Optimization of headspace solid-phase microextraction of volatile organic compounds from dry soil samples by porous coatings using COMSOL Multiphysics

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Headspace solid-phase microextraction (HSSPME) is one of the simplest and cost-efficient sample preparation approaches for determination of volatile organic compounds (VOCs) in soil. This study was aimed at the development of the model for numerical optimization of HSSPME of volatile organic compounds from dry soil samples by porous coatings using COMSOL Multiphysics (CMP). ‘Transport of Diluted Species in Porous Medium’ physics was used for modeling. Effect of sample mass, pressure, fiber-headspace and soil-headspace distribution constants on extraction profiles and time of 95% equilibrium has been studied using the developed model. Equilibrium extraction under atmospheric pressure (1 atm) can take up to 97 min, while under vacuum (0.0313 atm) – 2.3 min. Equilibration time under vacuum was 42-43 times lower than under 1 atm at all studied distribution constants and sample masses. The developed model was modified for optimization of pre-incubation time using ‘Transport of Diluted Species’ physics. According to the obtained plots, 95% equilibration time can reach 13.3 min and depends on both sample mass and soil-headspace distribution constant of the analyte. The developed model can be recommended for optimization of pressure, preincubation and extraction time when fiber-headspace and soil-headspace distribution constants, soil porosity and density are known.

Keywords: solid-phase microextraction; numerical modeling; COMSOL; soil analysis; volatile organic compounds; computational optimization.

COMSOL Multiphysics көмегімен кеуекті жабындар арқылы құрғақ топырақ сынамаларынан ұшпалы органикалық қосылыстардың бу-фазалы қатты фазалы микроэкстракциясын оңтайландыру

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Бу-фазалы қатты фазалы микроэкстракция (БҚФМЭ) топырақтағы ұшпалы органикалық қосылыстарды (ҰОҚ) анықтау үшін сынама дайындаудың қарапайым және үнемді әдістерінің бірі болып табылады. Бұл зерттеу COMSOL Multiphysics (CMP) көмегімен кеуекті жабындар арқылы құрғақ топырақ үлгілерінен БҚФМЭ ұшпалы органикалық қосылыстарды сандық оңтайландыру моделін әзірлеуге бағытталған. Модельдеу үшін «Сұйылтылған заттардың кеуекті ортада тасымалдануы» физикасы қолданылды. Әзірленген модельді пайдалана отырып, экстракциялық жабын мен газ фазасы арасындағы және топырақ пен газ фазасы арасындағы сынама массасының, қысымның, талданатын заттардың таралу константаларының экстракция профильдеріне әсері және 95% тепе-теңдікке жету уақыты зерттелді. Атмосфералық қысымда (1 атм) тепе-теңдікке жету 97 минутқа дейін, ал вакуумда (0,0313 атм) 2,3 минутқа дейін созылуы мүмкін. Вакуумдағы тепе-теңдік уақыты барлық зерттелген таралу константалары мен сынама массалары үшін 1 атм - ға қарағанда 42-43 есе төмен болды. Әзірленген модель «Сұйылтылған заттарды тасымалдау» физикасын қолдана отырып, алдын ала инкубациялау уақытын оңтайландыру үшін өзгертілді. Алынған графиктерге сәйкес, 95% тепе-теңдікті орнату уақыты 13,3 минутқа жетуі мүмкін және сынаманың массасына да, топырақ пен газ фазасы арасындағы талданатын заттың таралу константасына да байланысты. Әзірленген модель қысымды, алдын ала инкубациялау және экстракция уақытын оңтайландыру үшін ұсынылуы мүмкін, бұл кезде талданатын заттың экстракциялық жабын мен газ фазасы арасындағы, топырақ пен газ фазасы арасындағы таралу константалары, сонымен қатар кеуектілігі мен тығыздығы белгілі болуы қажет.

Түйін сөздер: қатты фазалы микроэкстракция; сандық модельдеу; COMSOL; топырақ талдауы; ұшпалы органикалық қосылыстар; компьютерлік оңтайландыру.

Оптимизация парофазной твердофазной микроэкстракции летучих органических соединений из образцов сухих почв пористыми покрытиями с использованием COMSOL Multiphysics

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Парофазная твердофазная микроэкстракция (ПТФМЭ) — один из самых простых и экономичных методов пробоподготовки для определения летучих органических соединений (ЛОС) в почве. Данное исследование было направлено на разработку модели численной оптимизации ПТФМЭ летучих органических соединений из образцов сухой почвы пористыми покрытиями с использованием COMSOL Multiphysics (CMP). Для моделирования использовали физику «Транспорт разбавленных веществ в пористой среде». С помощью разработанной модели изучено влияние массы образца, давления, констант распределения аналита между экстракционным покрытием и газовой фазой и между почвой и газовой фазой на профили экстракции и время достижения 95%-ного равновесия. Достижение равновесия при атмосферном давлении (1 атм) может занимать до 97 мин, а под вакуумом (0,0313 атм) – 2,3 мин. Время установления равновесия в вакууме было в 42-43 раза меньше, чем при 1 атм при всех исследованных константах распределения и массах образцов. Разработанная модель была модифицирована для оптимизации времени преинкубации с использованием физики «Транспорт разбавленных веществ». Согласно полученным графикам, время установления 95%-ного равновесия может достигать 13,3 мин и зависит как от массы образца, так и от константы распределения аналита между почвой и газовой фазой. Разработанная модель может быть рекомендована для оптимизации давления, времени преинкубации и экстракции, когда известны константы распределения аналита между экстракционным покрытием и газовой фазой, между почвой и газовой фазой, а также пористость и плотность почвы.

Ключевые слова: твердофазная микроэкстракция; численное моделирование; COMSOL; анализ почвы; летучие органические соединения; компьютерная оптимизация.

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Optimization of headspace solid-phase microextraction of volatile organic compounds from dry soil samples by porous coatings using COMSOL Multiphysics

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1. Introduction

Headspace solid-phase microextraction (HSSPME) is one of the simplest and cost-efficient sample preparation techniques for quantification of volatile organic compounds in soil samples [1, 2]. HSSPME is based on extraction of analytes by a small (typically, polymeric) coating located in a headspace above sample. It combines extraction, concentration, clean-up, and allows obtaining low detection limits. HSSPME-based analytical methods have been developed for quantitation of pesticides [3-5], volatile organic compounds [6], petroleum hydrocarbons [7, 8], chemical warfare agents [9,10], rocket fuel residuals [11, 12], phenols [13-15] and other pollutants in soil. Due to its simplicity, HSSPME has a great potential for on-site application [16-19].

Development of methods for quantification of volatile organic compounds in soil samples based on HSSPME is tedious because many parameters should be experimentally optimized – amount of sample, fiber coating, extraction temperature, pressure and time [20, 21]. Typically, parameters are optimized sequentially (one parameter per experiment) [20]. Design of experiments (DOE) is often used for enhancing the optimization process by decreasing the number of experiments [22]. COMSOL Multiphysics® (CMP) have been successfully used for a much simpler and faster computational optimization of HSSPME of volatile organic compounds from samples of air [23-25] and water [26, 27]. COMSOL Multiphysics® allows monitoring changes in concentrations of analytes in different locations of an extraction vessel and obtaining extraction profiles of analytes.

Fick's second law of diffusion has been used to model mass transport in the gas phase:

$$\frac{\partial c}{\partial t} = D\,\nabla^2 c \qquad (1)$$

where: c is the analyte concentration, mol/m^3; D is the diffusion coefficient of the analyte in a corresponding gas, m^2/s; t is time. Diffusion coefficient of an analyte in gas phase (D, cm^2/s) is typically estimated using Fuller et al. [28] method:

$$D = 0.001\,\frac{T^{1.75}\left(\frac{1}{M_a}+\frac{1}{M_h}\right)^{0.5}}{p\left[(V_a)^{1/3}+(V_h)^{1/3}\right]^2} \qquad (2)$$

where T is the temperature, K, M_a is the molecular mass of an analyte, g/mol, M_h is the molecular mass of a gas (e.g., air) in headspace, g/mol, p is the pressure, atm, V_a is the molecular diffusion volume of an analyte; V_h is the molecular diffusion volume of a gas in headspace.

Mass transport in a porous coating has been modeled using [23, 26]:

$$\left(\varepsilon + \rho\,K_p\right)\frac{\partial c}{\partial t} = D_e\,\nabla^2 c \qquad (3)$$

where: ε is a porosity of a porous material (0.366 for 85 µm Carboxen/polydimethylsiloxane, Car/PDMS, fiber [23]); ρ is a bulk density of a porous material (760 kg/m^3 for 85 µm Car/PDMS [23]); K_p is a distribution constant between coating and air, m^3/kg; D_e is the effective diffusivity in the coating, m^2/s, that can be determined using:

$$D_e = D\,\varepsilon\,/\,\sigma \qquad (4)$$

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where: D is the diffusion coefficient of an analyte in the gas inside the coating calculated by Eq. (2); σ is the tortuosity factor of the coating (1.317 for 85 µm Car/PDMS [23]) that is calculated from the corresponding porosity [29].

To our best knowledge, the modeling of HSSPME of VOCs from soil samples has not been described in the open literature. This research was aimed at developing the model for simulation of HSSPME of VOCs from dry soils. Modeling mass transport and adsorption of VOCs in dry soils should be similar to that in porous coatings because both of them are saturated with gas. Wet soils contain or are saturated with water, which will require developing of a different, more complex model.

2. Experiment

2.1 General modeling parameters

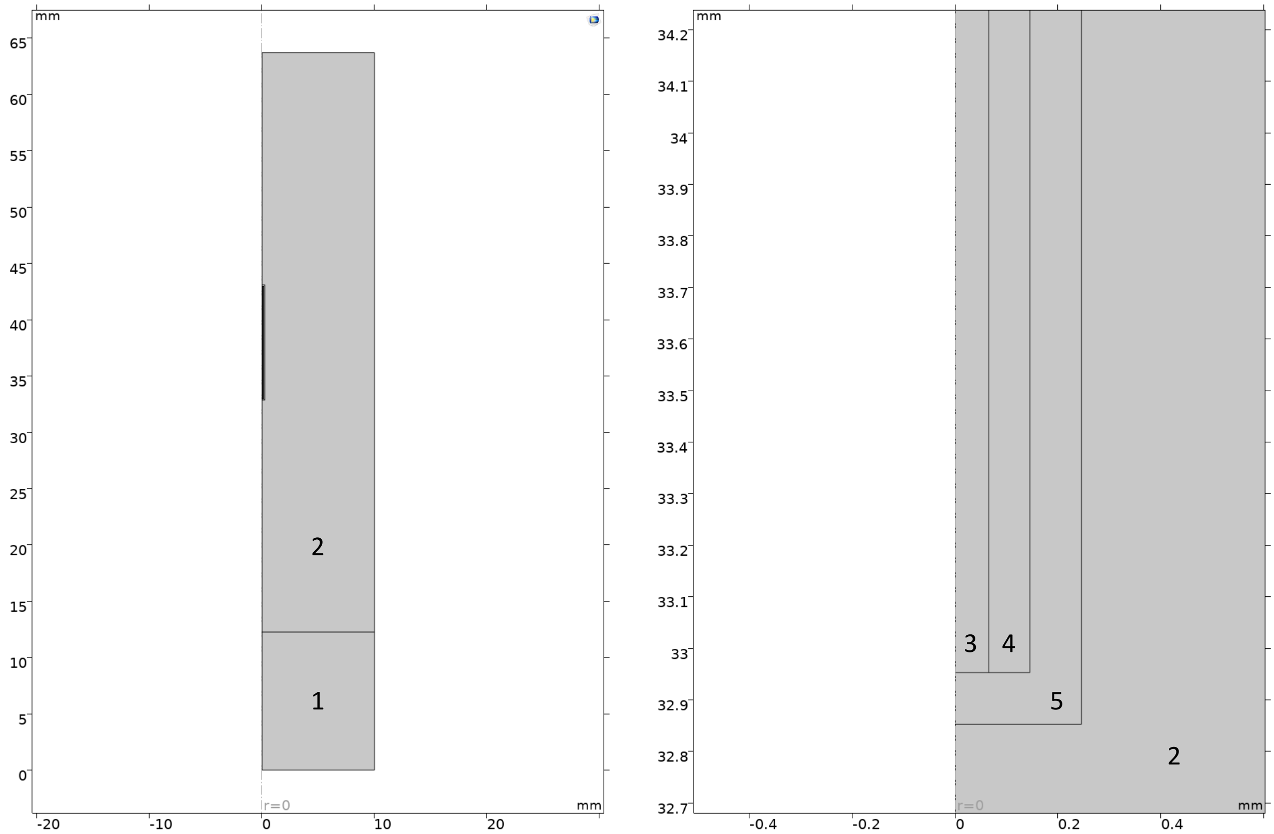
Modeling was conducted using COMSOL Multiphysics 5.6 (Burlington, MA, USA) software with Chemical Engineering module installed on a personal computer equipped with a six-core Core i7-8700 central processing unit (Intel, Santa Clara, CA, USA), 16 Gb of DDR4 random access memory (Apacer, Taiwan) and 250 Gb 860 Evo solid-state drive (Samsung, Seoul, Rep. of Korea).

2.2 Modeling of HSSPME

Two-dimensional (2D) axisymmetric model was built using ‘Transport of Diluted Species in Porous Media’ physics. The geometry (Figure 1) consisted of four main rectangular domains: soil, headspace, fiber core (0.13 x 10 mm) and fiber coating (0.08 x 10 mm). A small additional rectangle (0.49 x 10.2 mm) was built around the coating as proposed by Kenessov et al. [23] for improved modeling accuracy. Fiber core and coating were located in the center of the headspace. Mass transport in the headspace was modeled using Eq. (1). Headspace was considered static. Mass transport and adsorption in the coating and soil were modeled using Eq. (3).

Modeling was conducted for 85 µm Car/PDMS coating (Supelco, USA), the structure of which was thoroughly studied before [23]. Coating porosity, tortuosity factor and bulk density were set to 0.366, 1.317 and 760 kg/m^3, respectively. Porosity, tortuosity factor and bulk density of soil were set to typical values - 0.4, 1.3 and 1300 kg/m^3, respectively [30]. User defined adsorption isotherm was chosen for the adsorption modeling using:

$$c_p = c \cdot K_p \qquad (5)$$



Geometry components: 1 – soil, 2 – headspace, 3 – fiber core, 4 – SPME coating, 5 – additional rectangle around the coating where the initial concentration was set to zero.

Figure 1 – Geometry of the model for solid-phase microextraction of VOCs from soil

where c_p is the concentration adsorbed to the solid material, mol/kg; c is the concentration in gas inside a solid material, mol/m^3; K_p is the solid-headspace distribution constant, m^3/kg, calculated from the dimensionless solid-headspace constant (K_{sh}) using:

$$K_p = \frac{K_{sh} - \varepsilon}{\rho} \tag{6}$$

It was assumed that before HSSPME, the equilibrium between soil and headspace was established. Initial concentration of an analyte in headspace and soil gas before extraction (C_{oh}) was calculated using:

$$C_{oh} = \frac{C_{0s}\, m_s}{K_{ps}\, m_s + V_h + \varepsilon_s\, m_s/\rho_s} \tag{7}$$

where C_{0s} is the initial analyte concentration in soil before introducing it to the vial (mol/kg); K_{ps} is the soil-headspace distribution constant, m^3/kg; m_s and d_s are the mass (kg) and the bulk density (kg/m^3) of soil, respectively; V_h is the headspace volume (m^3), ε_s is the soil porosity. Initial analyte concentrations in the coating and in the small rectangle around the coating were set to zero.

Benzene was chosen as a model analyte for study because it has successfully been used (as one of the analytes) for developing the CMP models for air [23, 25] and water [26]. Two coating-headspace distribution constants (K_{fh}) were tested – 150000 and 8300, as reported by Prikryl and Sevcik [31] for 85 µm Car/PDMS and 65 µm polydimethylsiloxane/divinylbenzene (PDMS/DVB) fibers, respectively. Because the internal structure of PDMS/DVB is not reported in the available literature, parameters (dimensions, porosity, tortuosity factor and bulk density) for Car/PDMS were used for calculations at K_{fh} = 8300. Modeling was conducted using seven different dimensionless soil-headspace constants (K_{sh}): 1, 10, 100, 1000, 10000, 100000 and 1000000.

Diffusion coefficient of benzene in headspace was calculated using Eq. (2). Extraction temperature (298 K) and pressure (1 atm or 0.0313 atm) were assumed constant and homogeneous in all domains. Fuller diffusion volumes for benzene, air and water molecules were set to 90.7, 20.1 and 12.7 [28]. Fluid diffusion coefficients of benzene in gas inside the coating and the soil were set equal to the diffusion coefficient in headspace.

Extra fine free triangular mesh was used for the modeling. For better accuracy, resolution of narrow regions was increased to 10 and maximum element size was set to 0.2. All other study settings were set to default (Physics controlled).

During data processing, surface average derived values were calculated. 'Concentration species absorbed to the solid' were used for calculating concentration in the coating. Relative concentrations in the coating were calculated by dividing computed concentrations absorbed to the coating by equilibrium concentrations calculated using [21]:

$$[c_f] = \frac{K_{pf} C_{0s} m_s}{K_{pf} m_f + K_{ps} m_s + V_h + \dfrac{m_f \varepsilon_f}{\rho_f} + \dfrac{m_s \varepsilon_s}{\rho_s}} \tag{8}$$

where C_{0s} is the initial analyte concentration in soil before introducing it to the vial (mol/kg); K_{pf} is the coating-headspace distribution constant, m^3/kg; K_{ps} is the soil-headspace distribution constant, m^3/kg; m_f, ε_f and ρ_f are the mass (kg), porosity and the bulk density (kg/m^3) of the coating, respectively; m_s, ε_s and ρ_s are the mass (kg), porosity and the bulk density (kg/m^3) of soil, respectively; V_h is the headspace volume (m^3).

2.3 Modeling of pre-incubation

Two-dimensional (2D) axisymmetric model was built using two 'Transport of Diluted Species' physics. The geometry consisted of two main rectangular domains: soil and headspace. Equation (1) has been used to model mass transport in both soil and headspace. Apparent diffusion coefficient was set for simulating mass transport in soil [23]:

$$D_a = \frac{D\, \varepsilon_s}{\rho_s\, K_{sh}} \tag{9}$$

Fluxes to (or backward from) headspace (Flux$_1$ and Flux$_2$, respectively) at the soil-air boundary were set to [23]:

$$\begin{aligned} \mathrm{Flux}_1 &= 1000\frac{m}{s}(\mathrm{c}_s - c_h K_{sh}); \\ \mathrm{Flux}_2 &= 1000\,\frac{m}{s}(c_h K_{sh} - \mathrm{c}_s) \end{aligned} \tag{10}$$

where: 1000 m/s is the flux coefficient at the soil-headspace interface (set to a very high value as previously used [23]); c_s and c_h are concentrations of the analyte in soil and headspace at the interface, respectively, mol/m^3. Initial analyte concentration in headspace was set to zero.

Relative concentrations in the headspace were calculated by dividing computed concentrations in the headspace by equilibrium concentrations calculated using [21]:

$$[c_h] = \frac{C_{0s} m_s}{m_s/(\rho_s K_{sh}) + V_h} \tag{11}$$

3. Results and Discussion

3.1 Extraction profiles obtained during the modeling

The model allowed obtaining extraction profiles of benzene from headspace above 1 g of soil in 20 mL vial (Figure 2) using different values of the coating-headspace and soil-headspace distribution constants. At K_{fh} = 150000, the increase of K_{sh} from 100 to 1000 resulted in a substantially longer equilibration process. Time required for extracting 95% of the equilibrium benzene amount ($t_{0.95}$) increased from 33.7 to 65.3 min. At K_{fh} = 8300, the increase of K_{sh} from 100 to 1000 resulted in the increase of $t_{0.95}$ from 4.4 to 5.9 min. Equilibration at K_{fh} = 150000 takes about one order of magnitude longer time than at K_{fh} = 8300.

Such extraction profiles can be used for optimizing extraction time, which is typically chosen after the equilibrium is established. However, to minimize competition between analytes and matrix ingredients, extraction can be conducted at the linear range – when analyte concentration in a coating linearly increases with the increase of time [21].

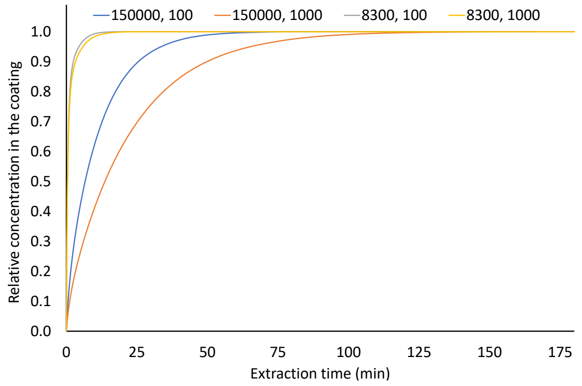


Figure 2 – Benzene solid-phase microextraction profiles from headspace above 1.00 g of soil in 20 mL vial at 1 atm simulated in CMP using two different K_{fh} (150000 and 8300) and K_{sh} (100 and 1000) values

3.2 Effect of sample mass under atmospheric pressure

Sample mass is an important parameter in HSSPME. Increase in a sample mass can result in an increased analyte amount in a coating and a lower detection limit. This parameter is particularly important when extraction effectiveness is high [21]. However, the increase of soil mass and height in the vial can slow down the equilibration process, which will be more affected by the mass transfer in soil – analytes located at the bottom of the vial will have to pass via a thicker level of soil to reach the headspace. In the case of HSSPME of VOCs from water, mass transfer in the sample can be enhanced by stirring, but this approach is impossible for soil. According to Eq. (3), the mass transfer rate in soil depends on the fluid diffusion coefficient, porosity, tortuosity factor and soil-headspace distribution constant.

CMP allows simulating the effect of soil mass on extraction profiles and optimization of this important parameter along with extraction time (Figure 3). At K_{fh} = 150000 and K_{sh} = 1, sample mass has a minor effect on the equilibration time (Figure 3A). At K_{fh} = 150000 and K_{sh} = 10, linear dependence of $t_{0.95}$ on the sample mass is observed. At K_{fh} = 150000 and K_{sh} = 100, linear dependence of $t_{0.95}$ on the sample mass is observed when increasing m_s from 2 to 10 g. At K_{fh} = 150000, K_{sh} = 100 and m_s = 10 g, $t_{0.95}$ reaches 97.0 min, the highest value in this study. At K_{fh} = 150000, K_{sh} = 100000 and 1000000, $t_{0.95}$ linearly decreases from 69.8-71.5 min to 52.3-54.0 min with the increase in m_s from 1 to 10 g. At K_{fh} = 150000 and K_{sh} = 10000, $t_{0.95}$ linearly decreases from 74.0 to 59.8 min with the increase in m_s from 2 to 10 g. At K_{fh} = 8300, $t_{0.95}$ values are not higher than 6 min meaning that equilibrium extraction can be conducted at any m_s with low time expenses (Figure 3B). The trends are similar to those at K_{fh} = 150000, except at K_{sh} = 100: $t_{0.95}$ increases when increasing m_s from 1 to 5 g followed by the decrease when m_s is increased to 10 g. At K_{fh} = 150000 and K_{sh} = 1000, $t_{0.95}$ increases when increasing m_s from 1 to 5 g followed by a slight decrease when m_s is increased to 10 g.

3.3 Effect of sample mass under vacuum conditions

HSSPME under vacuum conditions (Vac-HSSPME) can be used to achieve equilibrium faster [32-35]. This is mainly caused by the decreased diffusion coefficients in headspace under vacuum conditions [36]. The effect of vacuum when extracting VOCs from a dry soil is even more pronounced because it enhances mass transfer in the soil sample. As is seen from Eq. (4),

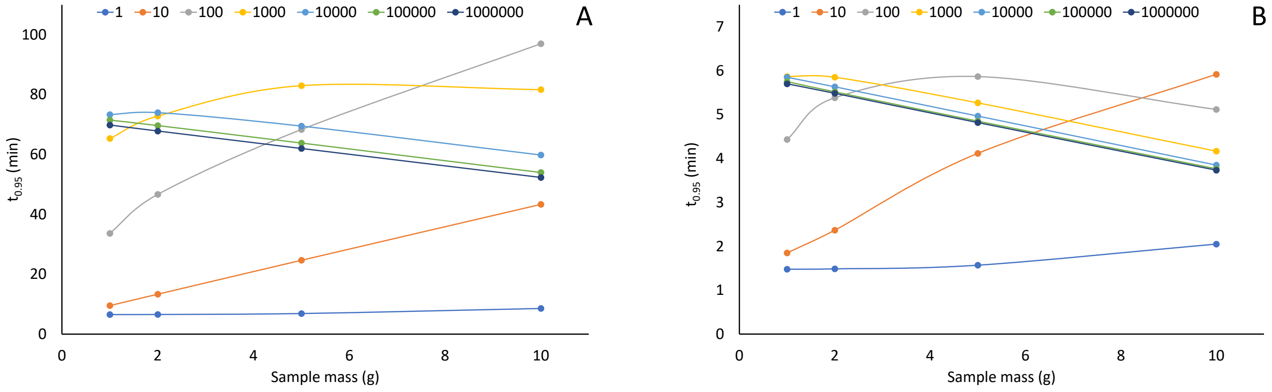


Figure 3 – Time required for extracting 95% of the equilibrium benzene amount ($t_{0.95}$) using coating-headspace distrbution constants 150000 (A) and 8300 (B) at 298 K, 1 atm and different soil-headspace distribution constants

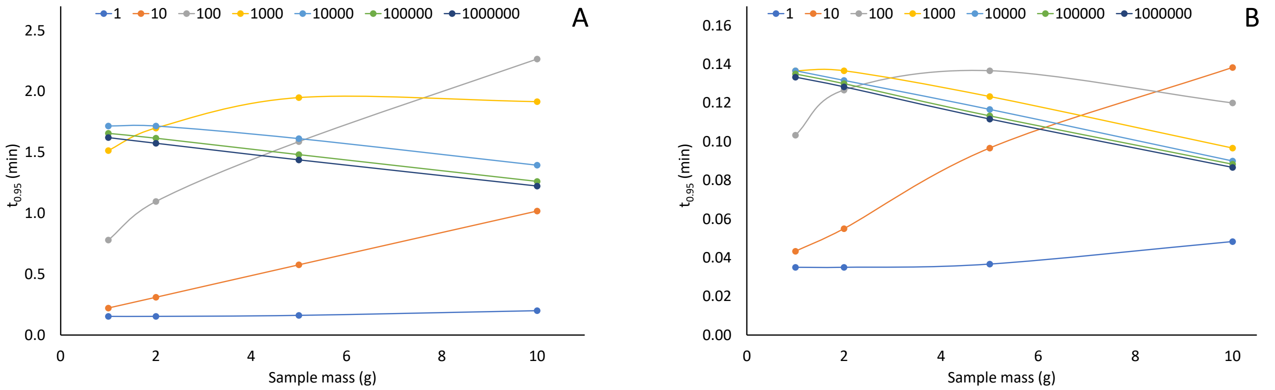


Figure 4 – Time required for extracting 95% of the equilibrium benzene amount ($t_{0.95}$) using coating-headspace distribution constants 150000 (A) and 8300 (B) at 298 K, 0.0313 atm and different soil-headspace distribution constants

effective diffusion coefficient in soil is directly proportional to the diffusion coefficient in soil gas that is the same as headspace. To estimate the effect of vacuum on $t_{0.95}$, a pressure in the model was set to 0.0313 atm corresponding to the saturated pressure of water at 298 K. Benzene diffusion coefficient in water vapor at 0.0313 atm was calculated using Eq. (2).

At K_{fh} = 150000, $t_{0.95}$ under vacuum were 0.15-2.3 min at all studied K_{sh} and m_s values (Figure 4A). The trends were similar to those at atmospheric pressure, and $t_{0.95}$ under vacuum were 42-43 times lower than under atmospheric pressure. At K_{fh} = 8300, $t_{0.95}$ under vacuum were 0.04-0.14 min at all studied K_{sh} and m_s values (Figure 4B). The trends were also similar to those at atmospheric pressure, and $t_{0.95}$ under vacuum were 42-43 times lower than under atmospheric pressure. The obtained results prove that the decrease of pressure in the vial substantially decreases equilibration time at all studied values of distribution constants and sample masses. CMP can be used to estimate the effect of vacuum and optimize extraction time under vacuum conditions.

3.4 Optimization of pre-incubation time

Pre-incubation time is an important parameter for achieving greatest accuracy and precision of methods based on HSSPME. It is required to establish the equilibrium between a sample and headspace in a vial before introducing and exposing an SPME fiber. Typically, pre-incubation time is optimized experimentally. Recently, CMP has been successfully used for optimization of preincubation time before HSSPME of VOCs from a water sample [26]. The model developed for HSSPME of VOCs from soil has been modified for optimization of pre-incubation time by removing SPME fiber and related domains from the geometry and physics. However, it was impossible to accurately set the initial concentration of the analyte in soil and soil gas, and another model was built using two ‘Transport of Diluted Species’ physics (for soil and headspace).

According to the modeling results, equilibration time ($t_{0.95}$) depends on both sample mass and soil-headspace distribution constant of the analyte (Figure 5). At K_{sh} = 1 and 10, $t_{0.95}$ increases linearly with the increase of sample mass. At K_{sh} = 100, $t_{0.95}$ increases linearly only in the range from 1 to 5 g followed by a decrease. At K_{sh} = 1000, 10000 and 1000000, $t_{0.95}$ decreases linearly when increasing a sample mass from 2 to 10 g. At K_{sh} = 100000, $t_{0.95}$ decreases linearly in the whole studied range of sample mass. Thus, the developed model can be used for optimizing the pre-incubation time.

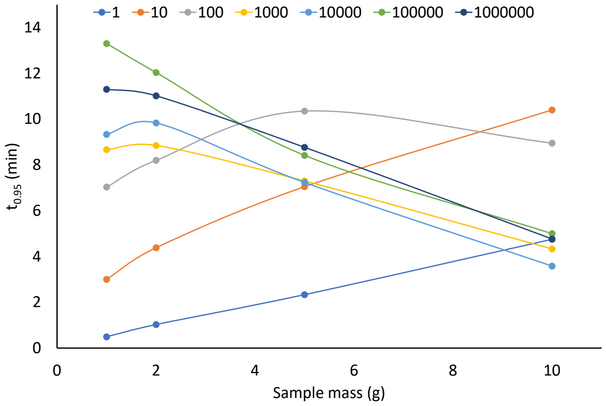


Figure 5 – Effect of sample mass on the time required for achieving 95% of the equilibrium of benzene between headspace and soil ($t_{0.95}$) at 298 K, 1 atm and different soil-headspace distribution constants

4. Conclusion

Thus, a new CMP model has been developed for optimizing HSSPME of VOCs from dry soil samples. For optimization, coating-headspace and soil-headspace distribution coefficients at the extraction temperature, coating and soil porosities and bulk densities should be known. Fluid diffusion coefficients can be estimated using Fuller method. Sample mass, geometry of the extraction vessel, location of the fiber, extraction time and pressure can be optimized using the model. Pre-incubation time can also be optimized after a minor modification of the main model. In addition to the optimization of extraction parameters, the model can be used for a better understanding of an extraction process, disclosing and solving various problems related with, e.g., poor accuracy and precision.

In the future, the developed model can be improved by considering soils saturated and unsaturated with water, which can be done using the 'Unsaturated Porous Medium' feature in the 'Transport of Diluted Species in Porous Medium' physics. Such modeling will require soil-water distribution constants, diffusion coefficients in water and volatilization rates for studied analytes. The model can be improved by adding a possibility of temperature optimization that will dependences of most modeling parameters on the temperature. Losses of unstable analytes during storage, pre-incubation and extraction of samples can also be potentially estimated in the developed model by adding Reactions to 'Transport of Diluted Species in Porous Medium' physics and providing corresponding equations for reaction rates.

Conflicts of interest

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

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