the amount and the pixel count of the crystalline product. (2) The volume (L) of the sample solution was estimated from the relation between the droplet volume and the droplet print diameter. Based on these estimations, the concentration of NH_4^+ (mol L^{-1}) was calculated from the NH_4^+ amount (*via* (1)) and the droplet volume of each sample solution (*via* (2)). Figure 3 shows two calibration curves based on these relations. In a double logarithmic plot of Fig. 3a, the slope for the low amount range was small. This method can be adopted for a sample with a large amount of NH_4^+ amount. From the second calibration curve shown in Fig. 3b, the sample solution volume was estimated from the droplet print diameter. In the double logarithmic plot, the variation showed high linearity and high reproducibility; this result demonstrated the high validity of the calibration curve.

Field application

To assess the applicability of these calibration curves, we conducted analyses of actual rain and fog water. The possibility of interference in NH_4^+ determination of various ion compounds in rain and fog water was a concern in field applications. The sample rain and fog water used for this study was collected on the mountainside of Mt. Oyama (680 m, located in western Kanagawa in Japan) using sampling equipment during 21 October – 24 November in 2010. After collection, it was filtrated with a 0.45-µm membrane filter. Our group investigated the effects of acid fog and acid rain on the environment of Mt. Oyama.[15] Using a microsyringe, 1 µL of the collected sample rain or fog water was dropped on the gelatin film as one drop. In this experiment, however, the actual individual raindrop was not dropped directly on the gelatin film. A comparison between the NH_4^+ concentration estimated using the Liesegang method described above and the results from the ion chromatography showed that these data mutually corresponded, especially at high NH_4^+ concentrations: 0.57 mM NH_4^+ using this method and 0.66 mM using ion chromatography. Results suggest that the NH_4^+ determination method proposed in this study is applicable to the analysis of individual raindrops in an actual environment. For further improvement, the optimization of setting conditions of the gelatin film such as $NaB(C_6H_5)_4$ concentration, glycerin concentration, and the selection of these additive reagents must be performed. Furthermore, the application of this method to individual rain or fog drops remains as a subject for additional investigation.

Conclusions

A novel method for the quantitative determination of NH_4^+ concentration in a droplet was proposed using Liesegang ring formation of $NH_4B(C_6H_5)_4$. We achieved high reliability using the relation between pixel count and NH_4^+ concentration. The relation between the droplet volume of the sample solution and the diameter of a droplet print on the gelatin film showed high reproducibility. The NH_4^+ concentration estimated using this method agreed well with results obtained using ion chromatography. Results show that this method of determining NH_4^+ is applicable to analysis of individual raindrops.

Supporting Information

Figure S1 presents crystalline formations in all NH_4Cl concentrations of the dropped sample solution (5 μM – 10 mM). Figure S2 presents crystalline formation by dropping actual fog water that had been collected at Mt. Oyama. These materials are available free of charge on the internet at http://www.jsac.or.jp/analsci/.

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