Comparison of aerosol acidity based on a direct measurement method and a chemical thermodynamic model

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Abstract

Aerosol acidity is an important parameter in aerosol science that affects many chemical reactions in the atmosphere, and it is often estimated using chemical thermodynamic models. The Extended Aerosol Inorganic Model IV (E-AIM IV) is frequently used for this purpose; however, due to the limited number of available direct measurement methods of aerosol acidity, there is still a certain degree of uncertainty with regard to how accurately the simulation results reflect reality. In this study, a new pH testing paper method for the direct measurement of aerosol pH is used to measure the pH (pH_{meas}) of aerosol particle samples. Based on the data of the ionic constituents of the samples, the E-AIM IV model is then used to estimate aerosol pH (pH_{est}). This study provides a comparison of pH_{meas} and pH_{est}, revealing that the relationship is satisfactorily approximated by a simple linear regression of pH_{est} = 1.05pH_{meas} + 0.38 (R^2 = 0.90). The strong correlation and slope very close to unity indicate that the pH testing paper method corroborates the outputs of the E-AIM IV model.

Keywords:
Aerosol pH; Extended Aerosol Inorganic Model IV; pH testing paper method.
1 INTRODUCTION

Atmospheric aerosol acidity, expressed in terms of pH, is an important parameter in atmospheric science. It significantly affects the gas/particle partitioning of semi-volatile species in the atmosphere, such as NH$_3$/NH$_4^+$ and HNO$_3$/NO$_3^-$ (Guo et al., 2017). Thereby, aerosol acidity indirectly affects inorganic nitrogen deposition in the ecosystem (Nenes et al., 2021). In addition, previous studies on human health assessment suggested that aerosol acidity plays an important role in the solubility of hazardous materials in aerosol particles (e.g., trace metals) (Deguillaume et al., 2005; Fang et al., 2017). Moreover, the human respiratory system can be affected adversely by direct inhalation of highly acidic particles (Dockery et al., 1996; Raizenne et al., 1996). Therefore, aerosol acidity has attracted increasing interest in atmospheric aerosol research. Obtaining information on aerosol acidity is beneficial for many related studies (Su et al., 2020).

Despite its importance, it is difficult to measure aerosol acidity, owing to the low water content and high ionic strength of aerosol particles. The thermodynamic models, such as the Extended Aerosol Inorganics Model IV (E-AIM IV; Wexler and Clegg, 2002), ISORROPIA II (Fountoukis and Nenes, 2007), SCAPE2 (Meng et al., 1995), and EQUISOLV II (Jacobson, 1999), were always used to estimate aerosol acidity in many previous studies. Among the thermodynamic models, the E-AIM IV model is regarded as the benchmark thermodynamic model for inorganic aerosol systems because it is based on the thermodynamic data of pure aqueous solutions and
mixtures (Wexler and Clegg, 2002; Pye et al., 2020) and its calculation is based only on the thermodynamic interactions between solute species (Zaveri et al., 2008; Hennigan et al., 2015). Several studies have demonstrated that the E-AIM IV model is more accurate and suitable for estimating aerosol acidity (Yao et al., 2006; Seinfeld and Pandis, 2016). For these reasons, the E-AIM IV model is one of the most commonly used methods in aerosol acidity studies. The importance of NH$_3$ for aerosol acidity has often been reported on the basis of the analysis of thermodynamic models (Song et al., 2018; Murphy et al., 2017; Hennigan et al., 2015), and the multiphase buffer theory of aerosol acidity has been proposed to explain the aerosol pH variations caused by NH$_3$ (Zheng et al., 2020; Zheng et al., 2022). However, NH$_3$ data are often unavailable because there is a scarcity of reliable observations of NH$_3$ with particulate NH$_4^+$, resulting in inaccurate estimations of aerosol pH. To overcome this issue, comprehensive tests using real atmospheric samples with direct pH measurements are needed to understand the validity of the E-AIM IV model.

In our previous study (Song and Osada, 2021), we built a pH testing paper method for aerosol acidity by using particle hygroscopic equilibrium under high relative humidity (RH). This method has the advantages of simplicity, operability, and inexpensive costs. However, because the reliable in-situ aerosol acidity is practically unobtainable, it is difficult to experimentally provide the accuracy of the pH testing paper method. Therefore, in this study we conducted a comparison
of the pH testing paper method and a widely used thermodynamic model (the E-AIM IV model) for some aerosol samples. By the comparison, the relationship between the pH testing paper method and the E-AIM model would be illustrated, thereby revealing the utility of the pH testing paper method for the study of aerosol acidity.

2 METHODS

2.1 Direct measurement of pH

A new pH testing paper method for aerosol acidity developed by Song and Osada (2021) was used to measure the pH of aerosol particle samples in this study. An airtight box with a constant RH of 92% was prepared with a KNO₃ saturated solution. One spot of the sample sheet was cut and placed in the high-RH airtight box to form droplets by hygroscopic equilibrium. The temperature for the chamber experiments (Song and Osada, 2021) was set at the average air temperature of the aerosol sampling period. The pH of the droplet formed from the collected aerosol particles was measured by the pH testing paper (902 05, Macherey-Nagel GmbH & Co. KG). This pH testing paper was selected from six pH testing papers through rigorous examinations, including the color responses accuracy examination using salt solutions with different ionic strengths, the realistic high-ionic-strength condition examination using hygroscopic equilibrium, and the pH measurement of atmospheric aerosol samples. The applicable range of this method is 0.5–5.5 pH units. The uncertainty of the pH testing paper is 0.5 pH units, which is provided by the manufacturer (902 05, Macherey-Nagel GmbH & Co. KG).
The limitation of this method is that approximately 12 μg fine (PM$_{0.2–2.0}$ in this study) particles are required to form a detectable droplet at 92% RH condition. Each aerosol sample was determined 3–5 spots to obtain an average as the acidity of that aerosol sample (RSTD is ca. 11%). Details of the pH testing paper method for aerosol acidity measurement are presented by Song and Osada (2021).

### 2.2 Aerosol samples and chemical analysis

The fine aerosol particle (0.2–2.0 μm) samples were collected on polytetrafluoroethylene (PTFE) sheets (25 mm diameter; T020A025A, Advantec Toyo Kaisha Ltd.) using an inertial impactor (Kawakami et al., 2008) located on the rooftop of the Environmental Studies Hall of the Higashiyama Campus of Nagoya University (35.16 °N, 136.97 °E) from October 2019 to January 2020. Ambient air was drawn into the inertial impactor at a flow rate of 26 L min$^{-1}$. To obtain the different mass accumulations of aerosols, ten runs of air sampling were conducted by controlling the sampling duration. All sample sheets were stored in air-tight polypropylene tubes and kept in a refrigerator until the laboratory experiments were performed.

For impactor sample collection, nineteen spots were formed on the PTFE sheets. One spot was used for the pH measurement by using the pH testing paper method. Seven spots were extracted using 13 mL of pure water for analyzing major ionic constituents (NH$_4^+$, SO$_4^{2−}$, NO$_3^−$, Na$^+$, Cl$^−$, Ca$^{2+}$, Mg$^{2+}$, and K$^+$).

### 2.3 E-AIM IV thermodynamic model estimation
The E-AIM IV model is a semi-empirical thermodynamic model used to calculate the gas–liquid–solid equilibrium in an aqueous aerosol system. It mainly focuses on the \( \text{H}^+–\text{NH}_4^+–\text{Na}^+–\text{SO}_4^{2–}–\text{NO}_3^{–}–\text{Cl}^{–}–\text{H}_2\text{O} \) mixture system under variable temperatures ranging from 263.15 K to 330 K and RH higher than 60% (http://www.aim.env.uea.ac.uk/aim/model4/model4a.php; Friese and Ebel, 2010). Based on various input parameters, the E-AIM IV model provides rigorously estimated parameters of aerosol acidity. In this study, the input data include the ionic concentrations of \( \text{NH}_4^+ \), \( \text{Na}^+ \), \( \text{SO}_4^{2–} \), \( \text{NO}_3^{–} \), and \( \text{Cl}^{–} \); the average temperature of the sampling period; a RH of 92%; and the \( \text{NH}_3 \) concentration. Details of input data for the E-AIM IV model are listed in Table S1. Owing to the lack of data regarding ammonia in the measurement box of the pH testing paper method, the input \( \text{NH}_3 \) concentration for the E-AIM IV model was assumed based on the the upper and lower limits of possible \( \text{NH}_3 \) concentrations in the measurement box, including (1) the ambient concentration in the atmosphere during each sampling period (\( \text{NH}_3\text{-Amb} \)) (Monitoring data of \( \text{NH}_3 \text{-Amb} \) is provided in Table S1 of the Supplementary Materials; and details of \( \text{NH}_3 \) measurement are presented by Osada (2020)); (2) the average (30 ppb) of the empirical concentration in the laboratories (Li and Harrison, 1990; Li et al., 2020); and (3) 0 ppb (no ammonia).

Based on the output results of the E-AIM IV model, the aerosol pH was calculated using Eq. (1), which is an operational definition endorsed by the International Union of Pure and Applied
Chemistry (IUPAC, 1997), following the work of pH determination of the standard buffer (Covington et al., 1985; Stumm and Morgan, 1996). Eq. (1) was transformed from the original pH definition of \( pH = -\log (a_H) \), where \( a_H \) is the activity of H⁺ (Stumm and Morgan, 1996):

\[
\text{pH}_m = -\log_{10}(a_{mH}) = -\log_{10}(\frac{\gamma_{H} m_H}{m_0})
\]

(1), where \( a_{mH} \) denotes the activity of H⁺ and \( \gamma_H \) represents the activity coefficients of the molality standard state. \( m_H \) is the molality of H⁺ (mol kg⁻¹; moles of H⁺ ion per kilogram of solvent, typically pure water), and \( m_0 \) is the unit molality (equal to 1 mol kg⁻¹ solvent).

In addition, the original pH definition has two other transformed formulas. Their differences have been discussed in several articles (Murphy et al., 2017; Jia et al., 2018; Pye et al., 2020). In this study, a simple comparison between the different pH formulas was also conducted. Details are provided in Supplementary Material.

3 RESULTS AND DISCUSSION

The annual average PM₂.₅ concentration in Nagoya is approximately 12 μg m⁻³ (https://www.city.nagoya.jp/kankyo/page/0000129706.html). To obtain sufficient fine particle samples to apply the pH testing paper method, the sampling time was set according to the real-time monitoring data of PM₂.₅ (https://soramame.env.go.jp/). The PM₂.₅ time-series data during the sampling periods are presented in Fig. S2 in Supplementary Material.
To reduce the effect of temperature on pH, the experimental temperature was set equal to the average outside air temperature during the sampling periods, before the pH measurement of aerosol particle samples was conducted. The RH in the chamber for the pH testing paper method was maintained at 92% by using the water vapor equilibrium of the KNO₃ saturated solution so that the fine particles on the sample sheet could form water droplets. The pH (pH\text{meas}) of the droplet was measured by pH testing paper, yielding a range of 2.1–2.7, with an average of 2.4 ± 0.2.

Using the E-AIM IV model and various input data, the pH (pH\text{est}) of the water droplet was estimated for the NH₃ concentration at the assumed ambient concentration (NH₃-Amb), average laboratory concentration (30 ppb), and 0 ppb. The pH\text{est} was calculated using Eq. (1). An analysis of the results showed that the pH\text{est} values were 1.29–2.35, 2.63–3.17, and 3.70–4.14, respectively, for the assumed ammonia concentrations of 0 ppb, NH₃-Amb, and 30 ppb. With the increase in the input ammonia concentration, the pH\text{est} values increased. This is because ammonia is an important atmospheric alkaline inorganic gas.

Fig. 1 presents a comparison between pH\text{meas} and pH\text{est}. Symbols were assigned colors according to the [NH₄⁺\text{modeled}]/[NH₄⁺\text{measured}] ratio. [NH₄⁺\text{modeled}] is the NH₄⁺ concentration in the gas–liquid–solid equilibrium condition estimated by the E-AIM IV model, and [NH₄⁺\text{measured}] is the NH₄⁺ concentration measured by ion chromatography. Among the
estimated results for the three ammonia concentrations (NH$_3$-Amb, 30 ppb, and 0 ppb), the best
correlation ($R^2 = 0.90$) between pH$_{est}$ and pH$_{meas}$ was obtained with NH$_3$-Amb, while no correlation
($R^2 = 0.08$) was found for 0 ppb. From the $[\text{NH}_4^+]_{\text{modeled}}/[\text{NH}_4^+]_{\text{measured}}$ ratio indicated by the
colors in Fig. 1, $[\text{NH}_4^+]_{\text{modeled}}$ for NH$_3$-Amb was closest to $[\text{NH}_4^+]_{\text{measured}}$. Because NH$_3$-Amb
provided the best match for the NH$_4^+$ concentrations in aerosol samples, the gas/particle
partitioning of NH$_4^+$/NH$_3$-Amb in the E-AIM IV model calculation was closer to the NH$_4^+$/NH$_3$
partitioning in the high-RH airtight box. By contrast, when input NH$_3$ was 30 ppb (triangles), the
ratio of $[\text{NH}_4^+]_{\text{modeled}}/[\text{NH}_4^+]_{\text{measured}}$ was higher than 1.0, indicating that the model results of NH$_4^+$
concentrations were an overestimation. Furthermore, the zero NH$_3$ concentration showed a
scattered relationship between pH$_{est}$ (hexagons) and pH$_{meas}$, and the results indicate that the NH$_3$
in the airtight box equilibrated with the NH$_4^+$ of the aerosol sample in the box. Because the NH$_4^+$
of the aerosol sample equilibrated with the ambient NH$_3$ concentration in the atmosphere, the E-
AIM IV model with NH$_3$-Amb input showed strong agreement with the results of the pH testing
paper method.

Although NH$_3$-Amb was used as the input, pH$_{meas}$ was not the same as pH$_{est}$. The remaining
offset was 0.5 pH units on average. This can be attributed to the assumed input NH$_3$
concentration for the E-AIM IV model. To determine the effect of NH$_3$ on the pH testing paper
method, pH$_{est}$ was calculated again with the E-AIM IV model, assuming additional ammonia
levels of 0 ppb, 0.5 ppb, 1.0 ppb, and the NH$_3$ ambient concentration (NH$_3$-Amb). As shown in Fig. 2, the minimum difference between pH$_{\text{est}}$ and pH$_{\text{meas}}$ appeared at ammonia concentrations of 0.5 and 1.0 ppb (red circles and green triangles). This suggests that the ammonia concentration in the high-RH airtight box was lower than the NH$_3$-Amb concentration. It is presumably because the H$^+$ in the KNO$_3$ saturated solution in the airtight box consumed a part of NH$_3$ to form NH$_4^+$, thereby achieving the equilibrium of NH$_3$/NH$_4^+$. Apart from this, the uncertainty of the E-AIM IV model estimation could cause the difference between pH$_{\text{est}}$ and pH$_{\text{meas}}$, which arises from the omission of non-volatile cations of K$^+$, Ca$^{2+}$, and Mg$^{2+}$ and organic acids. Previous studies show that the effect of K$^+$, Ca$^{2+}$, and Mg$^{2+}$ on aerosol pH$_{\text{est}}$ might be 0.2–0.5 pH units (Guo et al., 2017; Karydis et al., 2021) and the effect of organic acid was 0.07±0.03 (Song et al., 2018).

Comparing the relationship between the direct measurement results (pH$_{\text{meas}}$) and the model estimation results (pH$_{\text{est}}$), it was found that (1) pH$_{\text{est}} = 1.05\text{pH}_{\text{meas}} + 0.38$, where pH$_{\text{est}}$ is estimated with the NH$_3$-Amb, and (2) pH$_{\text{est}}' = 0.90\text{pH}_{\text{meas}} + 0.28$, where pH$_{\text{est}}'$ is estimated with the input NH$_3$ of 1 ppb. The above discussion suggests that the pH testing paper method provides valuable data on aerosol acidity without requiring knowledge concerning the ambient ammonia concentration during aerosol sampling.

4 CONCLUSIONS
This study compared aerosol acidity determined using a new pH testing paper method for direct measurement (pH$_{\text{meas}}$) with that using the chemical thermodynamic E-AIM IV model (pH$_{\text{est}}$). The comparison indicated that the results of both methods correlate strongly with one another. A strong correlation between pH$_{\text{meas}}$ and pH$_{\text{est}}$ was obtained ($R^2 = 0.90$) when NH$_3$ was input for the E-AIM IV model as the ambient concentration of the atmosphere. The pH$_{\text{est}}$ values could be approximated by a simple linear regression equation: pH$_{\text{est}} = 1.05$pH$_{\text{meas}} + 0.38$. In summary, our pH testing paper method was shown to perform in a highly satisfactory manner. It enabled the determination of aerosol pH for the aerosol sample without requiring knowledge of aerosol complete composition (Song and Osada, 2021), including non-volatile cations and organic acids. Thus, being a simpler and more economical approach, the pH testing paper method would be beneficial for improving our understanding of aerosol acidity.

ACKNOWLEDGMENTS

This study was partly supported by the Environment Research and Technology Development Fund (JPMEERF20165004) of the Environmental Restoration and Conservation Agency of Japan. The authors would like to acknowledge Dr. Sayako Ueda for helpful discussions.

REFERENCES


Factors controlling sea salt modification and dry deposition of nonsea-salt components to the ocean. J. Geophys. Res. Atmos. 113, D14216. https://doi.org/10.1029/2007JD009410


Fine-particle pH for Beijing winter haze as inferred from different thermodynamic equilibrium models. Atmos. Chem. Phys. 18 (10), 7423–7438. https://doi.org/10.5194/acp-18-7423-2018


Figure 1. Comparison of results measured using the new pH testing paper method and those estimated using the E-AIM IV model with three assumed NH$_3$ concentrations: the average concentration in the laboratory of 30 ppb, the average concentration of ambient ammonia during each sampling period (Amb. Conc.), and no ammonia (0 ppb). Colors indicate the ratio of the estimated NH$_4^+$ to the measured NH$_4^+$ ([NH$_4^+$]$_{modeled}$/[NH$_4^+$]$_{measured}$).
Figure 2. Comparison of the measured results of the new pH testing paper method and the estimated results of the E-AIM IV model with four assumed NH$_3$ concentrations: 0 ppb, 0.5 ppb, 1.0 ppb, and the average concentration of ambient ammonia during each sampling period (Amb. Conc.).