Response to Anonymous Referee #3

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 manuscript describes an improvement upon a recently published method (Craig et al. 2018) using image processing of colorimetric indicator paper to analyze the pH of atmosphere particles. The work is thorough and worthy of publication. There a few points I would suggest addressing and one major weakness to the manuscript. Overall, this method is an important step forward for determination of aerosol pH.

Responses and Revisions:

Thanks for the positive comments from the reviewer.

Comments and suggestions:

Specific Comments. The largest concern with the manuscript is that it all of the analysis is with pipetted solutions and not with actual lab-generated or ambient aerosol as far as I can tell. Both Craig et al. 2018 and Coddens et al. 2019 from the Grassian laboratory looked at suspended aqueous aerosol that were then impacted onto colorimetric indicator paper. This led to some unique results (e.g. size dependence of pH), which make it not surprising that the 0.1 microlitre samples herein rapidly changed after pipetting on the paper. Even running just a few aerosolized samples to verify the selection of the specified pH paper would greatly strengthen the manuscript.

Responses and Revisions:

Thanks for the comments.

We further performed experiments to confirm that the lab-generated aerosols could be collected onto pH papers by using two custom-made impactors. Moreover, our results also demonstrate that, with our proposed RGB model the pH paper method can be used to predict aerosol pH with a high accuracy (with a predicted pH uncertainty ≤ 0.5 unit). The application of the impactor setup as well as the pH paper method in real ambient cases will be explored in our future work. Details can be found in Section 2.2 and 4.2, in the revised manuscript. As shown below.

“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 $pH_{\mathrm{reference}}$ 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 $pH_{\mathrm{reference}}$ 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 $pH_{\mathrm{reference}}$ in the low pH range as $pH_{\mathrm{reference}} < 2.5$ (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., $2.5 < pH_{\mathrm{reference}} < 4.5$, 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."

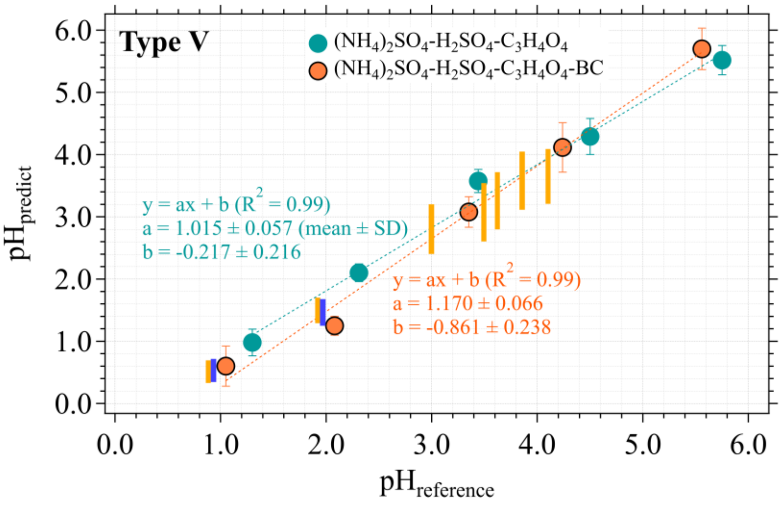


Figure 5: pH estimation using the type V pH paper for lab-generated aerosols with or without the co-existence of black carbon (BC). $pH_{predict}$ are calculated with the averaged coefficient vector [a, b, c] derived from five replicate calibration experiments with standard-buffer-generated aerosol samples. 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. A minor is the justification of using 2 microlitres samples overall based on a high volume sampler pulling hundreds of lpm for a couple of hours. With that kind of flow rate and timing, a sample is unlikely to retain this amount of water due to drying and, at a minimum would be vastly altered at the end of sampling versus what was initially collected. Losses of semi-volatile inorganic (e.g. ammonium/ammonia) and organic (e.g. carboxylic acids like acetic acid) species would be expected in that sampling setup.

Responses and Revisions:

Thanks for the comments.

As stated above, we further built two impactors. One piece of pH paper (5 × 5 mm) could be fixed on the impactor bottom plate and one camera was installed on the top of the impactor. During a sampling process, aerosols with certain sizes could impact on the pH paper and the induced color change could be captured by the camera. With this impactor setup, we were able to check the pH paper color at any sampling time without interrupting the sampling. Moreover, we would also expect a small difference between the surrounding environment of aerosols inside the impactor and that outside the impactor (i.e., ambient cases).

Therefore, for future ambient applications the estimated aerosol pH should be representative of the aerosol acidity under ambient cases. Based on our preliminary tests by using lab-generated aerosols, the impactor setup has been demonstrated to work well for aerosol collection and pH prediction, and therefore has a great potential for future application under ambient conditions. During our lab tests, an optimal aerosol sampling time was identified as 30 min and the generated aerosol concentrations were ~ 800 μg m^{-3} (measured under RH = 14%), the collected aerosols could cause a color change on the whole pH paper. And the colors on the whole area were even to the eye, indicating that the liquid aerosols had spread evenly across the pH paper. Thus, the whole pH paper area was used for subsequent image processing to get their RGB values. According to the measurement results under lab conditions, we further estimated a sampling time range of ~ 1 – 4 hours for ambient aerosols with a $PM_{2.5}$ concentration of ~ 100 μg m^{-3}, when using our impactors (with an estimated aerosol collection efficiency of 50% – 70%, based on APS and SMPS measurements) and with a sampling flow range of ~ 30 – 120 L min^{-1}.

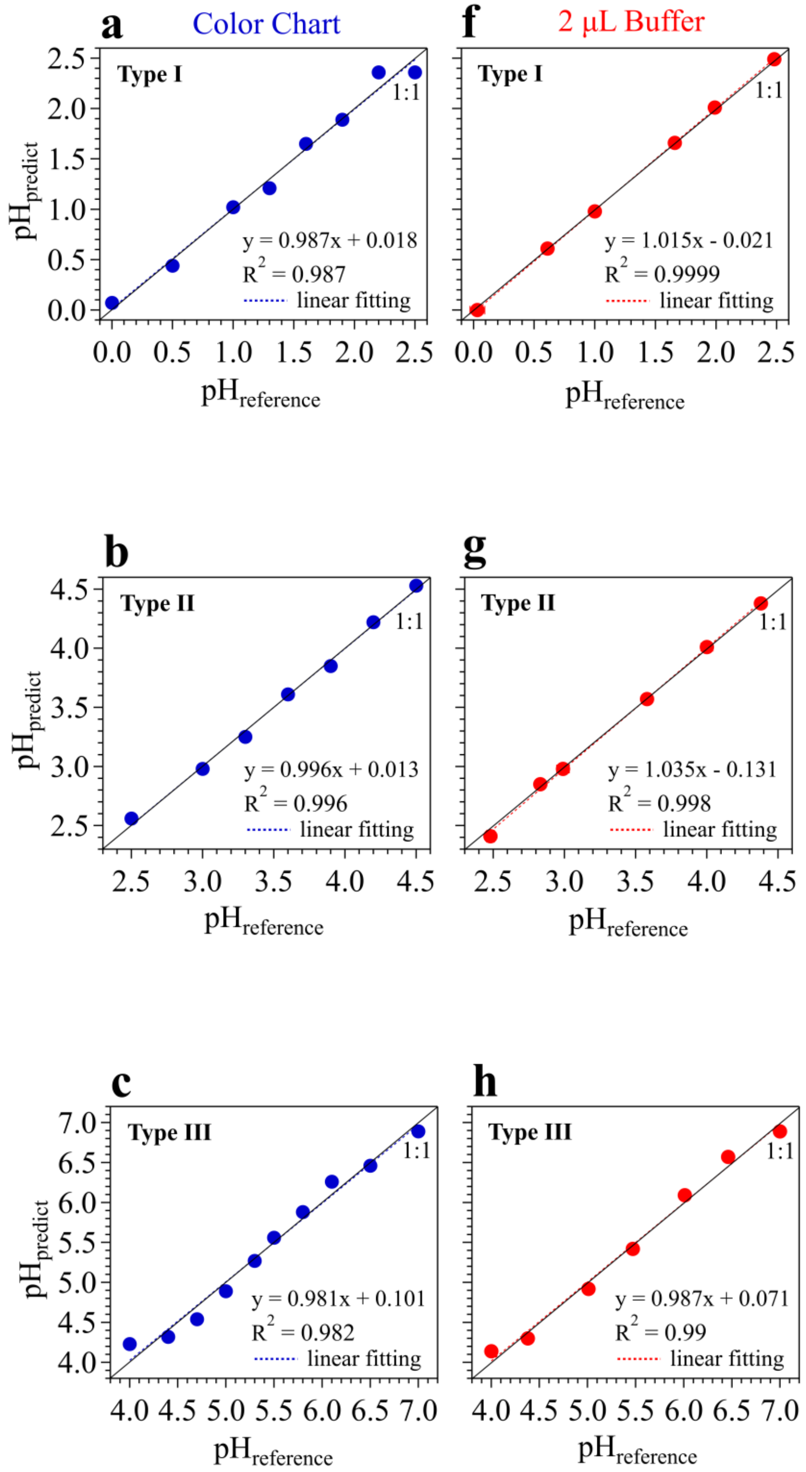
Comments and suggestions:

Specific Comments. For Figure 2 it would be helpful to include both x – and y – error bars on the points, with x representing the uncertainty in the predicted pH and y the uncertainty in the pH probe/buffer measurements. This would help to know if the uncertainties include the regression line for the points that do not fall exactly on it.

Responses and Revisions:

Thanks for the comments.

Both x- and y-error bars have been included in Figure 2. As shown below. Note that, since the uncertainty in the pH probe/buffer measurements were very small (with a standard deviation of ≤ 0.06), almost all the x-error bars are covered by the symbols.


a
Color Chart
Type I
y = 0.987x + 0.018
R^2 = 0.987
linear fitting
1:1
$pH_{predict}$
$pH_{reference}$
0.0 0.5 1.0 1.5 2.0 2.5
f
2 μL Buffer
Type I
y = 1.015x - 0.021
R^2 = 0.9999
linear fitting
1:1
b
Type II
y = 0.996x + 0.013
R^2 = 0.996
linear fitting
2.5 3.0 3.5 4.0 4.5
g
Type II
y = 1.035x - 0.131
R^2 = 0.998
linear fitting
c
Type III
y = 0.981x + 0.101
R^2 = 0.982
linear fitting
4.0 4.5 5.0 5.5 6.0 6.5 7.0
h
Type III
y = 0.987x + 0.071
R^2 = 0.99
linear fitting

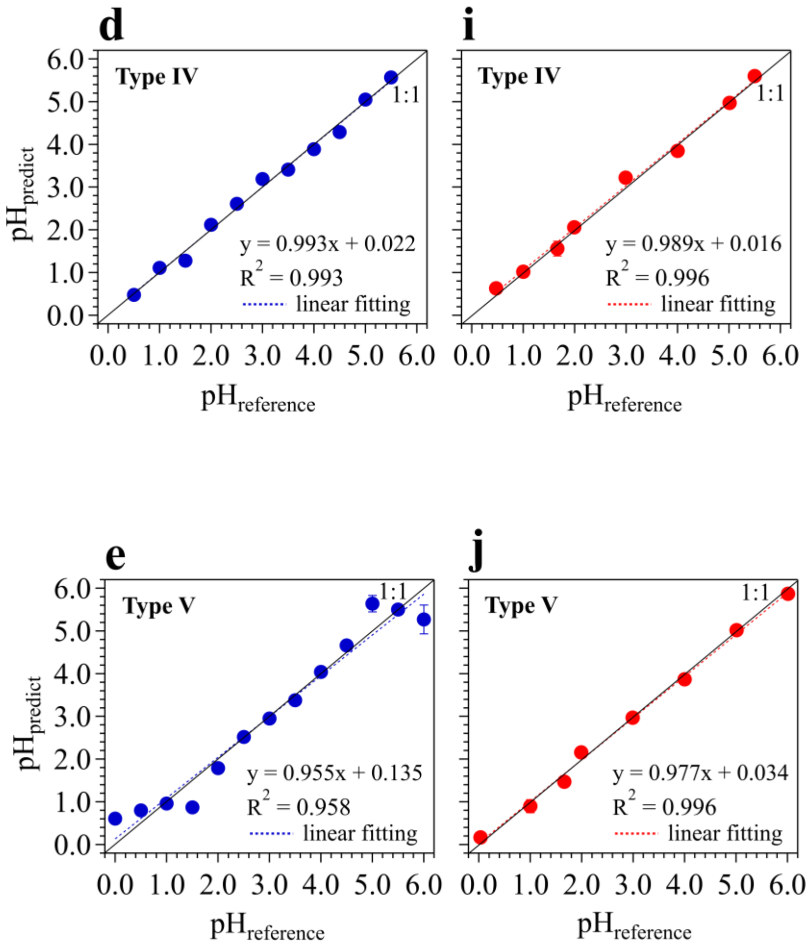


Figure 2: Predicted pH ($pH_{predict}$) using our RGB model versus the reference pH shown on the color chart and the pH-meter-probed-pH of the buffer samples (all denoted as $pH_{reference}$) respectively, for the five different pH papers: (a) and (f) Type I: 0 – 2.5, (b) and (g) Type II: 2.5 – 4.5, (c) and (h) Type III: 4.0 – 7.0, (d) and (i) Type IV: 0.5 – 5.5 and (e) and (j) Type V: 0 – 6.0. Blue symbols denote the established relationship based on color charts only. Red symbols represent the results for 2 µL of buffer droplets on pH papers. Both vertical and horizontal error bars represent the standard deviation of five to six replicate experiments. Note that the error bars in most of the panels are smaller than the symbols.

Comments and suggestions:

Specific Comments. This is a small point, but the term "outlier" is probably not the best for the point on Figure S4. If it is reproducible to the extent described it is by definition not an outlier. I think "anomalous" might be a better term, as this point would not be thrown out by the traditional Grubbs test of an outlier or other outlier tests.

Responses and Revisions:

Thanks for the comments.

We have changed the term “outlier” in Figure S4 into “anomalous”. And the related description in the manuscript has also been adjusted accordingly. As shown below.

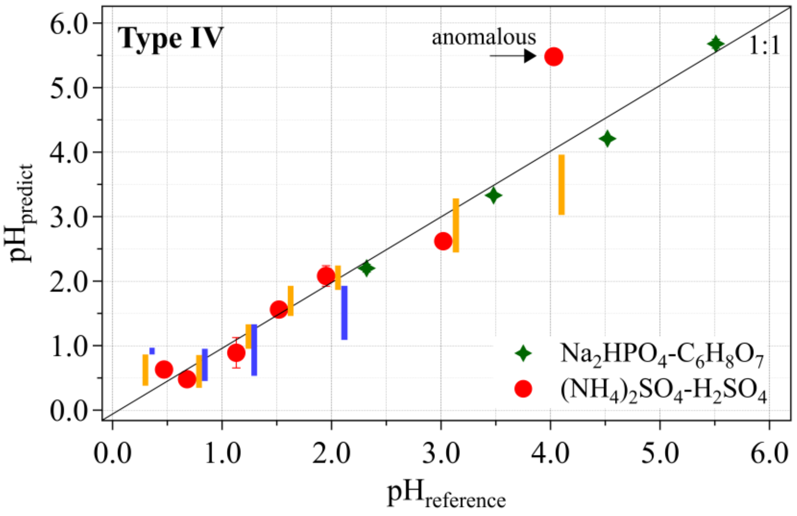


Figure S4. Estimation of samples pH using the type IV pH paper. The adopted samples include a series of 2 µL lab-prepared aerosol surrogates ($(NH_4)_2SO_4$-H_2SO_4, red dot) and self-prepared buffers (Na_2HPO_4-$C_6H_8O_7$, green star). $pH_{predict}$ are calculated with the averaged coefficient vector [*a*, *b*, *c*] derived from the standard buffers from three to six replicate experiments under constant photographing conditions. The error bars represent the standard deviation of three to six 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 larger than 2.5 µm in Craig et al. (2018). Note that, each orange or blue bar has the same $pH_{reference}$ as of the red symbol close to it.

“$pH_{predict}$ versus $pH_{reference}$ for the 2-µL-droplet samples on the type IV pH paper are shown in Fig. S4. Generally, the $pH_{predict}$ by the type IV pH paper are comparable with the $pH_{reference}$ at a lower pH range (i.e. $pH_{reference}$ = 0.46, 1.52 and 3.0). However, an anomalous point (highlighted by the arrow in Fig. S4) with 1.5 unit of overestimation in $pH_{predict}$ can be found at $pH_{reference}$ around 4. …**”**

Comments and suggestions:

Specific Comments. The last point would be to that though the mention “anti-interference” it would be useful for the authors to see if their RGB method would work with brown carbon or black carbon samples (or some other chromophoric aerosol) that also contain secondary species and water.

Responses and Revisions:

Thanks for the comments.

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. 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 Sect. 4.2 in the revised manuscript:

"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 $pH_{\mathrm{reference}}$ 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 $pH_{\mathrm{reference}}$ 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 (≤ 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 $pH_{\mathrm{reference}}$ in the low pH range as $pH_{\mathrm{reference}} < 2.5$ (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., $2.5 < pH_{\mathrm{reference}} < 4.5$, 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."

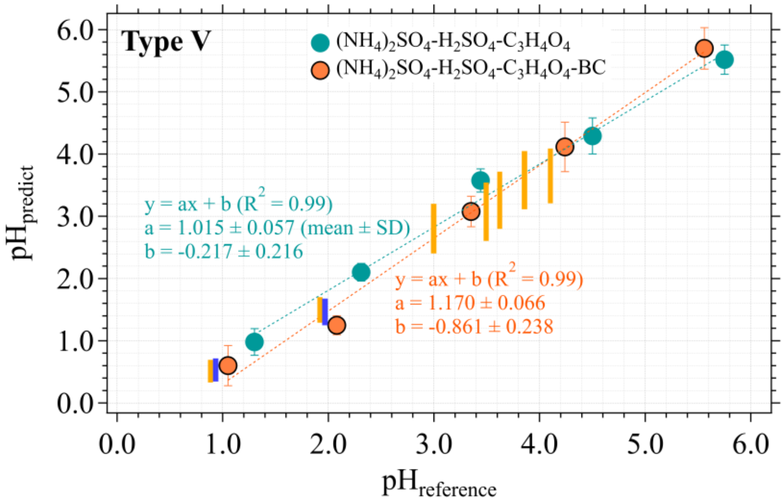


Figure 5: pH estimation using the type V pH paper for lab-generated aerosols with or without the co-existence of black carbon (BC). pH$_{predict}$ are calculated with the averaged coefficient vector [a, b, c] derived from five replicate calibration experiments with standard-buffer-generated aerosol samples. 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.

References

Chen, L., Zhang, F., Yan, P., Wang, X., Sun, L., Li, Y., Zhang, X., Sun, Y., and Li, Z.: The large proportion of black carbon (BC)-containing aerosols in the urban atmosphere, Environmental Pollution, 263, 114507, https://doi.org/10.1016/j.envpol.2020.114507, 2020.

Craig, R. L., Peterson, P. K., Nandy, L., Lei, Z., Hossain, M. A., Camarena, S., Dodson, R. A., Cook, R. D., Dutcher, C. S., and Ault, A. P.: Direct Determination of Aerosol pH: Size-Resolved Measurements of Submicrometer and Supermicrometer Aqueous Particles, Analytical Chemistry, 90, 11232-11239, 10.1021/acs.analchem.8b00586, 2018.

Kondo, Y., Sahu, L., Moteki, N., Khan, F., Takegawa, N., Liu, X., Koike, M., and Miyakawa, T.: Consistency and Traceability of Black Carbon Measurements Made by Laser-Induced Incandescence, Thermal-Optical Transmittance, and Filter-Based Photo-Absorption Techniques, Aerosol Science and Technology, 45, 295-312, 10.1080/02786826.2010.533215, 2011.

Wang, Q., Huang, R.-J., Zhao, Z., Cao, J., Ni, H., Tie, X., Zhao, S., Su, X., Han, Y., Shen, Z., Wang, Y., Zhang, N., Zhou, Y., and Corbin, J. C.: Physicochemical characteristics of black carbon aerosol and its radiative impact in a polluted urban area of China, Journal of Geophysical Research: Atmospheres, 121, 12,505-512,519, 10.1002/2016JD024748, 2016.