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HEADSPACE SOLID-PHASE MICROEXTRACTION OF ATMOSPHERIC ORGANIC AEROSOLS

M. Kirchner[1], E. Matisová[1], P. Kotianová[1], J. Leško[2†] and H. Puxbaum[3]*

[1]Department of Analytical Chemistry, [*]e-mail: matisova@chtf.stuba.sk
[2]Central Laboratory, Faculty of Chemical and Food Technology,
Slovak University of Technology, Radlinského 9, 812 37 Bratislava, Slovak Republic
[3]Institute for Chemical Technologies and Analytics, Vienna University of Technology,
Getreidemarkt 9/164/AC, A-1060 Vienna, Austria.

Abstract. *The possibilities to analyse organic atmospheric aerosols by headspace solid phase microextraction (HS-SPME) coupled with GC-MS were investigated. Aerosol samples from highway representing mainly aerosols produced by petroleum and diesel engines and country with low industrial pollution were collected on a quartz fibre filter. For HS-SPME extraction polydimetylsiloxane and polyacrylate fibres were chosen. Analytes were thermally desorbed from the filter to a headspace, and sorbed to a SPME fibre. Subsequently analytes were thermally desorbed from the fibre in GC injector in splitless mode, separated on a HP-5 column and detected. Various experimental parameters (time and temperature of sorption and desorption, GC temperature programme) were optimised. The uses of solvents or special sample preparation steps were avoided. The origin of large amounts of silicon compounds proved by GC-MS was determined to quartz fibre filter (used for aerosol sampling) and hydrolysis of polydimetylsiloxane stationary phase of SPME. The following groups of compounds were identified in atmospheric aerosols: phthalates, polyaromatic hydrocarbons, alkyl phenols, alkanes and oxygenated compounds as carboxylic acids and esters.*

Key words: *headspace SPME, capillary GC, GC-MS, atmospheric organic aerosols, semivolatile compounds*

Introduction

An aerosol is a dispersed system consisted of solid and liquid particles suspended in a gas. Atmosphere is an air cover of the Earth. The lowermost layer of atmophere is called troposphere. Troposphere consists of gases and diffused particles. This system is marked as atmospheric aerosol. A part of particles is emitted into atmosphere from natural or man-made sources on Earth's surface, while others come into being in the air by gas-to-particle conversion [1].

The particles suspended in the air consist of elements, inorganic and organic species. Our interest is pointing to organic compounds. Organics are components of solid particles or they are adsorbed on the surface of particles. The composition of particles is interesting from the point of view of the composition of atmosphere, and atmospheric chemistry and air pollution.

Atmospheric aerosol contains a wide range of organic compounds at very different concetration levels. Not all of them are known. Organic compounds with highest concetrations present in atmospheric aerosol can be divided into three big classes [1]: (1) hydrocarbons, (2) aromatic compounds, (3) organic acids and related compounds. Presence of these compounds (especially polyaromatic hydrocarbons) suggests potential implication in health impact because fine particles with diameter smaller than 2.5 μm are respirable [3].

Analysis of aerosols starts with sample collection. Sampling is usually performed by filters [1]. The aim of a subsequent separation procedure is to separate certain compounds or functional groups from the matrix by solvent extraction (Soxhlet or ultrasonic extraction), supercritical fluid extraction, or thermodesorption [2]. For the solvent extraction many solvents and its mixtures have been utilized. Extraction step of a sample preparation is followed by sample pretreatment steps. Solid particles are usually eliminated by filtration. If separation into different classes of organic compounds is necessary, the solution is submited to liquid chromatography (LC), solid phase extraction (SPE) or thin layer chromatography (TLC).

The widely used method for organic aerosol analysis has been a high resolution gas chromatography (HRGC) [2]. Combination of HRGC with a suitable detection, makes this method useful for qualitative and quantitative analysis. Mass spectrometric (MS) and flame ionization detector (FID) have been mostly applied [2].

Extraction and subsequent sample pretreatment brings a high risk of sample contamination. Therefore, other methods of isolation of target analytes are necessary. Criteria for a new isolation and preconcetration method of organic aerosol analysis are high sensitivity and minimum number of steps.

Solid Phase Microextraction (SPME) is an extraction method which combines preseparation and preconcetration in one step. Principle of SPME is based on the partitioning of an analyte between an extracting phase immobilized on a fused silica fiber and the matrix and/or its headspace [4]. SPME is a fast solventless sensitive technique. Several review articles have been published on SPME, where thermodynamic aspects and

application are discussed [5, 6]. SPME has been applied to extract volatile and semivolatile compounds from simple liquid matrices, such as water, and also very complex matrices, e.g. urine and blood [7]. Headspace solid phase microextraction (HS-SPME) has been applied also for the analysis of solid materials: soils [8 -10], fire debris [11], medicinal plants [12]. Polyaromatic hydrocarbons (PAHs) were determined by HS-SPME in sands and soils [13, 14]. Water addition to solid matrix significantly improves extraction of volatile [8, 9] and semivolatile organic compounds, e.g. PAHs [14, 15].

As organic species may be released from atmospheric aerosol by heat [2], we have investigated possibilities of HS-SPME as preconcetration and preseparation method for atmospheric aerosol analysis in combination with GC and GC-MS.

Experimental

Instrumentation. A manual SPME holder with 100 μm polydimetylsiloxane and 85 μm polyacrylate stationary phase fibers (Supelco, PA, USA) was used. The temperature of water bath for HS-SPME sampling was controlled by means of a device Thermostat Julabo f 25 (Julabo Labortechnik GmbH, Germany) with a precision of 0.01°C. Ultrasonic extraction was realized in an ultrasonic bath Teson 1 (Tesla, Vráble, Slovak Republic). Experiments with a flame ionization detector (FID, 320°C) were performed on a GC HP 5890 series II (Hewlett-Packard, Avondale, PA, USA), equipped with split/splitless injector (250°C) and an HP-5 column, 30 m x 0.32 mm I.D., film thickness 0.25 μm under temperature programmed conditions (45°C for 5 min, followed by 35°Cmin^{-1} to 88°C, then 4°Cmin^{-1} to 250°C, hold 20 min). Carrier gas He (Linde, Technoplyn, Bratislava, Slovak Republic) with a linear velocity 23 cm s^{-1} measured at isothermal conditions (100°C) suitable for trace analysis (purity of 99.999 %) was used.

GC-MS measurements were carried out on Kratos MS 25RFA (Carlo Erba - Kratos) with double focusation, equipped with column DB-5 MS (J&W Scientific), 30 m x 0.32 mm I.D., film thickness 0.25 μm, (45°C for 5 min, followed by 35°Cmin^{-1} to 88°C, then 8°Cmin^{-1} to 240°C, hold 20 min). Helium was used as the carrier gas. Electron impact ionization (70 eV) was used and mass spectra were collected over the range of 28 – 550 m/z. Scan rate was 0.6 s/d, interscan 0.3 s/d, temperature of ionization chamber 220°C.

Sample Handling, SPME Extraction and GC Analysis. The quartz fibre filters with diameter of 15 cm (Pallflex 2500QAT, Putman, Conn., USA) were used for aerosol sampling. Description of samples is shown in Table 1. Filters with aerosol samples were stored in freezer at -20°C. Blank filters (pure filters without sampled aerosol) were stored at room temperature.

Table 1. Properties of aerosol samples.

Sample No.	Sampling place	TSP* [μgm^{-3}]	TC* [μgm^{-3}]	BC* [μgm^{-3}]
1	Highway	-	76.0	1.30
2	Highway	96.4	67.3	1.48
3	Country side	16.4	5.5	0.78

*: TSP: Total Suspended Particles; TC: Total Carbon; BC: Black Carbon

A small part (~1.33 cm^2) was cut from the filter and placed into a 4 mL glass vial having open screw top closures fitted with teflon-lined septa (Chromacol, Herts, UK). To minimize possible non-homogeneity in composition of collected aerosols on the area of the filter, pieces were taken each next to other at one radius of the circular filter. The temperature of sampled vials was maintained by placing a vial in a small thermostated water bath. Constant temperatures (25 to 95°C) were achieved after 7 minutes. During the sampling stage SPME fiber was exposed in the headspace above quartz filter for the given period of time (extraction time). After extraction the fiber was immediately transferred into GC injector in splitless mode and desorbed at 250°C. After desorption time (5 min) elapsed GC injector was switched into split mode and fiber was cleaned for 2 additional minutes to prevent carryover.

In experiments with the addition of water to the quartz filter samples, deionized water (100 μL) was added prior to commencement of SPME extraction described above.

To ensure the reliability of analytical results, the blank runs of GC column, SPME fibre blank runs, and SPME-vials blank runs were performed in this study. Subsequently in the checked vial the sample or the control filter was analysed.

For semiquantitative analysis a standard solution of even n-alkanes in the range $C_8 – C_{28}$ in n-pentane (Merck, Darmstadt, Germany) was prepared at a concentration 1.2 μg/ml.

Liquid extracts were prepared from the same filter area as in HS-SPME method (1.33 cm^2). The cutted part of a filter was placed into a 4 mL vial and repeatedly extracted by a portion of dichlormethane (0.5 mL) at ambient temperature in ultrasonic bath for 15 minutes. Extracts were combined and dried under a gentle stream of nitrogen. The residue was dissolved in 25 μL of dichlormethane and stored in a refrigerator at 4°C before analysis.

Results and Discussion

Initial Fiber Selection and SPME Sampling. Important parameters influencing HS-SPME extraction process are fiber coating, temperature of sorption, fibre exposure time, the time of taking the sample [4, 16, 17]. The increased temperature is necessary for releasing semivolatile compounds present in aerosols into a headspace. Fibre exposure time to a headspace above a sample is important to be optimised to approach equilibrium, where the extraction yield is the highest. Selection of a fibre coating is important from the point of view of affinity of compounds to the fibre stationary phase, based on the principle of polarity. First, we chose non-polar PDMS fibre coating at selected temperatures (25, 45, 55, 75 °C) and fibre exposure times (5, 15, 30, 45 minutes) were tested with aerosol sample No.1. Aerosol samples No. 1, 2 (from highway) are similar with regard to total carbon and black carbon content. The growth of peak areas was observed with increasing temperature and exposure time as well as the range of boiling points of extracted compounds. The temperature of fibre desorption in the GC injector was initially set to 220 °C and the time of desorption was set to 1.5 min. With the growth of extracted amounts of compounds from aerosols, these conditions became insufficient for quantitative desorption and preventing carryover. Subsequently temperature of desorption was increased to 250°C, the maximum operation temperature for 100μm PDMS fibre. The period of desorption was increased to 5 min-

utes in splitless injector (which was subsequently switched into split injector and fibre was cleaned for 2 minutes). This step diminished the risk of the carryover. Increasing the sorption temperature caused the sorption of higher boiling compounds. Therefore, simultaneous adjustment of GC separation temperature program was necessary.

To achieve better efficiency of HS-SPME-GC, 100 μL of water was added directly to a sample in a vial. The water addition supports the releasing of compounds from solid matrix [8, 9, 14, 15]. The peaks areas have increased. However, peak areas of quartz fibre filter blank analysis with the water addition also increased.

Optimised HS-SPME and GC conditions and also water addition experiments were used for GC-MS measurements. The obtained data identified the most of largest peaks to trimethylsilyl compounds for both, aerosol sample and quartz filter blank analysis. Water addition to the sample and the blank filter significantly increased amounts of detected trimethylsilyl compounds. Typical ion of trimethylsilyl compounds was m/z 73; also other intensive ions with m/z 267, 281, 341, 355 with typical isotope intensity patterns for silicon (M+1, M+2) were present in spectra. As potential sources of trimethylsilyl compounds were considered: chromatographic column HP-5, SPME fibre with PDMS stationary phase, and quartz fibre filter. The stationary phase of chromatographic column HP-5 is made of 95%-polydimetylsiloxane, 5%-fenyl. Blank run on GC column did not show any eluting peaks with m/z 73, what excluded GC column from potential sources of trimethylsilyl compounds.

The stationary phase of the used SPME fibre is made of polydimetylsiloxane. The presence of water may cause a hydrolysis of PDMS fibre [18]. With water samples and HS-SPME analysis using PDMS fibre typical siloxanes peaks were observed [19]. PDMS fibre blank runs did not show any significant peaks. Every morning the fibre was conditioned in GC injector at maximum allowed operating temperature set by manufacturer (250°C) for 30 minutes. Subsequently the blank run was performed. Conditioning of the fibre could have caused releasing potentially present water and also hydrolysed fragments of PDMS stationary phase. Blank run on PDMS fibre was performed after each aerosol sample analysis. No peaks of siloxanes were confirmed. Blank runs were performed also with sampling vials to search a potential influence of air humidity on the decomposition of PDMS fibre. GC-MS experiments proved 3 small peaks of siloxanes in the whole GC run.

Quartz fibre filter is made of quartz and organic fibres. Mentioned trimethylsilyl compounds could have been released from the quartz filter.

Blank runs on water (deionised, redistilled and drinking) using 100 μm PDMS fibre resulted in chromatograms with large peaks eluting at the same retention times as sampled aerosols. GC-MS experiments proved trimethylsilyl character of the observed compounds. The most probable origin of trimethylsilyl compounds is hydrolysis of PDMS fibre; the other, but not probable source is water.

In order to exclude SPME fibre as a potential source of trimethylsilyl compounds, 85 μm polyacrylate fibre was selected for further experiments. The stationary phase is made of polyacrylate; therefore, it is not a source of trimethylsilyl compounds. The same operation conditions were used as for PDMS fibre. No trimethylsilyl compounds were detected in a blank run of PA fibre and in blank runs on the sampling vials. Analyses of quartz fibre filter, sampled aerosols and deionised water were also performed. Trimethylsilyl compounds were present in all samples of aerosols and also in control quartz fibre filter. In deionised water using 85 μm PA fibre, silica compounds were detected only in two small peaks.

The amounts of trimethylsilyl compounds found in control quartz fibre filter and aerosol samples analysis using PA fibre were, however, at much lower level compared to the results with PDMS fibre. This can be explained by the lower affinity of trimethylsilyl compounds released from the filter to polyacrylate. Filters with collected aerosols may contain ambient humidity of the environment where samples were collected. Humidity might be released during thermostating at an increased temperature into a headspace and impact PDMS stationary phase of the SPME fibre what caused its hydrolysis accelerated by the increased temperature. According to these results, the most probable sources of trimethylsilyl compounds are quartz fibre filter used for collection of aerosols and the hydrolysis of PDMS stationary phase of the SPME fibre in the presence of water (humidity).

HS-SPME Optimisation with PA Fibre. For better recoveries higher sorption temperatures were tested (65, 75, 85, 90, 95°C) at sorption time 30 min. For the selection of the best sorption conditions the evaluation of areas of 15 selected peaks was performed. Large and medium peaks within the whole chromatogram were chosen for the search. Two replicate aerosol samples (No. 2) for each sorption temperature were analysed. Average values of peak areas were compared (Figure 1). As expected, the amount of extracted compounds increased with the increased sorption time. From the graph in Figure 1 the following conclusions could be formulated. The extraction yield for the high boiling analytes highly depends on increasing temperature. With increasing temperature peak areas of less volatile compounds increase. Only peaks with maximal concentrations (peaks No. 9 – 11) were detected at the lowest sorption temperature (65°C). For the more volatile compounds (peaks No. 1,2) equilibrium between the gaseous phase and SPME stationary phase moves to the decreased sorption amount of the searched analytes at higher temperatures. The temperature of 90 °C was chosen as the sorption temperature in further analyses also with the prolonged period of the sorption time (45 min – included in Figure 1).

Typical chromatograms of a blank run of sampling vial and aerosol sample under optimised SPME sampling and GC conditions with PA fibre are shown in Figure 2.

A semiquantitative analysis of extracted compounds was performed. It is supposed according to literature [20, 21] and our GC-MS results, that organic compounds in aerosol samples posses the main part of the molecule of a hydrocarbon nature. Therefore, their response could approximate to n-alkanes response. A standard solution of even members of homologous series of n-alkanes in the range $C_8 - C_{28}$ with the concentration 1.2 μg/mL in pentane was used with splitless injection of 1 μL and detection with FID. The set of chromatographic conditions was the same as in the case of aerosol analysis. The obtained peak areas were used for the calculation of response factors. According to response factors of n-alkanes, the extracted amount of compounds from the aerosol sample No. 1,2 (highway) was calculated. Using PA fibre, the smallest peaks correspond to less

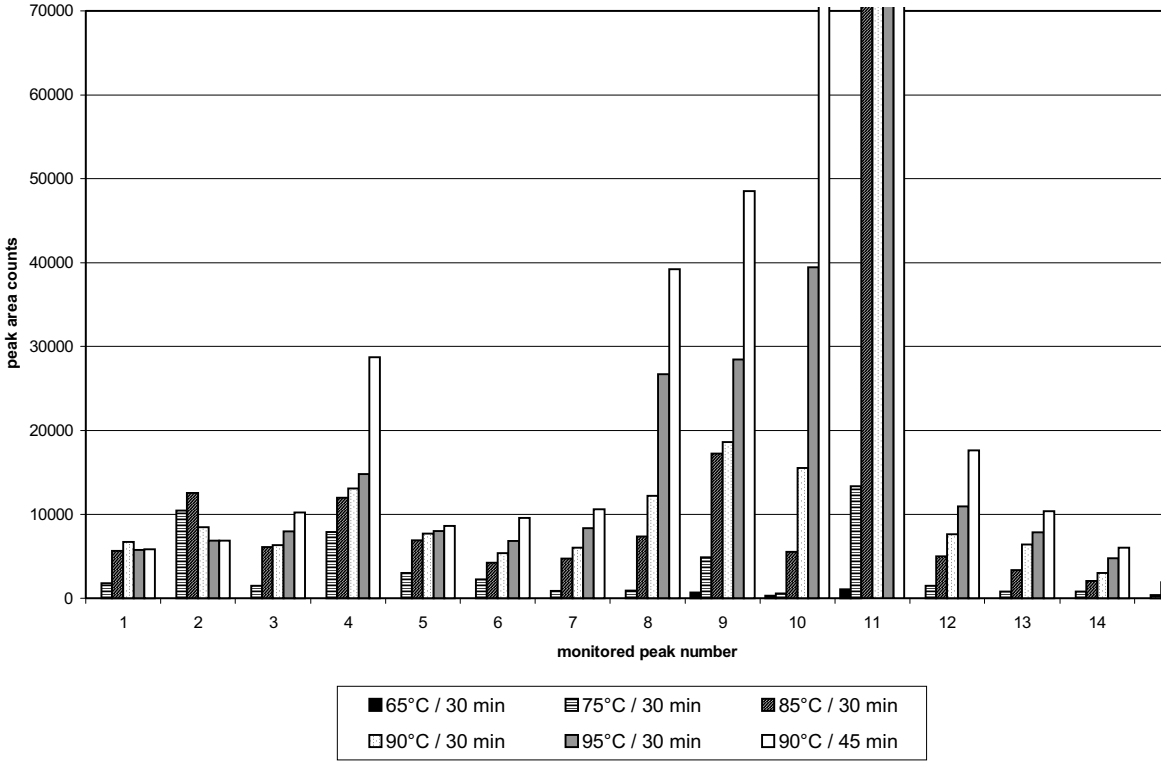

Figure 1. Dependence of selected peak areas on HS-SPME sorption conditions obtained with 85 μm PA fibre: temperature and time; aerosol sample No. 2.

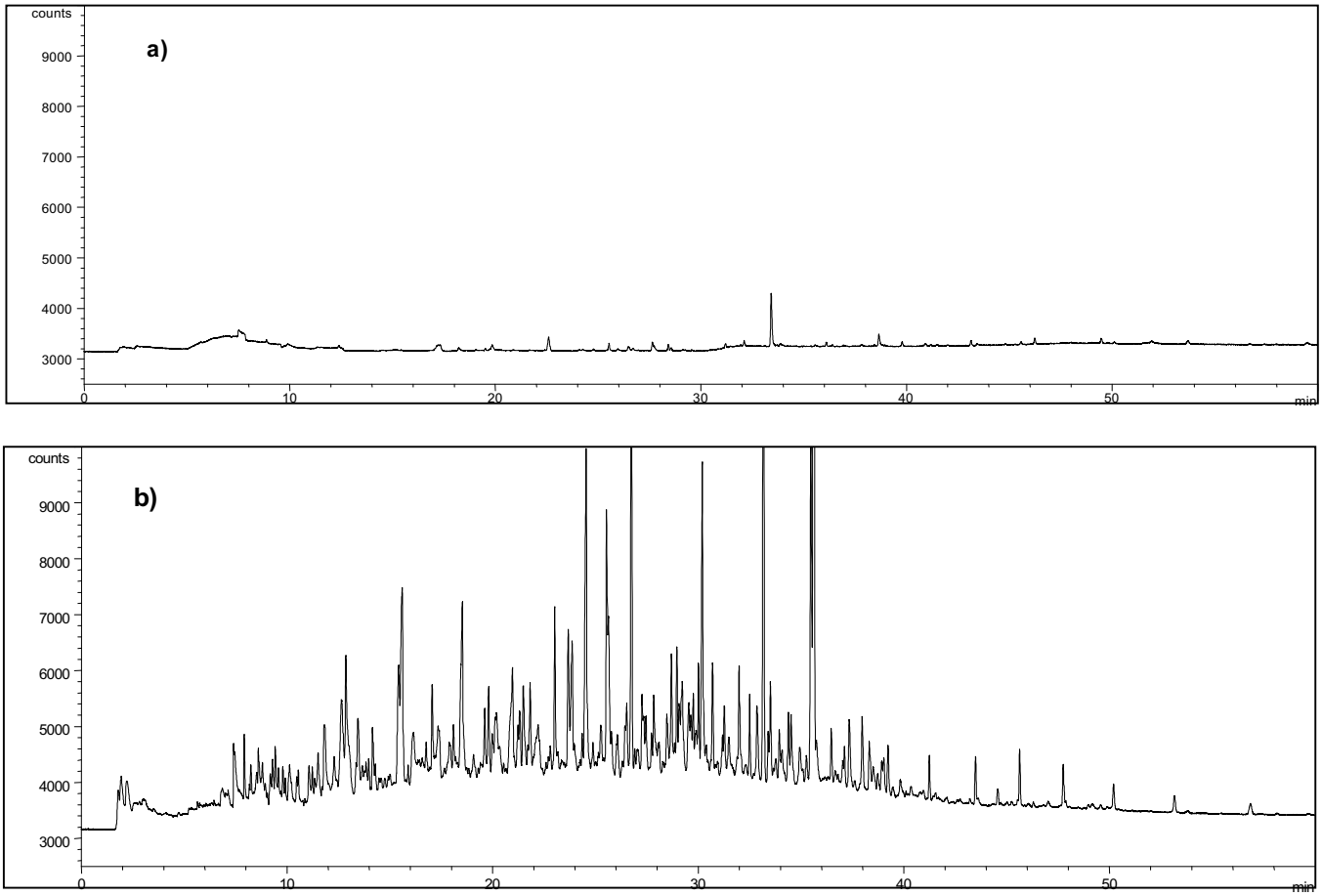

Figure 2. Chromatograms obtained using 85 μm PA fibre, a) vial blank, b) aerosol sample No. 2. Temperature of sorption 90°C, time of sorption 30 min, temperature of desorption 250°C, time of desorption 5 min, column HP-5, 30 m x 0.32 mm I.D. x 0.25 μm film thickness, temperature program: 45°C for 5 min, followed by 35°Cmin^{-1} to 88°C, then 4°Cmin^{-1} to 250°C, hold 20 min, detector FID.

than 0.01 ng, typically middle peaks response to about 1 – 5 ng, the highest peaks response to approximately 70 ng. The yields of analytes obtained using PDMS fibre were lower, typically middle peaks response to about 1 – 3 ng, the highest peak responses to 20 ng. Sampling aerosols in the clean country areas (country side, aerosol No. 3) peak areas correspond to less than 5 ng.

Liquid Extraction of Aerosol Samples. For the comparison of HS-SPME results, experiments with liquid extraction were realized. Following extracts were prepared: blank for extraction procedure, blank for quartz fibre filter and extract of aerosol sample No. 2. For the analysis splitless injection of 2 μL of extract with a solvent plug and detection with FID was used. Comparing liquid extraction yields to PA fibre extraction yields lower amount of detected extracted compounds was determined. Typically, peak areas of extract response to approximately 0.5 – 5 ng of n-alkanes. This fact is also caused by the fairly high dilution factor of the residue after extraction and a small amount of analytes introduced to GC system. Unquestionable advantage of HS-SPME approach is elimination of any solid particles or non-volatile compounds that are extracted by solvent extraction and subsequently are introduced into GC resulting in contamination of injector and front part of GC column.

GC-MS Identification. Identification of components in organic aerosol was based on information obtained from the comparison of the acquired spectra with library spectra, interpretation of the acquired mass spectra and mass chromatograms of selective ions of characteristic groups of compounds found in samples. The obtained spectra were of lower quality, in many cases mixed mass spectra were obtained. Organic aerosols represent multicomponent mixtures and a single column capillary GC is unable to resolve all compounds present in aerosols [21]. In the studied aerosol samples the following groups of compounds were proved: phthalates, aromatic hydrocarbons, phenols, aldehydes, ketones, related compounds of carboxylic acid. A summary of identified compounds from aerosol samples is shown in Table 2. Also control filters were analysed. Alkanes, carboxylic acids with a longer chain and siloxanes compounds were proved in quartz fibre filter blanks. The quartz fibre filters, used for aerosol sampling were not thermally treated before their usage, as the producer guarantees their purity.

Table 2. Summary of identified compounds in aerosol samples No. 1, 2, and 3.

	Samples	
No. 1	No. 2	No. 3
phthalic acid anhydride	1,2-cyclopentanediol	methylbenzaldehyde
butylbenzene	methylbenzaldehyde	phthalic acid anhydride
toluylen diisocyanate	phthalic acid anhydride	butylbenzene
hydroxybenzaldehyde	izobenzofuranone	toluylen diisocyanate
4-(methylthio)-benzaldehyd	hydroxybenzaldehyde	dimethyl phthalate
methyl-1,3-isobenzofuranedion	methyl-1,3-isobenzofuranedion	2,6-ditercbutyl-4-methyl-phenol
dimethyl phthalate	dimethyl phthalate	2,4-ditercbutylphenol
2,6-ditercbutyl-4-methyl-phenol	2,6-ditercbutyl-4-methyl-phenol	3,5-ditercbutyl-4-hydroxy-benzaldehyde
4-nitrophenol	2,4-ditercbutylphenol	diethylphthalate
diethylphthalate	4-nitrophenol	dodecanoic acid isopropylester
diphenylketone	diethylphthalate	diphenylketone
C9-alkylphenol*	diphenylketone	phenanthrene
C9-alkylphenol*	phenyl-2-propyl-phenol	anthracene
C9-alkylphenol*	anthracene	diisobutylphthalate
phenyl-2-propyl-phenol	diisobutylphthalate	morpholine derivate*
C9-alkylphenol*	morpholine derivate*	di-n-butylphthalate
C9-alkylphenol*	phthalate*	fluoranthene
anthracene	di-n-butylphatalate	pyrene
phthalate*	fluoranthene	
di-n-butylphatalate	pyrene	
anthracenedion		
naphthalic anhydride		
fluoranthene		
pyrene		

* No closer structual information avaible

Conclusions

HS-SPME is a fast and simple method for the analysis of atmospheric organic aerosol sampled on filters. The developed method is suitable as a screening method of semivolatile compounds present in organic aerosol in high concentrations, e.g. PAHs, phthalates. The amount of extracted compounds could be increased utilizing larger surface area of filters. The range and amount of less volatile compounds could be enlarged increasing sorption temperature. This would lead, however, to the shift of equilibrium of the most volatile compounds and their lower yields. HS-SPME-GC-MS with selective ion monitoring would increase sensitivity significantly. The method can be advantageously used also for the purity control on the volatile and semivolatile compounds of filters used for aerosol collection, and/or filters cleaning procedure, storage before the sampling of aerosols.

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