Supplement of Atmos. Meas. Tech., 14, 355–367, 2021
https://doi.org/10.5194/amt-14-355-2021-supplement
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Supplement of

On the calibration of FIGAERO-ToF-CIMS: importance and
impact of calibrant delivery for the particle-phase calibration

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

Table S1. Collection of literature-based $P_{sat}$ (Pa) values used in various published FIGAERO calibrations. $P_{sat}$ values used in this study are taken from Lopez-Hilfiker et al., (2014).

| Saturation pressure (Pa) | Lopez-Hilfiker et al., (2014) | Stark et al., (2017) | Nah et al., (2019) | Bannan et al., (2019) | Ye et al., (2019) | (Wang et al., 2020) | This study |
|--------------------------|--------------------------------|----------------------|--------------------|-----------------------|------------------|---------------------|------------|
| Glutaric acid            | 6.7 x 10^{-4}                  | 1 x 10^{-3}          | 1 x 10^{-3}        | 4 x 10^{-4}           | 2.6 x 10^{-4}    |                     |
| Cis-Pinonic acid         | 6 x 10^{-5}                    | 0.03                 | 7.8 x 10^{-4}      | 7.79 x 10^{-4}        |                  |                     |
| Pimelic acid             | 1.3 x 10^{-4}                  | 2.6 x 10^{-4}        |                    |                       |                  | 1.3 x 10^{-4}      |
| Erythritol               |                                |                      | 6.3 x 10^{-5}      |                       |                  |                     |
| Palmitic acid            | 1.4 x 10^{-4}                  | 2.0 x 10^{-5}        | 5 x 10^{-5}        | 2.8 x 10^{-5}         | 1.4 x 10^{-4}    |                     |
| Azelaic acid             | 6 x 10^{-6}                    | 6 x 10^{-6}          | 7.4 x 10^{-6}      | 1.4 x 10^{-6}         | 6 x 10^{-6}      |                     |
| Oleic acid               | 1 x 10^{-6}                    |                      |                    |                       |                  |                     |
| Stearic acid             | 1 x 10^{-5}                    | 2.5 x 10^{-6}        |                    |                       | 1 x 10^{-6}      |                     |
| Sebacic acid             | 1.5 x 10^{-6}                  | 1.5 x 10^{-6}        |                    |                       | 1.5 x 10^{-6}    |                     |
| Behenic acid             | 7 x 10^{-4}                    | 4.9 x 10^{-6}        |                    |                       |                  |                     |
| Oleic acid               | 1 x 10^{-5}                    |                      |                    |                       |                  | 1 x 10^{-5}        |
| Tricarballylic acid      | 3 x 10^{-7}                    |                      | 3.1 x 10^{-7}      | 3.1 x 10^{-7}         |                  |                     |
| Pinic acid               | 6 x 10^{-5}                    | 4.3 x 10^{-5}        | 3.2 x 10^{-5}      | 9.3 x 10^{-5}         |                  |                     |
| Citric acid              |                                |                      |                    | 2.7 x 10^{-10}        | 2.7 x 10^{-10}   |                     |
| Camphoric acid           |                                |                      |                    | 2 x 10^{-4}           | 2 x 10^{-5}      |                     |
| Dodecanoic/lauric acid   |                                |                      |                    | 0.01                  |                  |                     |
| Succinic acid            |                                |                      | 1.3 x 10^{-3}      |                       |                  |                     |
| Malonic acid             |                                |                      | 6.2 x 10^{-4}      |                       |                  |                     |
| Adipic acid              |                                |                      | 1.8 x 10^{-4}      |                       |                  |                     |
| Suberic acid             |                                |                      |                    | 2.23 x 10^{-5}        |                  |                     |
S2. Measurement schematics

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

S3. Measured $T_{\text{max}}$ values

Table S2. Average $T_{\text{max}}$ values ($^\circ$C) and standard deviations based on three repetitions, as shown in Figure 3 panel a). Used $P_{\text{sat}}$ (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$^{-1}$        | 49.9±4.4| 74.6 ± 3.1| 94.6 ± 2.8| 110.9 ± 2.4| 123 ± 2  |
| Conc. 0.01 g L$^{-1}$       | 38.5 ± 1.2| 58.5 ± 1.5| 76.8 ± 1.2| 90.9 ± 0.9|         |
| Conc. 0.003 g L$^{-1}$      | 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$^{-4}$| 3.05 x 10$^{-5}$| 1.29 x 10$^{-6}$| 9.2 x 10$^{-8}$|
Table S3. Average $T_{\text{max}}$ values (°C) and standard deviations based on three repetitions, as shown in 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$^{-1}$  | 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$^{-1}$  | 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$^{-1}$ | 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$^{-4}$ | 1.3 x 10$^{-4}$ | 1 x 10$^{-5}$ | 6 x 10$^{-6}$ | 1 x 10$^{-6}$ | 1.47 x 10$^{-6}$ |

Figure S2. Repeated Fig. 1 (dashed lines) with calibration lines from this study added for the atomizer method (green solid line) and the syringe method (for a solution concentration of 0.1 g L$^{-1}$, solid blue line). Both lines are for 30 min ramping times and the atomizer measurements used polydisperse aerosol with a median particle size of 60 nm. Green circles show the measured data where the line have been fitted.
S4. Error analysis for Figure 8.

Errors for deposited mass on the filter shown in Fig. 8 are determined with propagation of error for both methods. For syringe deposition the equation is of the form

\[ m_{\text{syringe}} = V_s C_s, \]

where \( V_s \) (ml) is the injected volume and \( C_s \) (g l\(^{-1}\)) is the mass concentration of the solution. The solution was prepared by weighting the analyte with a microscale and solving it to 200 ml of ACN to make 0.2 g/l solution. The stock solution was then diluted into 50 ml solution of 0.01 g/l concentration. To account for the dilution, the equation now becomes to form

\[ m_{\text{syringe}} = \frac{V_{\text{syr}}}{V_{\text{pip}}} \frac{V_{\text{fin}}}{V_{\text{sto}}} m_{\text{scale}}, \]

where \( V_{\text{syr}} \) is deposited volume to the filter, \( V_{\text{pip}} \) is volume pipetted from stock solution to make the dilute solution, \( V_{\text{fin}} \) is the volume final dilute solution, \( V_{\text{sto}} \) is the volume of the stock solution and \( m_{\text{scale}} \) is the analytes mass measured with the microscale. Now denoting

\[ R = \frac{V_{\text{syr}}}{V_{\text{pip}}} \frac{V_{\text{fin}}}{V_{\text{sto}}}, \]

we get the equation to the form

\[ m_{\text{syr}} = R m_{\text{scale}} \]

and formula for propagation of error becomes

\[ \Delta m_{\text{syringe}} = \sqrt{\left( \frac{\partial m_{\text{syr}}}{\partial R} \right)^2 \Delta R^2 + \left( \frac{\partial m_{\text{syr}}}{\partial m_{\text{scale}}} \right)^2 \Delta m_{\text{scale}}^2}, \]

\[ \Delta m_{\text{syringe}} = \sqrt{m_{\text{scale}}^2 \Delta R^2 + R^2 \Delta m_{\text{scale}}^2}, \]

where

\[ \Delta R = \sqrt{\left( \frac{V_{\text{pip}}}{V_{\text{fin}} V_{\text{sto}}} \right)^2 \Delta V_{\text{syr}}^2 + \left( \frac{V_{\text{syr}}}{V_{\text{fin}} V_{\text{sto}}} \right)^2 \Delta V_{\text{pip}}^2 + \left( -\frac{V_{\text{syr}} V_{\text{pip}}}{V_{\text{fin}}^2 V_{\text{sto}}} \right)^2 \Delta V_{\text{fin}}^2 + \left( -\frac{V_{\text{syr}} V_{\text{pip}}}{V_{\text{fin}} V_{\text{sto}}^2} \right)^2 \Delta V_{\text{sto}}^2}. \]

When using Class A glassware, tolerances for different measurement flasks can be found online.

 Atomizer deposition

Amount of deposited particulate mass can be calculated with equation

\[ m_{\text{atom}} = F t V_c, \]

where \( F \) is the flow through the filter [m\(^3\) s\(^{-1}\)], \( t \) [s] is the collection time and \( V_c \) [\( \mu \)g m\(^{-3}\)] is the particle mass concentration in the sample air. The propagation of error formula for this equation is of the form

\[ \Delta m_{\text{atom}} = \sqrt{\left( \frac{\partial m_{\text{atom}}}{\partial F} \right)^2 \Delta F^2 + \left( \frac{\partial m_{\text{atom}}}{\partial t} \right)^2 \Delta t^2 + \left( \frac{\partial m_{\text{atom}}}{\partial V_c} \right)^2 \Delta V_c^2}, \]

\[ \Delta m_{\text{atom}} = \sqrt{(t V_c)^2 \Delta F^2 + (F V_c)^2 \Delta t^2 + (F t)^2 \Delta V_c^2}. \]
where $\Delta F = 0.01 \times F$ (flow meter accuracy), $\Delta t = 1$ (assuming swift movement of the tray). When using monodisperse aerosol sampling method as shown in Fig. S1 b), particle mass concentration can be calculated by assuming spherical particle shape as

$$V_c = \frac{\rho d_p^3 \pi n}{6},$$

where $\rho$ is the density of the aerosol particles, $d_p$ is the set monodisperse particle size and $n$ is particle number concentration measured with CPC. The uncertainty of $V_c$ is then

$$\Delta V_c = \sqrt{\left(\frac{3\rho d_p^2 \pi}{6}\right)^2 \Delta d_p^2 + \left(\frac{\rho d_p^3 \pi}{6}\right)^2 \Delta n^2},$$

where $\Delta d_p = 0.01 \times d_p$ and $\Delta n = 0.1 \times n$ with instrumentation described in Sect. 2.4.

Y-axis errors for Figure 8 are calculated by assuming Poisson-type measurement error for CIMS measurements (Yan et al., 2016)

$$e_i = \frac{s_i}{\sqrt{\Delta t}} + a,$$

where $s_i$ is the measured signal, $\Delta t$ is the difference of two-time steps and $a$ is constant accounting for electrical noise.

When integrating over such data, we assumed error to be of the form

$$\Delta I = \pm \sqrt{1.96 \times \text{std}(S)^2 + \sum e_i^2},$$

where $\text{std}(S)$ is the standard deviation over the whole thermogram.

5. $P_{sat}$ of higher order PEGs

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

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

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

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