Multifactor colorimetric analysis on pH-indicator papers: an optimized approach for direct determination of ambient aerosol pH

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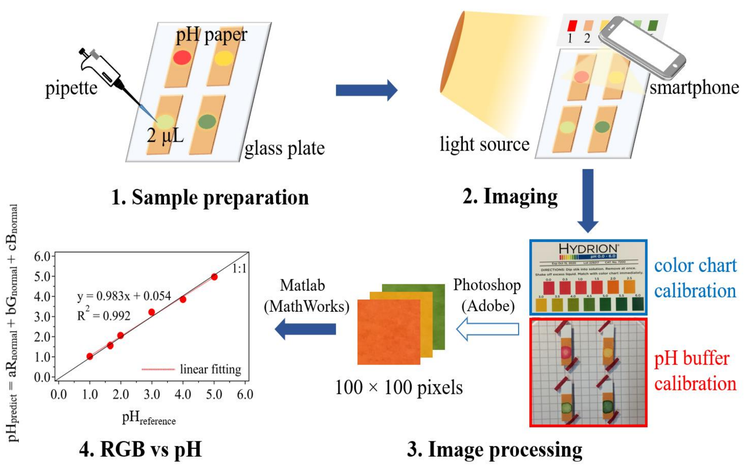
Abstract

Direct measurement of the acidity (pH) of ambient aerosol particles/droplets has long been a challenge for atmospheric scientists. A novel and facile method was introduced recently by Craig et al. (2018), where the pH of size-resolved aerosol droplets was directly measured by two types of pH-indicator papers (pH ranges: 0 – 2.5 and 2.5 – 4.5) combined with RGB-based colorimetric analyses using a model of G-B (G minus B) versus pH^2. Given the wide pH range of ambient aerosols, we optimize the RGB-based colorimetric analysis on pH papers with a wider detection range (pH ~ 0 to 6). Here, we propose a new model to establish the linear relationship between RGB values and pH: $pH_{predict} = a \times R_{normal} + b \times G_{normal} + c \times B_{normal}$. This model shows a wider applicability and higher accuracy than those in previous studies, and is thus recommended in future RGB-based colorimetric analyses on pH papers. Moreover, we identify one type of pH paper (Hydrion® Brilliant pH dip stiks, Lot Nr. 3110, Sigma-Aldrich) that is more applicable for ambient aerosols in terms of its wide pH detection range (0 to 6) and strong anti-interference capacity. The determined minimum sample mass (~ 180 µg) highlights its potential to predict aerosol pH with a high time resolution (e.g., ≤ 1 hour). We further show that the routinely adopted way of using pH color charts to predict aerosol pH may be biased by the mismatch between the standard colors on the color charts and the real colors of investigated samples. Thus, instead of using the producer-provided color chart, we suggest an in-situ calibration of pH papers with standard pH buffers.

Methods

1. Schematic of using the RGB-based colorimetric method for pH estimation.



2. RGB model

$$R_{\mathrm{normal}} = R/(R+G+B)$$

$$G_{\mathrm{normal}} = G/(R+G+B)$$

$$B_{\mathrm{normal}} = B/(R+G+B)$$

$$\mathrm{pH_{predict}} = aR_{normal} + bG_{normal} + cB_{normal}$$

Note: According to trichromatic theory, RGB are the three primary colors and their combination in varying proportions can generate any other specific color.

Results

1. Validation of the new RGB model

The validity of our new RGB model was checked through five types of pH papers. The colors on the color chart and of the standard buffer sample for each type of pH paper were analyzed through our RGB model and then the calculated $pH_{predict}$ were compared with the reference pH shown on the color chart and of the buffers.

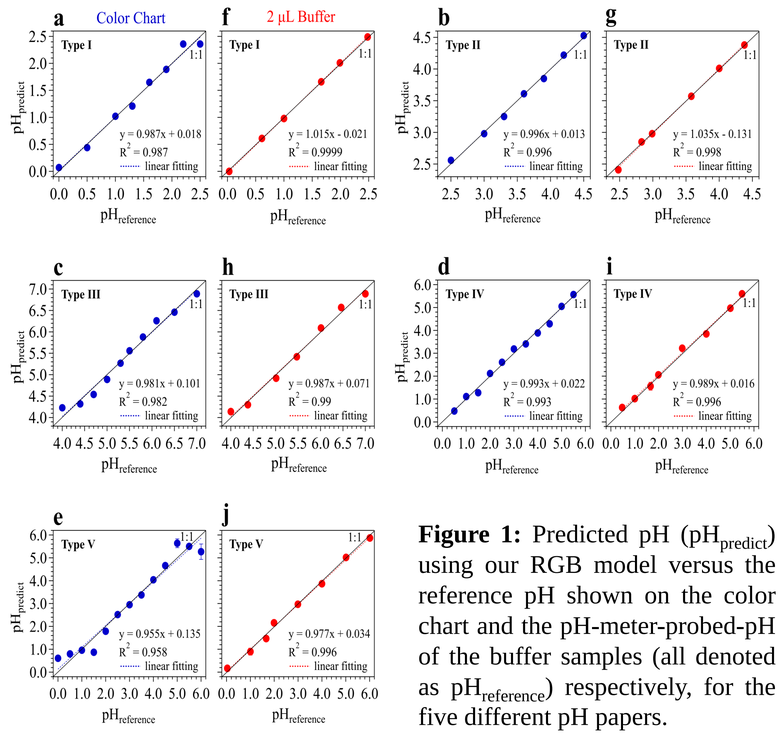


Figure 1: Predicted pH ($pH_{predict}$) using our RGB model versus the reference pH shown on the color chart and the pH-meter-probed-pH of the buffer samples (all denoted as $pH_{reference}$) respectively, for the five different pH papers.

We further compared our model with the other two models proposed in previous studies, in terms of evaluating their correlation coefficient, R^2.

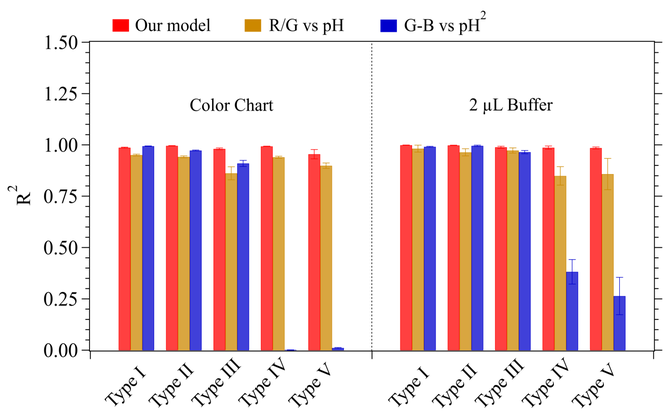


Figure 2. Comparison of the established linear correlation using different RGB models for the five types of pH papers adopted in this study.

2. Calibration with standard buffer solutions

A good linearity may not always be obtained from the color chart of some types of pH papers in some pH ranges. For example, in the 'color chart' column of Fig. 1. Actually, even small deviations found in the color-chart-derived calibration curves may lead to significant or non-negligible errors in measuring aerosol pH. We conducted a case study using the type IV pH paper combined with our RGB model to predict the pH of buffer samples by using the color-chart-derived coefficient vector [*a*, *b*, *c*], i.e., the color-chart-calibration method (Fig. 1d).

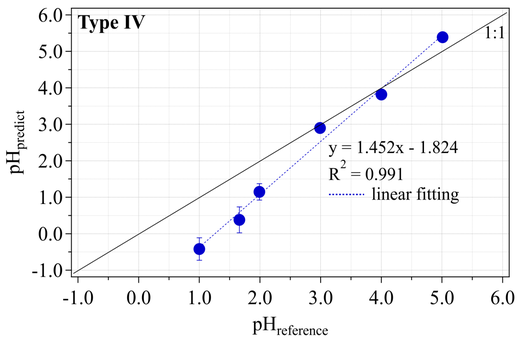


Figure 3. $pH_{predict}$ versus $pH_{reference}$ for 2 µL buffer samples on the type IV pH paper. The $pH_{predict}$ are calculated using the coefficient vector [*a*, *b*, *c*] derived from regression analysis on the color chart.

3. pH estimation for aerosol surrogates and chemical interference check

In order to test the feasibility of pH papers for pH prediction of aerosols, the pH papers with larger pH detection ranges were used to estimate the pH of lab-prepared aerosol surrogates ($(NH_4)_2SO_4$ - H_2SO_4). The results showed that only the Type V pH paper is suitable for future ambient aerosol pH prediction, due to its higher accuracy and strong anti-interference capacity. The identified minimum sample volume is 0.1 µL (~ 180 µg).

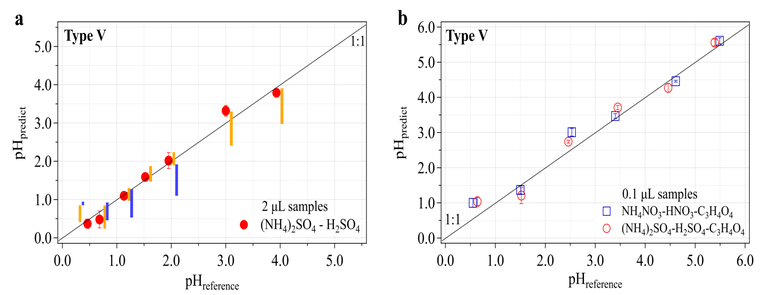


Figure 4: pH estimation using the type V pH paper for samples with different volumes: (a) 2 µL and (b) 0.1 µL. In (a), the heights of the orange and blue bars indicate the reported pH ranges measured with pH papers and Raman spectroscopy respectively, for $(NH_4)_2SO_4$ - H_2SO_4 aerosols with particle sizes larger than 2.5 µm in Craig et al. (2018). Each orange or blue bar has the same $pH_{reference}$ as of the red symbol close to it.

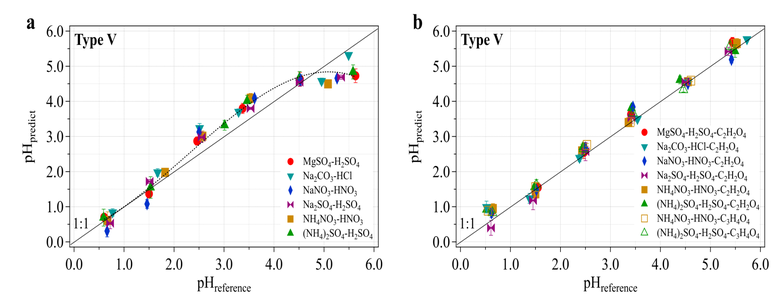


Figure 5: pH estimation using the type V pH paper for salt systems with only inorganic acids (a) and both inorganic and organic acids (b). $pH_{predict}$ are calculated with the averaged coefficient vector [*a*, *b*, *c*] derived from three replicate calibration experiments with standard buffers and under constant photographing conditions. The dotted line in (a) is used to guide the eye.

References

Craig, R. L., et al.: 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.

Li, G., et al.: Multifactor colorimetric analysis on pH-indicator papers: an optimized approach for direct determination of ambient aerosol pH, Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2019-394, in review, 2019.