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APPLICATION OF THE STEAM JET AEROSOL COLLECTOR (SJAC) FOR DIFFERENTIAL MEASUREMENTS OF ORGANIC COMPOUNDS IN THE GAS VERSUS PARTICLE PHASE.

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ABSTRACT

A new approach of using the Steam Jet Aerosol Collector (SJAC) for the determination of semivolatile organic compounds has been investigated. Gas phase and particle phase were investigated separately. The SJAC, an alternative for filter based sampling method, is one of condensational growth sampling systems which uses water as a condensational liquid. In our setup for the determination of the gas phase compounds an extra XAD adsorbent cartridge was applied. Collection of gas phase fraction takes place after particle phase collection; therefore no denuder technique is used. Collection efficiency for particles was examined with hydrophobic soot and octacosane particles. In order to estimate the amount of bias caused by the transfer of components from gas phase to the particle fraction, streams of individual organic compounds with different polarity in synthetic air were examined. Laboratory tests showed negligible amounts of gas phase material measured in the particle fraction and high collection efficiency for hydrophobic particles.

Key Words: Semi Volatile Organic Compounds, Aerosol Sampling, Gas-/Particle Portioning

1. INTRODUCTION

One of the most important issues of an analytical procedure is a representative sample. Both health and ecological impacts of semivolatile organic compounds (SVOC) depend on their chemical species and physical form of appearance. Therefore it is very important to be able to determine their concentration in the gas phase (Gp) and particulate phase (PM).

Theoretical predictions were developed to describe SVOC gas/particle partitioning. They are based either on the adsorption model using subcooled liquid vapour pressure (Pankow 1994), the absorption model using octanol-air partition coefficient K_{OA} (Finizio et al., 1997; Harner and Bildeman 1998), or combine black carbon adsorption and organic matter absorption (Dachs and Eisenreich 2000). Lohmann and Lammel (2004) showed that theoretical values of gas-particle partition coefficient K_p calculated according to different models disagree with each other and developed another model which combines diesel soot adsorption and organic matter absorption. Thus, finding a really unified method to predict SVOC partitioning seems to be rather difficult.

Aerosol collection of SVOC on the other hand, carried out most often by means of (denuder)/filter/adsorber techniques, is subjected to significant biases. Major physical sampling artefacts are caused by evaporation of components from PM (collected on the filter and inside denuder, blow off) and adsorption of Gp (to the filter and PM collected on the filter, blow on). Even 100 % overestimation of PM because of blow on or 20 % underestimation - from blow off can occur (Mader et al., 2003). Another source of error is chemical degradation. Because PMs exposed to high amount of air containing reactive gases (e.g. O_3, NO_x,) which pass through the collected material, can undergo chemical reactions, hence the determined amounts of target analytes can be inaccurate (e.g. for PAH Schauer et al., 2003).

Corrections for SVOC measurements developed so far still suffer from their underlying yet unrealistic assumptions (equilibrium condition for backup filter, 100% denuder efficiency) or do not take into account all possible biases during sampling (evaporation of SVOC from PM inside denuder). Recent comparison of filter/adsorber, filter/filter/adsorber , denuder/filter/adsorber and electrostatic precipitator/adsorber methods used for diesel exhaust measurements showed that none of these methods can be applied for accurate determination of K_p (Volckens and Leith 2003).

Aerosol growth technique is widely used in Condensation Particle Counters with butanol as a condensing liquid, and recently also with water. The Steam Jet Aerosol Collector (SJAC, Khlystov et al., 1995) and Gas and Aerosol Monitoring System (GAMS, Simon and Dasgupta 1995) were the first approaches using water condensation onto PM for chemical measurements of aerosol. This technique was later applied to other methods with different technical setups: Versatile aerosol concentration enrichment system (VACES, Kim et al., 2001), Particle-into-Liquid Collector (PILC, Weber et al. 2001), a condensation-growth and impaction system, (C-GIS, Sierau et al. 2003). All those approaches were specifically interested in water soluble fraction of PM.

SJAC was originally designed for online determination of inorganic ions (NH_4^+, SO_4^{2-}, NO_3^-, Cl^-) in the particle phase. In this concept the aerosol passes through a wet denuder (Keuken et al. 1989) in order to remove gas phase components (NH_3, HNO_3, HCl, SO_2). Rapid mixing the aerosol (cold stream) with the injected water steam (hot stream) creates supersaturation conditions. This causes condensational growth of particles to droplets sizes of several micron. Those are removed by means

of the cyclone with the cut point aerodynamic diameter of about 2 µm and are subsequently analysed online for inorganic compounds by ion chromatography.
In our work we adapted the original concept of the SJAC for sampling water soluble as well as insoluble organic compounds both in particle and gas phase.

2. EXPERIMENTAL PART

2.1. Technical setup

SJAC modification is based on the reverse to original sampling order concept. In this setup no denuder technique is used therefore collection of gas phase components follows particle phase collection (Figure 1). Ideally Gp and PM go through inlet to the mixing chamber, where steam is injected. Then water vapour starts to condense onto PM because of supersaturated conditions. Grown particles are removed by cyclone like in the original setup (aqueous solution of particle phase sample P). Gp compounds either absorb in water steam condensed inside the cooler (aqueous solution of gas phase sample G_1) or are adsorbed in the adsorbent cartridge containing XAD4 (gas phase sample G_2). The addition of the cooler prior to XAD4 adsorber was necessary in order to get rid of the high amount of water from the cyclone exhaust, which would cause increase of the pressure drop (XAD4 swelling) and lower sorption efficiency of the adsorbent.

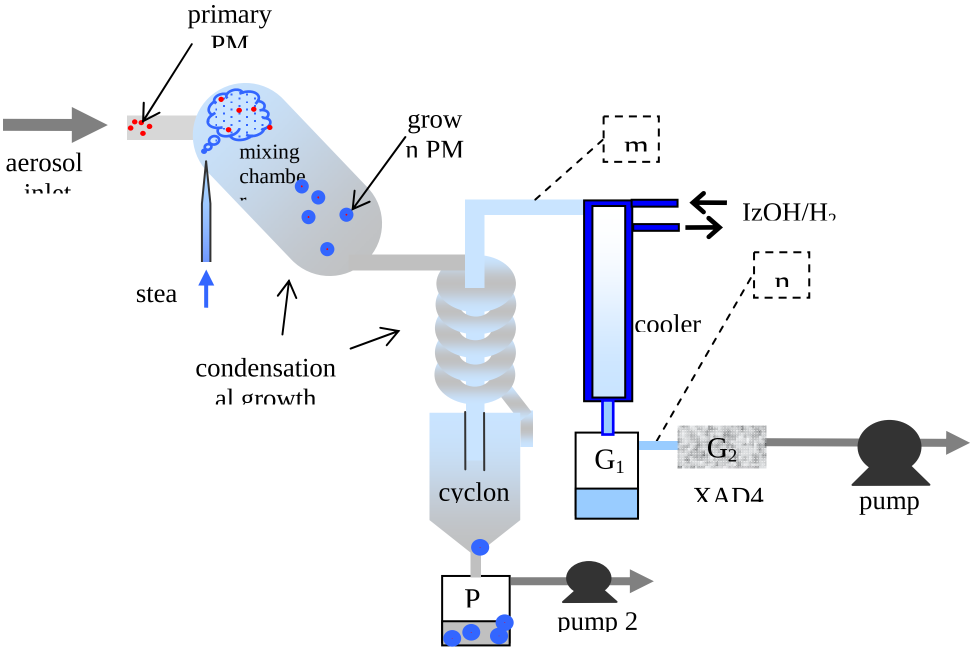


Figure 1. Setup of the modified SJAC for differential measurements of organic compounds in the gas and particle phase; P – particle sample, G_1, G_2 – gas phase samples; m, n – location of the SMPS sampling lines.

SJAC working conditions were as follows: flow rate of main air pump 1: 1m^3/h; flow rate of pump 2 (cyclone): ca. 200 ml/min, cooler temperature: 1°C. Steam was supplied by an electrically heated boiling pot (Figure 2a). Power optimum of boiling pot was found to be – 1.05 A, 200V. It corresponds to ca. 2.7 ml/min steam flow and is slightly higher then optimum steam flow rate used for inorganic compounds measurements (2.5 ml/min; Slanina et al., 2001).

Additionally a resistive heated capillary (Figure 2b) was tested for steam generation A stainless steel capillary (1 m length, 0.2 mm ID, 0.5 mm OD) was connected to the mixing chamber of the SJAC by means of a Teflon adapter and on the other side to a HPLC pump operating at flow rates 1.5 – 4 ml/min. In order to generate steam a direct electric current (2.5 A) was applied to the capillary.

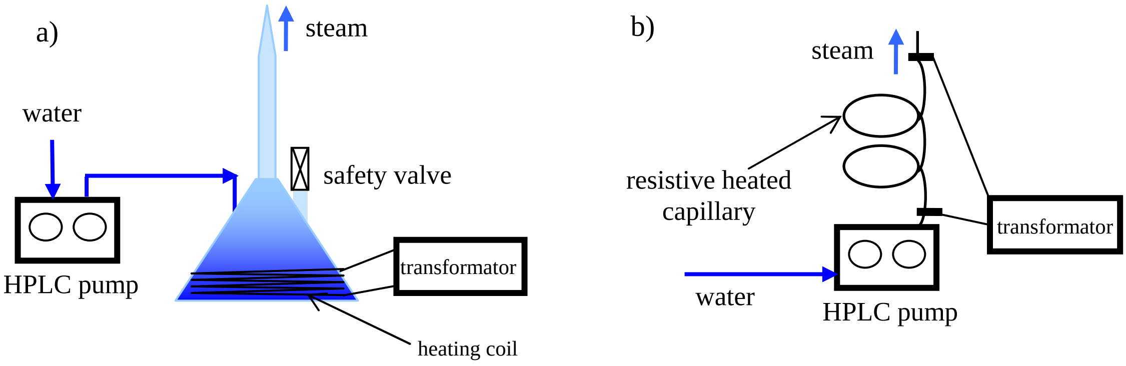


Figure 2. Different steam generators used with SJAC – original steamer – boiling pot (a) and resistive heated steal capillary (b)

2.2. Particle collection efficiency

Particle measurements were made by means of Scanning Mobility Particle Sizer (SMPS, Model 3936, TSI, USA) in the size range of 14.1 – 737 nm. PM measurements with different steam parameters were carried out and compared to measurements without steam application.

Particle collection efficiency was examined with two types of non volatile hydrophobic particles – soot and octacosane PM.

Soot particles were delivered from spark generator (GFG 1000, Palas, Germany). The smallest particles (with mean diameter of ca. 35 nm) were obtained with minimum spark frequency of about 3 Hz and were immediately diluted by means of synthetic air. 170 nm particles were generated by 800 Hz spark frequency and diluted like previously. 250 nm particles were generated by 300 Hz spark frequency and using a 20 L glass vessel for coagulation growth of primary soot particles.

SMPS sampling line was placed upstream the cooler (location “m” – Figure 1). In this case, in order to remove excess water, which would disturb the SMPS measurements, an additional heater and dryer in the sampling line of the SMPS were applied.

Octacosane condensation particles were generated by purging constant flow (ca. 150 ml/min) of nitrogen through a heated impinger vial containing octacosane. Subsequent cooling of the octacosane vapour led to homogeneous nucleation. A monodisperese aerosol with median diameter of 70 nm was obtained.

Because of the large active surface of the dryer, used in the experiments with the carbon particles, octacosane adsorption to drying material took place. Therefore SMPS sampling line had to be moved downstream the cooler (location "n" – Figure 1). In this case water concentration was much lower than in position "m" allowing for omission of heater and dryer. SMPS measurements in location "n" are subject to overestimation of SJAC efficiency because of additional supersaturation caused by the cooler. Yet negligible differences in SJAC collection efficiency of soot particles obtained from sampling location "m" and "n" proved validity of SMPS measurements of octacosane particles in position "n".

2.3. Transfer of gas phase to particle fraction

Pure vapours of individual SVOC (heptadecane, undecanol, naphthalene and metoxyacetophenol) with dilution air were applied in order to estimate the amount of bias caused by the transfer of components from gas phase to the particle fraction. Vapour generation took place simply by purging constant flow of particle free nitrogen (20 - 100 ml/ min, depending on the compound) through a thermostated impinger vial containing analysed compound (Figure 3).

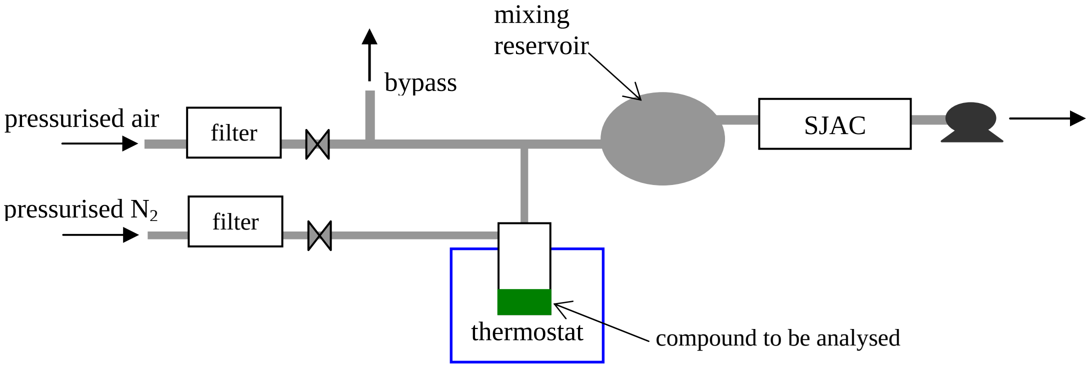


Figure 3. Gas phase measurements setup

2.4. Sample preparation

For aqueous samples – P and G_1 a liquid-liquid ultrasonic-assisted extraction with dichloromethane (3 x 30ml) was applied. XAD4 samples – G_2 were extracted by means of Accelerated Solvent Extraction (ASE® 200, Dionex, USA) based on modified Dionex Application Note 347 (Dionex Extraction Applications) – acetone/hexane 30/70 (v/v); 3 cycles; 100 °C, 100 bar. In order to minimise the blank concentration of XAD4 samples ASE extraction cells were used as an adsorbent container during sampling. Both extraction methods were followed by drying the extracts with sodium sulphate and reduction of solvent. For quantitative analysis GC-MS analysis (HP 6890) based on internal standard addition method was applied.

3. RESULTS AND DISCUSSION

3.1. Particle collection efficiency

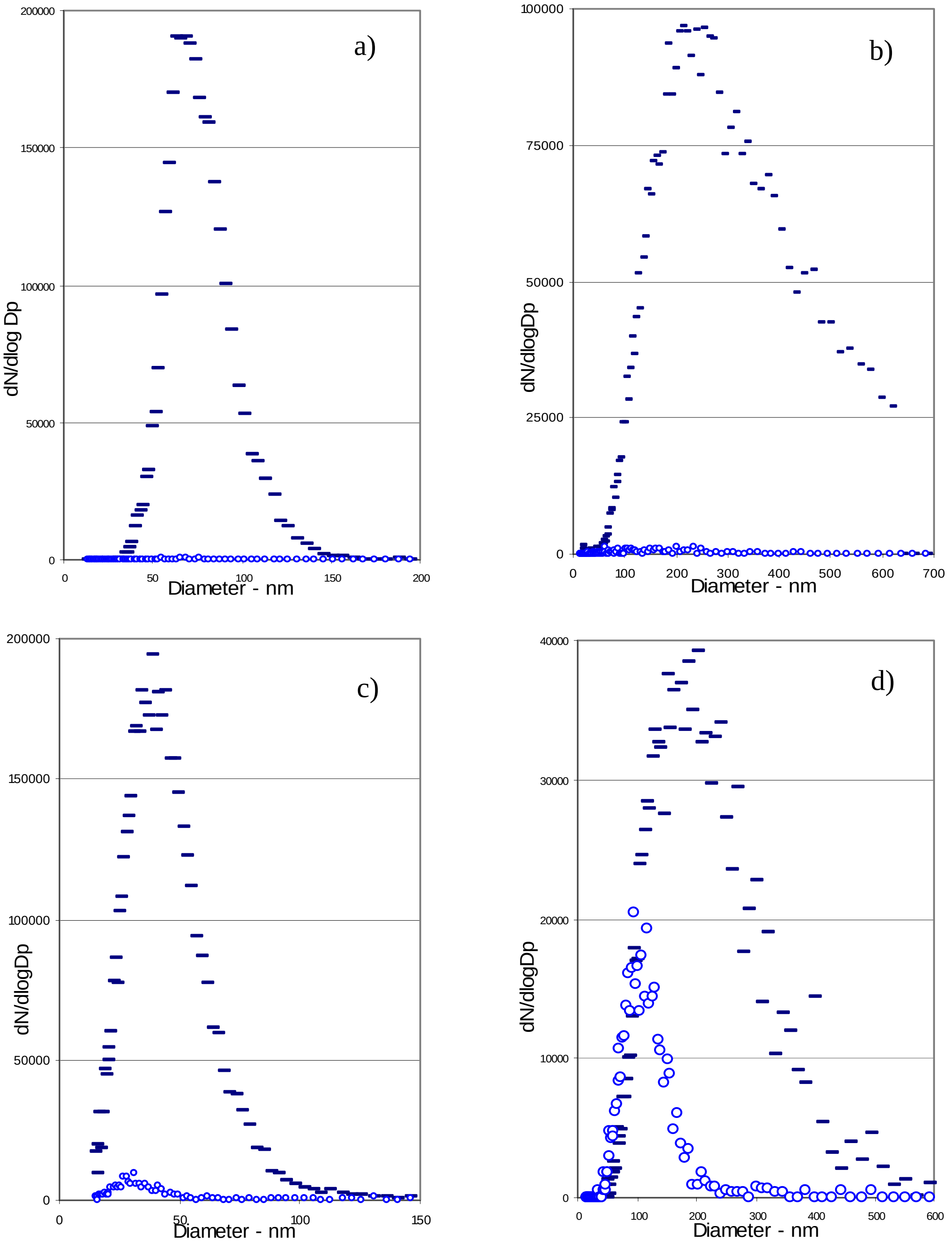


Figure 4. SJAC particle collection efficiency; primary size distribution ----- , size distribution after SJAC ooooo ; a – octacosane, mean diameter 70 nm, b – soot, mean diameter 250 nm, c – soot, mean diameter 35 nm, d – soot, mean diameter 170 nm with heated capillary as a steamer.

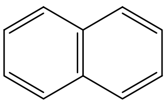
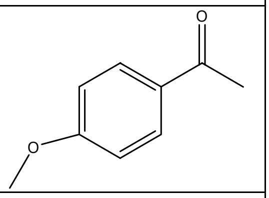
Hygroscopic growth of organic particles is weaker as for inorganic compounds (Weingartner et al., 1996). Therefore there was concern that the particle collection efficiency especially for small non polar particles will be low. The applied cyclone together with preceding mixing chamber working under supersaturation conditions was found to remove over 99% (number of particles) of soot particles as well as octacosane particles in general (Figure 4 a, b). Only for the smallest soot particles, with the mean diameter of ca. 35 nm, efficiency was slightly lower – 95% (Figure 4 c).

Applying a different steam generation technique (restitive heated steal capillary, Figure 2 b) with optimum steam flow rate of 2ml/min did not increase the collection efficiency – on the contrary – it was clearly lower (ca. 66% of particles number) than in case of original SJAC's boiling pot (Figure 4 d).

3.2. Transfer of gas phase to particle fraction

Wide ranges of water solubility and polarity of four individual test compounds were applied for gas phase bias measurements in order to cover a broad range of compounds in the ambient aerosol and to check those two properties impacting on behaviour of Gp in SJAC sampler (Table 1).

Table 1. Properties* of test compounds and concentration ranges applied in the experiments.

component	heptadecane	undecanol	naphthalene	metoxyacetophenol
water solubility [mg/l]	0.00029	19.1	31	2030
vapor pressure at 25 ^oC [mm Hg]	0.00023	0.003	0.085	0.08
log P (octanol-water)	8.7	4.3	3.3	1.8
chemical formula	$CH_3(CH_2)_{15}CH_3$	$CH_3(CH_2)_{10}OH$		
concentration range; [µg/m^3]	20 – 400	20 – 400	10 – 400	20 – 300

* SRC PhysProp Database - http://www.syrres.com/esc/physdemo.htm

"The worst scenario" assumes that polar, water soluble compounds will partly dissolve in the droplets and be removed by the cyclone and cause overestimation of particle sample P. Therefore for undecanol, naphthalene and methoxyacetophenone amount of the bias was expected to be higher than for the water insoluble heptadecane which supposes to have the smallest gas to particle fraction transfer and what follows the smallest percentage concentration of the particle fraction P during gas phase experiments.

Table 2. Average fractionation of gaseous test compounds between three samples of the modified SJAC during gas phase measurements; in percent with standard deviations, n=5-8.

sample:	gas phase sample G_1 (cooler)	gas phase sample G_2 (XAD–4)	particle phase sample P (cyclone)
heptadecane	0.0 ± 0.0	100.0 ± 0.0	0.0 ± 0.0
undecanol	9.5 ± 3.1	88.7 ± 1.7	0.0 ± 0.0
naphthalene	1.2 ± 0.2	98.6 ± 0.4	0.0 ± 0.0
metoxyacetophenol	73.5 ± 1.3	24.0 ± 1.1	2.4 ± 0.7

Percentage concentrations of each given fraction were calculated dividing the concentration of the fraction by the concentration of the sum of all fractions and multiply by 100%.

The bias caused by transfer from gas to particle fraction for haptadecane, undecanol and naphthalene was found to be negligible – average percentage concentrations in the particle sample P during gas phase experiments was found to be 0.0 (Table 2). Only in case of metoxyacetophenol, which has the highest water solubility, SJAC measurements showed bias caused by transfer from gas to particle fraction. Maximal percentage share of the sample P for this compound was 3 %. Hence it confirms that for much less water soluble compounds than metoxyacetophenol (e.g. alkanes and PAHs) correction for SJAC measurements is not necessary.

Distribution between gas phase samples G_1 and G_2 illustrates differences not only in water solubility but also volatility of examined compounds. G_1 fraction of naphthalene is lower than for undecanol but water solubility of naphthalene is higher then that of undecanol. This distribution pattern can be useful as a kind of “online pre-separation” of measured compounds according to water solubility and volatility of SVOC in complex matrices of organic aerosols.
The distribution pattern shown in table 2 has proved to be concentration independent for the used range of concentrations (Table 1) of test compounds.

Evaluation of the modified SJAC yielded negligible bias caused by transfer from gas to particle phase and high collection efficiency for ultrafine hydrophobic particles. Therefore SJAC is a potential method free from physical artefacts for SVOC aerosol measurements. Furthermore chemical degradation of particle phase material is likely to be lower than that for filter based methods – lack of PM contact with reactive air compounds. Hence the future examinations aim for field comparison of the modified SJAC with standard sampling methods.

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