Reviewer 1:

The manuscript examines water-soluble light-absorbing compounds in biomass burning fire plumes using on-line particle into liquid sampler (PILS) and offline size exclusion chromatography (SEC), both coupled to spectrophotometric detectors. The main messages of the manuscript are: (1) absorption coefficient of the BBOA particles sometimes increases and sometimes decreases with the plume age; (2) PILS and SEC data do not agree with each other due to effects of solvents on the absorption spectra of the analyzed chromophores. While the manuscript is potentially publishable, I have two major comments about the manuscript that will likely require a major revision or an even more drastic action.

We appreciate the detailed comments of the Reviewer. We have addressed each in detail below, where our responses are in highlighted blue and changes to the manuscript are indicated in **bold blue**. In summary, we agree with the comments of the Reviewer and have performed several new experiments to explore the effects of solvent composition on brown carbon absorption. This is reflected in new text and figures in both the manuscript and SI, described below.

1). The section describing the solvent effects will need to be significantly revised. The authors have misinterpreted the change in the spectrum of nitrocatechol as the effect of solvent polarity. Instead, this is quite simply an acid-base equilibrium between nitrocatechol (C6H5NO4, absorption peak at around 350 nm) and its anion (C6H4NO4-, absorption peak at around 450 nm). Common nitrophenols have pKa of the order of 7, leading to large differences in the absorption spectra recorded during LC separation using an acidified and non-acidified eluent. For example, see Figure 5 of Cornard et al. (2005), https://doi.org/10.1016/j.chemphys.2004.09.020, for the comparison of absorption spectra of the nitrocatechol and its anion. Also, see Figure S2 in Lin et al. (2017), https://doi.org/10.1021/acs.est.7b02276, which shows how spectra of eluted nitrocatechol and other nitrophenols change depending on the eluent pH.

The reviewer is correct regarding the pH effect on nitrocatechol. Nitrocatechol, having a pKa value of 6.84, is deprotonated in these conditions, resulting in a red shift. We have removed the text in section 3.4 that incorrectly explains the reason why we observed a red shift for 4-nitrocatetchol. We have moved and edited Figure 4b and moved it to the SI as part of Figure S6, where we show the wavelength dependent absorption of several compounds known to contribute to BrC absorption under various mobile phase conditions. The details of Figure 4, S6, and rewriting of section 3.4 are explained below.

From what I can gather from Figure 4 in this manuscript, the ammonium acetate buffer that the authors used for their SEC ACN+buffer experiments was sufficiently basic to significantly deprotonate nitrocatechol. In contrast, in their DIW only experiment, nitrocatechol was only partly deprotonated (there is a shoulder there corresponding to the 450 nm band of the anion but the majority of the nitrocatechol is not deprotonated). Was the buffer prepared to provide buffering at pH 5 or pH 9 in this work? I presume it is the latter. For more on this buffer and its dual pH buffering nature, I would recommend reading Konermann (2017), https://doi.org/10.1007/s13361-017-1739-3.

Ammonium acetate was dissolved in water and then combined with acetonitrile, which has a pH of 7.2. Ammonium acetate dissolved in water has an inherent buffering capacity between pH 3.75 to 5.75 and pH 8.25 to 10.25 (Konermann, 2017); however, with the addition of acetonitrile, the buffering ranges shifts to approximately 5.5±1 and pH 9 ±1 (Subirats et al., 2009). The pKa values of previously identified BrC compounds are within the inherent buffering range so we did not pH control the mobile phase.

The ammonium acetate solution was not pH adjusted and was inaccurately called a buffer in the manuscript. We should have referred to it as a mobile phase modifier. We have corrected this statement in sections 2.3, 3.4, and throughout the manuscript and SI:

Line 158 to 161: The isocratic method was run using a 1:1 mixture of acetonitrile and a buffer solution consisting of 18.2 MΩ·cm deionized water with 25 mM ammonium acetate at a flow rate of 1 mL min^{-1} and a sample injection volume of 100 µL.

This sentence was changed to:

Line 158 to 161: "The isocratic method was run using a 1:1 mixture of acetonitrile and 25 mM ammonium acetate at a flow rate of 1 mL min^{-1} and a sample injection volume of 100 µL."

In the SI:

Figure S4: Single-wavelength chromatogram at 250 nm of an aqueous sample run with equal parts buffer solution and methanol (black) and equal parts buffer solution and acetonitrile (orange).

This caption was changed to:

"Figure S4: Single-wavelength chromatogram at 250 nm of an aqueous sample run with equal parts 25 mM ammonium acetate solution and methanol (black) and equal parts 25 mM ammonium acetate solution and acetonitrile (orange)."

The following text was added to the SI:

"The default mobile phase used was equal parts acetonitrile and DIW with 25 mM ammonium acetate. When ammonium acetate is dissolved in water, sub-stoichiometric acidification converts acetate to acetic acid producing conditions that can stabilize pH at 4.75 (Konermann, 2017). The alkalinization of ammonium acetate solution generates NH$_3$ via the depronotation of NH$_4^+$, creating buffering capacity around the pK$_a$ of ammonium (9.25). Therefore, ammonium acetate dissolved in water has an inherent buffering capacity in acidic (pH at 4.75±1) and basic ranges (9.25±1) (Konermann, 2017). The addition of acetonitrile to ammonium acetate dissolved in water reduces the buffer capacity and shifts the buffering ranges of ammonium acetate dissolved in water to approximately pH 5.5±1 and pH 9 ±1 (Subirats et al., 2009). The purpose of the addition of the ammonium acetate to the mobile phase was to minimize electrostatic interactions between the compounds and the stationary phase of the column. This has proven effective in previous SEC-UV analyses of biomass burning derived samples investigating MW properties of fresh and aged BrC (Di Lorenzo et al., 2017; Wong et al., 2017; Lyu et al., 2021). If the electrostatic interactions are negligible, SEC separation is based on hydrodynamic volume, which is a function of MW and the density of the compounds (Pelekani et al., 1999). In Figure S6, there is a red shift when mobile phase conditions have a pH greater than the pK$_a$ of the single compound. However, Figure S7 shows that the wavelength-dependent absorption of SRFA looks

similar under all mobile phase conditions. This indicates that we do not anticipate pH impacting wavelength-dependent absorption in the SEC-UV analysis."

2). The strong pH dependence of the absorption spectra of nitrophenols (and some other brown carbon compounds) and the different acidities of working solvents used for the PILS and SEC portions of this work, make it very hard to faithfully compare the results obtained by these two methods. I presume that the complete lack of correlation between the two methods in Figure 3 must be at least in part due to these solvent acidity effects. Broadly speaking, this manuscript shows that choosing an inappropriate solvent for the measurements will lead to questionable results. Is this self-evident conclusion really worth publishing? Would the agreement be better if a more acidic buffer was used for the SEC portion of the work? Given that the atmospheric particles that are commonly acidic, why was a basic buffer selected for the separation? In my opinion these questions need to be carefully addressed before the manuscript can proceed to a publication. Additional experiments (and possibly a full re-analysis of samples with a different solvent for SEC) may be necessary to address these questions.

We agree with the Reviewer that an investigation on the impact of pH was warranted, and we have performed additional experiments to examine this question. To investigate the impact of mobile phase pH on wavelength dependent absorption, we adjusted the ammonium acetate solution to pH 5 and pH 9 prior to the addition of the acetonitrile. We selected four compounds that contribute to brown carbon absorption (4-nitrocatechol, vanillin, 7-hydroxycoumarin, 4-hydroxy-3-methoxy cinnamaldehyde, and mixture of the four compounds) and SRFA to run in the following mobile phases: DIW, DIW with 25 mM ammonium acetate, the default mobile phase (pH of 7.2), pH 5, and pH 9. As expected, we observed red shifting when the pH was greater than the pK_a of the compound. We acknowledge that numerous studies have investigated the impact directly acidifying and alkalinizing a SRFA sample have on absorption – there is a slight increase in absorption with increasing pH (Phillips et al., 2017).

To assess the impact of pH and mobile phase on a complex mixture, we also measured the absorption of a SRFA aqueous solution and a FIREX-AQ aqueous sample with the abovementioned mobile phases (Figure 4 and Figure S8). In contrast to the individual BrC compounds, no major changes in the spectral shape were observed under different mobile phase conditions. To confirm these results, we measured the absorption of SRFA in each solvent using an Agilent spectrophotometer (Figure S7).

The investigation of pH impact on absorption prompted the investigation of other plausible explanations to describe the discrepancies between the online BrC absorption measurements and offline SEC-UV measurements. Major differences between the online and offline analyses are the use of acetonitrile for the chromatographic separation and that the aqueous samples were stored prior to the SEC-UV analysis. These results are now described in the revised manuscript. Section 3.4 was retitled and re-written, and a description of the new methods was added as section 2.4.

"2.4 Absorption in different mobile phases

To assess the impact of pH and mobile-phase composition on wavelength-dependent absorption, the ammonium acetate solution was adjusted to pH 5 and pH 9 with acetic acid and ammonium hydroxide, respectively, prior to combining with acetonitrile. A 15 µg/mL in DIW solution of Suwannee River Fulvic Acid (SRFA II; International Humic Substances Society, Saint Paul, MN, USA) and a FIREX-AQ aqueous sample were injected onto the diode array detector without the SEC column in line with the following mobile phases: DIW only; 25 mM ammonium acetate solution; the default mobile phase (described in Sect. 2.3); 25 mM ammonium acetate

solution adjusted to pH 5; and 25 mM ammonium acetate solution adjusted to pH 9. Solutions of 4-nitrocatechol, 4-hydroxy-3-methoxy cinnamaldehyde, vanillin, and 7-hydroxycoumarin in DIW with concentrations of 3.9×10^{-8}, 3.4×10^{-8}, 3.9×10^{-8}, 3.7×10^{-8} mol/mL, respectively, were prepared and injected onto the diode array detector to observe differences in their absorption profiles. To confirm the diode array detector results, measurements of the SRFA solution were also made with UV-visible spectroscopy (8453; Agilent Technologies, Santa Clara, CA, USA) where the solution was mixed (1:1 ratio) with the various mobile phases prior to transferring to a cuvette for absorption measurements (Figure S7)."

Section 3.4 was titled:
Line 287: 3.4 Solvents affect the measured absorption spectra

This was changed to:

Line 327: "3.4 Investigating the impact of solvent effects, pH, and storage effects on absorption spectra"

Section 3.4 first addresses solvation effects (Lines 337 to 376):

"First, we assess solvation effects due to changes in the mobile phase composition. The PILS solubilizes BrC in pure water for the online measurements to facilitate absorption measurements (Weber et al., 2001). In contrast, the mobile phase used for the offline SEC-UV analysis was a mixture of acetonitrile and DIW with 25 mM ammonium acetate. Chromatographic packing materials are often incompatible with pure water and require a mixture with an organic solvent to elute compounds from the stationary phase or, in SEC separations, to prevent sorption to the stationary phase. For this reason, chromatographic partitioning-based separations occur in aqueous-organic mixtures, where the composition can be deliberately modified to optimize interactions of the target molecules between the stationary phase and mobile phase. In SEC, non-size exclusion interactions between the analyte and stationary phase are dominated by electrostatic and hydrophobic interactions (Hong et al., 2012). If the analyte and stationary phase are identically charged, ion exclusion effects can occur, resulting in an earlier elution time as the analyte is prevented from entering the pores. If the analyte and stationary phase are oppositely charged, adsorption can result, leading to a later elution time. Hydrophobic effects can occur if the analyte interacts with hydrophobic sites of the column matrix (Hong et al., 2012). The purpose of adding ammonium acetate to the mobile phase is to increase the ionic strength of the mobile phase and facilitate ion-pairing, which suppresses electrostatic interactions between the stationary phase and the polar and charged functional groups. The organic solvent used in our mobile phase was acetonitrile, which has been shown to be unreactive towards typical BrC components and has been recommended as an inert solvent for BrC extraction and analysis (Walser et al., 2008; Bateman et al., 2008; Chen et al., 2022). Therefore, we do not expect the mobile phase to chemically alter BrC compounds while effective at mitigating column stationary phase-analyte interactions.

While chemical changes caused by our mobile phase are unlikely, it is possible that other solvent effects on absorption could be occurring. Effects of solvent on molecular absorption are well established in the photochemistry literature (Lignell et al., 2014; Mo et al., 2017; Zheng et al., 2018; Lyu et al., 2021; Chen et al., 2022; Dalton et al., 2023). The polarity of the solvent affects the absorption wavelength by changing stabilization of the ground and/or excited states. With a decrease in solvent polarity, (acetonitrile-water is less polar relative to pure water), this can lead

to a decrease in stabilization of the ground state of BrC compounds (such as 4-nitrocatchol), but this effect is molecule dependent. The impact of solvation on red and blue spectral shifting will likely be several nanometers, which could contribute to the observed differences in the offline and online absorption measurements. Previous work has shown that acetonitrile is could disrupt π- π interactions between BrC molecules, which could cause the liberation of adsorbed low MW BrC chromophores from larger chromophores or disrupt BrC aggregates (Lyu et al., 2021). Smaller, less conjugated systems typically absorb in the ultraviolet-blue wavelength region, and their $\pi \rightarrow \pi*$ transition red shifts when more conjugated systems are fused together (Gorkowski et al., 2022). Thus, we would expect absorption measurements in the presence of acetonitrile to be blue-shifted relative to those in pure water. This represents a possible explanation for greater absorption intensity at lower wavelengths measured in the offline SEC-UV analysis compared to the online analysis."

The influence of solvent pH in Section 3.4 now reads (Line 377 to 407):

"Second, we assess the pH of the sample matrix, which is known to affect the absorption profile of BrC compounds. Multiple studies have investigated the impact of pH on wavelength-dependent absorption. For example, Phillips et al. 2017 directly adjusted the pH of SRFA and biomass-burning derived aqueous extracts (with sodium hydroxide or hydrochloric acid) and observed no measurable shift in the spectra to shorter or longer wavelengths; however they did observe that as the pH increased, there was an increase in the magnitude of absorption, which was more pronounced at higher wavelengths. The pH of the default mobile phase solution was 7.2, while the pH of the deionized water solutions in the PILS was approximately 5 (due to carbon dioxide dissolution). To investigate the impact pH has on BrC absorption, we measured several compounds that have been shown to contribute to BrC absorption (4-nitrocatechol, vanillin, 7-hydroxycoumarin, 4-hydroxy-3-methoxy cinnamaldehyde, and mixture of the four compounds) under different solvent and pH conditions: DIW, DIW with 25 mM ammonium acetate, as well as the mobile phase at pH 5, 7.2, and 9. When the matrix conditions have a pH greater than the pK_a of the compound in question, the species will deprotonate, resulting in a shift to longer wavelengths (Hinrichs et al., 2016). For compounds with a pK_a between 5 and 9 (i.e., 4-nitrocatechol, 7-hydroxycoumarin, vanillin), we observed this phenomenon (Figure S6). To assess the impact of pH and mobile phase on a complex mixture, we also measured the absorption of a SRFA aqueous solution and a FIREX-AQ aqueous sample with the abovementioned mobile phases (Figure 4 and Figure S8). In contrast to the individual BrC compounds, no major changes in the spectral shape were observed under different mobile phase conditions. To confirm these results, we measured the absorption of SRFA in each solvent using a separate spectrophotometer (Figure S7). This suggests that the pK_a of the majority of functional groups in the absorbing compounds present were less than 5 or above 9. Nitroaromatic compounds typically have pK_a values between 5 and 8; suggesting low levels of this class of compounds present in the aqueous samples. This observation is comparable to the online BrC-PILS analysis; for aqueous absorption, Washenfelder et al. 2022 observed the average absorption contribution at 365 nm of 4-nitrocatchol was less than 1.1 % and the summed contribution to absorption by 2-nitrophenol, 4-nitrophenol, 4-nitrocatechol, 4-nitroguaiacol, and 2,4-dinitrophenolate was less than 3.6 %. Since the absorption profile of SRFA and the FIREX-AQ sample appear similar in all mobile phase conditions, we have no evidence that pH of the mobile phase in the SEC separation conditions impacts the wavelength dependent absorption of the FIREX-AQ aqueous samples."

The influence of storage effects in section 3.4 reads (Line 408 to 444):

"Third, we assess the potential effect of storage on the aqueous samples measured by SEC-UV. A recent study by Resch et al. 2023 observed that biomass burning-derived filter extracts

stored at temperatures above freezing may undergo compositional changes that can increase in signal for various compounds. Hydrolysis reactions include converting alkenes to alcohols and esters to carboxylic acids, and the breakdown of oligomers. The hydrolysis of oligomers such as dimer esters stored in an aqueous solution can result in an increase in precursor monomers as decomposition products leading to an increase in signal (Zhao et al., 2018; Resch et al., 2023). Further, ammonium and alkylamines have been observed in high levels in biomass burning aerosols (Di Lorenzo et al., 2018); aqueous reactions between dicarbonyls (e.g., glyoxal, methylglyoxal) with ammonium and amines may also contribute to an increase in absorption intensity at pH 4 to 7 (Powelson et al., 2014; Yang et al., 2023). The FIREX-AQ aqueous samples had a pH of 5 and were stored at 4 °C for two years prior to analysis. Assuming they contained dicarbonyl compounds and reduced nitrogenous species, it is possible reactions leading to products that can contribute to greater absorption during storage occurred. To further investigate the impacts of storage on a complex aqueous mixture, we measured the absorption spectra of two SRFA solutions: one freshly made and one stored for one year at 4 °C. We observed an increase in absorption in the aged SRFA solution, in which integrated absorption was 39 % higher than the freshly-made solution. This same effect was also observed with SRHA solutions (Figure S14). Thus, it is possible that processes during storage could have led to increased absorption measured in the offline SEC samples.

Among the three processes discussed here, we conclude that the storage of aqueous extracts is the most plausible explanation for the higher absorption observed in the offline samples from FIREX-AQ. If hydrolysis reactions are occurring, we might expect this to impact the MW profile (i.e., SEC elution times). We examined the MW profile of freshly-made and one year-aged SRFA solutions (Figure 4C). The increase in absorption with storage does not measurably affect the molecular size-resolved absorption of the mixtures. The same effect was observed for SRHA (Figure S14). This demonstrates that any storage-induced changes in these complex mixtures of organic molecules have a minimal impact on the molecular weight relative to the wide MW range of the SEC column. The MW of the BrC species would have to change by ~ 100 Da to be noticeable on the MW scale of our separation (250 Da to 75 kDa). Such a drastic change in MW is unlikely the case in most hydrolysis reactions. Thus, our results above in which we broadly categorize MW species to be less than or greater than 500 Da are likely robust. The SEC separation of the aqueous samples signify that low MW (<500 Da) chromophores contribute more to total absorption than higher MW (>500 Da), this finding is supported by previous SEC-UV analyses of BrC aged less than 10 hrs (Di Lorenzo et al., 2017; Lyu et al. 2021). The consistent MW profiles between the freshly-made and stored solutions of SRFA and SRHA reasonably suggest that storage did not have a major impact on the MW of BrC."
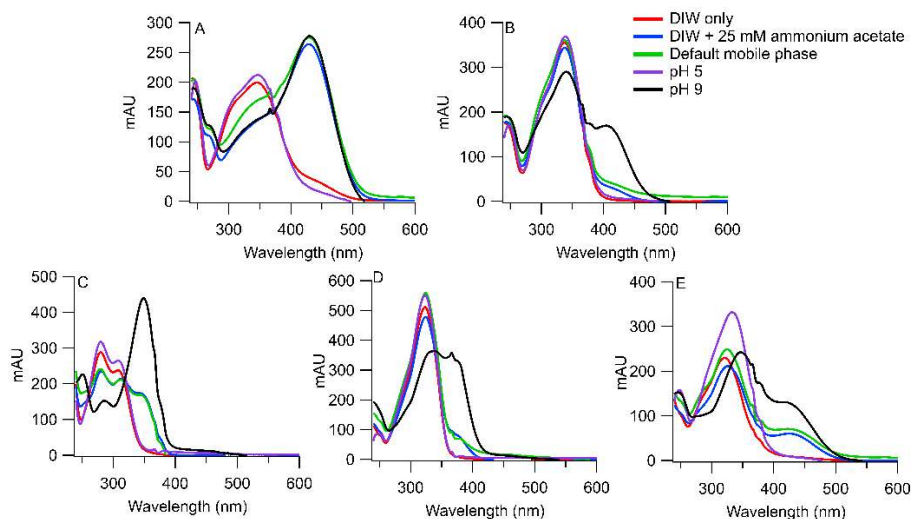
nitrocatechol (b) 4-hydroxy-3-methoxy cinnamaldehyde (c) vanillin (d) 7-hydroxycoumarin and (e) a mixture of the four compounds by a diode array detector. The default mobile phase consists of 1:1 mixture of acetonitrile and DIW with 25 mM ammonium acetate. The purple and black traces represent pH controlled mobile phases, where the pH of the ammonium acetate solution was adjusted to pH 5 and pH 9 prior to the addition of the acetonitrile."
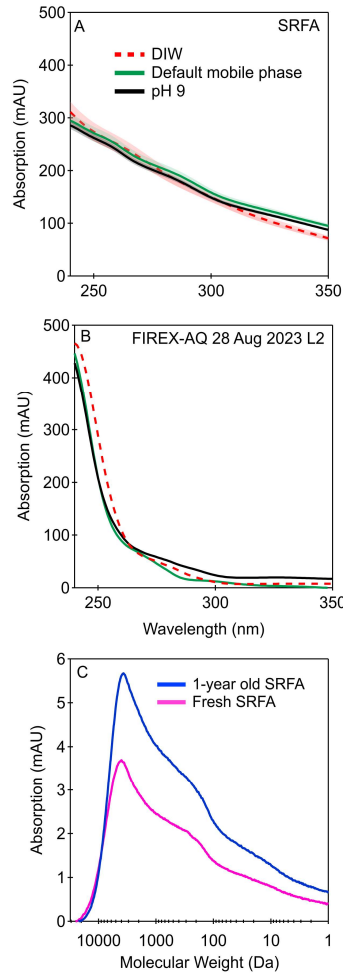
"Figure 4. Absorption as a function of wavelength of (a) SRFA and (b) a FIREX-AQ aqueous sample collected on 28 Aug 2019 L3 with varying mobile phases. (c) Molecular weight profile of a freshly-made 15 µg/mL SRFA solution and the same solution one year later. The shaded region represents the coefficient of variation for absorption at each wavelength using n = 3 DIW."
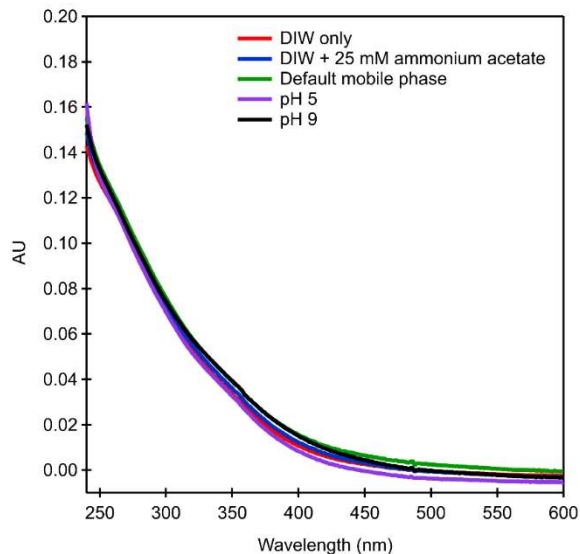
"Figure S7. Absorption as a function of wavelength of SRFA measured using a Agilent 8453 UV-visible Spectroscopy System. A solution of 15 μg/mL SRFA was diluted by 50 % by the mobile phase and then transferred to the cuvette prior to measurement. The default mobile phase consists of 1:1 mixture of acetonitrile and DIW with 25 mM ammonium acetate. The purple and orange traces represent pH controlled mobile phases, where the pH of the ammonium acetate solution was adjusted to pH 5 and pH 9 prior to the addition of the acetonitrile."
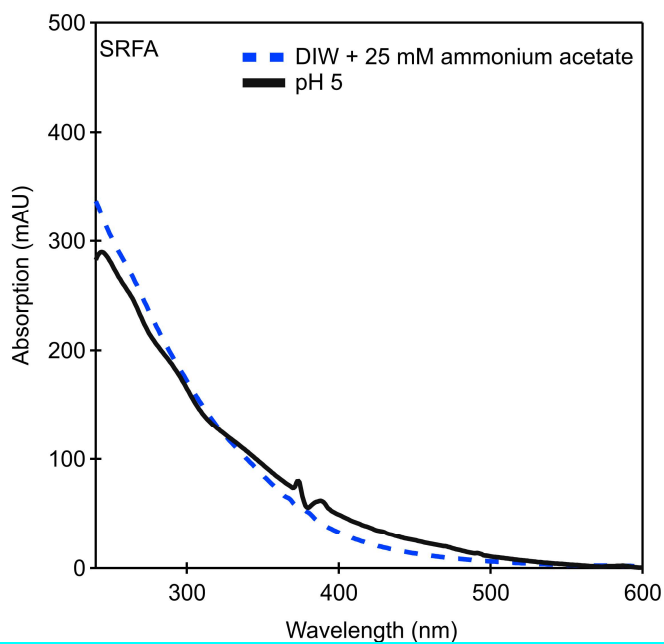
"Figure S8. Absorption as a function of wavelength of SRFA measured in a 25 mM ammonium acetate solution and in a mobile phases controlled to pH 5."
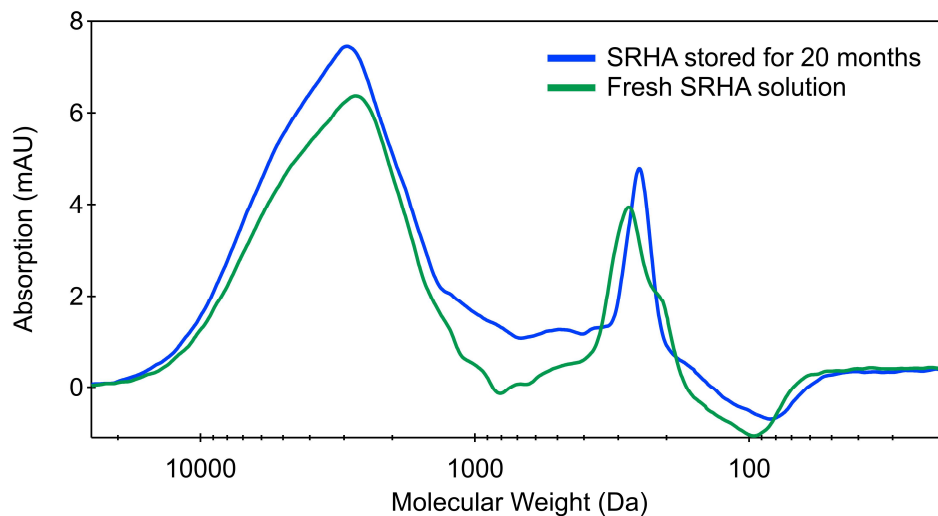
"Figure S14. Size separation of a fresh SRHA solution which was then re-run 20 months later."

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