Reply to Prof. Grieshop

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Note and general comments

Note: I am a referee for the paper but am posting my review with my name as much of my response is informed by a highly related (and complementary) paper that a former student and I published on a similar topic (Saha and Grieshop 2016). It appears that the authors of this paper may not be aware of our paper, and I wished to be transparent so thought it most appropriate to post this review under my name.

This paper presents results from a series of chamber experiments in which a-pinene was oxidized with ozone and OH and the resulting aerosol measured in-situ and via measurements of particulate matter. A-pinene ozonolysis is a well-studied system, but a number of open questions remain, with the product distribution (typically quantified in terms of volatility) and phase-partitioning kinetics being among two of the most pressing ones. This paper adds to the literature discussing this system by including cutting-edge chemical analyses of particles formed from both ozonolysis and particles thus formed and then perturbed via OH oxidation and additional dilution. A number of different experimental arrangements – e.g. use of thermodenuder (TD), analysis of PTR-MS measurements of gas-phase and vapors driven off a filter, ESI-MS analysis of filter samples and multi-chamber dilution studies – provide valuable data sets by which the partitioning and chemical composition of this SOA can be probed. This is a system and a topic of great interest to ACP readers, and as such I believe this is highly appropriate venue for this analysis. This is an interesting and creative set of experiments resulting in data collected with cutting edge techniques. However, while the data appear to be carefully collected, I find some of the interpretation of these data could be improved and that some of the resulting conclusions are insufficiently supported by the analysis. Therefore, I suggest that this paper be substantially revised before publication is considered.

Reply

Thank you for your valuable comments. We very much appreciate the time and effort you spent reviewing our paper and welcome the opportunity to improve its clarity and accuracy. We apologize that we did not refer to your recent work (Saha and Grieshop, 2016) in the original manuscript; we have rectified this oversight and now cite your results.

Comment 1

The title and tone of discussion don't give proper weight to previous work that has shown that the partitioning of a-pinene SOA is not well-represented by 'traditional' yield experiments. As the other reviewer suggested, this is not a 'new' insight, and so more effort should be made to put the present results into the proper context, including that provided by our paper and others with more detailed chemical analyses that well preceded ours.

Reply

We agree with the comment. Taking into account these comments and comment 9 by the other reviewer, we replaced the title with the following new one:

Studying volatility from composition, dilution, and heating measurements of secondary organic aerosols formed during α-pinene ozonolysis

Comment 2

Inter-experiment variation is an important theme that should be explored. There is relatively little comparison between sets of experiments conducted at similar conditions to establish repeatability of efforts (which seem to be good for TD results, based on Runs 2, 3 and 4 in Fig. 4c) and also to more systematically explore the influence of different experimental conditions (e.g. OH scavenger, RH) on the measurements. One complication, especially to interpreting TD results is that OA concentration varies quite substantially (Table 1). Our paper showed that smog chamber OA concentration has a systematic effect on its observed evaporation. These data are collected at a range of concentrations, though a number of other parameters were simultaneously changed and so it's difficult to say whether the effect of individual changes can be extracted. In addition to inter-experimental variability, I'm also curious about possible explanations for the quite substantial variation in volatility distributions from different methods (Fig. 4 panels) – are there any cases in which experiments show better or worse agreement? What might explain these differences?

Reply

Responding to this comment and comment 10 by you, we cited your paper and added the following discussion on the dependence of TD data on mass concentration. The following text is added in lines 296–302:

Saha and Grieshop (2016) reported that SOA volatility increases with increasing mass concentration in the range of 5–445 µg m^{-3}. Although we also obtained TD-AMS data between 964 and 2,400 µg m^{-3} in runs 1, 2, 3, 4, and 6 (black symbols), our results showed no clear trend with mass concentration. We surmise that the observed dispersion is probably caused by either the large variation in the present MFR data or differences in the mass concentration ranges between the current and previous studies. The variations between black symbols at 50 °C are greater than those at higher temperatures. A major reason for such variations may be the difference between the sensor temperature and the TD effective temperature.

Furthermore, we added discussion about experimental uncertainties in volatility distributions obtained by different methods. In the revised manuscript, we discussed the volatility distribution of LC/MS further, and we calculated additional results employing a third saturation concentration parameterization method (Fig. 4c). We also check the sensitivity of transmission efficiency (Fig. 4d). we compared the results in Figs. 4a, 4b, 4c, and 4d with the results of the TD-AMS analysis (Fig. 4e), and discussed potential reasons for differences in shape of the volatility distributions. Following this comment and comment 5 by the other reviewer, the following text has been added in lines 315–318:

The volatility distributions in Figures 4a, 4b, 4c, and 4d (LC/MS) have different shapes than Figure 4e (TD-AMS). The shapes of the volatility distributions obtained from LC/MS analysis may be affected by uncertainties in saturation concentration and sensitivity parameterizations as well as the existence of undetected molecules. The shape of the volatility distributions obtained from the TD-AMS may be influenced by heat-induced reactions.

Comment 3

I have some major concerns about the collection and analysis of the room temperature evaporation data. In considering these results, I'd ask the authors to take a careful look at our paper (Saha and Grieshop 2016) and also work by Saleh et al. (Saleh et al. 2011, 2013), especially their chamber experiments considering time scales of equilibration. An important point is that equilibration rates cannot be readily separated from volatility in this type of experiment, and so the authors should not compare the assumed equilibrium of particles calculated based on yield experiment data (horizontal lines in Fig. 5) with dynamic equilibration data unless the consistency is somehow proven (e.g. the actual equilibrium state of the system is known). This disconnect especially stands out here because the authors have presented volatility distributions showing much lower volatility, so it is strange to compare 'equilibrium' dictated by another experimental approach (yield experiments) when other parts of your paper are essentially arguing that these are wrong. A better way to compare equilibrium properties is by comparing volatility distributions. Normalized time scales (see Saleh et al. papers referenced above) can be used to compare equilibration time scales for such experiments. As it is, this figure suggests that equilibration time scales for the low and high RH experiments are very different, but this difference may be due to differences in volatility or other experimental conditions. If this is the case, the volatility distributions in Fig. 4 may be *able explain this difference. As both our paper and (Saleh et al. 2013) point out, if you assume the wrong volatility you can easily conflate 'slow' evaporation due to a kinetic limitation (as you suggest), when it's really just that (as your chemical analyses suggest) the aerosol is much less volatile than yield data suggest. This is an assumption that we show may be at play in the 'kinetic limitation' ascribed to slow evaporation by Vaden et al. (2011). In addition, since different chambers (Teflon-coated steel vs. FEP membrane) were used for the different experiments, it's impossible to say what influence different wall characteristics may have of on the observed evaporation. As it is, there is far too little evidence to support the statements on Line 279-284 about 'irreversible' partitioning and the RH-dependence of evaporation and viscosity. There is good evidence elsewhere that RH dependencies may be important, but I don't find what is presented here convincing. For example, the data don't support the statement (L282-283) that that 'gas/particle partitioning was virtually irreversible'. This level of dilution is insufficient to probe the irreversibility of partitioning for compounds with C* less than 10^1 or 10^2 ug/m3, which comprise the majority of the material in your distribution (Fig. 4) but not the Lane et al. (2008) distribution used to calculate equilibrium partitioning.*

Reply

Following the comment, we carefully read papers the suggested papers (Saha and Grieshop (2016) and Saleh et al. (2011; 2013)). Revisions are made to descriptions in the introduction as described in the reply to specific comment 1. We removed straight lines drawn in Fig. 5 because we agree with your suggestions. We determined equilibration scaling time to be 24–46 min for the present dilution data. Scaling results are shown in Figure R1. We revised the last paragraph of section 3.4 (lines 334–346 of the manuscript) as follows to discuss scaling factors measured in present study:

The equilibration scaling time, defined by Saleh et al. (2011; 2013), was used to characterize slow SOA evaporation. The equilibration scaling time was determined to be 24–38 min and 33–46 min for α-pinene SOA particles generated in dry and humid experiments, respectively. The results are not compared between dry and humid experiments here because the chamber systems differ between these experiments. The current results of a 24–46 min equilibration time scale imply that the gas–particle equilibrium approximation could be applied for evaporation of α-pinene SOAs under atmospheric conditions, as suggested by previous workers (Saleh et al., 2013; Saha and Grieshop, 2016). The theoretical equilibration scaling time was also evaluated using eq. 3 in Saleh et al. (2013), where the accommodation coefficient was set to a recommended value of 0.1 for α-pinene SOAs. The theoretical equilibration scaling time was determined to be 24–41 min, which was similar to the experimental results: 24–46 min. These results suggest that kinetic inhibition may be a possible reason of slow evaporation. The present results based on SOA particles contrast with previous results based on semi-volatile diesel particles, which evaporate instantaneously after dilution (Fujitani et al., 2012). Kinetic inhibition during dilution-induced SOA evaporation may occur because SOA particles include low or extremely low volatility organic compounds.

Consequently, we also revised the abstract. The text in lines 18–22 of the manuscript has been revised as follows:

The volume fraction remaining of SOAs decreased with time and the equilibration time scale was determined to be 24 – 46 min for SOA evaporation, suggesting that kinetic inhibition may be a possible reason for slow evaporation. The kinetic inhibition may occur because SOA particles contain compounds that are less volatile than those of semi-volatile products.

We determine volatility distributions from dilution data in the region 1–1000 μg m^{-3} because the dilution data obtained in present study are only available in a region C* >1 μg m^{-3}. These results are added to Figure 4 of the revised manuscript and Table S3 of the supplementary material. We discuss these results in lines 347–354 as follows:

The volatility distributions determined from dilution data are compared with those determined from SOA yield curves (Lane et al., 2008) as shown in Figure 4f. We determined the volatility distributions from dilution data assuming gas–particle equilibrium using the VFR data measured 3 h after the dilution. The volatility distributions were only calculated in the range 1-1000 μg m^{-3} because dilution data are only available for C^* > several μg m^{-3}. The average $\log_{10} C^*$ values determined from dilution measurements (1.00–1.60) are lower than that determined from SOA yield curves (2.26); these results of dilution experiments might be consistent with the results of LC/MS and TD-AMS. However, note that the volatility determined from dilution experiments will be underestimated due kinetic inhibition.

Furthermore, we removed discussion of reversibility. We only discussed slow evaporation using scaling factors as described above.

Reply

Specific comment 1

L42-43 – Discussion of dilution results is limited, and the body of literature lumped as 'later research' should be further discussed. This is a logical place to discuss Saleh et al. (2013).

Reply

We added the citations of Saha and Grieshop (2016) and Saleh et al. (2013) and revised sentences in lines

40–47 as follows:

Yet another technique used to study volatility distribution is dilution-induced evaporation. Grieshop et al. (2007) diluted SOA particles in a reactor and studied the reversibility of gas–particle partitioning. Later workers (Vaden et al., 2011; Saleh et al.; 2013; Wilson et al., 2015; Yli-Juuti et al., 2017) diluted SOA particles instantaneously in an external chamber. Saleh et al. (2011; 2013) defined the equilibration time scale of SOA evaporation, and reported that the equilibration time scale is several minutes to several tens of minutes for α-pinene SOA particles (Saleh et al., 2013). Slow evaporation could be due to the presence of low-volatility materials in SOAs, kinetic inhibition, or some combined effect (Saha and Grieshop, 2016). Therefore, data from dilution-induced evaporation measurements would be determined not only by product volatility but also by the particle phase.

Specific comment 2

L90 – It would be helpful to compare density numbers determined here with those from other studies. In general, more comparison of results with the wealth of other studies of this model aerosol system would help to place this study in its proper context relative to the literature.

Reply

We added the following text in lines 95–96 of the manuscript:

The density determined in this study is close to literature values: 1.32 ± 0.10 g cm^{-3} (Ng et al. 2007) and 1.24 ± 0.03 (Malloy et al., 2009).

Specific comment 3

L97-98 - Discussion of the use of pinonic acid as a reference for the thermodenuder (TD) measurements should be discussed, along with more generally the approach used for interpreting TD measurements to yield Fig 4c. Is the T_50 method of Faulhaber et al. (2009) used with only a single 'calibration' compound (pinonic acid) to develop the calibration? Or were more calibration compounds used? Was the calibration from Faulhaber used directly? If so, do the results for your single calibration compound match well with that from their calibration? It is not clear if your TD has exactly the same residence time as the one used there, which would be an important pre-requisite for applying this calibration.

Reply

We used the results of T-50 calibration from Faulhaber et al. (2009) directly because the present TD has a residence time close to that used for their TD. We confirm their calibration results explain the results of the TD-AMS measurements of pinonic acid particles well. A T-50 of pinonic acid particles was determined to be 35.4 deg C; and the $\log_{10}$ C* value was calculated to be 1.7 ± 1.0 by a method of Faulhaber et al. (2009). The result of $\log_{10}$ C* determined by this method was close to that determined for pinonic acid by SPARC (2.25). We added the following text in lines 308–311 of the manuscript:

We used the results of the calibration curve from Faulhaber et al. (2009) directly because the TD in our study has a residence time close to that used for their TD. We confirmed that their calibration results are consistent with our results for pinonic acid particles.

Specific comment 4

Line 102-104 – I would be curious to see how wall losses of vapors might affect the determination of the distribution of gas-phase constituents in the chamber at the end of the experiment and how this, and also sampling/storage conditions might affect what was sampled on the chamber walls. Also, during the desorption of the filters, was the PTR-MS signal observed to return to background? In both your and our work, we find materials that remain in the particle phase (not on filters) in a TD to up to 120 C (393 K) with substantial residence times, so I'd be curious to see how PTR-MS-identified products evolve during desorption and if everything was actually desorbed from the filters. In general, no PTR-MS data are shown apart from the points shown in Fig. S2 in the supplement. Is there any reason these data are not further discussed?

Reply

From PTR-MS data, we determined the saturation concentrations only for the compounds that are detected between m/z 151 and 229. The PTR-MS data were not used to determine the volatility distribution of gaseous products in this study. When we measure vapors in the chamber, the ion signals of m/z 151–229 decreased slowly due to wall loss after α-pinene is consumed by the ozonolysis; however, the lifetime of the detected compounds were longer than the gas-particle equilibration time scale (that is determined to be <1 h in this study). This suggests that we can apply the assumption of gas-particle equilibrium for the detected compounds. We estimated the maximum fraction of the total vapor wall loss to the total vapor mass. As per the reply to the comment 1 made by reviewer #1, we compared the amount of gaseous products detected by the PTR-MS with an expected value, which was calculated from a difference between the amounts of consumed reactants and formed SOAs. We estimated the loss of gaseous compounds to be up to 40 %.

The PTR-MS data in Figure S2 were estimated from the results of run 6. The thermogram of the filter analysis and the temporal variations of ion signals at m/z 185 and m/z 187, which are attributed to pinonic acid and pinic acid, respectively, are shown in Figure R2. As shown in the figure, the PTR-MS signal was observed to return to background levels. The temperature dependence of vapor pressure of pinic acid over a flat surface has been reported by Bilde and Pandis (2001). The vapor pressure of pinic acid at 368 K (95 ºC) was calculated to be 0.19 Pa (= 1.4×10^{-3} Torr). From the relationship between the absorption equilibrium constant and the vapor pressure of compound (Odum et al., 1996), the $F_{i,OM}/A_i$ ratio was derived as 0.1 (Mo was set to 960 μg m^{-3} (run 6) as a maximum particle level at 95 ºC; MW_{om} was set to 200; and, ζ was set to 1). As Prof. Grieshop pointed out, not everything might be desorbed from the particles; however ≥90 % of pinic acid exists in the gas phase at 368 K (95 ºC).

We did not discuss results of PTR-MS in detail because the results will be presented in a separate paper. We have added the following description in lines 112-115 of the manuscript.

The ion signals of m/z 151–229 were only used for the evaluations of saturation concentration. The signals of *m/z* < 151 were not used because there would be interference from fragment ions. The signals of *m/z* > 229 were not detected due to the low sensitivity of the quadruple mass spectrometer.

Specific comment 5

Line 109 and 152-153 – A brief description of the analytical method would be helpful. For example, some mention of the source/significance of sodium adducts would be helpful, especially for those (like me) unfamiliar with this quirk of ESI analysis.

Reply

We added the following text in lines 168–170:

Species that do not generate stable positive ions through protonation were ionized by clustering with Na^+ cations that are naturally present in the solvent chemicals and glassware (Kruve et al., 2013; Zhang et al., 2017).

Specific comment 6

Line 241 – Error of +/- 2 – it is not clear what units this error is reported in? Possibly a factor of 2?

Reply

This sentence explains the error of $\log_{10} C^*$. We revised this sentence (lines 270–272 in the new manuscript) as follows:

The C^* values predicted for dimers by the 1D function agreed with the SPARC results within an error of two orders of magnitude; in contrast, the 2D function predicted C^* values five to six orders of magnitude higher than the SPARC results.

Specific comment 7

Line 212-215 – While a line can be drawn through these data points, and shows a reasonably high R^2 value, there seems to be a discontinuity in this relation at a logC of around -3 or -4, with the clusters of data at either side of this showing a much shallower relationship between MW and logC*. For example, if you exclude the lower volatility data, you would have a much different dependence. How does this affect your results? Is there any reason for this discontinuity, perhaps due to the oxidation state or other properties of the compounds in these two clusters?*

Reply

The carbon oxidation states will differ significantly between the products of m/z >=300 and <300 based on the present LC/MS results. We treated data sets in these two regions separately and fitted two different straight lines. These results are shown in Figure S3 and Table S2 in the revised supplementary material. We discussed this third fitting method as follows in lines 242–245 of the manuscript:

The third parameterization technique is the binary fit method. In Figure S2, the linear function overestimates molecular weights in the region $\log_{10} C^*$ = -3 to 0. There are significant differences between the carbon oxidation states for the products with m/z ≥300 and <300, according to our current LC/MS results. We fitted these two data sets separately for better approximation as shown in Figure S3.

Furthermore, the volatility distributions determined using this binary fit are shown in Figure 4 of the revised manuscript. We discuss these results in lines 275–281 of the manuscript as follows:

The volatility distributions determined using the binary fitting method (Fig. 4c) have different shapes compared to those obtained using the 1D and 2D fits, suggesting that the shape of the volatility distribution obtained by LC/MS data depends on the saturation concentration parameterization. Table S2 shows that the binary fit provides a better approximation for MBTCA than the 1D and 2D fits although the binary fit provides worse approximations for dimers than the 1D fit. Table S3 compares the average $\log_{10} C^*$ values determined for volatility distributions obtained in this study. The average $\log_{10} C^*$ values determined for the binary fit (-2.19 to -2.76) were close to or lower than those determined for 1D fit (-2.71 to -0.83) and lower than those determined for 2D fit (-0.61 to 1.44).

Specific comment 8

L221-223 – This may be a very normal assumption to make for a TOF-MS, but I would like to see it justified, either with a reference or calibration data. How sensitive are results (e.g. volatility distributions) to any uncertainty in this?

Reply

For example, the TOF-MS transmission correction is discussed in Heinritzi et al. (2016). We cite this paper in the revised manuscript. We calculated volatility distributions without transmission correction and added these results to Figure 4 of the revised manuscript and Table S3 of the supplementary material. We discuss these results in lines 282–287 of the manuscript as follows:

As a sensitivity check of the transmission correction, we calculated volatility distributions obtained by a 1D fit without accounting for the transmission correction (Figure 4d). The average $\log_{10} C^*$ values determined without the transmission correction (-3.55 to -1.38) are close to or lower than those determined with the transmission correction (-2.71 to -0.83). The average $\log_{10} C^*$ values determined for all LC/MS data (-3.55 to 1.44) are lower than those determined for the yield curve (2.66), suggesting that α-pinene SOAs have a lower volatility than that expected from yield curve analysis.

Specific comment 9

L242-244 – I don't quite understand this statement. How were 2D function results 'adjusted'? I'm assuming this is referring to the range of compounds fit by the 2D function? This statement and its implications should be clarified.

Reply

We revised this sentence (lines 272–274 in the manuscript) as follows:

The accuracy of the results predicted by the 2D function was worse than those predicted by 1D function because the 2D function was fitted not only to the data of α-pinene oxidation products but also that of other organic compounds.

In addition we revised the sentences in lines 239–241 of the manuscript as follows:

The 2D function was fitted to EVAPORATION data for various organic compounds including not only α -pinene oxidation products, but also other organic compounds present in the atmosphere.

Specific comment 10

Line 250-255 – The level of agreement should be better described (perhaps by comparing others' data to yours). Also, I note that there is quite a bit of scatter in observed evaporation, especially at 50 deg. C, where there is nearly a factor of 2 range in VFR (~0.4 to 0.7) for the alpha-pinene SOA systems. It is stated that data were similar 'to within experimental uncertainties', but these uncertainties are not stated *or discussed. As noted above, comparing results collected for experiments at the same conditions (Coa, scavenger, RH, etc.) can constrain inter-experiment variability and then be used to discuss whether any observed differences may be ascribed to these conditions or uncontrolled variability in the experiments.*

Reply

A probable reason of data variations is the error of thermodenuder temperature. We added the following sentences in lines 300–302:

The variations between black symbols at 50 °C are greater than those at higher temperatures. A major reason for such variations may be the difference between the sensor temperature and the TD effective temperature.

Specific comment 11

Line 291 – Our study and various others that our paper discussed and cite, many of which were also cited here (e.g. (Ehn et al. 2014; Zhang et al. 2015)) have pointed towards the prevalence of very low volatility compounds in pinene SOA in contrast to existing yield-experiment-based parameterizations. It may be true that you are the first who arrived at the results via application for ESI-MS, but that is not how I read this sentence.

Reply

I revised these sentences (lines 359–362 of the manuscript) as follows:

To the best of our knowledge, this study is the first to analyse HOMs by column separation and to compare the product volatility distribution determined by chemical analysis with those determined by particle evaporation measurements. The HOM detection by column separation is a valuable contribution to the current research because this technique could potentially be applied to molecular identification.

Specific comment 12

Line 293-294 – Since a VBS model by itself doesn't assume an evaporation rate, it's hard to make this comparison. Also, as noted, volatility and evaporation kinetics are conflated in the comparison in this paper, so insufficient evidence is presented to make this claim. In chemical transport models, the assumption is that frequently made that equilibrium partitioning adequately describes what happens within time steps of on the order of a ~hour. Our paper argues that this is probably a fine assumption for alpha-pinene SOA produced in our lab under atmospheric conditions, though the assumption cannot be made in interpreting thermodenuder measurements.

Reply

We revised this paragraph (lines 363–368 of the manuscript) as follows:

The first-generation products formed during α-pinene ozonolysis were found to include compounds less volatile than those predicted from SOA yield curves, and the equilibration time scale of dilution-induced evaporation was found to be several tens of minutes. These findings support recent results of SOA chemical composition studies and SOA evaporation studies. In the current VBS model, the product volatility distributions determined by SOA yield curves are employed. Further improvement of the atmospheric simulation model will be necessary to explain both laboratory and ambient SOA levels.

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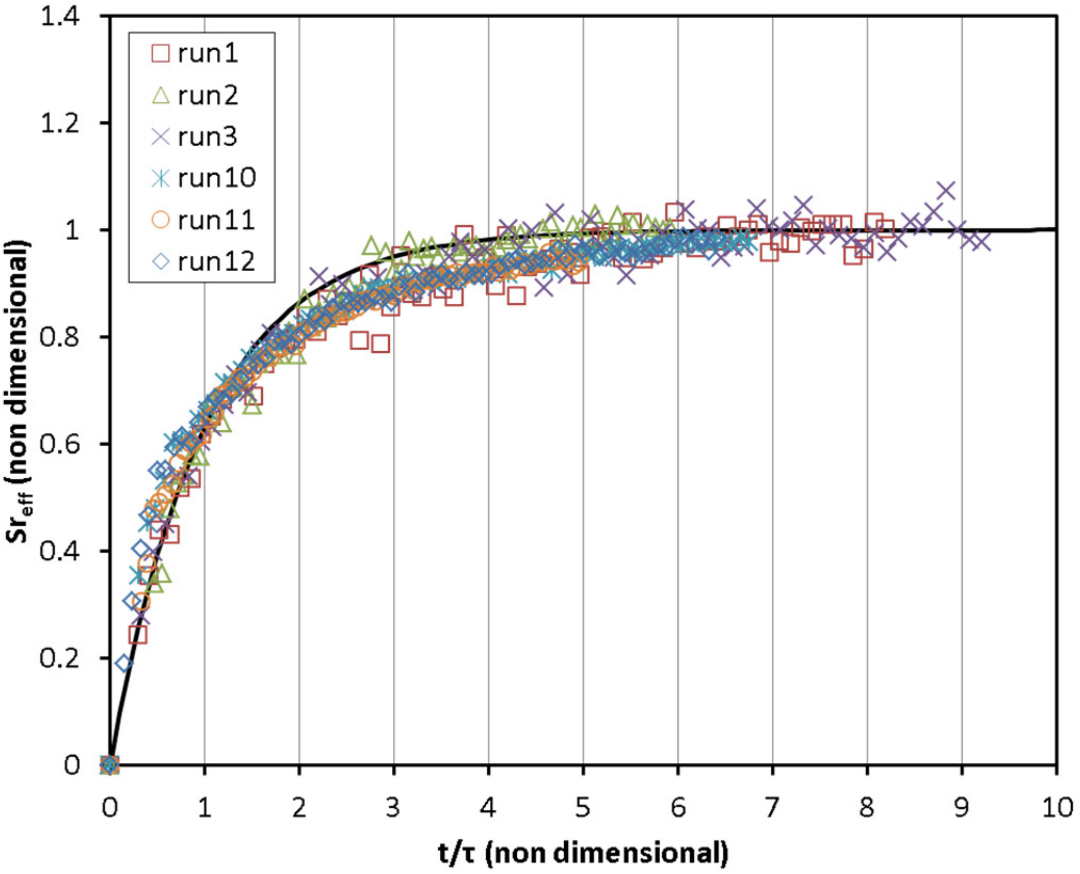

Figure R1: SR_{eff} calculated form present dilution data plotted as a function of t/τ; where SR_{eff} is defined in eq. 1 of Saleh et al. (2013); t is time; and τ is equilibration time scale. The curve represents a first-order approximation to the dynamic response. This curve underestimates and overestimates experimental data in a region t/τ = 0–1 and 1–5, respectively, which is likely due to higher-order dynamic responses of a complex aerosol system.

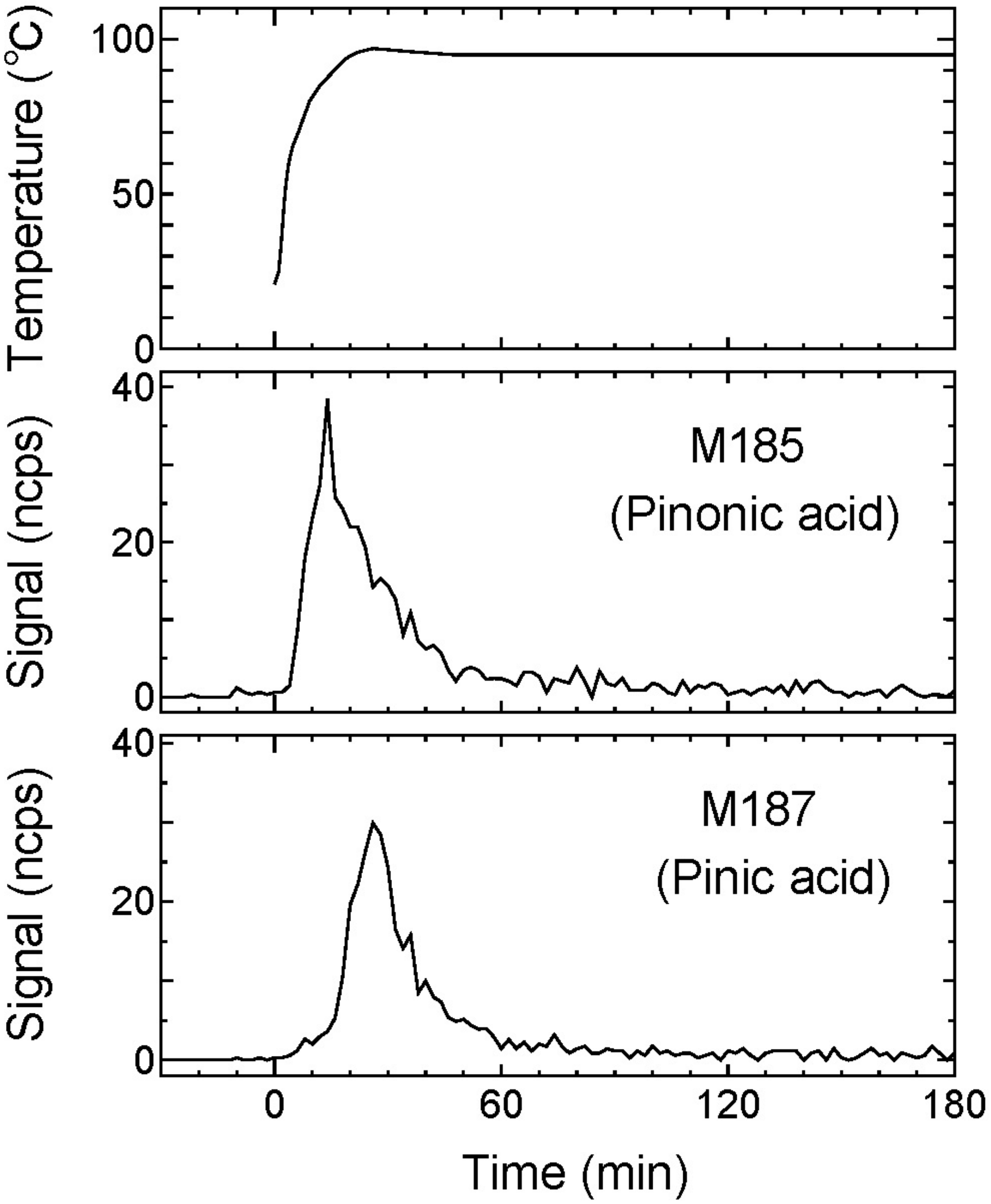

Figure R2: (a) Thermogram of the filter analysis. Temporal variations of ion signals at (b) m/z 185 and (c) m/z 187 during the filter analysis.