

On the challenges of measuring semi-volatile organic compound aerosols using personal samplers

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Abstract Aerosols from Semi-Volatile Organic Compounds (SVOCs) are usually partitioned in workplace air between the particulate and vapour phases. Personal samplers that are used for the occupational monitoring of such aerosols should be able to trap both phases. In this study the dynamic changes in the partitioning of model SVOC aerosols are shown from an experimental point of view. Furthermore, the partitioning between filter and adsorber substrates of a personal sampler were compared for both aerosol sampling and spiking technique. In every comparison the spiking technique had more SVOC left on the filter substrate than by aerosol sampling. The difference between methods ranged from 13 to 52%. Based on these results, further measurements were undertaken to study the differences in evaporation rates of filters clogged with SVOC aerosol particles and that of spiked filters.

Herausforderungen bei der Messung semi-volatiler organischer Substanzen mittels personengetragener Aerosolsammler

Zusammenfassung Aerosole aus semi-volatilen organischen Substanzen (SVOC) können gleichzeitig als Partikel und als Dampf in der Luft auftreten. Personengetragene Aerosolsammler sollen in der Lage sein, beide Phasen solcher Aerosole aufzunehmen. In dieser Studie werden dynamische Änderungen der Gas-Partikel-Verteilung von SVOC-Modellaerosolen aus experimenteller Sicht dargestellt. Darüber hinaus werden die Verteilungen von Substanzen auf Filtern und Adsorbieren eines Aerosolsammlers nach Anwendung der Aerosolprobenahme- und Dotiertechnik miteinander verglichen. Alle Vergleiche ergaben, dass Filter nach Anwendung der Dotiertechnik eine höhere SVOC-Masse als bei der Aerosolprobenahme aufwiesen. Der Unterschied zwischen beiden Methoden betrug in der Massenkonzentration 13 bis 52%. Aufgrund dieser Ergebnisse wurden weitere Messungen zur Untersuchung von Verdampfungsraten auf zweierlei Filtern (dotiert oder mit SVOC-Aerosolpartikeln belegt) durchgeführt.

1 Introduction

Aerosols from Semi-Volatile Organic Compounds (SVOCs) represent an important challenge to industrial hygienists due to toxicological as well as sampling issues [1]. SVOCs are often partitioned between the particulate and vapour phases of an aerosol. Their presence in workplace air is most commonly monitored using personal samplers equipped with fibrous filters. However, collected particulate mass

can evaporate from the filters [2] or vapour can condense onto collected particles or on the filter. Due to these evaporation-condensation effects, the personal aerosol samplers currently used do not reflect the particle-vapour-distribution of SVOC aerosols accurately. If a sampler fails to collect both phases of an aerosol, a significant underestimation of airborne pollutants could be the consequence.

Since sampling artefacts could lead to a biased health risk assessment, separate particle-vapour quantification can be important. The separate analysis of both phases should be considered because inhaled SVOC aerosol particles and vapours behave differently when inhaled in the respiratory tract. Vapours for example can be exhaled if they are not soluble in body fluids. If this is not the case, vapours are adsorbed into the lung tissue. Furthermore, the deposition of particles in the respiratory tract depends on the particle aerodynamic size [3; 4], with smaller particles reaching deeper into the lung.

One possibility to account for the vapour-particle partitioning of SVOC aerosols is to use a denuder as a vapour trapping tool. Because of their different diffusion coefficients, particles will flow through the denuder channels, while vapour molecules will diffuse to the denuder wall where they should be ab- or adsorbed [5]. Small and portable denuders like the multi-channel silicone rubber traps are very suitable for both the vapour collection of nonpolar SVOCs and the transmission of particles in the 0.3 to 2 μm size range [6; 7]. Therefore, artefact-free separation of both SVOC phases may be possible if using low flow rate personal air samplers combined with multi-channel silicone rubber traps.

For the development of personal samplers and methods for the analysis of SVOC aerosols, many laboratories resort to "filter spiking" experiments [8], where known amounts of compounds of interest are placed on filters as a way to simulate the sampling and partitioning of workplace aerosols. Downstream of the filters, adsorbers can be attached to account for the mass evaporated from filters. Air is sampled using a personal sampling pump and the filter and sorbent can be thermally desorbed or extracted with a solvent and analysed. Based on the subsequent results, the spiking method provides an indication if the tested SVOCs should be sampled as particulate phase on filters, as vapour phase on adsorbers or mixed-phase aerosol on combined filter-adsorber personal samplers.

2 Materials and Methods

2.1 Generation and characterisation of SVOC aerosols

Aerosols from several SVOCs (diethylene glycol, n-tetradecane, n-hexadecane, n-octadecane) with various particle sizes were generated using a Topas SLG 270 (Topas GmbH, Germany) aerosol generator and mixed with nitrogen in a Flow Tube (FT) inside a temperature controlled environmental chamber (HPZ 90/50, Heraeus Vötsch, Germany);

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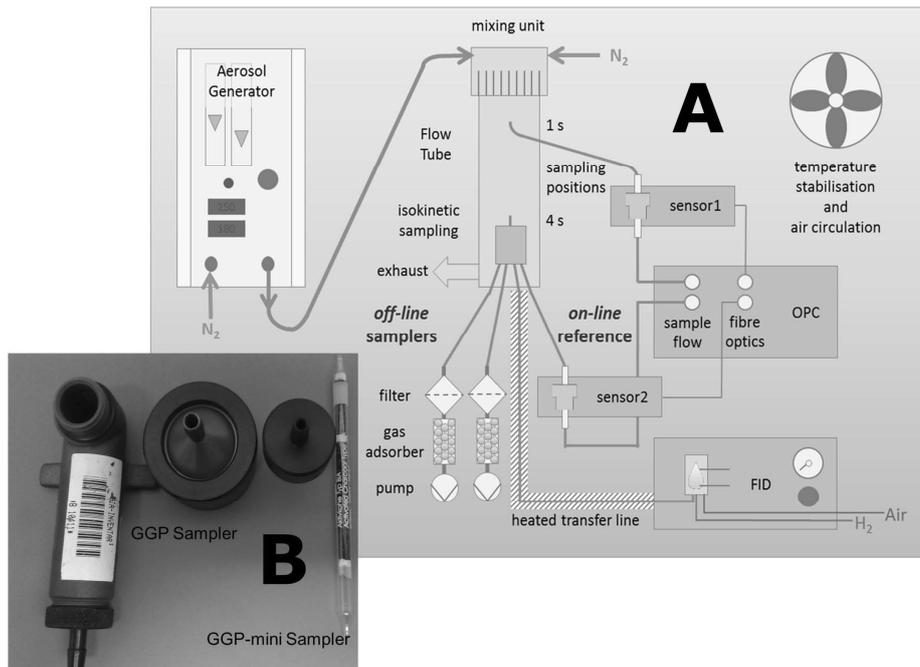


Figure 1. A: Experimental setup inside the temperature-controlled chamber. B: GGP and GGP-mini aerosol personal samplers used for the occupational monitoring of SVOCs in Germany.

Figure 1-A). The chamber was operated for the purpose of this study at temperatures ranging from 10 to 35 °C.

The particle-vapour partitioning of the generated SVOC aerosols in the FT was assessed using an on-line reference [9; 10] comprised of a Welas 3000 optical particle sizer (OPC, Palas GmbH, Germany) for the determination of the particle mass and a JUM 109A flame ionisation detector (FID, JUM Engineering GmbH, Germany) for measuring the total SVOC concentration. The OPC comprised two separate sensors placed in the upper and lower part of the FT, separated by about three seconds of residence time (Figure 1). By alternately measuring with both sensors, the changes in the particle size distribution (PSD) and therefore in particle mass could be monitored within the residence time between the sensors. Interested readers can find more details about this setup in the following referenced paper [9].

Off-line samplers like GGP and GGP-mini (Figure 1-B) [11 to 13] were used to determine the particle-vapour par-

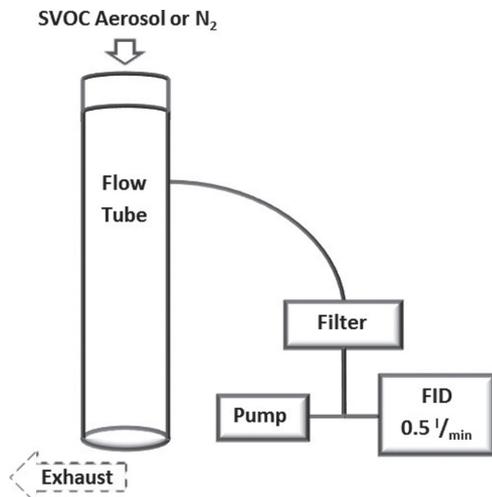


Figure 2. Experimental setup for the determination of SVOC evaporation from filters.

tioning of SVOC aerosols as measured by filter-adsorber type personal aerosol samplers. Parallel measurements using on-line and off-line methods were conducted to investigate and predict the sampling bias regarding the particle-vapour partitioning caused by off-line samplers.

2.2 Filter spiking

Glass fibre filters with a diameter of 37 mm (MN 85/90, Macherey-Nagel) were spiked with known quantities of SVOCs by means of a microliter syringe. Three SVOCs of different volatility were tested with regard to their partitioning between filter and adsorber substrates after simulating two hours of sampling. Air was drawn through the filter-adsorber combination at a flow rate of 3.5 l/min for two hours. Subsequent analysis of the filters and adsorbers by solvent extraction allowed comparing the partitioning of the spiking

technique with that of aerosol sampling (Table).

2.3 Monitoring of the mass evaporated from clogged filters

A FID was set up downstream of a filter holder containing 37 mm filters. The FID measured the evaporation flux of SVOCs during particle collection and during the subsequent evaporation of collected particles or spiked filters (Figure 2). A sampling pump was used to reach the target flowrate of 3.5 l/min.

3 Results and discussion

3.1 Dynamic partitioning of model SVOC aerosols in ambient air

Aerosols of SVOC will usually be partitioned between the gas and particle phase. The particle-vapour partitioning of an aerosol can fluctuate strongly with changing temperature and residence time. Figure 3 shows the mass percentage of particles (the difference up to 100 % represented by the vapour phase) from an 18 mg/m³ generated n-hexadecane aerosol inside the flow tube. The particle mass was measured at two locations in the FT separated by three seconds of residence time (Figure 3, left axis). The aerosol distribution at 11 °C was dominated by the condensed phase, with up to 90% particle fraction. In contrast, at 35 °C only 20% of the aerosol could be found in the particle phase. The particle mass evaporated between the two sampling points also varies with temperature, with about 2 mg/m³ evaporated particle mass at 15 °C, 5 mg/m³ at 25 °C and 7 mg/m³ at 30 °C. This goes to show that the partitioning of SVOC aerosols is continuously changing with temperature and distance from the emission source. Furthermore, the separate quantification of the gaseous and particulate phases might be required for compounds with a degree of toxicity that is strongly depending on the physical state of the aerosol.

The relative humidity of the ambient air can also play a major role on the partitioning of water-soluble SVOCs and on the time required for such droplets to evaporate. Figure 4 shows the PSD of diethylene glycol (DEG) particles with an initial diameter of 1 μm and the PSD of these particles after three seconds of residence time at 70, 40 and 0% of relative humidity (RH). Figure 4 shows that at 0% RH DEG particles evaporated completely. By contrast, at higher RH values, higher water content is being sorbed by the DEG particles, leading to a homogeneous mixture and therefore decreasing the vapour pressure on the droplet-air interface. As a result, water-soluble particles will remain in the air for longer time periods.

3.2 Assessment of the partitioning between the filter and adsorber substrates for the spiking technique in comparison to aerosol sampling

Filter spiking followed by drawing of air with a sampling pump is widely used in laboratories that develop samplers and methods for SVOC sampling. However, this technique might not be fully comparable to sampling of particle-vapour mixtures. The Table shows the partitioning obtained for both aerosol sampling and spiking measurements. For each of the six comparisons, the amount of material remaining on the filters was higher for the spiking tests. Conversely, more SVOC was transferred in the sorbent tube by the passing air in the case of aerosol sampling. The differences between the two techniques ranged from 13 to 52%. Neither the volatility of the substances tested nor the concentrations affected the differences observed. This goes to show that even though the results obtained with spiking technique provide a good estimation if a compound should be sampled using filters (particles), sorbent tubes (vapours) or a combination of both (mixed phase), differences to actual aerosol sampling will arise. This should be kept in mind, especially when compounds tested are almost entirely found on the filters. Though the spiking test might recommend the sampling of the compound only with filter cassettes, finer aerosol particles might lead to evaporative losses that should be accounted for.

3.3 Assessment of the evaporative flux behind filters clogged with particles or spiked

Figure 5 shows the time-dependent variation of the DEG mass measured behind a filter during collection of DEG aerosol particles (black dots) and evaporation of the sampled DEG droplets (grey dots). During the initial phase of sampling, the vapour concentration passing the filter is low and increases rapidly until it stabilises at about 90% of the final concentration. At first, the fibrous filter will adsorb vapour and will act like a source of vapour once a sufficient

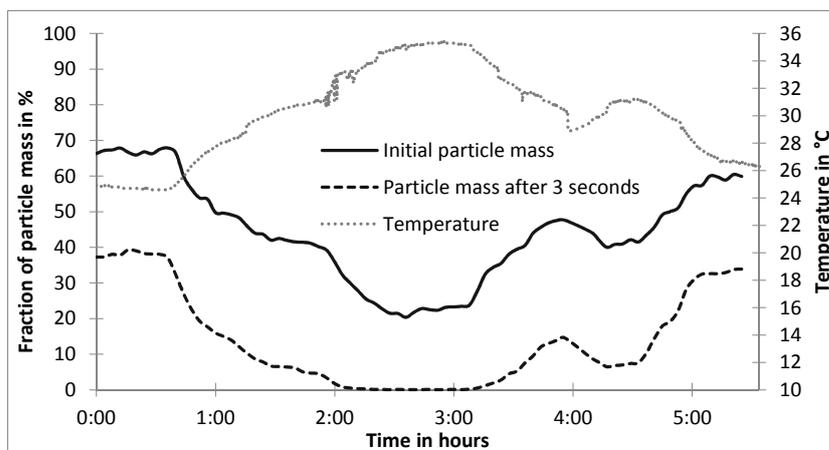
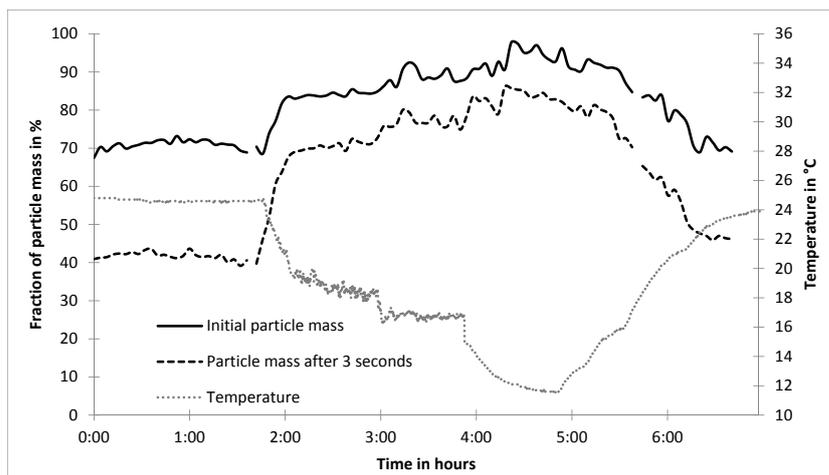


Figure 3. Time-dependent variation of the percentual particle mass (left axis) in relation to temperature in the experimental chamber (right axis) for n-hexadecane aerosol (mass concentration of 18 mg/m^3). The upper figure shows the variation for decreasing temperature (25 \rightarrow 11 $^\circ\text{C}$) while the bottom figure for increasing temperature (25 \rightarrow 35 $^\circ\text{C}$).

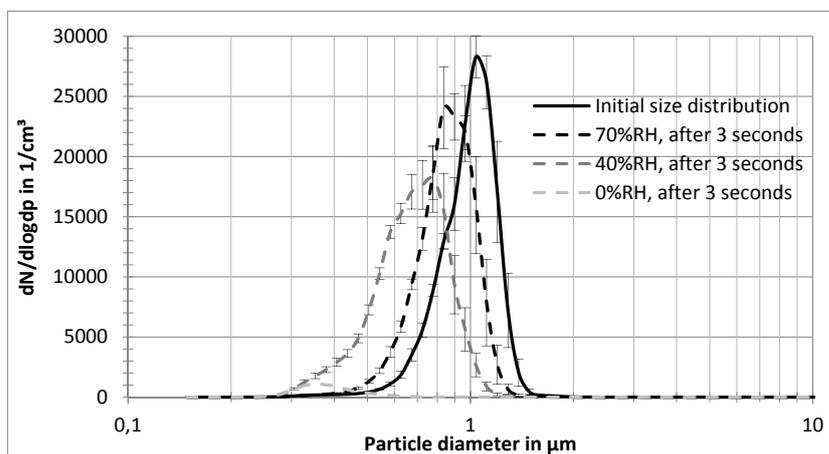


Figure 4. Particle size distribution of the initially generated diethylene glycol (DEG) aerosol and after three seconds of residence time for 70, 40 and 0% relative humidity (RH).

amount of particles are trapped. At this point, the vapour concentration exiting the filter reaches a plateau. After turning off the aerosol generator, only pure nitrogen was aspirated through the filter. Despite the fact that no further DEG was found upstream of the filter, the vapour concentration behind it remained constant. This goes to show that the collected particles evaporate and saturate the aspirated air flow with vapours. The main parameter limiting the evaporation of SVOC from the filter is the ability of

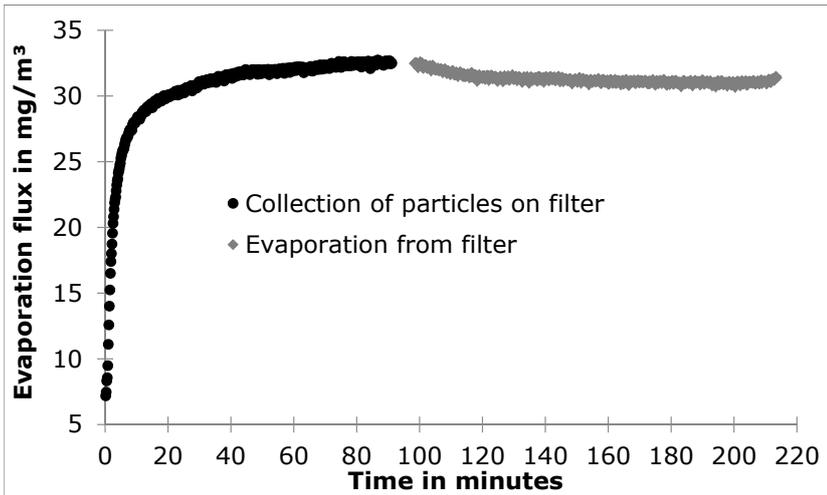


Figure 5. Time-dependent concentration of diethylene glycol (DEG) vapour measured behind a filter during the collection and subsequent evaporation from the filter.

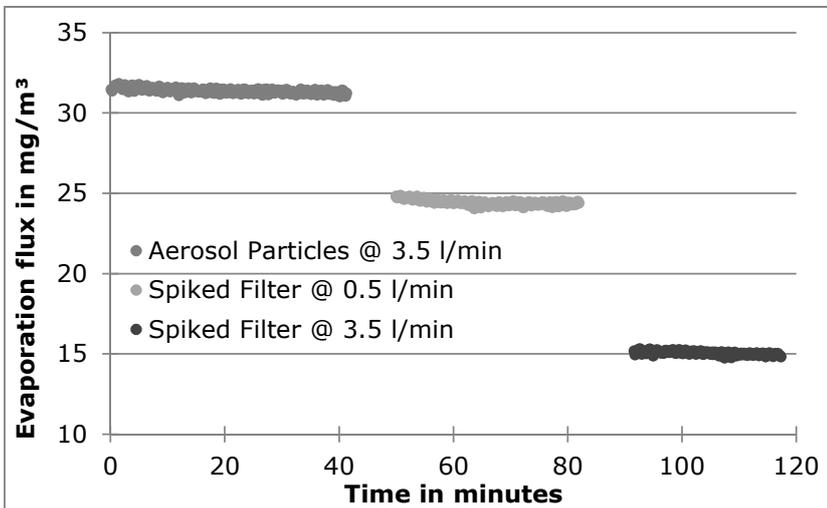


Figure 6. Evaporation flux measured after filters clogged with aerosol particles and spiked with diethylene glycol (DEG).

Partitioning of SVOCs – comparison between filter spiking technique and aerosol sampling.

Substance	Method	Filter		Adsorber		Total in mg/m ³	Difference in %
		in mg/m ³	in %	in mg/m ³	in %		
n-Octadecane	Spiking	2.6	82.3	0.6	17.7	3.2	29.1
	Aerosol	1.7	53.1	1.5	46.9	3.2	
n-Hexadecane	Spiking	5.2	75.1	1.7	24.9	6.9	52.0
	Aerosol	1.9	23.2	6.3	76.8	8.2	
n-Hexadecane	Spiking	20.9	84.8	3.7	15.2	24.6	41.3
	Aerosol	12.3	43.5	16	56.5	28.3	
n-Tetradecane	Spiking	12.6	19.0	53.6	81.0	66.2	19.0
	Aerosol	0	0.0	71.7	100	71.7	
n-Tetradecane	Spiking	45.0	34.3	86.0	65.7	131.0	25.7
	Aerosol	13.2	8.6	139.5	91.4	152.7	
n-Tetradecane	Spiking	71.0	41.3	101.0	58.7	172.0	13.3
	Aerosol	56.8	28.0	146.4	72.0	203.2	

the sampled air to transport the vapours. The maximum amount of material being transported is given by the gas phase saturation concentration, which is a function of a compounds vapour pressure at the given temperature.

The vapour concentration downstream of DEG-spiked filters was measured at two flow rates and compared to that from the particle-clogged filter. By comparing the evaporation flux between particle-clogged and spiked filters, a difference of more than factor two is visible (Figure 6). With the spiking technique, larger and more compact droplets will be placed on the filters. This in turn leads to a lower surface to volume ratio compared to the sampling of aerosol particles. This reduced surface will lead to substantially less evaporation through diffusion of material into the air stream passing the filter. By increasing the flow rate through the filter, the relative residence time of the aspirated air and therefore the contact time with the diffusing vapour decreases. This is reflected in Figure 6, where an almost 60% increase in the evaporation flux was measured when reducing the flow rate from 3.5 to 0.5 l/min. This goes to show that lower flow rates through the filter will lead to an increased enrichment of the aspirated air with vapour.

4 Conclusions and outlook

The results presented in this study furthermore demonstrate the dynamic partitioning of SVOC aerosols between the particle and vapour phases. This dynamic partitioning should be accounted for in cases where different toxicological effects are expected for each phase. Improved personal samplers will be needed to achieve this goal [14]. Furthermore it was shown that the spiking technique used for method development and prediction of partitioning underestimate evaporation from filters compared with actual aerosol sampling. Alternative ways to micro-dose smaller droplets on filters [15] in a defined pattern might lead to results that are closer to actual aerosol sampling.

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