# Modeling solid-phase microextraction of volatile organic compounds by porous coatings using finite element analysis

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## Abstract

Experimental optimization of analytical methods based on solid-phase microextraction (SPME) is a complex and labor-intensive process associated with uncertainties. Using theoretical basics of SPME and finite element analysis software for the optimization proved to be an efficient alternative. In this study, an improved finite element analysis-based model for SPME of volatile organic compounds (VOCs) by porous coatings was developed mainly focussing on the mass transport in coatings. Benzene and the Carboxen/polydimethylsiloxane (Car/PDMS) coating were used as the model VOC and a porous SPME coating, respectively. It has been established that in

the coating, volumetric fractions of Carboxen, PDMS, and air are 33, 42 and 25%, respectively. It has been proven that Knudsen diffusion in micropores can slow down a mass transport of analytes in the coating. For Car/PDMS coating, mass transport of benzene is mostly characterized by a molecular diffusion, which can be explained by a large fraction of macro- and mesopores. It has been shown that the developed model can be used to model the extraction of VOCs from air and water samples encountered in a typical SPME development method procedure. It was possible to determine system equilibration times and use them to optimize sample volume and Henry's law constant. The developed model is relatively simple, fast, and can be recommended for optimization of extraction parameters for other analytes and SPME coatings. The diffusivity of analytes in a coating is an important property needed for improved characterization of existing and new SPME polymers and analytical method optimization.

**Keywords:** SPME; Carboxen; volatile organic compounds; benzene; transport in porous media; COMSOL Multiphysics.

## 1. Introduction

Solid-phase microextraction (SPME) is one of the simplest and most perspective sample preparation approaches for the quantification of organic compounds in various samples [1]. This technology is based on the transfer of analytes from a sample into a micro (thin polymeric layer) coating followed by their complete thermal desorption to an analytical instrument. SPME combines sampling and several sample preparation steps – extraction, concentration, and cleanup. In most cases, SPME can be fully automated using commercial autosamplers, for which SPME became the standard option in addition to liquid and headspace injection.

According to Scopus and Web of Science databases, thousands of articles have been published describing the development and application of analytical methods based on SPME.

However, optimization of SPME-based methods remains very time- and labor-intensive because many parameters need to be optimized [2]. Optimization of SPME parameters is one of the main steps required in method development and often uses a common-sense, 'trial-and-error' experimental design. The commonly optimized parameters are fiber coating type and dimensions, extraction temperature and time, pH, amount of salt added to a sample, sample/headspace ratio, agitation/stirring rate, pressure in a vial, desorption temperature and time. Because the selection of parameters tested and the lack of proper control and training, SPME-based methods often result in lower accuracy compared to methods involving conventional sample preparation techniques, which hinders their implementation in routine laboratories and adoption as standard methods. Thus clearly, it is challenging to recognize many potentially important sources of uncertainties during typical experimental optimization of SPME, and there is a need to develop a more focused, improved approach to the optimization process itself.

One of the most important resources for optimization of SPME-based methods is the theory of the method, which is well established [3–8] yet underutilized. The theory is often used by method developers only as a tool to explain the results of the experimental optimization. The rare use of the theory for direct method optimization can be caused by its complexity and insufficient mathematical background, or computing resources available to many developers. This problem can be solved by using a simplified software for mathematical modeling, which does not require advanced skills.

COMSOL Multiphysics was proven to be an effective tool to model SPME of organic compounds from various matrices and optimize method parameters [9–14]. Using this software, the sorption/desorption behavior was predicted for calibrant-loaded extraction phase (CL-EP) for an aqueous sample [9]. The presence of the binding matrix was determined to be a limiting factor, i.e., as the source of shorter equilibrium time for SPME [11]. Kenessov et al. [14] discovered that

the poor accuracy of time-weighted average sampling of volatile organic compounds from air using retracted porous SPME fibers was caused by slow mass transport of analytes in the coating.

The software uses the finite element analysis (FEA) method for solving differential equations governing mass and energy balance, which can be used to describe various physical and chemical processes. For the modeling, a user must create a process 'geometry' (physical shape and dimensions), choose a suitable physics, provide all required parameters and settings from a user menu. As the result of the modeling, it is possible to predict and visualize an analyte concentration in each point of geometry in different time moments, obtain extraction profiles at different extraction parameters and model unusual sampling conditions (worst cases).

Despite the major initial progress with modeling, currently available models based on COMSOL Multiphysics still use several simplifications for mass transport of analytes in adsorptive (porous) coatings. During their modeling, Kenessov et al. [14] considered Carboxen/polydimethylsiloxane (Car/PDMS) and polydimethylsiloxane/divinylbenzene (PDMS/DVB) coatings as a single porous structure. However, these coatings have a much more complex structure. They consist of solid (Carboxen 1006 or DVB) particles attached to each other and to the silica rod using cross-linked PDMS. The diameter of Carboxen particles in the coating is 1~5 µm, with the average of ~2 µm [15]. Mean diameter of micropores of Carboxen particles is 1.2 nm [3] meaning that the diffusion of small-sized molecules in the micropores can be driven by Knudsen diffusion, which is much slower than a molecular diffusion [16].

Many important specifications of the commercial fibers are not reported in the scientific literature as that information could be either proprietary or difficult to obtain without sophisticated equipment. For example, there is no information on the ratio between PDMS, Carboxen, and air in the coating, which makes it impossible to build the accurate model because the ratio can affect the mass transport rate of analytes in the coating. Still, in some cases, an estimate of specific parameters can be obtained experimentally.

This research is aimed to develop an improved model, which describes VOCs mass transport in commercial porous SPME coatings and allows obtaining extraction profiles consistent with experimental results. Benzene (a ubiquitous and toxic pollutant in the air, water, and soil) was selected as a model VOC. Carboxen/PDMS was selected as a model porous (adsorptive) SPME coating because it is recommended for extractions of a wide range of VOCs and is often used for exploratory work for method development.

## 2. Experimental

### 2.1. General modeling parameters

Modeling was conducted using COMSOL Multiphysics 5.4 (Burlington, MA, USA) software with Chemical Engineering module installed on a personal computer equipped with a six-core Core i7-8700 central processing unit (Intel, Santa Clara, CA, USA), 16 Gb of DDR4 random access memory (Apacer, Taiwan) and 250 Gb 860 Evo solid-state drive (Samsung, Seoul, Rep. of Korea).

Modeling was conducted using 'Transport of Diluted Species' and 'Transport of Diluted Species in Porous Media' physics in a 'time-dependent' mode using previously used parameters [14]. Convection was deactivated in transport mechanisms as there was no air movement in the modeled systems. Default equations of COMSOL Multiphysics were used for the modeling, i.e.:

$$\frac{\partial c}{\partial t} = \nabla \left( D \, \nabla c \right) \tag{1}$$

$$\left( \varepsilon + \rho \, K_p \right) \frac{\partial c}{\partial t} = \nabla \left( D \, \nabla c \right) \tag{2}$$

where: $c$ is the analyte concentration, mol m$^{-3}$; $D$ is the diffusion coefficient, m$^2$ s$^{-1}$; $t$ is time; $\varepsilon$ is a porosity of a porous material; $\rho$ is a density of a porous material, kg m$^{-3}$; $K_p$ is a distribution constant between coating and air, m$^3$ kg$^{-1}$.

The diffusion coefficient of benzene in the air was set to $8.8 \cdot 10^{-6}$ m$^2$ s$^{-1}$ [14]. The distribution constant for benzene between coating and air was set to 150,000 [17]. Simulations were conducted for 23-ga 85-µm Car/PDMS Stableflex® fiber (Supelco, Bellefonte, PA, USA) with a core diameter of 130 µm and length of 80 mm; the coating thickness and length were 80 µm and 10 mm, respectively [3]. The porosity and tortuosity of Carboxen particles were set to 0.37 and 1.315, respectively [14]. The 'extra fine free triangular mesh' was used for the modeling. To provide better meshing at the coating-air interface, the resolution of narrow regions was increased to '5'.

For two-dimensional (2D) geometry, the analyte amount extracted by the coating was calculated by multiplying surface average concentration in the coating by the coating volume, or surface averaged concentration adsorbed to the solid by the coating mass. For three-dimensional (3D) geometry, volume averaged concentrations were used for similar calculations.

### 2.2. Effect of the diffusion coefficient in the SPME coating on the extraction process

When modeling using single apparent diffusion coefficient for the whole coating, 'Transport of Diluted Species' physics was used separately for air and the coating. Two-dimensional axisymmetric geometry was used for the modeling. Fluxes from (or backward to) air (*Flux$_1$* and *Flux$_2$*, respectively) at the coating-air boundaries were simulated similarly as previously shown for absorptive coatings by Kenessov et al. [14]:

$$Flux_1 = k\left(c_a - \frac{c_f}{K_{fa}}\right); \quad Flux_2 = k\left(\frac{c_f}{K_{fa}} - c_a\right) \tag{3}$$

where: $k$ is the flux coefficient, m s$^{-1}$; $c_a$ and $c_f$ are concentrations of the analyte in air and coating at the boundary layer, respectively, mol m$^{-3}$; $K_{fa}$ is the dimensionless distribution constant for benzene between SPME coating and air. A 20-mL headspace vial (i.d. = 20.0 mm, height = 63.7 mm) with initial concentration 0.641 µmol m$^{-3}$ and the same constant concentration at outer boundaries was used to model the extraction from open air with a constant concentration.

*2.3. Experimental study of the structure and composition of Car/PDMS fiber coating*

Thermogravimetric analysis was conducted using synchronous thermal analyzer STA 449 F3 Jupiter (NETZSCH, Germany) to estimate the ratio of Carboxen and PDMS in a commercial SPME coating. The analyzed coating (L = 10 mm) was separated from the base and divided into 1-2 mm pieces. Sample weight was obtained using two pairs of microbalances: XP56 (Mettler Toledo, Switzerland) and CPA2P (Sartorius, Germany). Sample weight on both instruments was identical and resulted in 0.462 mg. Full sample was placed in $Al_2O_3$ crucible, evacuated in a sample chamber at $10^{-2}$ mbar, followed by argon (99.998%, NIIKM, Moscow, Russia) flow. The experiment was performed in dynamic mode with constant purging with argon at 20 mL min$^{-1}$. An empty crucible was used as a reference sample. Temperature rise was performed from 20 °C to 1000 °C at the rate of 10 °C min$^{-1}$. System management, data collection, and processing were performed using NETZSCH-Proteus software. Microphotographs of the 85-µm Car/PDMS coating were obtained using scanning electron microscope SIGMA VP (Zeiss, Germany). Vacuum deposition of a conductive layer of gold on the surface of samples was carried out using the Q150T ES system (Quorum Technologies, United Kingdom).

*2.4 Modeling of the effect of benzene diffusion coefficient in Carboxen particles on the mass transport of the analyte in the coating*

Modeling was conducted in three dimensions on the 4.64 × 4.64 × 46.4 µm (W × D × H) block, which was split to 20 smaller (4.64 × 4.64 × 2.32 µm) blocks. Ten small blocks from one side corresponded to air, while remaining ten small blocks corresponded to the piece (slice) of the Car/PDMS coating. There were two studied geometries of the coating – with and without particles. Visual representation of the geometries is provided in Fig. A.1 in Supplementary Material. For the second geometry, separate transport parameters were set for particles and space (air) between them.

At the end of the side with blocks filled with air, benzene concentration 0.641 $\mu\text{mol}\cdot\text{m}^{-3}$ was set. For the model without particles, coating porosity ($\varepsilon_c$) was calculated using:

$$\varepsilon_c = \varepsilon_i + \varepsilon_p(1 - \varepsilon_i) \tag{4}$$

where: $\varepsilon_i$ is the inter-particle porosity; $\varepsilon_p$ is the porosity of particles. Coating density ($\rho_c$) was calculated using:

$$\rho_c = \rho_p(1 - \varepsilon_i) \tag{5}$$

where: $\rho_p$ is the density of Carboxen particles. Tortuosity model was chosen in the software to calculate the effective diffusivity. Tortuosity ($\tau$) was calculated from the corresponding porosity:

$$\tau = \varepsilon + 1.5(1 - \varepsilon) \tag{6}$$

Knudsen diffusion coefficient in pores of particles ($D_K = 1.14\cdot10^{-7}$ $\text{m}^2$ $\text{s}^{-1}$) was calculated using [18]:

$$D_K = 3.068\, r\, \sqrt{T/M} \tag{7}$$

where: $r$ is the average pore radius (0.6 nm); $T$ is the temperature (298 K); $M$ is the molecular mass ($78\cdot10^{-3}$ $\text{kg mol}^{-1}$). Net diffusion coefficient in pores ($D_P = 1.14\cdot10^{-7}$ $\text{m}^2$ $\text{s}^{-1}$) was calculated using [5,19]:

$$D_P = (D_G^{-1} + D_K^{-1})^{-1} = 1.12 \cdot 10^{-7}\,\text{m}^2\text{s}^{-1} \tag{8}$$

where $D_G$ is benzene diffusion coefficient in the air ($8.8\cdot10^{-6}$ $\text{m}^2$ $\text{s}^{-1}$).

### 2.5. Experimental study of benzene mass transport in Car/PDMS fiber

### 2.5.1 Description of the experiment

Sixty 20-mL headspace vials were crimped simultaneously with samples used for the determination of benzene concentration in the laboratory air. At this moment, the atmospheric pressure in the laboratory was 700±10 mmHg. The temperature during the crimping and whole experiment was 24±2 °C. To estimate equilibrium response of the analyte, four prepared samples were extracted for 8 h with two exposed 85-μm Car/PDMS fibers in duplicates. That procedure

was followed by a 30-min extraction by exposed fiber in two replicates to monitor MSD sensitivity changes for quality assurance and control. Eighteen samples were extracted by two retracted (Z = 0 mm) 85-µm Car/PDMS fibers for 2, 5, 10, 20, 60, 120, 240, 480 and 960 min using Combi-PAL (CTC Analytics, Switzerland) autosampler installed on a 6890N/5973N GC-MS (Agilent, USA) equipped with split/splitless inlet and SPME liner (i.d. = 0.75 mm, Supelco, Bellefonte, PA, USA). The position of the retracted fiber was controlled using CTC Cycle Editor available in MSD ChemStation (E.02.02) software. After extraction, the fiber was introduced into the GC inlet working in splitless mode for 5 min at 250 °C. Separation was conducted using 30 m × 0.25 mm DB-35ms (Agilent, USA) column (0.25 µm film) under the constant helium (>99.995%, Orenburg-Tehgas, Russia) flow equal to 1.0 mL min$^{-1}$. Oven temperature was programmed from 70 °C (held for 1 min) to 190 °C (held for 1 min) at the rate of 20 °C min$^{-1}$. MS detection was conducted in selected ion monitoring (SIM) mode of the ion with m z$^{-1}$ 78, dwell time was 100 ms.

To monitor GC-MS instrument sensitivity changes, every fiber change was followed by a 30-min extraction by the exposed fiber in two replicates. Amount of the extracted benzene relative to the equilibrium value (%) was calculated by the following formula

$$n = \frac{S_r \times S_c}{S_f \times S_e} \times 100\% \tag{9}$$

where: $n$ is a relative amount of benzene collected on fiber, %; $S_r$ is the peak area after extraction by the retracted fiber at variable extraction time, a.u.; $S_f$ is a peak area of 8-h extraction by exposed fiber, a.u.; $S_c$ is a peak area after 30-min extraction by the exposed fiber following the extraction by a retracted fiber at variable extraction time, a.u., $S_e$ is a peak area after 30-min extraction by the exposed fiber following the 8-h extraction by an exposed fiber, a.u.

### 2.5.2 Modeling parameters

Two-dimensional axisymmetric geometry included the 20-mL vial (i.d. = 20 mm, height = 63.7 mm), 23-ga protecting needle, Stableflex® Car/PDMS fiber core and coating. The internal

diameter of the protecting needle was established using a digital USB microscope (China) capable of 1,000× zoom. SPME assembly with retracted fiber and caliper photos were taken from an equal distance. Internal diameter (i.d., mm) was calculated using:

$$i.d. = L\frac{p_1}{p_2} \tag{10}$$

where: $L$ is the distance between marks on the caliper (1 mm); $p_1$ is the internal diameter of protecting needle, pixels; $p_2$ is the distance between marks on caliper, pixels. Distance in pixels was calculated using Paint.NET 4.1.5 (dotPDN LLC, USA) software.

The diffusion coefficient of benzene in laboratory air was set to $9.55 \cdot 10^{-6}$ m$^2$ s$^{-1}$. This value was obtained by adjusting the diffusion coefficient at standard conditions ($8.8 \cdot 10^{-6}$ m$^2$ s$^{-1}$) to the actual atmospheric pressure and temperature in the laboratory. The computation was completed in the range between 0 and 57,600 s at the step of 100 s. The initial value for benzene concentration in the laboratory air inside the vial during the experiment (0.435 µmol m$^{-3}$) was determined using standard addition calibration using the method developed by Baimatova et al. [20]. Initial benzene concentration in the coating was set to zero.

### 2.6 Application of the model to SPME of analytes from air

Extraction of benzene was modeled from sample containers having volumes of 20, 125, 250 and 1000 mL filled with air at $C_0 = 0.641$ µmol m$^{-3}$. Internal diameters of containers were 20, 40, 60 and 100 mm. Extraction from infinite volume was also tested. The computation was completed in the range between 0 and 10,000 s with the 10-s interval.

### 2.7 Application of the model to headspace SPME of analytes from water

Extraction of benzene was modeled from the 20-mL vial (i.d. = 20 mm) filled with 1, 2, 5, 8 and 12 mL of the water sample with initial benzene concentration of 0.641 mmol m$^{-3}$. Analyte transport in water was modeled using 'Transport of Diluted Species' physics. Flux at the air-water

interface was modeled according to the equation (3). Henry's law constant was set to 0.227 [21]. To simulate the ideal sample stirring, the flux coefficient was set to a sufficiently high value of 1000 m s$^{-1}$. Analyte diffusion coefficient in water was set equal to the that in the air ($8.8 \cdot 10^{-6}$ m$^2$ s$^{-1}$). The fiber was located 10 mm above the water surface. The computation was completed in the range between 0 and 10,000 s with the 10-s interval.

## 3. Results and Discussion

### 3.1 Effect of the diffusion coefficient in the SPME coating on the extraction process

The apparent diffusion coefficient is often used as a single parameter characterizing the rate of mass transport of a chemical in a complex medium. It allows predicting how quickly the compound will be distributed in the studied material, e.g., porous adsorbent or soil. According to the results (Fig. 1), the decrease of the apparent diffusion coefficient of benzene in (inside) the coating slows down benzene extraction process from the air. The effect is less pronounced when decreasing $D_a$ from $10^{-10}$ down to $10^{-11}$ m$^2$ s$^{-1}$ because, in this range, diffusion of the analyte in the air is a limiting stage of the extraction process. Further decrease of $D_a$ makes the mass transport of the analyte inside the coating the limiting stage. The obtained results prove that proper characterization of the analyte mass transport in the coating is very important for accurate modeling of the whole extraction process. The lack of scientific knowledge about this complex process complicates the development of the accurate model.

During this stage of the study, it has been confirmed that the apparent diffusion coefficient in the coating can be determined by the following formula [14] without any loss of accuracy:

$$D_a = \frac{D\,\epsilon}{\tau\,K_{fa}} \tag{11}$$

where: $D$ is the diffusion coefficient of the analyte in the air; $\varepsilon$ is the total porosity of the coating;

$\tau$ is the tortuosity of the coating; $K_{fa}$ is the distribution constant between fiber and air. In this case, the results of the modeling were the same as the results obtained using 'Transport of Diluted Species in Porous Media physics', which was recently used by Kenessov et al. [14]. However, the use of this approach for modeling the extraction by an exposed fiber required adding a small additional rectangle around the coating where initial concentration must be set to zero. In the remaining part of the vial, the concentration was set to 0.641 μmol m$^{-3}$. Without this important modification, incorrect results of the modeling were obtained, and the mass conservation law was violated. In further modeling, both approaches were used to validate the obtained results.
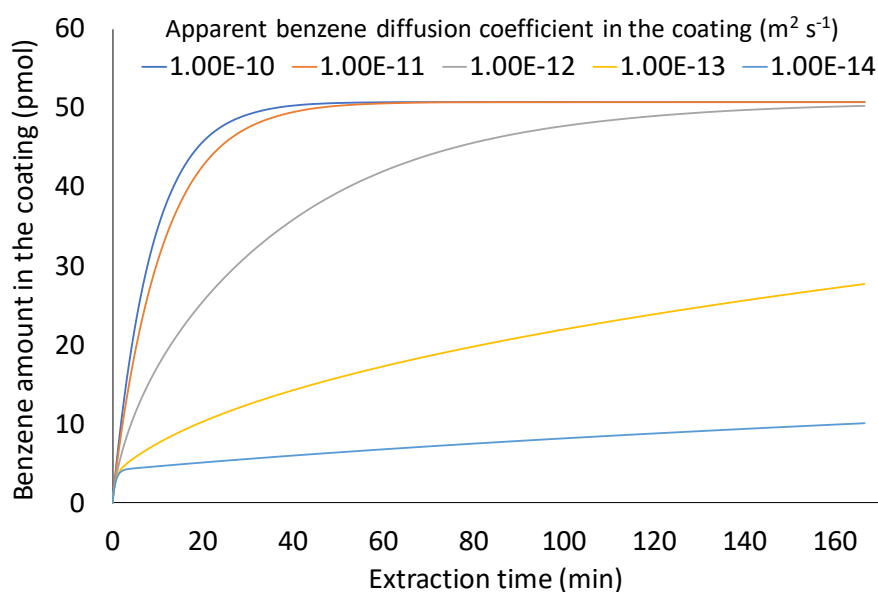
**Fig. 1** Effect of the apparent diffusion coefficient of benzene inside the 85-μm Carboxen/PDMS coating on benzene extraction profile from the air ($C = 0.641$ μmol m$^{-3}$)

### 3.2. Structure and composition of Car/PDMS fiber coating

In the previous section, a simplified homogeneous model of analyte mass transport in SPME coating was used. In reality, it is much more complicated because commercial adsorptive fibers have a quite complex structure and chemical composition. Car/PDMS fiber consists of Carboxen 1006 particles, cross-linked PDMS binder, air and a Stableflex core [3]. There is a very limited amount of publicaly available information about this type of coating in the literature because it is considered proprietary [14]. Without this information, development of a more accurate model is impossible. In a personal communication with the manufacturer (Sigma-Aldrich Chemie) representatives [22], it has been disclosed that the density of Carboxen particles is ~1 g mL$^{-1}$. The volume of air between particles was not known by the manufacturer, and the ratio between PDMS and Carboxen was proprietary. This stage of the study was aimed at estimating the ratio between volumes and masses of Carboxen, PDMS and air in the coating experimentally.

During the thermogravimetric analysis (Fig. 1) of SPME where elevated temperature causes breakdown and release of volatile fractions, the coating mass dropped by 62% (286 µg), which can be related to the PDMS 'glue' (acting as a binder) and polymeric part of the StableFlex core of the SPME assembly. Considering the dimensions of the StableFlex core, which consists of an 80-µm silica core and a 20-µm 'plastic-like' polymer [3], the mass of the latter is 63 µg. Thus, the resulting mass of PDMS 'glue' is 286 - 63 = 223 µg. The remaining portion (38%; 176 µg) corresponds to solid Carboxen particles, which have much higher thermal stability. Because the densities of PDMS glue and polymeric part of the StableFlex® core are not known, they were assumed to be 1 g mL$^{-1}$. Taking into account that the density of Carboxen particles is also 1 g mL$^{-1}$, they occupy 176 µL (33% of the reported total coating volume of 528 µL [3]). PDMS and air between Carboxen particles occupy 42 and 24 % of the coating volume, respectively. These results are supported by SEM microphotographs of the Car/PDMS coating (Fig. 3) where spherical Carboxen particles (d

~ 0.5-3 µm) covered with PDMS are clearly visible. There is a significant amount of PDMS between particles, which allow retaining them together.
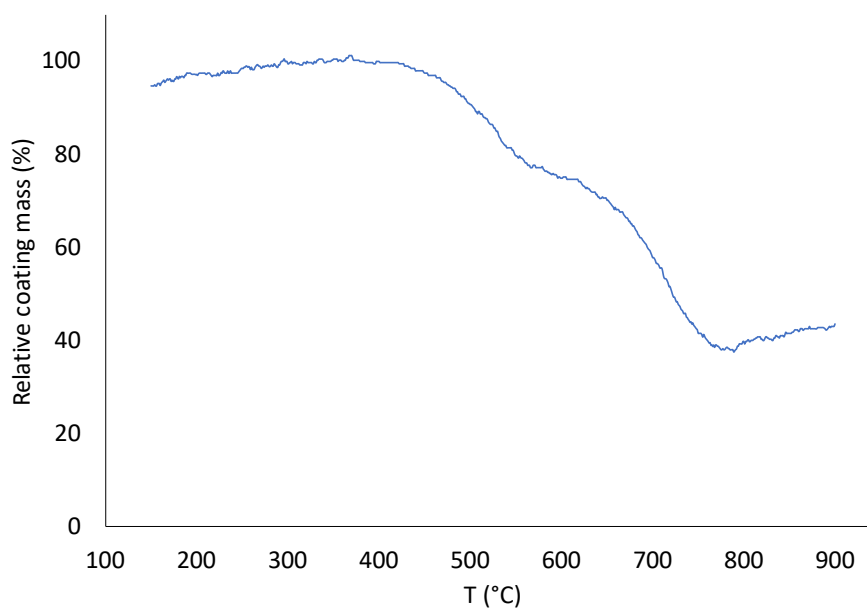
**Fig. 2** Thermogravimetric curve of 85-µm Car/PDMS coating in the range of 150~900 °C
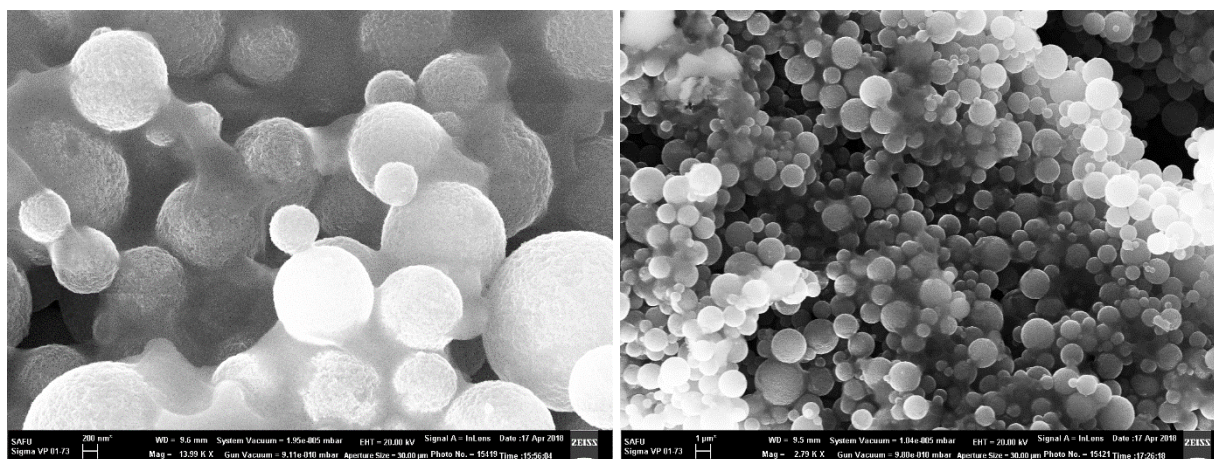
**Fig. 3** Scanning electron microscope image of Car/PDMS fiber. Carboxen phase is represented by ~0.5 to ~3 µm porous spheres. Each particle is covered with a layer of PDMS, which is also represented by darker shaded 'bonds' between spheres with occasional larger 'blobs.'

*3.3 Effect of benzene diffusion coefficient inside Carboxen particles on the mass transport of the analyte in the coating*

The experimentally determined coating structure was used to build the 3D model of a small section of the coating. Building the whole coating with separate particles was not feasible at this time because it would take a very long time and/or significant computational resources. The use of 2D geometry would not have been appropriate because each 'slice' of the coating is different, and it is impossible to model a single slice properly describing the coating. PDMS phase was not included into the model for its simplification; all space between particles was assumed to be filled with air. It was done mainly because the analyte distribution constant between PDMS and Carboxen was not known (but it generally accepted that Car/PDMS provides much higher fiber-air benzene distribution constant than PDMS - 150,000 [17] versus 301 [3], respectively). Carboxen particle size was set to 2 µm, the distance between the surfaces of the particles was 0.32 µm so that the particles take 33% of the total volume of the coating section. According to equations (4-6) and the results presented in Section 3.2, coating porosity, density and tortuosity were set to 0.792, 330 kg m$^{-3}$ and 1.104, respectively.

Results of the modeling proved that the analyte diffusion coefficient inside Carboxen particles affects its mass transport in the coating. When the mass transport of the analyte in particles is driven by Knudsen diffusion ($D_p = 1.12 \cdot 10^{-7}$ m$^2$ s$^{-1}$), the overall mass transport in the coating is slower compared to the molecular diffusion-driven process ($D_p = 8.8 \cdot 10^{-6}$ m$^2$ s$^{-1}$). This is likely because of the faster equilibration of particles' surface with surrounding air under slower Knudsen diffusion.

When the mass transport inside particles was driven by molecular diffusion as in the space (voids) between particles, it was possible to obtain the same results using a simplified homogeneous model (both 2D and 3D geometries). It means that in this case, the geometry of the coating does not affect the results of modeling. The only parameter affecting the whole process is

the distribution constant between coating and air. However, when the diffusion coefficient inside particles was not equal to the diffusion coefficient in voids, it was impossible to find the homogeneous model, which would provide the same results of the modeling.
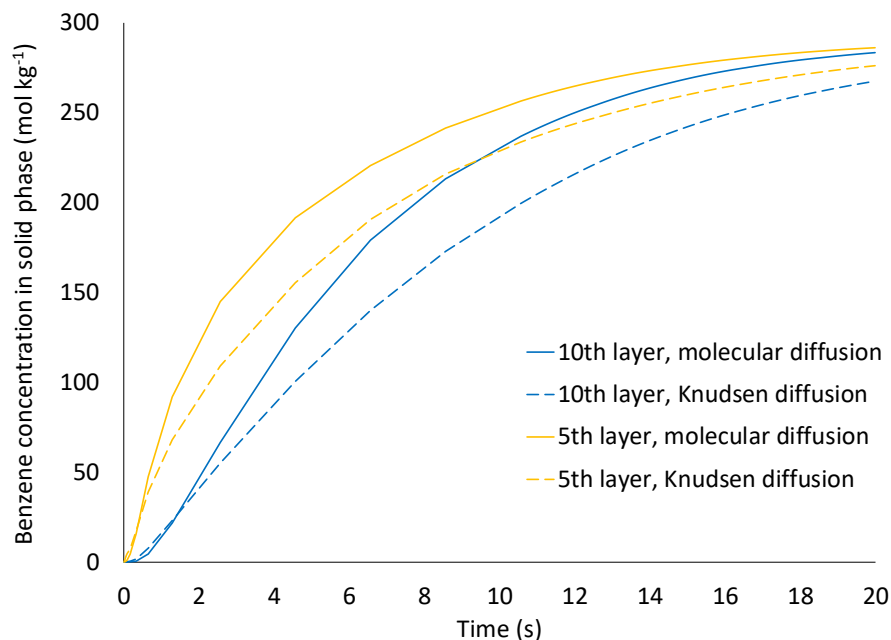
**Fig. 4.** Effect of a primary benzene diffusion mechanism in particles on its concentration profiles in 10th and 5th rows of particles

### 3.4. Experimental study of benzene mass transport in Car/PDMS fiber

As it was previously shown by Kenessov et al. [14], SPME of VOCs strongly depends on the mass transport rate in the coating when it is retracted inside a protecting needle (in the case of time-weighted average sampling, TWA-SPME). In this case, the tip of the fiber can be equilibrated (saturated) with analytes extracted from the surrounding air because of the slow mass transport of analyte to the remainder of the coating. As was proven, this process is more pronounced at lower diffusion path lengths (i.e., shorter retraction depths). In the present study, the lowest possible $Z$ (0 mm) was chosen to maintain the highest possible flux of the analyte to the fiber tip.

According to the Sigma-Aldrich needle gauge chart [23], 23-ga needles have a nominal I.D. of 340 µm, which was previously used for modeling purposes [14]. Due to the reproducible

differences observed between experimental and theoretical results of TWA SPME sampling, it was hypothesized that such discrepancies can be caused by the higher internal diameter of the protecting needle of a SPME assembly. Four photos for caliper scale and five microphotographs for protecting needle were used to accurately determine the internal diameter. The measured value was $476\pm11$ µm, which is ~40% higher than the reported value and 7% higher than the value (444 µm) recently obtained by Tursumbayeva [24]. Such differences result in ~2× higher cross-sectional area of the protecting needle and TWA sampling rates by retracted fiber which were obtained during the modeling [14].

The obtained experimental extraction profile of benzene was very similar to the extraction profile obtained using the developed model. After 16-h extraction, 79% of the equilibrium amount of analyte has been extracted. Differences between experimental and theoretical values were within standard deviations and experimental error. Such differences can also be caused by the presence of PDMS in the coating and some impact of Knudsen diffusion, which were not considered during the modeling. Despite this, the obtained results prove that the simplified homogeneous model is quite accurate and can be used to model SPME of VOCs from gaseous samples by Carboxen/PDMS fiber. This is due to the combination of the macro-, meso- and micropores in the Carboxen 1006, which is considered as the ideal material for SPME coatings [3].
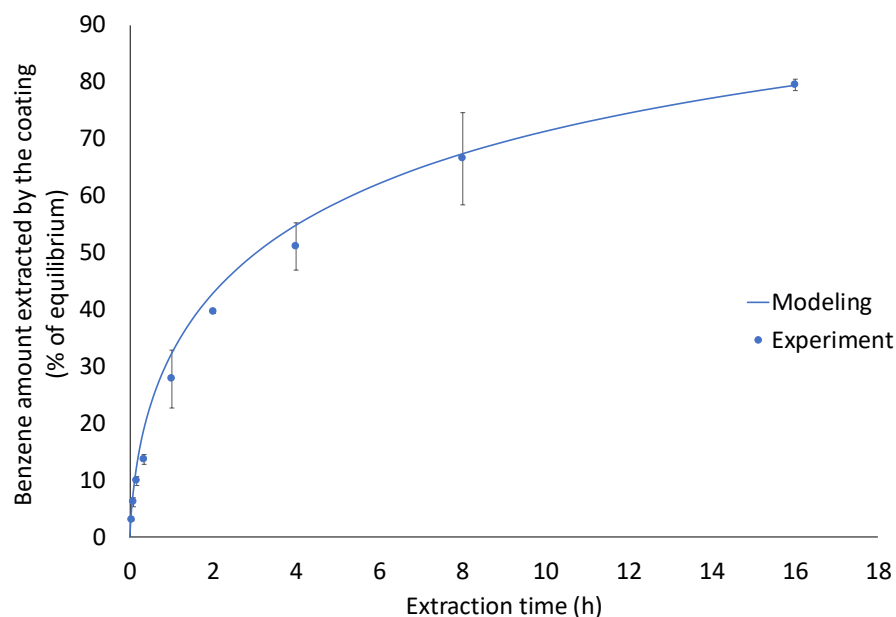
**Fig. 5.** Experimental and theoretical benzene extraction profiles from the air by retracted ($Z = 0$ mm) 85-µm Car/PDMS fiber at $T = 24{\pm}2$ °C and $p = 700{\pm}10$ mmHg.

*3.5 Application of the model to air sampling using SPME*

The developed model allowed obtaining benzene sampling profiles from sampling containers of a different volume – from 20 mL to the infinite value. From the obtained plots (Fig. 6), it could be seen that the increase of a sample container volume from 20 to 1000 mL results in the increase of a complete (100.0%) equilibration time from 16.5 to 58.8 min. At these volumes, 95% of the equilibrium amounts were extracted after 6.0 and 27.0 min, respectively. The increase of the volume over 1000 mL did not result in an increased equilibration time despite an 'infinite' volume allowed extracting 8% greater amount of the analyte.
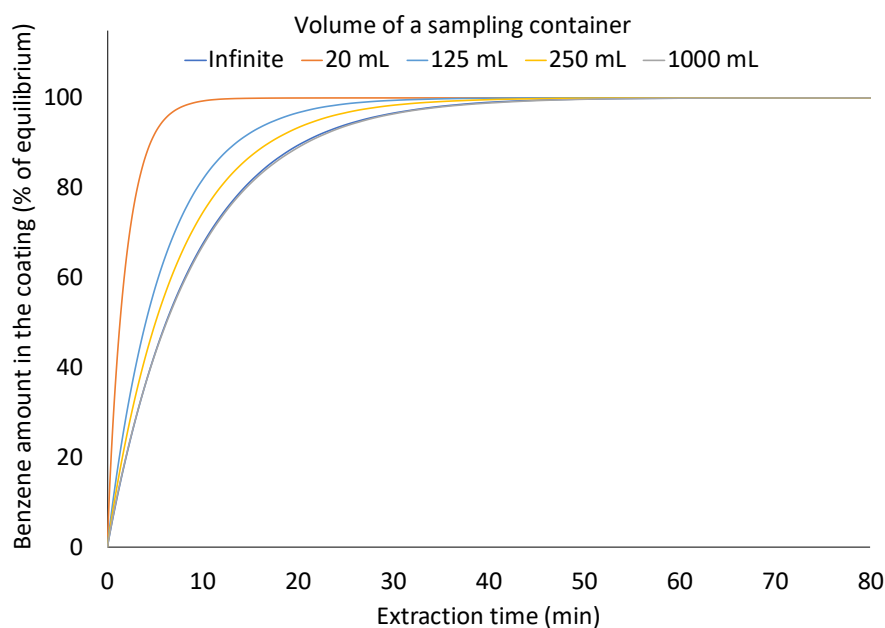
**Fig. 6.** Effect of the volume of air sampling container on extraction profiles of benzene by

Car/PDMS fiber at $T = 298$ K, $p = 1$ atm.

*3.6 Application of the model to benzene extraction from water samples*

The developed model can also be used for obtaining extraction profiles of volatile and semi-volatile compounds from water and other liquid samples. To simplify the modeling, the analyte mass transport in the liquid phase was assumed not to be the limiting stage of the extraction process, which can be achieved with the ideal stirring. According to the obtained plot (Fig. 7a), the increase of the sample volume requires longer equilibration time. At the volume of 1 mL, 95% of the equilibrium amount was extracted after 7.7 min. The increase of the sample volume to 2 mL increase the 95% equilibration time to 11.5 min. The use of the 12-mL sample required 19.3 min for equilibration. Along with the increase of extraction effectiveness by 41%, the increase of Henry's law constant from 0.227 to 1.000 ($V = 12$ mL) resulted in the further decrease of the equilibration time (Fig. 7b) to 9.3 min. This can be achieved by, e.g., adding salt to the sample before the extraction as it is a common practice in SPME method optimization.
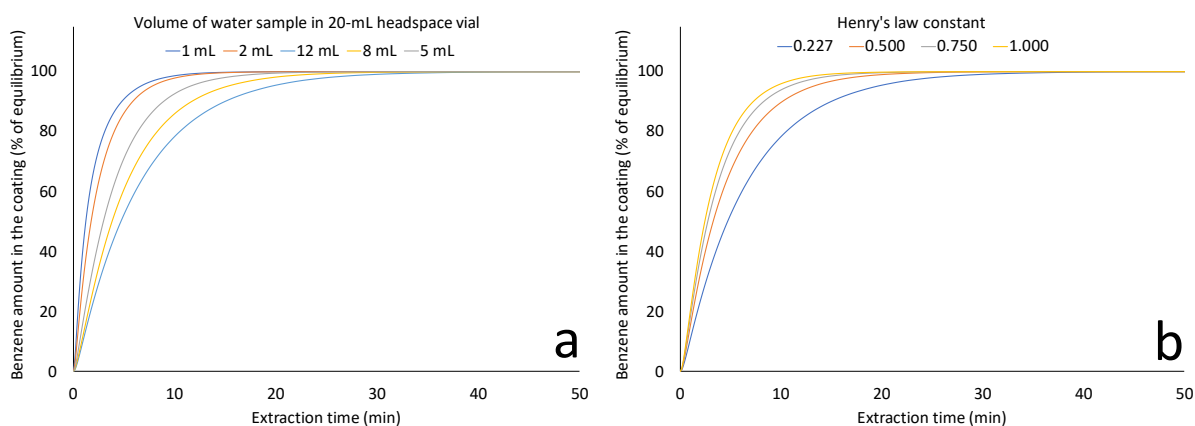
**Fig. 7** Effects of the water sample volume (a) and Henry's law constant (b) on extraction profiles of benzene by Car/PDMS fiber from 20-mL headspace vial at $T = 25$ °C and $p = 760$ mmHg under the ideal stirring.

## 4. Conclusion

In this research, the need to improve SPME-based method development process was addressed. An improved, finite element analysis-based model for VOC transport into a porous SPME coating was developed. The rationale for developing the model was to identify potentially important sources of uncertainties during typical experimental optimization of SPME, and thus to the optimization process itself.  Benzene and the Car/PDMS coating were used as a model VOC and a porous SPME coating. The effects of several parameters used to develop SPME-based method were studied. These included the diffusion coefficient in the SPME coating (assumed to be filled by air) and the diffusion coefficient inside the Carboxen particles. Combination of modeling and experimental methods (i.e., thermogravimetric analysis) allowed to determine the internal structure of the Car/PDMS coating. It has been established that volumetric fractions of Carboxen, PDMS and air in the coating are 33, 42 and 25%, respectively. In addition, measurements of the internal diameter of 23-ga protecting needle were equal to 476±11 μm, ~40% greater than nominal, suggesting that physical dimensions of SPME need to verified for some applications. The obtained experimental data allowed improving the recently developed numerical model of SPME using

Car/PDMS fiber and compared reasonably well with experimental data. It has been proven that Knudsen diffusion in micropores, which is slower than molecular diffusion characteristic for larger pores) can slow down a mass transport of analytes inside the coating. For Car/PDMS coating, mass transport of benzene is mostly characterized by a molecular diffusion, which can be explained by a large fraction of macro- and mesopores. For a more microporous coating, the effect of Knudsen diffusion can be more pronounced, which will require either building of a more complex model or using the simplified model proposed in this study at lower accuracy.

It has been shown that the developed model can be used to model the extraction of VOCs from air and water samples encountered in a typical SPME development method procedure. It was possible to determine system equilibration times and use them to optimize sample volume and Henry's law constant (e.g., by salting out effect). The developed model is relatively simple, fast (i.e., takes <5 min to obtain results), and can be recommended for optimization of extraction parameters for other analytes and sample types. The model can be further improved for studying effects of temperature, pH, salt addition, headspace pressure, extraction geometry and other parameters. The experimental methodology for studying benzene diffusivity in the Car/PDMS coating proved to be an efficient tool, which can be recommended for testing other types of coatings, particularly those being developed. In addition to distribution constants [25], the diffusivity of analytes in a coating is an important property needed for improved characterization of existing and new SPME fibers and analytical method optimization.

**Conflicts of interest**

The authors declare no conflicts of interest in relation to this research.

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