Reviewer #1

Minor/technical comments:
page 9356: Although SI units have to be used, please mention also the imperial units: 25 mm OD tube = 1" tube; 19 mm OD tube = 3/4" tube.

This has been added to the locations in the text where we describe inlet dimensions and parameters.

page 9358: What exactly is the effect of heating the IMR?

The IMR is heated to minimize memory from material partitioning to the IMR walls, and to keep the ionization region at a constant temperature when sampling. It should be noted that heating the IMR also increases the evaporation rate of particles that are present in the gas phase sample flow. For our operation temperatures (50-60 °C) and the residence time of the IMR (~100 ms), the rate of evaporation of aerosol into the gas phase is slow, so its effect is small (see response to Reviewer #2 below). At higher IMR temperatures or longer residence times, evaporation from the particle phase into the gas phase could be significant. We therefore chose 50 – 60 °C as a reasonable compromise. For ionization techniques which rely on adducts, for example Iodide or Nitrate (Aljawhary et al., 2013; Jokinen et al., 2012)*, increased IMR temperature changes the adduct stability and therefore the ionization efficiency. Therefore, calibrations at the chosen IMR temperature are required.*

page 9363: Is there a reference for the acetate Q-CIMS?

The Q-CIMS we used is similar to the one described by (Kercher et al., 2009) *but with different declustering field strengths and employs the same ionization technique described by* (Veres et al., 2008)*. The instrument was operated in acetate ionization only for the purposes of this manuscript.*

Figures:
Figure 6b is not mentioned in the text. But the figure caption is rather long, and some of the information would better be placed in the text in section 3.3.

We have now called out Figure 6b and moved some text from the caption into section 3.3 of the text.

Figure 7: Why are thermograms now plotted vs time and not vs temperature?

We plot the thermograms as a function of time because it is easier to visualize the full evolution of signal during a thermogram (ramp and soak) using the time axis. The signal continues to evolve during the "soak", even though the temperature is constant.

Reviewer #2

1. It might be mentioned that although particles are present in the sampled air during gas analysis, they are not analyzed because they do no evaporate in the CIMS (at least that is my understanding of the way this works). This might not be the case with other instruments coupled to the FIGAERO.

We have added the following sentences to the manuscript. "We estimate that for our ionization region temperature and residence time (T_{IMR} 50-60 C and τ_{IMR}~100 ms) evaporation of particle phase compounds is a relatively minor contribution to the observed gas-phase concentrations. The coupling of the FIGAERO to detectors or ionization regions that operate at higher temperatures or longer residence times would likely result in a contamination of the gas phase signals by vaporized particles and would require different quality

controls to evaluate the effect of volatilizing particles inside the instrument (Yatavelli and Thornton, 2010)."

We have calculated the evaporation rate for an example compound using the Hertz-Knudsen equation (Cappa et al., 2007)

$$J_e(T) = \frac{\gamma_e p^0(T)}{\sqrt{2\pi mkT}}$$

where $J_e(T)$ is the evaporation flux (molecules m^{-2} s^{-1}), $p^0(T)$ is the vapor pressure (Pa), m is the molecular mass (kg $molecule^{-1}$), k is the Boltzmann's constant (J K^{-1}), T is the temperature (K), and γ_e is called the evaporation coefficient and is considered to be temperature independent and equal to unity. For our calculations we assume a typical aerosol surface area of 200 $\mu m^2/cm^3$ and a vapor pressure consistent with a semi-volatile, for example pinic acid [$p^0(298\ K) = 4.2e\text{-}5$ Pa] (Bilde and Pandis, 2001). *We estimate the mass lost due to evaporation in the transit through the IMR to be .6% of the mass of a 50 nm particle consistent with other calculations for a similar IMR geometry*(Yatavelli and Thornton, 2010).

A method to estimate the upper limit of volatilizing aerosol in the gas phase sample stream can be obtained by periodically pulling the gas phase sample flow across a Teflon filter to remove particles and thereby measure the effect of volatilizing particles; however when sampling through a filter (similar to the case of the particle blanking manifold) it is possible to confound the loss of particulate mass with the loss of low volatility compounds present in the gas phase which can condense on the filter membrane and therefore appear as volatilizing particles.

2. Page 9367, lines 4-6: It has been shown that Teflon readily absorbs organic compounds that would normally be entirely in the gas phase (Matsunaga and Ziemann, AST, 2010), so this statement may not be true. In addition, because the FIGAERO is constructed of Teflon it is probably worthwhile discussing the possible effects of absorption of organic compounds. Some of the issues are touched on here in the context of adsorption, but that effect is likely to be minor compared to absorption, which is much more substantial and can occur on short timescales (a few minutes).

We thank the reviewer for pointing this out. In the FIGAERO, we cannot distinguish between absorption and adsorption artifacts, but measure the sum of them on the Teflon filter by using a blanking filter as described in section 3.2 of the text. We have added the absorption artifact statement and the Matsunaga reference to the text.

3. It might be useful to evaluate losses of gaseous and particulate organics during sampling and analysis by conducting experiments with a homologous series of monoacids, for example. I think with the CIMS one would expect about the same signal from all compounds regardless of carbon number, so that differences in measured concentrations could be used to evaluate losses within the system.

We agree this is a useful endeavor. However, in our instrument there are a variety of parameters that will affect the detection efficiency (i.e. the measured sensitivity) in addition to the inlet transmission efficiency, such as the chemical ionization efficiency and the mass-to-charge dependent transmission efficiency of the ion optics. We have been systematically studying the sensitivity of the acetate ionization efficiency to different carboxylic acids to decouple effects of mass dependent ion transmission and ionization efficiency. Until this work is completed, we can't reliably evaluate the losses of a large suite of compounds during sampling/analysis.

That said, the losses within sampling inlets will be highly dependent upon the inlet material, length, diameter, and flow velocities – often different from application to application and thus not generalizable. Our expectation is that very low volatility acids will have lower overall transmission, and thus sensitivity, due to the likelihood that thermal decomposition will become competitive with desorption, and strong partitioning to sampling surfaces downstream.

4. Section 3.3. I am not quite sure why the authors chose to correlate compound desorption temperatures with enthalpy of vaporization rather than vapor pressure (e.g., at 25C), as has been done by others with reasonable success (e.g., Ziemann, JPCA, 2002; Faulhaber et al., AMT, 2009). Although both correlations have their caveats, it seems that estimating an effective vapor pressure is more useful than an effective heat of vaporization, since gas-particle partitioning depends on the former not the latter. Effective heats of vaporization, as usually defined based on the temperature-dependent evaporation of a complex aerosol, seem to have less use since they do not reflect the heats of vaporization of individual compounds but instead the distribution of vapor pressures of the compounds in the mixture.

We agree it is possible to correlate desorption temperatures with vapor pressures and that ultimately these are what control gas-particle partitioning. We chose enthalpy of sublimation because there tends to be somewhat more consistency in this value between various studies than for the corresponding sub-cooled vapor pressures at 298K. Indeed, we assume that this type of relationship (which would need to be established for any other instrument or configuration) would be used to convert each detected elemental composition's desorption temperature to an effective vapor pressure. Often literature values of measured vapor pressures can vary by many orders of magnitude whereas enthalpy determinations have smaller reported uncertainties, typically on the order of 10% (see Table 2). We have nonetheless added a correlation with vapor pressures of the same compounds that were used for the development of the enthalpy of sublimation relationship (see attached figure). This revised figure will replace Figure 6 in the existing text.

It is important to note that with our method we measure the effective heats of vaporization of individual molecular components within an aerosol sample, not just the effective heat of vaporization of the bulk sample as done with thermal denuders. An estimate of the bulk value, for the functionalities detectable by CI, can then be derived from the sum ion signal.

5. Section 3.4. The authors might be interested to know that the behavior observed for m/z 185 ($C_9H_{13}O_4^-$) in Figure 5, which is presumably pinic acid, has been reported previously for the temperature-programmed thermal desorption of SOA formed from this same reaction (Docherty et al. EST, 2005). In that study pinic acid was monitored by EI-MS and a large low-temperature peak and high-temperature tail indicative of the monomer and oligomers, respectively, was observed.

We thank the reviewer for reminding us about this previous finding. This has been added as a reference in section 3.4 where we discuss the multi modal thermograms.

Technical Comments

1. Page 9376, lines 11-13: It sounds like the authors are saying that thermograms, thermal desorption information, and thermal separation have not previously been used in OA analysis. This is obviously not the case, since a number of groups have done so, but perhaps something else was meant. I suggest clarifying the sentence.

This sentence has been rewritten to read:

"The FIGAERO thermograms provide additional insight into the role of thermal decomposition and add an additional degree of separation to the aerosol composition data, which until now has remained unexplored with negative-ion HRTOF-CIMS."

References:

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ID	Comp.	Chemical Name	ΔH_{sub} kJ/mol	T_{max} (ºC)	p(298 K) 10^{-5} Pa	Source
a	$C_4H_{10}O_4$	Erythritol	135± 2	52.9	--	NIST
b	$C_7H_{12}O_4$	Pimelic Acid	127± 20	37.6	9-17	(Salo et al., 2010)
c	$C_6H_{10}O_5$	Levoglucosan	125 ± 10	61.5	20	(May et al., 2012; Oja and Suuberg, 1999)
d	$C_{10}H_{20}O_2$	Decanoic Acid	119± 2	<32.4	5400	NIST (Cappa et al., 2008)
e	$C_{10}H_{16}O_3$	Pinonic Acid	90± 7	<32.4	.4-7	(Salo et al., 2010)
f	$C_9H_{14}O_4$	Pinic Acid	109±21	61.5	4-10	(Salo et al., 2010)
g	$C_9H_{16}O_4$	Azelaic Acid	178±10	71.4	.6	(Bilde et al., 2003)
h	$C_{10}H_{18}O_4$	Sebacic Acid	161 ± 4	72.9	.147	NIST (Chattopadhyay and Ziemann, 2005)
i	$C_{13}H_{26}O_2$	Tridecylic Acid	141 ± 10	39.2	140	NIST(Chattopadhyay and Ziemann, 2005)
j	$C_{12}H_{22}O_4$	Dodecanedioic Acid	153 ± 4	71.9	6e-3-.242	NIST, (Chattopadhyay and Ziemann, 2005)
k	$C_{16}H_{32}O_2$	Hexadecanoic Acid	154 ± 4	65.3	.39-29	NIST (Cappa et al., 2008)
l	$C_{14}H_{26}O_4$	Decanedioic Acid	161 ± 4	70.0	.1-1	NIST, (Yatavelli and Thornton, 2010)
m	$C_{16}H_{32}O_3$	Hydroxy-Hexadecanoic Acid	149 ± 10	81.5	.653	(Vasiliou et al., 1999)
n	$C_{18}H_{32}O_2$	Oleic Acid	136 ± 8	71.9	.066-2.66	(Neuman et al., 1999) (Williams et al., 2006; Yatavelli et al., 2012)
o	$C_{18}H_{36}O_2$	Octadecanoic Acid	167 ± 4	79.5	.056-.19	NIST (Voisin et al., 2003)
p	$C_{18}H_{36}O_3$	Hydroxy-Stearic Acid	172 ± 10	89.7	.0865	Calc (Aljawhary et

						al., 2013; Mohr et al., 2013; Yatavelli et al., 2012)
q	$C_{22}H_{44}O_2$	Docosanoic Acid	193 ± 8	92.7	7e-4	NIST,(Aljawhary et al., 2013; Mohr et al., 2013; Yatavelli et al., 2012)
r	$C_{23}H_{46}O_2$	Tricosanoic Acid	197 ± 8	99.8	--	Calc
s	$C_{22}H_{42}O_3$	Hydroxy-Docosanoic Acid	250 ± 15	96.8	--	Calc

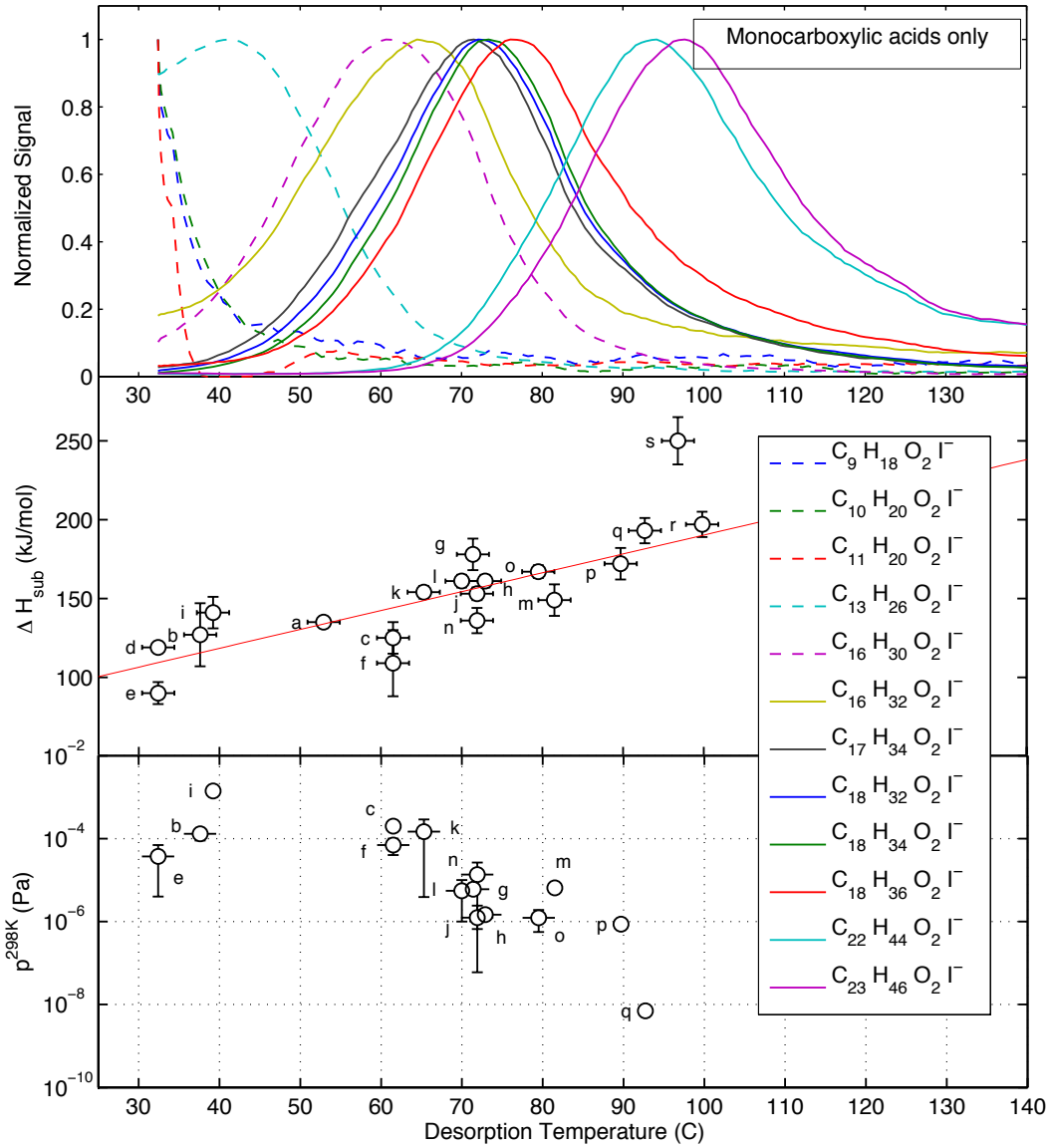

Figure 6. Top. Thermograms from a series of mono carboxylic acids are shown as detected by a FIGAERO-HRToF-CIMS operating in the field employing Iodide adduct ionization. The acids were part of a single mixture of several organic compounds that was deposited manually *via* a micro-syringe onto the FIGAERO filter, and then the filter was subjected to a standard thermal desorption. The series of acids each desorb with a single signal maximum (mode), signifying little contamination from other ions (see text). Middle. ΔH_{sub} values for compounds in the deposited mixture from the literature (open symbols) or estimated here using group contribution methods (dots) are plotted *versus* the temperature at which the compound's signal reached a maximum in the desorption (T_{max}, see text). Letters correspond to the identifier (ID) listed in Table 2. Bottom. Literature vapor pressures over the solid scattered with maximum desorption temperature. The relationship is less clear than enthalpy of sublimation likely resulting from the larger relative uncertainties in the measured vapor pressures.