Online Supplementary Material

Development of a personal aerosol sampler for monitoring the particle-vapour fractionation of SVOCs in workplaces †

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† Online Supplementary Material available

Materials and methods

The personal D-GPS aerosol sampler

The portable D-GPS sampler was designed to match the aerosol sampling characteristics of the GGP-Mini sampler (Breuer et al., 2015), therefore the shape and dimensions of the D-GPS inlet are similar to that of the GGP-Mini. The D-GPS sampler consists of a conical shaped inlet attached to a thermal desorption (TD) tube with the purpose of achieving an aspiration velocity of 1.25 m s^{-1} for the flow rate of 0.5 l min^{-1}.

The inlet is attached to a denuder consisting of 22 silicone rubber tubes (55 mm length, 0.3 mm inner diameter (ID), 0.5 mm outer diameter (OD), Detakta, Germany) inside a TD tube (89 mm length, 6.35 mm OD). The denuder is used to trap incoming SVOCs vapour, while allowing the particle phase to pass through its channels with minimal losses. The gaseous molecules reach the silicone rubber tube walls due to their high diffusion coefficients and are sorbed by the silicone rubber. A filter holder assembly (Figure S1) made of stainless steel, connects a denuder upstream, an adsorber tube downstream and a 13 mm filter (MN 85/90, Munktell, Sweden) in between.

The adsorber tube downstream of the filter was used to account for the particle mass that evaporates from the filters (*blow-off* effect). TD tubes of the same dimensions as the denuders described above were used. Three layers of graphitised carbon black (GCB) adsorber, each weighing 60 mg, separated by glass wool, were inserted into the TD liners. The three GCB adsorbers were, in the direction of the airflow: Carbotrap® B (20-40 mesh), Carbotrap® Y (20-40 mesh) and Carboxen® 569 (20-45 mesh) (Supelco GmbH, Germany). The adsorbers were placed in this order to trap semi-volatile compounds evaporated from particulates collected on the filter first and more volatile compounds in the second and third layer. The subsequent thermal desorption of the adsorber layers was done in reverse order.

The sampler can be attached to a worker by using a clip and is protected from accidental breakage by plastic tubes. The sampler is operated with a personal sampling pump (GilAir Plus, Sensidyne, USA).

Laboratory characterisation of the personal D-GPS aerosol sampler

The sampler was tested for its ability to separately trap vapours and particles of test aerosols under controlled laboratory conditions. The measurements were taken in a HPZ 90/50 temperature-controlled chamber (Heraeus Vötsch, Germany). The sampling setup is illustrated in Figure S2. *n*-Hexadecane was chosen as a model substance for the controlled laboratory study mainly based on its vapor pressure, partitioning at room temperature and low toxicity, which favoured the handling thereof. Substances with higher vapour pressures (i.e. *n*-tetradecane) would partition mostly in the gas phase, while substances with a lower vapour pressure (i.e. *n*-octadecane) will partition, for the given laboratory setup and conditions, mostly in the particle phase. The decision was therefore taken to use *n*-hexadecane for the purpose of comparing the actual partition of an SVOC aerosol to that of a reference system for a range of particle/vapour ratios (25-71 % as particles). The gas-particle fractionation of the generated *n*-hexadecane aerosols was measured with two or three D-GPS samplers in parallel and compared to an *on-line* reference. The *on-line* reference consisted of a flame ionisation detector (FID, model 109A, JUM Engineering, Germany) for the quantification of the total hydrocarbon content (total aerosol mass concentration) and an optical particle counter (OPC, model Welas 3000, Palas, Germany) to measure the particle mass concentrations of the generated aerosol. Here, series measurements were carried out with both *on-line* reference devices. The gas phase mass concentration was determined by subtracting the measured particle mass concentration from the measured total aerosol mass concentration.

A Sinclair-La Mer type aerosol generator (model SLG 270, Topas Germany), was used to produce the *n*-hexadecane aerosols. The generated aerosols were diluted with nitrogen and conveyed to a flow tube. The gas-particle fractionation, as measured by the *on-line* reference was varied by adjusting the temperature, the number of condensation nuclei and the dilution ratio. A detailed description of the aerosol generation system and reference method can be found in the literature (Dragan et al., 2014; Breuer et al., 2015; Dragan et al., 2015).

Parallel sampling with both *on-line* reference and *off-line* D-GPS samplers was done through the use of an isokinetic sampling head, as described by Breuer and Dragan (Breuer et al., 2015; Dragan et al., 2015). The isokinetic sampling head ensured that the samples taken by each instrument were representative. The D-GPS samplers were connected to GilAir Plus sampling pumps, set to a flow rate of 0.335 l min^{-1} for 10 min. After sampling, the TD tubes were hermetically sealed using TD endcaps (Shimadzu, Japan), while the filters were placed in capped glass vials. Prior to analysis, the filters were placed in TD tubes. Quantification of the *off-line* samples was done by thermal desorption coupled to gas chromatography-mass spectrometry (TD-GC-MS). Regarding the *off-line* sampling measurements, the minimum number of replicates was 4, while the minimum number of *on-line* series measurement replicates was 2.

The denuders, filters and adsorbers were thermally extracted using a TD-20 thermal desorber (Shimadzu, Japan) and analysed with a GC-MS system (GC-MS-QP2010 Ultra, Shimadzu, Japan). In this way, a routine analysis of the three substrates can be established, while also minimising the use of solvents. The thermal desorption was performed with a desorption flow rate of 60 ml min^{-1} at 250 °C and lasted 30 min for the silicone rubber denuders, 300 °C and 30 min for filters and 350 °C and 45 min for adsorbers. Extracted compounds were at first concentrated on a Tenax TD trap cooled at 5 °C and then re-desorbed at 330 °C with a split ratio of 500 to the GC. Separation was done on a BP20 polar column

(0.22 mm ID, 0.25 µm film thickness, SGE, Australia). The column was heated at a rate of 20 °C min^{-1} up to 150 °C, 5 °C min^{-1} up to 350 °C followed by 10 min of isothermal heating, with a total run time of 65 min (denuder and filter) and 80 min (adsorber). The mass spectrometer was operated in scan mode for m/z 35-500, scan rate 3.3 Hz. Quantification of the analytes mass was performed using a 6-point calibration curve.

In order to evaluate the implemented *off-line* replicate samples, a statistical outlier test (TRIMMEAN) was carried out using MS-Excel. Here, no statistical outliers were found. The percentual particle and gas phase fractions in Figure 2 were calculated with the following formulas:

Particle phase [%] = Particle concentration [mg m^{-3}] / Total concentration [mg m^{-3}] * 100
Vapour phase [%] = Vapour concentration [mg m^{-3}] / Total concentration [mg m^{-3}] * 100
Total concentration [mg m^{-3}] = Particle concentration [mg m^{-3}] + Vapour concentration [mg m^{-3}]

References

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Dragan GC, Karg E, Nordsieck HO*, et al.* (2014) Short-term evaporation of semi-volatile n-alkane aerosol particles: experimental and computational approach. *Environmental Engineering and Management Journal*; 13: 1775-85.

Figures and tables

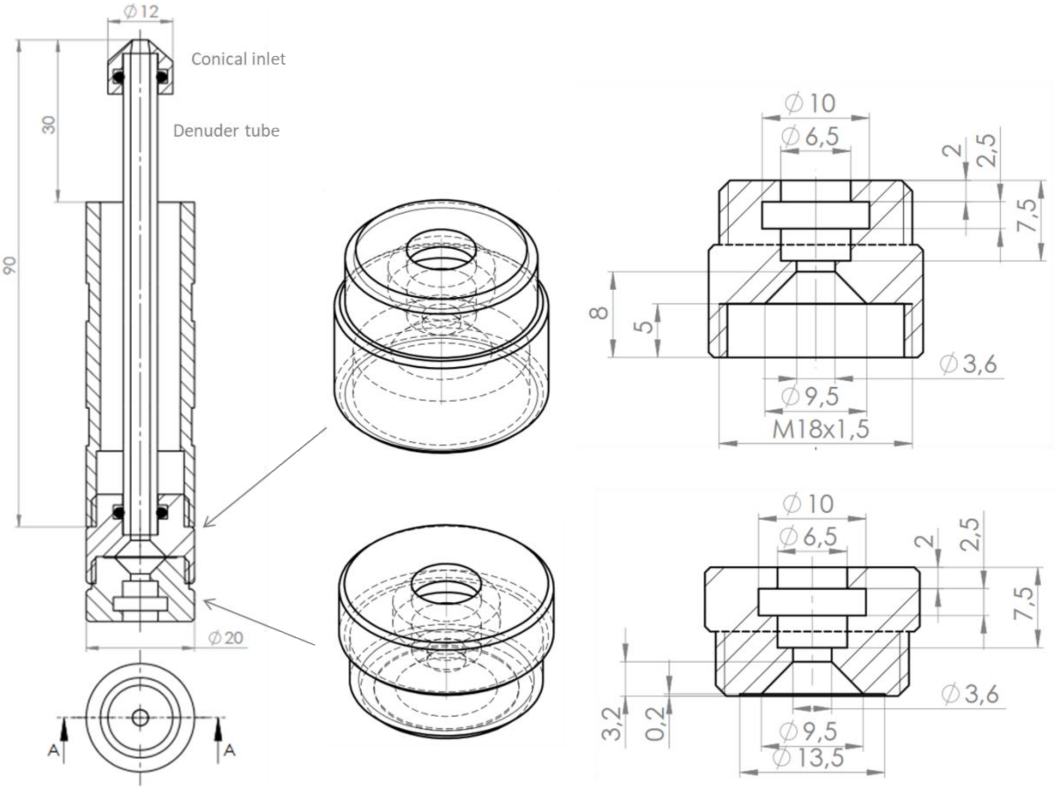

Figure S1 Technical drawing of a filter holder assembly of the D-GPS (denuder-gas-particle separation) sampler made of stainless steel.

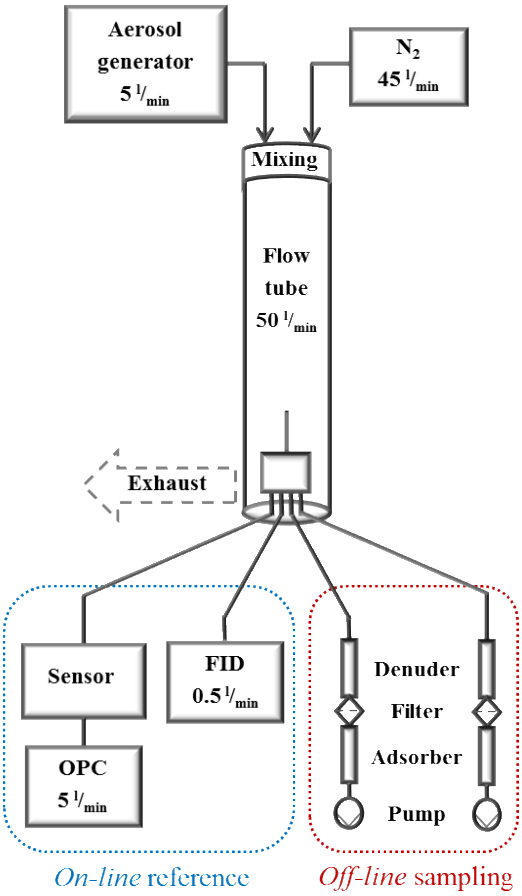

Figure S2 Experimental setup for the laboratory characterisation of the D-GPS personal aerosol sampler with *n*-hexadecane aerosols. The aerosols vapour and particle fractions were sampled with two (or three) *off-line* D-GPS samplers (consisting of a denuder, filter and adsorber) in parallel and were compared to the *on-line* reference. The *on-line* reference consisted of the optical particle counter (OPC) and flame ionisation detector (FID).

Table S1 Aerosol, particle and gas phase mass concentrations [mg m^{-3}] determined via *on-line* reference and *off-line* D-GPS sampler for six different particle to gas phase mass concentration ratios (right column) of an *n*-hexadecane aerosol as determined by the *on-line* technique. The minimum number of replicates was 4 (*off-line* sampling) and 2 (*on-line* series measurements). Each ± value represents one standard deviation. Each value given for the *off-line* aerosol mass concentration in brackets is the percentual recovery rate. Each ± value represents one standard deviation.

	On-line	***Off-line***	**Mass conc. ratio**
Aerosol mass concentration [mg m^{-3}]	7.7 ± 0.24	6.8 ± 0.20 (88.5 ± 2.3 %)	25:75
	8.6 ± 0.16	8.1 ± 0.28 (93.4 ± 4 %)	29:71
	9.3 ± 0.08	8.2 ± 0.08 (88.9 ± 0.7 %)	32:68
	9.3 ± 0.16	8.9 ± 0.55 (95.9 ± 6.1 %)	51:49
	10.1 ± 0.21	9.7 ± 0.34 (95.8 ± 3.6 %)	52:48
	10.6 ± 0.12	12 ± 0.48 (112.9 ± 4.5 %)	71:29
Particle mass concentration [mg m^{-3}]	1.9 ± 0.05	1.1 ± 0.13	25:75
	2.5 ± 0.11	1.4 ± 0.28	29:71
	3 ± 0.07	1.2 ± 0.16	32:68
	4.7 ± 0.11	3.4 ± 0.41	51:49
	5.3 ± 0.06	3.4 ± 0.32	52:48
	7.5 ± 0.23	6 ± 0.27	71:29
Gas phase mass concentration [mg m^{-3}]	5.8 ± 0.13	5.7 ± 0.13	25:75
	6.1 ± 0.21	6.7 ± 0.10	29:71
	6.3 ± 0.15	7.1 ± 0.16	32:68
	4.6 ± 0.25	5.5 ± 0.21	51:49
	4.8 ± 0.17	6.3 ± 0.13	52:48
	3.1 ± 0.21	6 ± 0.38	71:29