

Interactive comment on “Multifactor colorimetric analysis on pH-indicator papers: an optimized approach for direct determination of ambient aerosol pH” by Guo Li et al.

Anonymous Referee #2

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The authors build on the work of Craig et al using particles collected on pH indicator paper as a way to quantify actual ambient particle pH. The focus of this work is on the analysis of the color of the pH paper, not if the overall concept is of collecting particles on pH paper to determine pH is feasible. For example, there is no assessment in this work of the Craig et al method. The authors point out the challenging issues with determining particle pH; the small amounts of water that one has to work with, and that the liquid concentrations of the all the ions in the particle must be precisely maintained throughout the whole period spanning particle collection to pH measurement. The latter means no gradients in water or ions on the pH paper, no changes in T, RH, concentrations of semivolatile gases (ie, HNO₃, HCl, organic acids) from ambient to

the environment of the pH indicator strip during sampling or during pH analysis based on color. Achieving these criteria seems extremely difficult and at this point has never been proven to be accurate for fine particles, as far as I can tell by looking at the Craig et al results for PM_{2.5}. Furthermore, the authors use a highly simplified way of applying the surrogate for particle water to the pH paper and justify the amount of water in the tests with unrealistic (possibly meaningless) calculations. So the question is, is this research worthy of publication if the fundamental method on which it is based is possibly flawed (or impossible to achieve in practice), even if the colorimetric analysis, the main focus of this paper is reasonable? My suggestion is that the paper not be published until the authors 1) provide a detailed assessment of the results of Craig et al. discussing if it is viable and if so under what conditions (example, mainly just $D_p > 2.5$ μm , collected cloud water, etc), and 2) show that they can actually use this approach to accurately measure pH of real ambient particles, which is the objective of this research, otherwise there is an implied indorsement of this approach. 3) Assess the overall pH uncertainty of an actual process/instrument that could utilize their color analysis for different types of aerosols (ie, fine, coarse, cloud/fog water) under different ambient conditions (concentrations, RH). Alternatively, the authors could change the focus of the paper to simply one on using a smart phone to assess the color of pH paper, which may be of value when the pH indicator paper is used in the method it was intended for, measuring pH of bulk solutions.

More details are provided below:

In the Title or Abstract please specify what size of particles the method will be used to determine particle pH.

This paper does not address the fundamental question if the overall concept of Craig et al is practical or valid, nor does it critically assess the Craig results. The authors simply accept the method. The Craig et al data show that there is significant difficulty with the method for particles smaller than 2.5 μm . The authors should first assess if the approach is feasible (see discussion on this below) before claiming to have developed

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a method for measuring particle pH.

pH paper is used to measure pH of a large bulk solution, particles collected on a spot are not equivalent to this process. Please discuss the issues for accurate pH measurement with indicator paper due to these differences. This could include, evaporation of water from the paper, changes in ion activities when added to the paper and adsorbed by the paper (ie, wicked away from the original spot of application). Some of these points are discussed later in the paper, it would be good if this was discussed first.

The approach to test the method is to start with a bulk solution of known pH and then pipet a small amount ($2 \mu\text{L}$) on to pH paper in a lab with no environmental controls (T, RH =?) to simulate particle collection, then to measure pH by color analyses. The authors state this amount of liquid could be obtained for the following situation (quoted from the paper lines 139-143):

This adopted small volume ($2 \mu\text{L}$) was based on calculation of the available amounts of liquid aerosols for aerosol sampling under a typically polluted conditions (with $\text{PM}_{2.5}$ mass concentration around $100 \mu\text{g m}^{-3}$) with high relative humidity ($\geq 80\%$), and assuming a sampling flow rate of several hundred liter per minute (e.g., can be achieved by a Tisch Environmental $\text{PM}_{2.5}$ high volume air sampler, see <https://tisch-env.com/high-volume-air-sampler/pm2.5>) and a sampling time of a few (2 - 4) hours. Please comment on how typical these conditions are.

The discussion from the paper copied above seems to only consider how much particle liquid water is available in theory, not how it will be actually collected and how this will compare to the pipetting of $2\mu\text{L}$. Since the measurement is based on liquid water on the filter, one needs to know the size (surface area) of the filter (ie, how much area the collected water will be spread over). Is the liquid water spread evenly across (and possibly within the filter)? How would one maintain identical conditions on the filter as in ambient air during the sample and analysis time, which is critical to an accurate pH measurement? Can pH paper be used as a particle filter, if not how does one filter the

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particles and then use the pH paper, ie do the authors envision collecting the water on the filter and then use the pH paper to measure pH of that water, is this possible?

How big of a spot (ie, diameter) on the pH paper is the liquid when 2 μL are pipetted onto the paper? Does spot size matter? Is it practically possible to collect particles in that spot size so as to mimic the experiments performed here? For example, given the conditions above and the sample flow rate is there a device that can achieve this. The high volume sampler suggested collects particle over a large area (ie, a filter), so as noted above the question is, will this work as a method to collect the particles? Presumably to collect a spot of particle water, one would have to do this with an impactor. To not change the concentration of the ions that exists in the particle, the wicking away of the water on the collection paper would have to be limited, or at least the ions wicked away at the same rate as water. With an impactor the drop spreading would be enhanced by the air jet moving along the surface of the collection paper. Furthermore, how will pressure drops across the impactor or filter affect the determined pH (ie, loss of liquid water, etc). One should also consider other possible sampling issues that could alter pH from ambient?

It is noted in Section 4.2 that the pH could be determined by this method for much smaller volumes, requiring a lower sampling time and/or lower sampler flow rate. However, as notes, evaporation then becomes important and the measurements must be made rapidly, ie < 3 sec (for the conditions in their lab, ie what was the ambient RH in the lab). Again, is it really possible (practical) to actually use such small liquid samples as described in this approach?

Given all the possible issues with accurate pH determination of fine PM with this method, combined with the uncertainty in interpreting the pH indicator color (line 235-236), and that it is noted by the authors that uncertainty in pH can have huge impacts on pH dependent multiphase chemical processes (lines 86-87), is this method really a reasonable way to determine particle pH? The authors need to supply an actual estimate in the uncertainty in the pH determined by this method so that one can assess

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the impact it will have when these pH values are used.

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