

1 Supplement information for  
 2 Ylisirniö et. al. AMT-2020-254

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4 S1. Different  $P_{sat}$  values used in FIGAERO-ToF-CIMS calibrations in different studies

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6 *Table S1. Collection of literature-based  $P_{sat}$  (Pa) values used in various published FIGAERO*  
 7 *calibrations.*

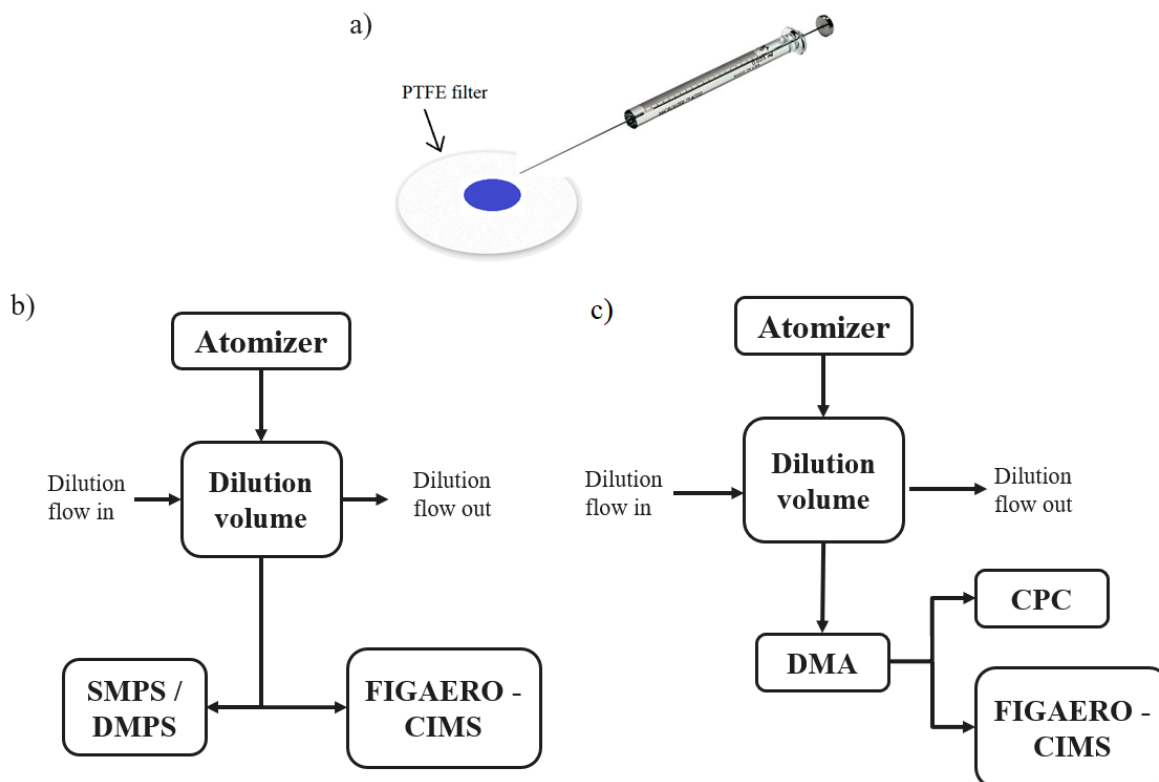
<b>Saturation pressure (Pa)</b>	<b>Lopez-Hilfiker et al., (2014)</b>	<b>Stark et al., (2017)</b>	<b>Nah et al., (2019)</b>	<b>Bannan et al., (2019)</b>	<b>Ye et al., (2019)</b>
Glutaric acid		$6.7 \times 10^{-4}$	$1 \times 10^{-3}$	$1 \times 10^{-3}$	$4 \times 10^{-4}$
Cis-Pinonic acid	$6 \times 10^{-5}$	0.03	$7.8 \times 10^{-4}$	$7.79 \times 10^{-4}$	
Pimelic acid	$1 \times 10^{-4}$		$2.6 \times 10^{-4}$		
Erythritol			$6.3 \times 10^{-5}$		
Palmitic acid	$1 \times 10^{-4}$		$2.0 \times 10^{-5}$		$5 \times 10^{-5}$
Azelaic acid	$6 \times 10^{-6}$	$6 \times 10^{-6}$	$7.4 \times 10^{-6}$		
Oleic acid	$1 \times 10^{-6}$				
Stearic acid	$1 \times 10^{-5}$		$2.5 \times 10^{-6}$		
Sebacic acid	$1.5 \times 10^{-6}$		$1.5 \times 10^{-6}$		
Behenic acid	$7 \times 10^{-4}$		$4.9 \times 10^{-8}$		
Oleic acid	$(0.066 - 2.66) \times 10^{-5}$				
Tricarballic acid		$3 \times 10^{-7}$			$3.1 \times 10^{-7}$
Pinic acid	$6 \times 10^{-5}$	$4.3 \times 10^{-5}$		$3.2 \times 10^{-5}$	$9.3 \times 10^{-5}$
Citric acid					$2.7 \times 10^{-10}$
Camphoric acid					$2 \times 10^{-4}$
Dodecanoic/lauric acid					0.01
Succinic acid				$1.3 \times 10^{-3}$	
Malonic acid				$6.2 \times 10^{-4}$	
Adipic acid				$1.8 \times 10^{-4}$	
Suberic acid				$2.23 \times 10^{-5}$	

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11 S2. Measurement schematics



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 13 *Figure S1. Panel a) illustration of the syringe deposition method. Measurement setup schematics for*  
 14 *the atomizer method either with b) polydisperse particles or c) monodisperse particles. The dilution*  
 15 *volume is used in the atomizer method to ensure complete evaporation of the solvent before particle*  
 16 *characterization.*

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 18 S3. Measured  $T_{max}$  values

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 20 *Table S2. Average  $T_{max}$  values ( $^{\circ}\text{C}$ ) and standard deviations based on three repetitions, as shown in*  
 21 *Figure 3 panel a). Used  $P_{sat}$  (Pa), based on Krieger et al., (2018), are shown in the bottom row.*

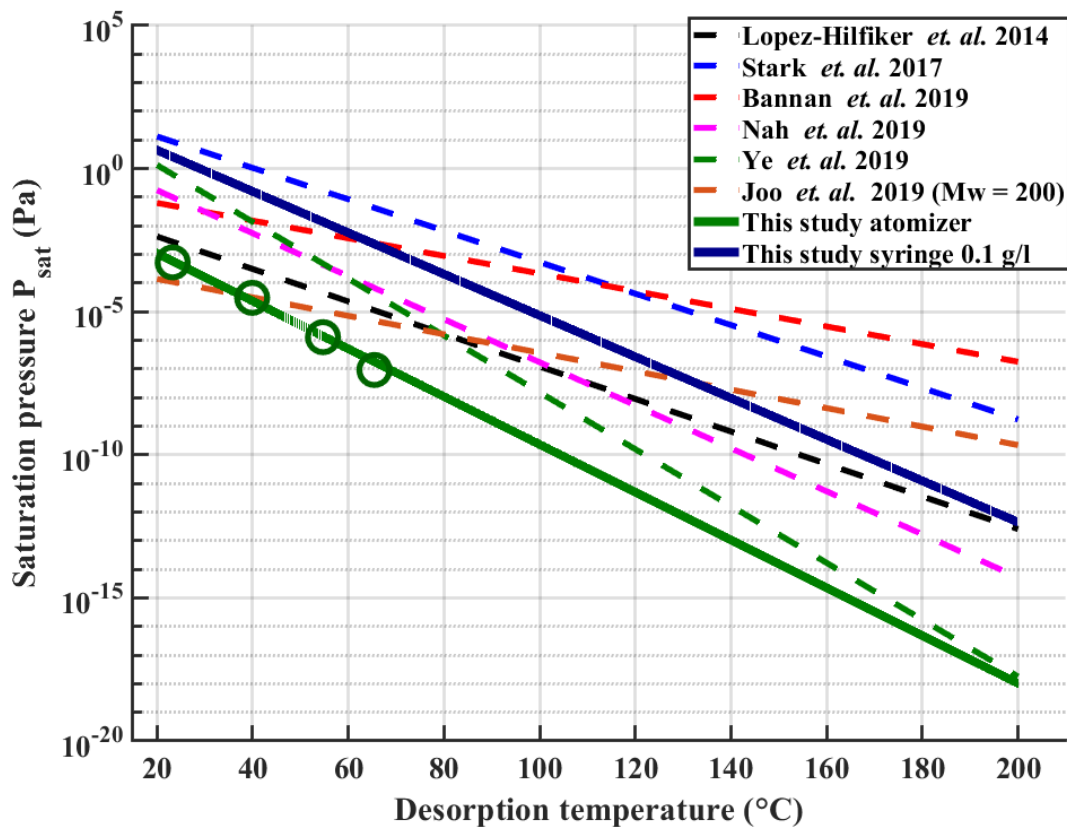
Experiment	PEG-4	PEG-5	PEG-6	PEG-7	PEG-8
Conc. 0.1 g L <sup>-1</sup>	49.9±4.4	74.6 ± 3.1	94.6 ± 2.8	110.9 ± 2.4	123 ± 2
Conc. 0.01 g L <sup>-1</sup>		38.5 ± 1.2	58.5 ± 1.5	76.8 ± 1.2	90.9 ± 0.9
Conc. 0.003 g L <sup>-1</sup>		36.7 ± 1.9	57 ± 2.5	73.1 ± 2.9	88.7 ± 2.8
Atomizer		23.3 ± 0.5	39.9 ± 0.4	54.7 ± 0.4	65.5 ± 0.2
Saturation pressure (Pa)	0.0169	5.29 x 10 <sup>-4</sup>	3.05 x 10 <sup>-5</sup>	1.29 x 10 <sup>-6</sup>	9.2 x 10 <sup>-8</sup>

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25 Table S3. Average  $T_{max}$  values ( $^{\circ}\text{C}$ ) and standard deviations based on three repetitions, as shown in  
 26 Figure 3 panel b). Used saturation pressure (Pa) values are shown in the bottom row.

Experiment	Palmitic acid	Pimelic acid	Oleic acid	Azelaic acid	Stearic acid	Sebacic acid
Conc. 0.5 g L <sup>-1</sup>	55.8 ± 0.3	54 ± 0.1	61.8 ± 2.8	63.3 ± 0.3	64.7 ± 0.5	73.1 ± 0.1
Conc. 0.1 g L <sup>-1</sup>	48.9 ± 1	46.1 ± 1.1	51.2 ± 1.8	54.8 ± 1.2	55.8 ± 1	62.6 ± 1.2
Conc. 0.01 g L <sup>-1</sup>	40.6 ± 1.2	39.5 ± 2	43.9 ± 2.8	41.5 ± 1.5	44.8 ± 2.5	46.1 ± 0.4
Atomizer	36.6 ± 0.6	34 ± 0.4	34.7 ± 0.8	40.2 ± 0.7	43.5 ± 0.6	49.4 ± 1
Saturation pressure (Pa)	1.4 x 10 <sup>-4</sup>	1.3 x 10 <sup>-4</sup>	1 x 10 <sup>-5</sup>	6 x 10 <sup>-6</sup>	1 x 10 <sup>-6</sup>	1.47 x 10 <sup>-6</sup>

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 29 Figure S2. Repeated Fig. 1 (dashed lines) with calibration lines from this study added for the atomizer  
 30 method (green solid line) and the syringe method (for a solution concentration of 0.1 g L<sup>-1</sup>, solid blue  
 31 line). Both lines are for 30 min ramping times and the atomizer measurements used polydisperse aerosol  
 32 with a median particle size of 60 nm. Green circles show the measured data where the line have been  
 33 fitted.

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35 S4.  $P_{sat}$  of higher order PEGs

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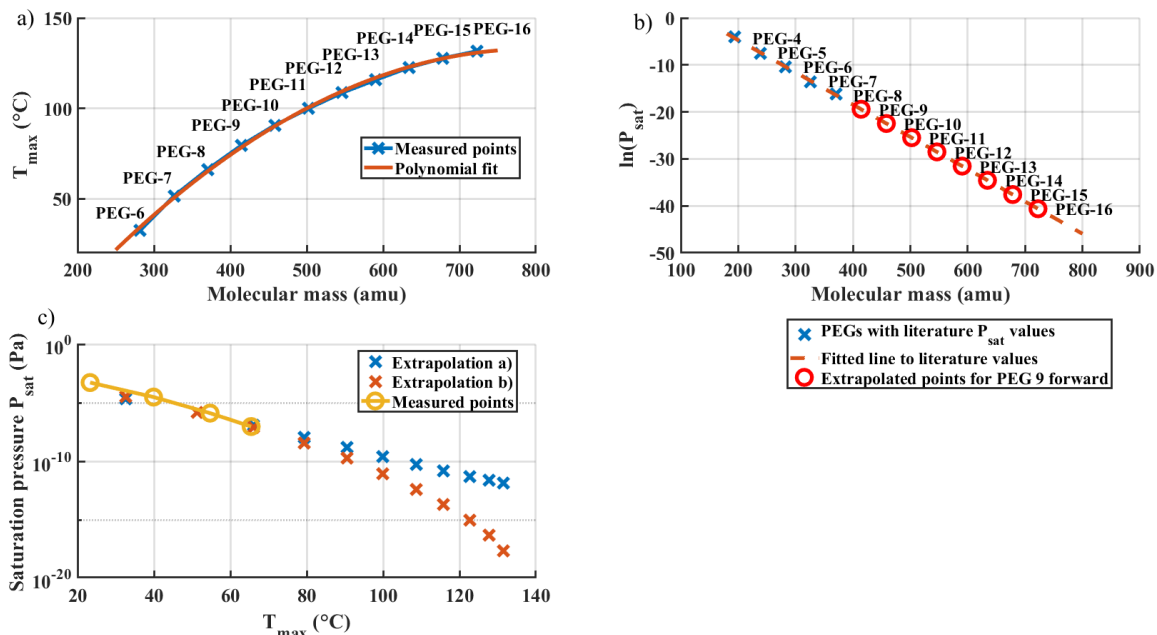
37 We performed additional  $T_{max}$  measurements of an atomized PEG-400 solution (Sigma Aldrich),  
 38 which contains different PEGs so that the average molecular mass of the solution is about 400 g/mol.  
 39 Detected PEGs ranged from PEG-6 to PEG-16. Fig. S3 a) shows measured  $T_{max}$  values of different  
 40 PEGs versus the molecular mass of the compounds. The measured points follow well a second order  
 41 polynomial fitted to the points. It should be noted that  $T_{max}$  values of PEG-400 are about 5-7 °C higher  
 42 than values measured for individual PEGs, possibly due to additional stabilization compounds in the  
 43 product. Figure S3 b) shows a somewhat bold log-linear extrapolation of saturation pressures from  
 44 measured PEGs (4-8) up to PEG-16.

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46 In Fig S3 c) we show two extrapolations for  $P_{sat}$  vs. measured  $T_{max}$ . Extrapolation a) was done by  
 47 substituting  $T_{max}$  values in eq. (2) with the polynomial fit to molecular mass ( $T_{max} = d Mw^2 + e Mw +$   
 48  $f$ , where  $Mw$  is molecular weight and  $d$ ,  $e$  and  $d$  are fitted constants), shown in Fig. S3a, while using  
 49 fit coefficients  $a$  and  $b$  from eq. (2). I.e., extrapolation a) estimates  $P_{sat}$  values based on molecular  
 50 mass. Extrapolation b) was done by directly fitting the normal logarithm of  $P_{sat}$  vs molecular mass  
 51 (Fig. S3 b).

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53 As can be seen, the two extrapolation methods for  $P_{sat}$  lead to substantially different extended  
 54 calibration curves in the higher desorption temperatures. Our results anyhow strongly suggest that  
 55 higher order PEGs could be used for extending the volatility calibration range, if their saturation  
 56 vapor pressures were established by accurate independent measurements or estimated with high  
 57 enough certainty.



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59 *Figure S3. Panel a) measured  $T_{max}$  values (crosses) vs. molecular mass of the PEGs contained in the*  
 60 *PEG-400 mixture, and a polynomial fit applied to the data. Panel b) natural logarithm of saturation*  
 61 *pressure vs. PEG molecular mass, and a linear fit to the literature-supported data sub-set (crosses),*  
 62 *extrapolated to extend to all other PEGs (circles). Panel c) saturation pressure  $P_{sat}$  vs  $T_{max}$  extrapolated*  
 63 *to cover all PEG, using extrapolations based on the fitted functions in panels a) and b).*

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