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Assessment of physicochemical properties of sorbent materials in passive and active sampling systems towards gaseous nitrogen-containing compounds

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Kinetics
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A B S T R A C T

The adsorption and desorption behavior of volatile nitrogen-containing compounds in vapor phase by solid-phase microextraction Arrow (SPME-Arrow) and in-tube extraction (ITEX) sampling systems, were investigated experimentally using gas chromatography-mass spectrometry. Three different SPME-Arrow coating materials, DVB/PDMS, MCM-41, and MCM-41-TP and two ITEX adsorbents, TENAX-GR and MCM-41-TP were compared to clarify the selectivity of the sorbents towards nitrogen-containing compounds. In addition, saturated vapor pressures for these compounds were estimated, both experimentally and theoretically. In this study, the adsorption of nitrogen-containing compounds on various adsorbents followed the Elovich model well, while a pseudo-first-order kinetics model best described the desorption kinetics. Pore volume and pore sizes of the coating sorbents were essential parameters for the determination of the adsorption performance for the SPME-Arrow sampling system. MCM-41-TP coating with the smallest pore size gave the slowest adsorption rate compared to that of DVB/PDMS and MCM-41 in the SPME-Arrow sampling system. Both adsorbent and adsorbate properties, such as hydrophobicity and basicity, affected the adsorption and desorption kinetics in SPME-Arrow system. The adsorption and desorption rates of studied C₅H₅N isomers in the MCM-41 and MCM-41-TP sorbent materials of SPME-Arrow system were higher for dipropylamine and triethylamine (branched amines) than hexylamine (linear chain amines). DVB/PDMS-SPME-Arrow gave fast adsorption rates for the aromatic-ringed pyridine and o-toluidine. All studied nitrogen-containing compounds demonstrated high desorption rates with DVB/PDMS-SPME-Arrow. Chemisorption and physisorption were the sorption mechanisms in MCM-41- and MCM-41-TP SPME-Arrow, but additional experiments are needed to confirm this. An active sampling technique ITEX gave comparable adsorption and desorption rates on the selective MCM-41-TP and universal TENAX-GR sorbent materials for all the compounds studied. Vapor pressures of nitrogen-containing compounds were experimentally estimated by using retention index approach and these values were compared with the theoretical ones, calculated using the CONductor-like Screening MOdel for Real Solvent (COSMO-RS) model. Both values agreed well with those found in the literature proving that these methods can be successfully used in predicting VOC’s vapor pressures, e.g. for the formation of secondary organic aerosols.

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1. Introduction

Nitrogen-containing compounds emitted to the environment are essential components of organic aerosols that take part in the formation of air pollution. Organic aerosols, that can be produced via several reactions or mechanisms in the air, play critical roles by affecting air quality and global climate, and by increasing concern about the human health hazards [1–3]. Hence, the knowledge of formation and chemical composition of organic aerosols are needed to understand certain aspects of these environmental issues. Nitrogen-containing compounds are very challenging to an-

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alyze or determine due to their volatility, high polarity, and presence as mixtures with low concentrations. The lack of reliable analytical methods causes difficulties in studying the specific role of nitrogen-containing compounds in the atmosphere [4–6].

The selection of proper sampling techniques with selective sorbent materials has become the crucial step for the collection of nitrogen-containing compounds from air samples before the final analysis. An accurate sampling and measurement of compounds requires a knowledge of the physicochemical properties that control their partitioning between gas and particle phases in the environment. These properties can also be exploited for the collection of compounds by adsorption onto the sorbent material of the sampling device, and for their desorption/release for the analysis, e.g. by gas chromatography–mass spectrometry (GC–MS) [7,8].

A solid-phase microextraction (SPME) Arrow and an in-tube extraction (ITEX) are two different sampling techniques that during the recent years have attracted a great interest as miniaturized air sampling systems due to their small sizes, environmentally friendly and their easy operation and automation. They also offer short sampling times and straightforward quantification. These techniques have successfully been used for the collection of volatile organic compounds from environment and food samples [2,9–11]. SPME-Arrow is a passive sampling system where the analytes move by diffusion from the sample medium (higher concentration) to the sampler medium (lower concentration) until the equilibrium is reached between these two media. In an active sampling system such as ITEX, extra pressure or vacuum are needed as the driving force to move the air through the tube packed with adsorbent [12,13]. Only gas phase can be collected by SPME-Arrow system, while ITEX sampler can collect both gases and particles.

Our recent studies have demonstrated that functionalized mesoporous silica-based sorbents, namely Mobil Composition of Matter No. 41 (MCM-41) and titanium hydrogen phosphate-modified MCM-41 (MCM-41-T), used as coating material in SPME-Arrow and as packed sorbent material in ITEX tube, can be successfully exploited by to selectively collect nitrogen-containing compounds from air [2,14]. In this study, the mass transfer mechanism of nitrogen-containing compounds from air to SPME-Arrow and ITEX sampling sorbents and from the sorbents to GC–MS was successfully studied by adsorption and desorption kinetics. Three different materials, MCM-41, MCM-41-TP, and Divinylbenzene/Polydimethylsiloxane (DVB/PDMS) were used as sorbent coatings in SPME-Arrow sampling system, and the ITEX tube was packed with two different adsorbent materials, MCM-41-TP and TENAX-GR. The adsorption kinetic models were studied to find the optimal sampling process for better sampling selectivity and optimum conditions, while the desorption kinetic models helped to find the optimal conditions for desorption of the analytes trapped by the sorbent to the analytical instrument resulting in improved quantification.

In addition to adsorption and desorption kinetics, another physicochemical property of atmospheric trace gases, namely saturation vapor pressures, were studied. The saturation vapor pressure is needed to determine their atmospheric behavior and impact, such as to predict the mass distribution of condensing and evaporating nitrogen-containing compounds between gas and particle phase in the atmosphere [15–18]. Nitrogen-containing compounds belong to the sources of the atmospheric aerosol particles, since when they are oxidized by atmospheric oxidants such as OH, NO2, O3, and Cl radicals, they form lower volatility products and then condense to form secondary organic aerosols, and later become the major contributor to particulate material (PM) phase, such as PM 2.5. Correct vapor pressure data is important for the characterization of compound partitioning onto atmospheric organic aerosols, since the gas/particle partitioning process depends on the vapor pressure values [19].

In this study, the saturation vapor pressures of selected nitrogen-containing compounds were experimentally estimated using retention index (Iₖ) approach after GC–MS analysis [15], and the values were compared to those obtained theoretically from computational modeling. The Conductor-like Screening MOdel for Real Solvent (COSMO-RS) model as implemented in the COSMO-conf and COSMOTHERM programs, was utilized to calculate electrostatic interactions between molecules in order to determine the saturation vapor pressure of compounds [19,20].

2. Material and methods

2.1. Reagents and materials

Pentane (95%) was purchased from Lab Scan Analytical Science (Sowinski, Poland), Dichloromethane (≥99.8%) and hexane (≥97%) were purchased from Honeywell (Seelze, Germany). Heptane (p.a.), nonane (99%), and decane (98%) were purchased from E Merck (Darmstadt, Germany). Octane (95%) was purchased from JT Baker (Deventer, Holland). Isobutyramine (99%), hexylamine (99%), and 1-methylimidazole (99%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Diprolyamine (∼100%), undecane (99%) and o-toluidine (≥99.5%) were purchased from Fluka (Buchs, Switzerland). Triethylamine (≥99%) was purchased from Merck KGaA (Darmstadt, Germany). Pyridine (∼100%) was purchased from VWR Chemicals (Fontenay-sous-Bois, France).

Empty ITEXs and bare Arrows were provided by BGB Analytik AG (Zurich, Switzerland). Divinylbenzene/PDMS-SPME-Arrow (DVB/PDMS-SPME-Arrow) was purchased from CTC Analytics AG (Zwingen, Switzerland). TENAX-GR was purchased from Alltech (Illiwild, USA). The mesoporous silica materials, MCM-41 and MCM-41-TP, materials were synthesized via sol-gel template as described in our previous publication [14]. The ITEX packing and SPME-Arrow coating instruction was described in detail in our previous studies [10,14].

2.2. Instrumentation

A lab-made permeation system was employed to create the gas-phase of selected model compounds [10]. A PAL Cycle Composer and PAL RTC autosampler that were used for the sample collection and desorption were provided by CTC Analytics (Zwingen, Switzerland). An Agilent 6890 N gas chromatograph coupled with an Agilent 5975C mass selective detector (Agilent Technologies, Pittsburg, PA, USA) was used for both kinetics and vapor pressure studies. The GC capillary column used for the kinetics studies was an InertCap for amines (30 m length x 0.25 mm I.D., without any information for the film thickness, GL Sciences, Tokyo, Japan). Whereas a GC capillary column with the dimension of 30 m (HP-1), 0.25 mm I.D. and 0.1 μm phase thickness (Agilent Technologies, USA) was used for vapor pressure study. A two-meter-long deactivated retention gap with 0.53 mm I.D was employed for both kinetics and vapor pressure studies and it was connected to the main analytical column using a glass press-fit connector (BGB Analytik, Switzerland).

2.3. On-line dynamic ITEX and SPME procedures for sampling through the permeation system

The permeation system used to create gas-phase sample from our model compounds is similar to that designed and applied in our previous studies [2,10,11]. Briefly, our permeation system consisted of a metal cylinder used to put vials containing our model compounds. A constant nitrogen flow (50 ml min⁻¹) was introduced into the metal cylinder that was kept in the permeation system’s oven at 30 °C in order to flush the permeated model
compounds out. A second and third nitrogen flow were used for the dilution, with the total dilution of up to 1:10,492, and the diluted gas-phase samples were guided to the extraction port of the auto sampler. Up to seven concentrations were used for the kinetics studies (Supplemental Table S1), with the compound dilution range between 1:357 and 1:10,492 (Supplemental Table S2). Whereas for vapor pressure study only used one dilution factor, which was 1:228.

2.4. Gas chromatography – mass spectrometry analysis

2.4.1. Kinetic study

SPME-Arrow systems with three different coating materials (MCM-41, MCM-41-TP, and DVB/PDMS) and two ITEX systems with two different adsorbents (MCM-41-TP and TENAX-GR) were compared in term of their kinetics in collecting the vapor of the model compounds from the permeation system (as adsorption kinetics study), and in releasing the analytes from the sorbents to GC inlet (as desorption kinetics study). The model analytes used in the kinetics study were isobutylamine, triethylamine, pyridine, dipropylamine, hexylamine, and o-toluidine.

For adsorption kinetics study, the important parameter studied was the adsorption time, which varied between 2 min and 30 min for both ITEX and SPME-Arrow systems. The gas sample containing six model compounds was collected from the permeation system at the temperature of 23 °C. 1 min desorption at the GC inlet was done at 250 °C in SPME-Arrow and at 250 °C by autosampler ITEX tool with the desorption volume and rate of 800 µL and 50 µL.s⁻¹, respectively. The adsorption kinetics studies were conducted in seven different concentrations for SPME-Arrow and six different concentrations for ITEX systems (Supplemental Table S1).

Whereas for desorption kinetics study, Origin 2022b was used to design the experiment using a central composite design 2² + star, axial distance 1.291 (orthogonal), involving 11 experiments (3 center points) per adsorbent material. The parameters studied were desorption temperature and desorption time. The extraction time was the same for all the experiments, which was 20 min sampling time for SPME-Arrow system, and 15 min for ITEX system. The sample collection temperature for both ITEX and SPME-Arrow systems was 23 °C, while the desorption temperatures varied from 180 to 280 °C for both techniques. The range of desorption time in SPME-Arrow was varied from 20 to 100 s for each desorption temperature. Whereas for ITEX system, the length of desorption time was calculated by the ITEX desorption flow rate which was from 20 to 80 µL.s⁻¹. Concentrations of the compounds used for adsorption kinetics studies are listed in Supplemental Table S1.

The injection was done in all the studies in splitless mode, while the programmed temperature in the GC oven was from 40 °C (held for 3 min) to 250 °C at a rate of 25 °C min⁻¹ and then held for 5 min. The temperature of transfer line, ion source and quadrupole in the MSD were 250, 230 and 150 °C, respectively.

Electron ionization (EI, 70 eV) was utilized, and the scan range was from m/z of 15 to 350. Helium (99.996%, AGA, Espoo, Finland) was used as the carrier gas at a constant flow rate of 1.2 mL.min⁻¹. Three replicates of each experiment were made, and average retention times and peak areas were used in the calculations.

2.4.2. Vapor pressure study

All vapor pressure experiments were performed using GC–MS with SPME-Arrow as the sampling device. The model compounds selected for vapor pressure study were triethylamine, pyridine, dipropylamine, 1-methylimidazole, hexylamine, and o-toluidine. Isobutylamine was not used since it was too volatile. DVB/PDMS-SPME-Arrow sampler was used to study vapor pressures of model compounds. The SPME-Arrow conditioning was carried out in the auto sampler heating module at 250 °C for 10 min, followed by 10 min adsorption of model compounds collected from the permeation system, and then desorption in the GC inlet for one minute. The injector temperatures varied, i.e. 100, 150, 200, and 250 °C. For the helium flow rate, instead of working on a constant flow mode, the vapor pressure study was done in a constant pressure of 70.0 kPa. All the runs were performed in isothermal conditions, in which the GC oven was kept at six to eight isothermal temperatures of five degrees’ difference in order to build an ln(T/T0) plot for each different desorption or injector temperature. The temperature range for the measurement was between 35 and 80 °C for each model compound. The length of the experiments depended on the isothermal oven temperature used, and it was typically about 20 – 45 min. The interface between the GC and the MS was maintained as the same temperatures as the column (from 35 to 80 °C), while the ionization source and quadrupole temperature were kept at 230 °C and 150 °C, respectively. Electron impact ionization (EI) was used at 70 eV electron energy, and ions from 29 to 300 amu were scanned. Three replicates of each experiment were made, and average retention times and peak areas were used in the calculations.

2.5. Calculations

2.5.1. Calculation of adsorption kinetic rate constants

The adsorption and desorption kinetics calculations were conducted using Python 3.9.15 with support libraries Matplotlib, Scipy, Numpy and lmfit. The Non-linear least squares model fitting was done using the Levenberg-Marquardt algorithm implemented in the lmfit library.

The kinetic rate constants were calculated from measured desorbed amount. The raw adsorption data was fitted to the Elovic model to calculate the adsorption kinetic rate with the formula given by:

\[
\frac{dq}{dt} = ae^{-bt}
\]

(1)

where \(a\) and \(b\) are constants during any one experiment. The constant \(a\) is regarded as the initial adsorption rate because \(dq/dt\) approaches \(a\) when \(q\) approaches 0, and it depends on the activation energy. Where \(q\) is the quantity of gas adsorbed during time \(t\). The parameter \(b\) is related to the surface coverage and activation energy for adsorption during any experiment [21–24].

The integrated form of Eq. (1) is:

\[
q(t) = \frac{1}{b} \left( \ln \left( t + \frac{1}{ab} \right) - \ln ab \right)
\]

(2)

Parameters from Eq. (2) can be found using nonlinear regression.

2.5.2. Calculation of desorption kinetic rate constants and thermodynamics

In this study, all desorption experimental data was fitted by a pseudo-first-order (PFO) kinetic model and expressed as:

\[
q = q_0 (1 - e^{-kt})
\]

(3)

Where \(q\) is the eluted amount, \(q_0\) is the adsorbed amount at the start of the desorption, (in this model fit the maximum amount of compound that can elute from the adsorbent). The measured amount in the experiments is presented as a compound’s peak area. Assuming that the adsorbed amount \(q\) is desorbing with the rate constant \(k_d\).

Since various desorption temperatures were applied, the desorption thermodynamics could also be observed. The Gibbs free
energy ($G$) was calculated using Eq. (4) at various desorption temperatures [25]:

$$
\Delta G = -R_c T \ln \left( \frac{k_e h}{k_b T} \right) 
$$  \hspace{1cm} (4)

Where $k_b$ is the Boltzmann constant, $T$ the temperature, $h$ the Planck constant, $R_c$ the gas constant, and $\Delta G$ is the Gibbs free energy of activation for the desorption process.

The resulting values for the $\Delta G$ at each temperature were used for the plot that was fitted by:

$$
\Delta G = \Delta H - T \Delta S
$$  \hspace{1cm} (5)

From a linear regression, the values for the enthalpy $\Delta H$ and entropy $\Delta S$ were obtained.

2.5.3. Calculation of vapor pressures

Vapor pressures can be estimated using retention indices ($I_k$) approach [15], which uses the series of n-alkane for the logarithmic interpolation. The data collected for the experiments was retention time and was used to calculate the analyze retention indices and then plot the data points for drawing an $I_k (T)/T$ plot for each different desorption temperature.

The $I_k$ of targeted compounds that were analyzed using GC in the isothermal conditions, was calculated using Eq. (6).

$$
I_k = 100z + 100 \ln \frac{R_{k(z)}}{R_{k(z+1)}}
$$  \hspace{1cm} (6)

Where $z$ is the number of carbon atoms of n-alkane eluting just before the analyze $x$; $z + 1$ is the number of carbon atoms of n-alkane eluting right after the analyze $x$; $R_{k(x)}$ is the retention time of the analyze; while $R_{k(z)}$ and $R_{k(z+1)}$ are the retention times of n-alkane eluting just before and right after the analytes, respectively. After calculating the analyze retention index ($I_k$) obtained from different isothermal temperature runs and the next step was to make an $I_k (T)/T$ plot, and then extrapolate it in order to get the $I_k$ of analyte at 25 °C (298.15 K).

The Clausius-Clapeyron equation was derived to determine the vapor pressure of n-alkanes at 298 K, see Eq. (7) below:

$$
\ln \left( \frac{p}{p_0} \right) = \frac{(A_0 + A_1 T + A_2 T^2)}{T}
$$  \hspace{1cm} (7)

Where $p$ is the n-alkane vapor pressure, $p_0$ is a normal pressure (101,325 Pa), $T_0$ is the temperature at which the constants were determined, and $T$ is the temperature where the experiment was conducted (room temperature, 25 °C). $A_0$, $A_1$, and $A_2$ are constants of appropriate n-alkanes in which the values were taken from literature [26].

$$
\ln p = \ln p_0 + \frac{(100z - I_k) \ln \left( \frac{p}{p_0} \right)}{100}
$$  \hspace{1cm} (8)

Equation (8) was used to estimate the vapor pressure ($p$) of the analyze after knowing the analyte's retention index ($I_k$) at 298 K and the vapor pressures of the n-alkanes eluting before ($p_{0z}$) and after ($p_{0(z + 1)}$) the analyze.

2.5.3.1. Calculation of saturation vapor pressure using COSMO-RS model

The saturation vapor pressures of all model compounds were also estimated using a three-step approach exploiting COSMOconf and COSMOTHERM programs that utilized the COSMO-RS model [20,27]. First, the COSMOconf program executes a conformer sampling routine. The final conformer structures are calculated on a density functional theory level of theory (DFT implemented in the TurboMole program, B38-PW86 functional, TZVPD basis, using multipole accelerated RI-approximation) with the application of Conductor-like Screening Model for Real Solvents (COSMO-RS), a continuum solvation model. The detailed COSMOconf routine can be found in its manual [28]. As the COSMO-RS model provides free energies for conformers optimized for the liquid phase, the second step is the calculation of the conformers in the gas phase on the same level of theory. In the third step, the COSMOTHERM program [29] calculates a saturation vapor pressure, where it weights multiple conformers according to their overall population in the solvent that is determined by the Boltzmann distribution of states with different free energies. The temperature for the calculation was 25.0 °C.

3. Results and discussions

3.1. Adsorption kinetics

The adsorption kinetics can be used to evaluate the adsorption rates and mass transfer mechanism of the analytes to the adsorbent. To investigate the rate-limiting step in the mass transfer of analytes through the adsorbent, adsorption of 2–30 min was performed with each material. The determination of the model adsorption parameters allows to design the adsorption mechanism pathways, to express the dependence of the surface properties of the adsorbent on the sorption results, and to determine the adsorbent capacities to aid the sampling analysis [30]. From the adsorption and desorption kinetic models, we can predict the adsorbent-adsorbate behavior.

In this study, various models were tested for the description of an adsorption kinetic process, such as PFO, pseudo-second orders (PSO), and Elovich model. However, only the last one worked in our study.

Supplemental Table S3 shows the original data used to model the adsorption kinetic rates of the nitrogen-containing compounds adsorbed by the MCM-41-TP-ITEX. The PFO and PSO model did not fit well with this data because the adsorption curves did not provide any clear equilibrium for SPME-Arrow or breakthrough for ITEX sampler at the studied conditions. In addition, the Elovich model worked well with our experimental data and might explain the possibility of chemisorption involved during the adsorption process since some other studies reported that this model is commonly used to describe chemical adsorption of gas onto solid adsorbent [23,31–33]. In this work, only the model fit to the Elovich model is shown. While both PFO and PSO data are not shown due to the poor fit of the models. The instance of the PFO model fit to DVB/PDMS is displayed in the Supplemental Figure S1. Other adsorbents, as well as the use of the PSO model showed similar model fits.

In general, the Elovich model helps to predict the mass and surface diffusion [21]. As can be seen from Fig. 1, the curve shapes are concave upward so that it can be assumed that a surface diffusion model is dominant mechanism of the intraparticle mass transfer for all the sorbent materials [34,35]. Even though in our case SPME-Arrow system including the MCM-41 and MCM-41-TP sorbents with an acidic side (from silica and the –TP group) on the surface gives better selectivity toward basic analytes such as nitrogen-containing compounds, the adsorption is mostly surface diffusion that belongs to a physical adsorption or mixed with small chemical adsorption. Adsorption kinetics of VOCs through the mesoporous silica is a complex process. Moreover, there is limited information in the literature relating to the adsorption kinetics of nitrogen-containing compounds in mesoporous materials. The transport mechanism was simplified by assuming that the intraparticle transport is governed either by pore or surface diffusion, or both for the more rigorous model. However, there have been some reports in the literature on mesoporous adsorbents, that provide weak adsorbent-adsorbate interactions as well [36,37]. In our case, we did not achieve the plateau shape because there was no pore condensation on the mesoporous silica meaning that further
experiments with much longer adsorption times would be needed to prove this theory.

The conformity between experimental data and the model-predicted values were expressed by the coefficient of determination ($R^2$), with value close to or equal to 1. A moderately high $R^2$ value ($R^2 > 0.800$) indicates that the model could describe the adsorption kinetics of model compounds to the selected sorbent materials. In our case, we used peak areas as the measured amount of analytes adsorbed ($q$). The sampling time was between 2 and 30 min. The initial adsorption parameter $a$ and the Elovich desorption constant $b$ were calculated by fitting the adsorption data using nonlinear regression to Eq. (2).

The plot of peak area vs. $\ln(t)$ in Fig. 1 indicates that the adsorption is in accordance with the Elovich equation with $R^2$ above 0.800, except for hexylamine adsorbed by MCM-41-SPME-Arrow giving the $R^2$ of 0.796.

In passive SPME-Arrow sampling, the pore size played an important role due to the random diffusion of molecules onto the pore channels. The pore sizes of DVB/PDMS, MCM-41, and MCM-41-TP in SPME-Arrow were 40 nm, 3.8 nm, and 3.5 nm, respec-
Table 1  
Kinetics parameters and error deviation data related to the adsorption of selected compounds onto several SPME-Arrow and iTEx sorbent materials using Elovich Eq. (2).

<table>
<thead>
<tr>
<th>Compounds</th>
<th>a (area s⁻¹)</th>
<th>b (l/area)</th>
<th>R²</th>
<th>1/ab (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isobutylamine</td>
<td>5.06</td>
<td>1.3 x 10⁻⁹</td>
<td>0.959</td>
<td>1.5 x 10⁻¹</td>
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<tr>
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<td>1.000</td>
<td>1.8 x 10⁻¹</td>
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<tr>
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<td>0.977</td>
<td>1.3 x 10⁻³</td>
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<tr>
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<td>4.7 x 10⁻¹</td>
<td>0.992</td>
<td>5.5 x 10⁻¹</td>
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<tr>
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<td>0.856</td>
<td>1.9 x 10⁻³</td>
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<td>o-Toluidine</td>
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<td>5.6 x 10⁻¹</td>
<td>0.950</td>
<td>9.2 x 10⁻²</td>
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<th>b (l/area)</th>
<th>R²</th>
<th>1/ab (s)</th>
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<th>b (l/area)</th>
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<td>6.4 x 10⁻¹⁰</td>
<td>0.971</td>
<td>6.7 x 10⁻⁸</td>
</tr>
<tr>
<td>Pyridine</td>
<td>38.9</td>
<td>4.2 x 10⁻⁹</td>
<td>0.969</td>
<td>6.1 x 10⁻⁵</td>
</tr>
<tr>
<td>Dipropylamine</td>
<td>1.3 x 10⁻¹</td>
<td>2.8 x 10⁻¹⁰</td>
<td>0.954</td>
<td>2.7 x 10⁻⁸</td>
</tr>
<tr>
<td>Hexylamine</td>
<td>26.3</td>
<td>9.2 x 10⁻¹¹</td>
<td>0.927</td>
<td>4.1 x 10⁻⁸</td>
</tr>
<tr>
<td>o-Toluidine</td>
<td>8.0</td>
<td>3.3 x 10⁻¹⁰</td>
<td>0.908</td>
<td>3.7 x 10⁻⁸</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compounds</th>
<th>a (area s⁻¹)</th>
<th>b (l/area)</th>
<th>R²</th>
<th>1/ab (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isobutylamine</td>
<td>1.8 x 10⁻²</td>
<td>1.1 x 10⁻⁵</td>
<td>0.941</td>
<td>4.8 x 10⁻⁶</td>
</tr>
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<td>Triethylamine</td>
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<td>0.994</td>
<td>2.3 x 10⁻⁶</td>
</tr>
<tr>
<td>Pyridine</td>
<td>3.1 x 10⁻²</td>
<td>7.9 x 10⁻⁵</td>
<td>0.989</td>
<td>4.1 x 10⁻⁶</td>
</tr>
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<td>Dipropylamine</td>
<td>1.6 x 10⁻²</td>
<td>9.2 x 10⁻⁵</td>
<td>0.984</td>
<td>7.0 x 10⁻⁶</td>
</tr>
<tr>
<td>Hexylamine</td>
<td>5.0 x 10⁻²</td>
<td>1.9 x 10⁻⁵</td>
<td>0.949</td>
<td>1.1 x 10⁻⁶</td>
</tr>
<tr>
<td>o-Toluidine</td>
<td>72.2</td>
<td>1.4 x 10⁻⁵</td>
<td>0.947</td>
<td>9.7 x 10⁻⁷</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compounds</th>
<th>a (area s⁻¹)</th>
<th>b (l/area)</th>
<th>R²</th>
<th>1/ab (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isobutylamine</td>
<td>2.1 x 10⁻²</td>
<td>9.8 x 10⁻¹¹</td>
<td>0.922</td>
<td>4.8 x 10⁻⁷</td>
</tr>
<tr>
<td>Triethylamine</td>
<td>2.2 x 10⁻³</td>
<td>2.6 x 10⁻⁹</td>
<td>0.985</td>
<td>1.7 x 10⁻⁷</td>
</tr>
<tr>
<td>Pyridine</td>
<td>4.4 x 10⁻²</td>
<td>1.3 x 10⁻⁹</td>
<td>0.953</td>
<td>1.8 x 10⁻⁶</td>
</tr>
<tr>
<td>Dipropylamine</td>
<td>1.8 x 10⁻³</td>
<td>1.7 x 10⁻⁹</td>
<td>0.953</td>
<td>3.2 x 10⁻⁶</td>
</tr>
<tr>
<td>Hexylamine</td>
<td>3.0 x 10⁻³</td>
<td>9.8 x 10⁻¹⁰</td>
<td>0.915</td>
<td>3.4 x 10⁻⁷</td>
</tr>
<tr>
<td>o-Toluidine</td>
<td>53.8</td>
<td>8.1 x 10⁻¹</td>
<td>0.904</td>
<td>2.3 x 10⁻⁸</td>
</tr>
</tbody>
</table>

DVB/PDMS-SPME-Arrow allowed slightly faster adsorption rates for aromatic compounds, i.e. pyridine and o-toluidine, presumably due to larger pore sizes and π-π interactions with the aromatic ring.

In the case of C₆H₁₃N isothers extracted by MCM-41 and MCM-41-Tp as SPME-Arrow sorbent material, triethylamine (tertiary amine) had the highest a constant followed by dipropylamine (secondary amine) and hexylamine (primary amine), demonstrating that in the gas phase branched amines had faster initial adsorption rates onto our materials compared to other nitrogen-containing compounds. For primary amine o-toluidine, an aryl group attached to the amine group decreased its basicity giving the lowest a constant compared to other primary amines (i.e. isobutylamine and hexylamine) [39]. Since in the gas phase the inductive effect of the alky groups spreads the positive charge into the protonated form causing the following basicity order; tertiary (most basic) > secondary > primary (least basic). Since the surfaces of MCM-41 and MCM-41-Tp coating materials contain silica and –TP in SPME-Arrow with an acidic side, the most basic amines posed fastest adsorption rates.

Amines act as bases, and their basicity varies from molecule to molecule, depending on the availability of the nitrogen’s lone electron pair, and the electronic properties of the attached substituent groups such as alky groups that enhance the basicity or aryl groups that diminish it. In the gas phase, since no solvent is used, we do not take into consideration the degree of solvation of the conjugate pair by the solvent (steric consideration). If the case of aqueous solution, the order of basicity will be secondary > primary > tertiary amines.

Aromatic heterocyclic amine pyridine gave slower a constant than triethylamine and dipropylamine. It is less basic due to the nitrogen atom that is directly linked to an aromatic ring structure, and affects its electron withdrawing properties. The sp² nitrogen that is a part of one double bond hybridized, increases s-character and brings it closer to the nitrogen nucleus, thus reducing its tendency to bond to a proton compared to sp³ hybridized nitrogen. The effect of the aromatic ring that decreases the basicity of the amine can be strengthened depending on the substituents on the ring and on the nitrogen. The presence of the lone electron pair in the nitrogen affects the aromatic ring, because the nitrogen can less electron density to the ring, and then the ring becomes much more reactive [39].

In the case of SPME-Arrow with DVB/PDMS sorbent, that has a more neutral and hydrophobic surface, the branched amines (i.e. triethylamine and dipropylamine) also had larger a and b constants than the primary amines (i.e. hexylamine) indicating faster initial adsorption rates and larger surface coverage. The properties of modeled nitrogen-containing compounds are shown in Table 2. Triethylamine (tertiary amine, log Kₒ/w = 1.45) as the least hydrophobic analyte among the studied C₆H₁₃N, gave a faster initial adsorption rate than the most hydrophobic hexylamine (primary amine, log Kₒ/w = 2.06), but slower than dipropylamine (secondary amine, log Kₒ/w = 1.67). Small primary amine isobutylamine has a log Kₒ/w below 1, indicating its low hydrophobicity nature. Thus, as expected, isobutylamine had a low affinity towards the DVB/PDMS sorbent in SPME-Arrow resulting in slow initial adsorption rates. In contrast, pyridine with the lowest log Kₒ/w (least hydrophobic) showed fast initial adsorption rates most probably due to strong π-π interaction with the DVB in DVB/PDMS-SPME-Arrow [40,41].

Another model compound that also has an aromatic ring, o-toluidine, demonstrated a slightly slower adsorption rate than pyridine.

In the case of active iTEx sampling technique, the adsorption rate of the selective MCM-41-Tp and universal TENAX-GR sorbent materials were comparable (Table 1). TENAX GR is made of 23% graphite carbon added during the polymerization of TENAX. It is composed of a weak acidic porous polymer based on 2,6-diphenyl-p-phenylene [46,47]. The particle size of graphite is
50 nm. MCM-41-TP sorbent material is more acidic than that of TENAX-GR.

For MCM-41-TP-ITEX, the order of the initial adsorption rate was similar to that of MCM-41-TP-SPME-Arrow, in which C₆H₅N₃, triethylamine (tertiary amine) had the fastest adsorption rate followed by dipropylamine (secondary amine) and hexylamine (primary amine). The same was true also for compounds with aromatic rings, in which o-toluidine gave slower adsorption rate than pyridine due to the aryl group attached to the amine group. The only differences were found for the primary amines, isobutylamine and hexylamine, which gave by ITEX sampling system much faster adsorption rate compared to that obtained by the passive sampling technique SPME-Arrow. Generally, as seen from Table 1, active ITEX sampling methods gave higher adsorption rates than the passive SPME-Arrow, most probably due to the aid of the pump that speed up the sample enrichment. TENAX-GR with a weak acidic porous polymer, gave also a similar adsorption rate trends as the MCM-41-TP-ITEX system.

3.2. Desorption kinetics

Desorption kinetics also helps to understand the rate off passage from one equilibrium state to another one. When adsorbed compounds desorb from the surface, this is mostly regarded as a uniform process. In this study, the pseudo-first-order (PFO) model was used to study the desorption of targeted analytes from the adsorbent materials using two different techniques, passive SPME-Arrow and active ITEX sampling systems. In SPME-Arrow desorption was done with the help of heat and time, while in the active ITEX sampling, in addition to heat, gas flow pushing the analytes out from the adsorbent was exploited.

The desorption results for all the selected compounds are presented in Supplemental Figs. S2 – S6, while all fitting results are summarized in Supplemental Tables S4 and S5. The number of data points used in the model fit was 9 for all the models, except for MCM-41-TP-ITEX and TENAX-GR-ITEX, where only 5 data points were used. The PFO parameter k_d was used to describe how fast the desorption was achieved [48]. Small k_d values were obtained when the desorption was slow.

As can be seen from Supplemental Tables S4 and S5, PFO represents good fitting model for the desorption study, with only 6% gave the low fitting (R² < 0.7) and 72% was in very good agreement with the R² > 0.9. Overall, the desorption rate was getting higher at higher temperatures for all the analytes desorbed from the adsorbents. Despite the fact that the desorption at 200 and 220 °C showed mostly highest fit to the PFO model (Figs. 2 and 3, Tables S4 and S5). The used first order kinetics also indicated the presence of single surface species.

Pyridine and dipropylamine demonstrated fast initial desorption rate towards the DVB/PDMS material in SPME-Arrow due to the sorbent’s polarity and hydrophobicity, and very good fitting (R² > 0.9) was achieved when the compounds were desorbed at the temperatures between 180 – 220 °C. Triethylamine and hexylamine both displayed narrow temperature ranges for desorption, ranging from 180 to 200 °C and 220 to 240 °C, respectively. For isobutylamine and o-toluidine, the temperature range for desorption was the largest, ranging from 180 to 240 °C.

Desorption of the primary amines (i.e. isobutylamine and hexylamine) at 180 °C from MCM-41-TP-SPME-Arrow did not fit well to the PFO model (R² < 0.5), most probably due to the strong bond between the active site of the adsorbent with the analytes. Isobutylamine that is more volatile than hexylamine gave a good fitting (R² > 0.9) with the PFO at 200 °C and hexylamine at 220 °C. o-Toluidine, however, indicated better fit at 180 °C with the R² of 0.879. The fitting of dipropylamine, which belongs to secondary amines, was worse at 180 °C (R² = 0.831), but improved at 200 °C. While other amines, such as an aromatic and tertiary amines, provided good PFO model fit starting from 180 °C. We can conclude that PFO model fits very well with aromatic and tertiary amines at low temperatures.

Amines desorbed by the MCM-41-TP-SPME-Arrow fitted well with PFO, except for pyridine at the temperature of 180 °C and isobutylamine at the temperature under 220°C.

In the case of ITEX with MCM-41-TP packed sorbent, all the experiments gave good model fit with the R² > 0.9, except desorption of o-toluidine at highest temperatures with R² > 0.7, and hexylamine whose desorption at 180 °C gave R² >0.8. TENAX GR as ITEX sorbent provided good fit for all the model compounds at any desorption temperatures and values were comparable to those obtained by MCM-41-TP-ITEX system.

DVB/PDMS as SPME-Arrow coating material gave faster desorption rates than SPME-Arrow system with MCM-41 and MCM-41-TP as sorbents. The fast desorption rate by DVB/PDMS-SPME-Arrow may be caused by rapid release of analytes from low affinity sorption sites during desorption process. Most presumably the analytes were attached onto DVB/PDMS in SPME-Arrow only via physisorption meaning that weak van der Waals forces are involved resulting in easy desorption, especially in passive SPME-Arrow sampling technique. Van der Waals forces contribute to the physisorption when the molecules are sufficiently close and mechanism of physisorption can be considered non-selective.

The relatively small increase in k_d rates and values in desorption experiments by SPME-Arrow with MCM-41 and MCM-41-TP coatings indicated the desorption process from higher affinity sorption sites [49], supporting that in addition to physisorption, chemical adsorption may be involved (even though not dominant) and provides selectivity. Chemical adsorption including chemical bonding, coordination, acid-base interactions and redox reaction are considered stable, therefore the desorption does not easily occur [50]. In this study, the silanol groups on the mesoporous silica surface might interact with the nitrogen atom in the amine groups that were responsible for the hydrogen bonding [51–53]. With relatively low energies of 1–40 kJ mol⁻¹, hydrogen bonding is stronger than van der Waals force but weaker than ionic or covalent bonds.

### Table 2

Properties of selected nitrogen-containing compounds.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Molecular formula</th>
<th>Category of amine</th>
<th>Molecular weight</th>
<th>Log K_sw [42]</th>
<th>Δf H°gas (kJ/mol) [43–45]</th>
<th>ΔVap H° (kJ/mol) at 760 mmHg</th>
<th>Boiling point (°C) at 760 mmHg</th>
<th>Vapor pressure (mm Hg) at 25 °C [44,45]</th>
<th>Dipole moment (D) [44,45]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isobutylamine</td>
<td>CH₃N₂</td>
<td>Primary</td>
<td>73.1</td>
<td>0.73</td>
<td>−98.6</td>
<td>30.6</td>
<td>68.0</td>
<td>138.0</td>
<td>1.27</td>
</tr>
<tr>
<td>Triethylamine</td>
<td>CH₃N₃</td>
<td>Tertiary</td>
<td>101.2</td>
<td>1.45</td>
<td>−92.9</td>
<td>31.0</td>
<td>89.3</td>
<td>57.1</td>
<td>0.66</td>
</tr>
<tr>
<td>Pyridine</td>
<td>CH₅N</td>
<td>Aromatic</td>
<td>79.1</td>
<td>0.65</td>
<td>140.7</td>
<td>34.0</td>
<td>115.5</td>
<td>20.8</td>
<td>2.19</td>
</tr>
<tr>
<td>Dipropylamine</td>
<td>CH₃N₂</td>
<td>Secondary</td>
<td>101.2</td>
<td>1.67</td>
<td>−116.5</td>
<td>38.1</td>
<td>109.3</td>
<td>20.1</td>
<td>No data</td>
</tr>
<tr>
<td>Hexylamine</td>
<td>CH₃N₂</td>
<td>Primary</td>
<td>101.2</td>
<td>2.06</td>
<td>−193.9</td>
<td>45.1</td>
<td>130.0</td>
<td>8.0</td>
<td>1.59</td>
</tr>
<tr>
<td>o-Toluidine</td>
<td>C₆H₅N₂</td>
<td>Primary</td>
<td>107.2</td>
<td>1.32</td>
<td>53.2</td>
<td>57.9</td>
<td>200.0</td>
<td>0.3</td>
<td>1.60</td>
</tr>
</tbody>
</table>
Given this low energy, the intramolecular hydrogen bonding can be broken at high temperature [54]. The desorption temperatures in our study ranged from 180 to 280 °C. Raised temperature make molecules more kinetically energetic, which weakens their hydrogen bonds.

In addition to hydrogen bonding, the mesoporous silica surfaces could interact with gaseous amines via Lewis and Brønsted mechanisms, indicating chemical interactions that fall within chemical adsorption [53,56,57]. Along with silanol group, the titanium phosphate (–TP) grafted on mesoporous silica (MCM-41–TP), increases the sorbent’s Lewis and Brønsted acidity [58]. This can be understood since the adsorption process is complicated and can involve more than one interaction. Pham et al. reported that MCM-41 possesses a Brønsted acid site that was determined by its interaction with pyridine [57]. Since amines have a lone electron pair that is used to accept proton, amines act as a Brønsted-Lowry base. However, the nitrogen-containing compounds that were adsorbed, were most probably not in the charge state, which may have contributed to the weak chemical adsorption [59].

This study supports our previous studies [2,14], showing that there is also interaction between basic analytes (i.e. nitrogen containing compounds) and active site of the material (silica and –TP.

Fig. 2. Pseudo-first-order plots for analyte desorption at 200 °C.
group) that PFO model does not describe well. However, with the good fitting of almost all experiments, PFO model could be used to predict the desorption kinetic rates of small gaseous molecules with the selective SPME-Arrow materials MCM-41 and MCM-41-TP that have proved good selectivity towards nitrogen containing compounds [2,14].

For active ITEX sampling, MCM-TP sorbent material gave higher desorption rates especially for isobutylamine, triethylamine, dipropylamine, and o-toludine than TENAX-GR, and similar rates for pyridine and hexylamine. Active sampling uses extra pressure as the driving force to actively push samples to be desorbed. This is most probably the reason why MCM-TP is more selective for nitrogen-containing compounds, although having faster desorption rate than TENAX-GR. We can conclude that ITEX sampling system gave higher adsorption rates due to the active sampling principle, and faster desorption rate is better for the analysis, especially when gas chromatography is used with need for quick injection.

3.3. Thermodynamic process of gas desorption

Since we used peak areas as the measured amount of analytes, not mole, the resulting values for the desorption rate constant \(k_d\) were used to calculate thermodynamics parameters using Eqs. (4) and (5). Gibbs free energy of the system can predict

---

**Fig. 3.** Pseudo-first-order plots for analyte desorption at 220 °C.
the thermodynamic process, for instance if the process reduces the free energy of the system, then the process is spontaneous. From the formula, the process is spontaneous when enthalpy decreases and entropy increases.

Calculated thermodynamic parameter for desorption of selected nitrogen-containing compounds from several adsorbents using both passive SPME-Arrow and active ITEX techniques are reported in Supplemental Table S6. The thermodynamics parameters were calculated at room temperature (25 °C or 298.15 K) where the adsorbate-sorbent interaction in DVB/PDMS-SPME-Arrow in general showed higher enthalpy contribution (ΔH) and small entropy contribution (ΔS-T) compared to those in mesoporous silica resulting in higher Gibbs free energy. In the case of ITEX sampling system, the dynamic technique resulted in comparable Gibbs free energy values. The positive enthalpy (ΔH) values suggested that the process was endothermic, while negative value indicated that the process was releasing heat (exothermic). The increased heat caused an increase in the desorbed amount of molecules, which attributed to the fact that the desorbed molecules should overcome a higher energy barrier and evaporate back to the gaseous phase more quickly. The affinity of the adsorbent towards the adsorbate is reflected by the entropy (ΔS) value. The negative entropy (ΔS) indicates generally decreased order, in this case, probably a decreased degree of randomness at the solid-gas interface during the desorption process [60].

3.4. Vapor pressure calculations

To simulate the behavior of chemical compounds in the environment, there have been many efforts directed towards developing models based on their physicochemical properties. Saturated vapor pressure is one of many properties and the most fundamental parameter to study the distribution of substances in the environment, including in the atmosphere. The vapor pressures of compounds at a given temperature can be regarded as a measurement of maximum amount or solubility of the compound in the vapor or air phase. In this sense, the vapor pressure influences the volatility of the substances, and is crucial to predict the adsorption of these compounds to airborne particulate matter (PM), the temporal and spatial distribution of SOA should be defined, as well as the removal of these compounds from the atmosphere by for instance, rainfall or dry deposition [61].

In this study, six nitrogen-containing compounds, present in the environment produced by either biogenic or anthropogenic emission, namely triethylamine, pyridine, dipropylamine, hexylamine, 1-methylimidazole, and o-toluidine were selected as model compounds for vapor pressure determination. For the experimental method, the saturation vapor pressures were determined with the aid of retention index data obtained from isothermal GC experiments coupled with mass spectrometry. As reported by Hartonen et al. [15], GC–MS method with retention index approach provides an excellent alternative for the determination of the saturation vapor pressures. In this study for the experimental measurement of vapor pressures by GC–MS, a non-polar column, HP-1 MS was used. The selection of a non-polar column was critical to avoid some polar interactions such as weak hydrogen bonding and dipole-induced dipole interactions since they will increase the retention times of model compounds relative to those of the n-alkane reference compounds, resulting in the lower vapor pressure values [15]. Therefore, only dispersive interactions governed by van der Walls forces were allowed since this interaction weaken quicker with a higher oven temperature [62]. The selection of thin column thickness (i.e. 0.1 μm) was due to the non-polar nature of the HP-1 column that contains 100% polydimethylsiloxane (in which all the –R groups are methyl groups) [15,63]. Thicker stationary phase prolongs the retention time of n-alkanes due to their stronger interactions with the stationary phase, opposite to the more polar nitrogen-containing compounds that were not retain anymore. This contributed to the deviation of the nitrogen-containing compounds’ retention indices and vapor pressures. Four injector temperatures were also used in order to compare the accuracy of vapor pressure values towards the values found from the literature. In this experiment, we did not include isobutylamine in the kinetics studies, since due to its high volatility it was difficult to run reliably alkane that elutes before isobutylamine for its retention index calculations.

Table 3 shows the linear equations and R² values of retention indices plots (y axis) versus column temperatures (x axis) to obtain the ln kₐ of analyte at the temperature of 25 °C. Whereas Table 4 shows the vapor pressure data obtained from Eqs. (7) and (8). Results in Table 4 are also compared with the computational modeling data using COSMO programs. All the data was also compared to that found from the literature.

As can be seen from Table 4, triethylamine that is produced by biogenic and anthropogenic sources such as emitted by cattle and sewage [1], has according to the literature vapor pressures of 52.6 at 20 °C and 57.1 mmHg at 25 °C [64]. Among six model compounds, triethylamine has the highest vapor pressure at 25 °C suggesting that triethylamine is the most volatile and then the easiest to be measured experimentally due to its higher gas-phase concentrations [61]. This finding is supported by the results seen in Table 4. By using GC–MS technique, the higher the vapor pressure, the most accurate results were obtained when the experiment was carried out at lower injector temperatures. Pyridine and dipropylamine with vapor pressures of 20.7 and 20.1 at 25 °C respectively, gave more accurate results when they were measured at the injector temperature of 150 °C. Whereas hexylamine and 1-methylimidazole which are less volatile, needed higher injector temperatures (200 to 250 °C) for accurate results. o-Toluidine had a big bias if compared to the vapor pressure values from the literature.

Triethylamine, dipropylamine, and hexylamine have the same molecular formula as C₈H₁₈N. However, as one would expect already from their structures, they gave different vapor pressure values. The molecular structure of the individual compound influences the energy needed for the evaporation, thus also affecting its vapor pressure. Branched compounds tend to exhibit higher vapor pressures than corresponding linear isomers, thus the more branched they are, the more volatile they are, resulting in the higher vapor pressure values. The function of the structure of the molecule affects the vaporization thermodynamics, for instance, the number of carbon atoms, the location of branches in a molecule, and the presence of aromatic rings [68]. These structural factors are regarded as group contributors in which the compounds are broken down into constituent groups, and the vapor pressure is also determined by group-group interaction parameter.

The larger errors appeared for o-toluidine as the experimental value was not similar to that obtained by theoretical calculations nor found from literature. This could be caused by the o-toluidine characterization that was strongly influenced by the characterization of the methyl group that is in ortho position to the NH₂, so that deviation between experimental and theoretical values is pretty high [51]. In addition, deviation on estimating or studying vapor pressures of branched aromatic compounds was higher than that of the linear chain compounds. The results for highly branched compounds have been usually less reliable than the results for the compounds including only simple substitutions on a non-branched molecule [69].

The laboratory results were also compared to the results calculated by using the COSMOconf and COSMOTHERM programs that
Table 3
Parameters in linear equations and $R^2$ values obtained from $I_0(T)/T$ plots.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Linear equation</th>
<th>$R^2$</th>
<th>$100,^\circ C$</th>
<th>$150,^\circ C$</th>
<th>$200,^\circ C$</th>
<th>$250,^\circ C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triethylamine</td>
<td>$y = -4.3x + 2154$</td>
<td>0.990</td>
<td>55.4</td>
<td>52.7</td>
<td>78.0</td>
<td>133.3</td>
</tr>
<tr>
<td>Hexylamine</td>
<td>$y = -0.9x + 1159$</td>
<td>0.992</td>
<td>11.1</td>
<td>14.7</td>
<td>15.8</td>
<td>13.5</td>
</tr>
<tr>
<td>1-Me Imidazole</td>
<td>$y = -0.6x + 1159$</td>
<td>0.998</td>
<td>5.1</td>
<td>6.0</td>
<td>6.7</td>
<td>6.9</td>
</tr>
<tr>
<td>Pyridine</td>
<td>$y = 0.1x + 1002$</td>
<td>0.996</td>
<td>12.8</td>
<td>19.0</td>
<td>17.8</td>
<td>14.6</td>
</tr>
<tr>
<td>o-Toluidine</td>
<td>$y = 0.1x + 1005$</td>
<td>0.993</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
</tr>
</tbody>
</table>

$^a$ Experimentally determined by using a static method [64].
$^b$ [45].
$^c$ [55].
$^d$ Experimentally determined as a function of pyridine concentration in isooctane at 25 °C by using chromatography method. The vapor pressure data then was then treated from Henry’s law constant [66].
$^e$ [67].

Table 4
Vapor pressures ($p$) at 25 °C measured experimentally by GC–MS (retention indices $I_0$, approach), samples collected by SPME-Arrow coated by DVB/PDMS. Theoretical values were theoretically calculated using CosmoTherm Program.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Literature</th>
<th>Theoretical (modeling)</th>
<th>Experimental using $I_0$ with injector T of:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>100 °C</td>
<td>150 °C</td>
</tr>
<tr>
<td>Triethylamine</td>
<td>C$_3$H$_7$N</td>
<td>57.1$^a$</td>
<td>69.0</td>
<td>55.4</td>
</tr>
<tr>
<td>Dipropylamine</td>
<td>C$_3$H$_7$N</td>
<td>20.1$^b$</td>
<td>29.6</td>
<td>11.1</td>
</tr>
<tr>
<td>Hexylamine</td>
<td>C$_3$H$_7$N</td>
<td>8.0$^c$</td>
<td>9.8</td>
<td>5.1</td>
</tr>
<tr>
<td>1-Me Imidazole</td>
<td>C$_4$H$_7$N</td>
<td>0.5$^d$</td>
<td>0.4</td>
<td>0.2</td>
</tr>
<tr>
<td>Pyridine</td>
<td>C$_5$H$_7$N</td>
<td>20.7$^e$</td>
<td>13.2</td>
<td>12.8</td>
</tr>
<tr>
<td>o-Toluidine</td>
<td>C$_7$H$_7$N</td>
<td>0.3$^e$</td>
<td>0.34</td>
<td>0.9</td>
</tr>
</tbody>
</table>

$^a$ Experimentally determined by using a static method [64].
$^b$ [45].
$^c$ [55].
$^d$ Experimentally determined as a function of pyridine concentration in isooctane at 25 °C by using chromatography method. The vapor pressure data then was then treated from Henry’s law constant [66].
$^e$ [67].

4. Conclusions

It is essential to describe precisely the kinetics of adsorption and desorption in different adsorbent–adsorbate systems, and in varied experimental conditions to study adsorbent behavior towards targeted nitrogen containing compounds. Elovich model successfully described the adsorption kinetics, while pseudo-first-order kinetic model was used to describe desorption kinetics with good model fits. Physiosorption was the main adsorption mechanism for sorbents studied, in particular for the DVB/PDMS sorbent in SPME-Arrow. Chemical adsorption was also detected for MCM-41 and MCM-41-TP sorbent materials in SPME-Arrow from the desorption kinetics study, but more studies with longer sampling times are needed. MCM-41-TP as SPME-Arrow coating provided smooth diffusion and consistent behavior but unfortunately with very low adsorption rates and capacity. Hence, in terms of

utilize the COSMO-RS model. For the model, some structural and functional groups were defined by COSMOconf program to make the group contribution method. This program methodically searches for conformers, remove unstable and redundant conformers, and optimizes the rest with quantum chemistry. The energy or stability of each compound conformer was then computed. The conformers were calculated separately and then the values were combined based on conformer stabilities.

The computed saturation vapor pressures were in very good agreement with the experimental values, maximally deviating by a factor of three, corresponding to the expected deviations of a factor of 3.68 that are given by the COSMO-RS developers [28]. A known source of error for COSMO-RS is due to an abundance of functional groups, as COSMO-RS overestimates the impact of intramolecular hydrogen bonds, [20] however, our model compounds selected have only one functional group.

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selectivity and adsorption rate, passive sampling technique SPME-Arrow with MCM-41 coating sorbent is recommended for the collection of nitrogen-containing compounds. Pore structures, such as pore volume and pore size were essential parameters for the determination of the adsorption performance. In addition, characteristic of adsorbent, such as acidity and hydrophobicity affect both adsorption and desorption rates of the nitrogen-containing compounds. In both MCM-41- and MCM-41-TP SPME-Arrow systems, adsorption and desorption rates of C8H8N isomers were faster for branched-chain amines dipropylamine and triethylamine than for linear chain amine hexylamine. MCM-41- SPME-Arrow was excellent to capture small amines, such as isobutylamine compared to other materials under study. Pyridine and α-toluidine with aromatic rings gave higher adsorption rates with DVB/PDMS-SPME-Arrow sampler. In addition, DVB/PDMS-SPME-Arrow system gave fastest desorption rates for all modeled nitrogen-containing compounds. Active ITEX sampling system provided higher adsorption and faster desorption rates making it better for the analysis by gas chromatography that needs fast desorption from the injector to capillary column.

The saturation vapor pressures of the model compounds were also studied by comparing their literature values with those achieved in our laboratory experiments using GC–MS (Kováts retention index). The results provided by the modeling, i.e. combination of the COSMOconf and COSMOTHERM programs that utilize the COSMO-RS model, were comparable with only small deviations. It is better to analyze more volatile analytes at lower GC injector temperatures, and vice versa. In our experiments, the adsorption and desorption of more volatile compounds were affected by the properties of sorbent, such as acidity, basicity, and hydrophobicity.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Eka Dian Pusfitasari: Conceptualization, Formal analysis, Visualization, Data curation, Software, Writing – original draft. Jose Ruiz-Jimenez: Conceptualization, Visualization, Supervision. Jörgen Samuelsson: Software, Visualization, Writing – review & editing. Vitus Besel: Software, Visualization. Torgny Forstedt: Visualization, Writing – review & editing. Kari Hartonen: Conceptualization, Supervision, Visualization, Writing – review & editing. Marja-Liisa Riekkola: Conceptualization, Supervision, Visualization, Funding acquisition, Writing – review & editing.

Data availability

Data will be made available on request.

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Supplementary materials

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References
