Response to Anonymous Referee #1

We thank the reviewer for the constructive suggestions/comments. Below we provide a point-by-point response to individual comment (Reviewer comments and suggestions are in italics, responses and revisions are in plain font; revised parts in responses are marked with red color; page numbers refer to the modified AMTD version).

Comments and suggestions:

Overall Comments. This work proposed a new model to establish the correlation between the color of samples on pH-indicator papers and their measured pH. This model was based on RGB analysis of the images of samples. Good agreement between the model-predicted pH and reference pH for pH paper color charts as well as standard buffers were observed for all the tested types of pH papers. The minimum liquid sample mass/volume needed for the type V pH paper is identified as ~ 180 μg/0.1 μL. Aerosol pH measurement is important for understanding the properties of aerosols. This work provided an improved model to do this. It is of scientific interest, and conclusions are supported by the data.

Responses and Revisions:

Thanks for the positive comments and feedback from the reviewer.

Comments and suggestions:

Specific Comments. However, two major concerns are: 1. The real application of this method is not performed. In real application, there will be many solid particles as well, which also have color (for example, black carbon) and may interfere with the measurement. This needs to be clarified.

Responses and Revisions:

Good suggestion.

To further test the feasibility of our method for real aerosol samples, we generated aerosol particles under laboratory conditions and collected them on pH papers by using two custom-made impactors which were connected in series during the aerosol sampling. In addition, the potential interference of black carbon (BC) on aerosol pH prediction was also examined. Generally, we could reasonably predict the pH of lab-generated aerosols based on the colorimetric analysis method proposed in the manuscript. The results also confirm the technical feasibility of collecting aerosol particles on pH papers through impactors. Moreover, the potential interference of BC on aerosol pH prediction was proved to be non-significant when we adopted a BC concentration representative of ambient BC levels. Details can be found in the revised part as follows:

"2.2 pH buffers, aerosol sample solutions and lab-generated aerosols

…To test the feasibility of the colorimetric analysis method towards real aerosols, the prepared aerosol sample solutions (i.e., the inorganic and organic mixtures) were further used to generate aerosol particles through an aerosol generator under laboratory conditions. The lab-generated aerosols were collected onto the type V pH paper through two custom-made impactors, which had different cutoff sizes and were connected in series. Before collection, the nebulized aerosols were firstly mixed with humidified and HEPA-filtered air to reach a relative humidity (RH) of 90 ± 1.5% and a total flow rate of 28.6 L min^{-1}. To minimize water exchange between the generated aerosol flow and the humidified aerosol-free air flow, the RH of the air flow was maintained similar to that of the aerosol flow. With the sampling flow rate of 28.6 L min^{-1}, the upstream impactor had a cutoff diameter (d_{50}) of ~ 2.2 µm (identified by an UV-APS, model 3314, TSI Inc.) and the downstream impactor had a d_{50} of ~ 0.40 µm (identified by a SMPS, model 3082, TSI Inc.). These two impactors produced a total pressure drop of 57 mbar in the aerosol line (measured by a digital pressure meter, model GMH 3111, GHM Messtechnik GmbH, Germany). To validate our method, one wifi endoscope camera was installed on the top of the downstream impactor (with a collected particle size range of 0.40 - 2.2 µm) to capture the images of one pH paper (5 × 5 mm) fixed on the impactor bottom plate. In practice, we could install a camera for each impactor. In order to apply our RGB model (Sect. 2.4), a series of standard buffers were also adopted to generate aerosols with the same experimental configuration mentioned above.

Given that in real ambient case some light-absorbing particles, such as black carbon (BC), may interfere with the displayed color of pH papers and thereof cause biased pH prediction, commercial soot samples (fullerene soot, Lot Nr. L20W054, Alfa Aesar, Germany) were additionally mixed into the aerosol sample solutions for aerosol generation to check their potential impact on the predicted aerosol pH. To achieve that, pure BC suspension was firstly prepared with de-ionized water and then a 15-minute ultrasonic treatment was performed to enhance the dispersion of BC particles inside the suspension. The mass concentration of BC particles (measured under dry conditions with a RH = 14%) generated from this suspension was quantified by the SMPS as ~ 240 µg m^{-3} using the density of fullerene soot of 1.72 g cm^{-3} (Kondo et al., 2011). 5 mL of this suspension was additionally mixed into 10 mL of pre-prepared aerosol sample solution, and this mixture was finally used for aerosol generation. A total mass concentration of the generated aerosols (measured under dry conditions with a RH = 14%) was determined by the SMPS as ~ 800 µg m^{-3} using a density of 1.7 g cm^{-3}. This density was obtained by averaging the densities of different components weighted by their respective volume in the aerosol sample solution mixed with BC. Note that the BC mass fraction was ~ 10%, representing a typical BC contribution in ambient aerosols (Wang et al., 2016; Chen et al., 2020)."

"4.2 Black carbon (BC) interference

To apply the pH paper method to ambient aerosols, another potential interference on the captured pH paper color would come from some light-absorbing aerosols such as black carbon (BC) or brown carbon (BrC). Therefore, we further examined the potential interference of BC on the predicted pH of lab-generated aerosols. Details regarding the aerosol generation and collection can be found in Sect. 2.2.

Figure 5 shows pH_{predict} versus $pH_{\text{reference}}$ for the generated aerosol particles (i.e., $(NH_4)_2SO_4$-H_2SO_4-$C_3H_4O_4$) with and without the co-existence of BC. Note that $pH_{\text{reference}}$ refers to the pH of bulk solutions used for aerosol generation. Generally, within the examined pH range no significant difference can be found between the pH_{predict} of aerosols with BC and that of the aerosols without BC. The linear fitting (i.e., the orange and blue dashed lines in Fig. 5) for each type of dataset shows that the pH_{predict} for aerosols with BC is slightly lower than the samples without BC at the low pH side but an opposite trend can be found in the high pH side. This statistically small difference is further confirmed by running two-sample *t*-tests with Matlab, as shown in Table S4. Even this difference ($\leq$ 0.5 unit) is slight and acceptable, it indicates the existence of potential interferences of BC on the predicted aerosol pH, and related mechanisms may need to be explored in future studies. Note that for our lab experiments the adopted BC amount accounted for ~ 10 % of the total aerosol mass, which reflects the typical BC contributions in ambient aerosols (Wang et al., 2016; Chen et al., 2020).

Moreover, both types of aerosols display a lower pH_{predict} than $pH_{\text{reference}}$ in the low pH range as $pH_{\text{reference}} < 2.5$ (Fig. 5). Within the same lower pH range, significantly reduced aerosol pH (versus the pH of bulk solutions) predicted by both pH papers and Raman spectroscopy were also found in Craig et al. (2018) for lab-generated aerosols, as indicated by the neighbored orange and blue bars in Fig. 5. Their results (Craig et al., 2018) further revealed that the markedly-lower-pH_{predict} trend weakened at the higher pH range (i.e., $2.5 < pH_{\text{reference}} < 4.5$, see the orange bars in Fig. 5). The authors argued that the decreased aerosol pH found for smaller-size particles (with aerodynamic diameter < 2.5 μm) could be attributed to ammonia partitioning and water loss (Craig et al., 2018). Even with controlled RH for the aerosol dilution air flow in this study (Sect. 2.2), we cannot totally exclude the impact of water loss on the predicted aerosol pH, considering that under such a high RH (~ 90 %) a small difference between the RH of the generated aerosol flow and that of the dilution flow may cause non-negligible water exchange between aerosols and the carrying gas.

In addition, the results shown in Fig. 5 further demonstrate the technical feasibility of using our custom-made impactors for aerosol collection. More importantly, with this impactor setup, we could monitor the change of the pH paper color at any sampling time without interrupting the sampling. Thus, when used for future ambient aerosol collection we would expect a small difference between the surrounding environment of aerosols inside the impactors and ambient conditions."

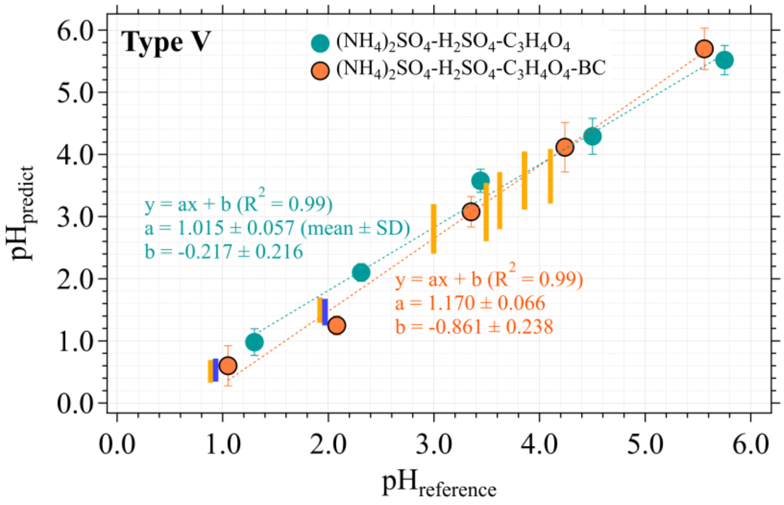

Figure 5: pH estimation using the type V pH paper for lab-generated aerosols with or without the co-existence of black carbon (BC). $pH_{predict}$ are calculated with the averaged coefficient vector [a, b, c] derived from five replicate calibration experiments with standard-buffer-generated aerosol samples. The error bars represent the standard deviation of three replicate experiments. The heights of the orange and blue bars indicate the reported pH ranges measured with pH papers and Raman spectroscopy respectively, for $(NH_4)_2SO_4$ - H_2SO_4 aerosols with particle sizes in the range of 0.4 - 2.5 µm in Craig et al. (2018). At $pH_{reference} < 2.5$, each orange or blue bar has the same $pH_{reference}$ as of the orange symbol close to it. Image processing of the collected aerosol samples follows a similar procedure as described in Sect. 2.3.

Comments and suggestions:

Specific Comments. 2. In this work, a mobile phone camera is used to capture the color, which limits the minimum liquid sample mass/volume needed for the type V pH paper. Even 0.1µL is still too much. The measured pH value will be a collective result of many aerosols. To get pH information of one individual aerosol is more interesting. Using an optical microscope may be more accurate and can further reduce the limits.

Responses and Revisions:

Thanks for the comments.

To the best of our knowledge, currently available techniques for measuring the pH of one individual aerosol include Raman microspectroscopy (Rindelaub et al., 2016; Wei et al., 2018; Lei et al., 2020) and aerosol optical tweezers (Boyer et al., 2020), which are all deployed in laboratories. Generally speaking, these techniques are mainly used for probing the pH of aerosols/droplets with larger sizes than we have in this study (0.4 – 2.2 µm in diameter). For example, the investigated aerosols had a diameter size range of 6 – 10 µm for the aerosol optical tweezer technique used by Boyer et al. (2020). And the Raman microspectroscopy was used to measure the pH of droplets with a diameter range of 10 – 30 μm and 13.3 – 25.7 μm in the work of Rindelaub et al. (2016) and Wei et al. (2018), respectively. Even though in the most recent study Lei et al. (2020) examined the pH of submicron aerosols, their experiments were performed through using Raman spectroscopy coupled to atomic force microscopy under well-controlled laboratory conditions. For our pH paper method and the way of aerosol sampling, collecting a large amount of aerosols on the pH paper seems to be the only available and feasible approach for pH estimation of submicron particles. More importantly, our method can be easily used for ambient aerosol pH prediction and therefore our way of exploring the aerosol pH would be more representative of ambient cases.

References

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