Preconcentrating sensor systems toward indoor low-concentration VOC detection by goal-oriented, sequential, inverse design strategy

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A R T I C L E   I N F O

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List of symbols

A B S T R A C T

The techniques capable of accurately and effectively detecting low-concentration volatile organic compounds (VOCs) are promising for environmental contaminant monitoring and non-invasive disease diagnosis. However, low-concentration measurement and selective quantification of multiple components are two major challenges for VOC detection. This work proposes the idea of a sensing system that incorporates preconcentration and multiple sensor arrays to address the two challenges. The design principles and strategies of the sensing system were discussed, as well as the key requirements and challenges of each step of the design process. We further developed a goal-oriented, sequential, inverse design method for an accurate sensing system of indoor VOCs, enabling the realization of high cross-selectivity detection. We also demonstrate the potential and feasibility of the sensing system with a preconcentrator through illustrative examples. The proposed system is expected to be scalable and intermittent, moving it closer to reliable, commercial, and portable near-real-time determinations of specific VOC concentrations. It would promote the effectiveness of indoor air quality (IAQ) assessments and interventions.

1. Introduction

Real-time sensing of volatile organic compounds (VOCs) is essential for environmental and health monitoring. The hazardous VOC gases in indoor spaces, such as building environments and industrial spaces, are a diverse family of organic compounds with sub-ppm concentrations [1, 2]. The demand for portable and reliable gas detection to measure the dynamic and transient distribution of VOC gases is spurring the design of intelligent and enabling gas sensors.

Sensor technologies for VOCs, including electrochemical [3], semiconductor and colorimetric sensors [4], are attractive due to their tunability, portability, fast response time, and ease of miniaturization properties [5]. Currently, indoor VOC sensing is challenging mainly because most VOCs appear in low concentrations, often below the detection limits of sensors. Meanwhile, pollutants often appear in a mixture with complex components and wide concentration ranges [6].

Despite scientists’ dedication to improving the sensitivity of sensors [7], most standalone micro-sensors and micro-sensor arrays are still not suitable for accurate quantitative analysis of airborne VOCs at ppm levels due to the lack of selectivity [8, 9]. Considerable efforts have been devoted to the exploration of new materials to enhance gas sensors’ performance under lower concentrations [10]. In some studies, the sensor’s detection limit can reach 1 ppm for specific target gases [11]. Some sensors, like the photoionization detector (PID), have a low limit of detection (LOD) (approximately 1 ppb, depending on the VOC) but lack selectivity, simply reporting a total equivalent isobutylene VOC concentration [12]. So far, high selectivity for single or few VOCs such as toluene [13], 1-octen-3-ol [14] and acetone [15] have been demonstrated, but the selective detection in a mixture of VOCs is significantly more challenging. There are some selective portable detectors, mainly utilizing micro-gas chromatography or techniques similar to mass spectrometry, such as ion-mobility spectrometers [16]. However, these systems tend to be large, time-consuming and expensive. Furthermore,
sensing systems to overcome the insufficient detection of low-concentration VOCs [17].

It is a great challenge to solve the trade-off problem of low detection limit, high selectivity and fast response in developing effective VOC sensing systems. There is an urgent need to develop a small, low-cost system that can distinguish multi-component VOCs in low concentration. Previous studies have explored the use of preconcentrators in sensing systems to overcome the insufficient detection of low-concentration VOCs [1,18,19]. Preconcentrators can improve the LOD by collecting and concentrating the analytes for a certain period and allow discrimination between VOCs [27,28], combining these two technologies to build a sensing system may be more promising to solve the challenging problem. Exploring the coupling relationship between three key steps in the design process, investigate the possible advances of this approach, and discuss its applicability for fast and accurate measurement of VOCs under different scenarios.

2. Design processes and principles for sensors with preconcentrator

2.1. Detection processes for a sensing system with preconcentrator

Fig. 1 provides an overview of the detection process in a sensing system that incorporates a preconcentrator and a sensor array. The preconcentrator operates based on the principle of VOC adsorption on adsorbents, followed by rapid thermal desorption. In Step 1, the preconcentrator is employed to capture target VOCs in environmental air, which typically have concentrations lower than the LOD of sensors. The VOCs are driven through the preconcentrator and adsorbed by the adsorbents at ambient temperatures. In Step 2, after a specific adsorption period, the preconcentrator will be rapidly heated by the Joule effect, reaching high temperatures within a wide range of 150–350 °C. Subsequently, the adsorbed VOCs are immediately released at concentrations greater than the sensor’s LOD. In Step 3, the high concentrations of desorbed VOCs flow through the sensor arrays with the airflow. The sensor array, including multi-sensors, should decouple and measure the concentrations of each released VOC.

The preconcentrator. Numerous designs of preconcentrators utilizing adsorption/desorption phenomena have been reported to date [20,29–31]. The designs vary in terms of the adsorption materials, desorption technologies, and other factors, such as heating methods. Some researchers have specifically focused on optimizing the microstructure design for better adsorption effects. The microstructures reported in the literature can be categorized into four types: cavity layout, tube type, planar coating, and three-dimensional (3D) structures, as shown in Fig. 2.
For cavity-layout preconcentrators, the adsorbed material is usually filled directly and compactly in the cavity and heated by a planar hotplate [11]. Tube-type preconcentrators employ a similar sorbent filling method but are heated by wrapping heating wires [16]. Planar coating type preconcentrators consist of a planar substrate coated with an adsorbent selective to the target molecules [19]. The design is relatively easy to fabricate and offers low power consumption. However, owing to its configuration, the amount of adsorbent that can be hosted in these devices is limited, which reduces the adsorption capacity and, therefore, their preconcentration performance. This major drawback has led to a change of trend in preconcentrator design to shift progressively from planar to 3D structures. Several 3D-type preconcentrators with diverse geometries have been proposed in the literature, such as circular spirals [32], arrays of parallel channels [30], or channels with square micro-posts [33]. These innovative 3D structures aim to overcome the limitations of planar designs by maximizing the adsorbent surface area and enhancing the preconcentration performance.

Other research focuses on developing high-performance adsorbents. Adsorbent materials can be categorized as carbonaceous-based, metal-based, MOF-based, oxide-based, silicon-based, and polymer-based [8]. Each type has its strengths and limits. Carbonaceous materials, such as graphed carbon, have been extensively studied for preconcentration due to their ease of preparation, low cost, and availability [27, 36]. However, carbon-based materials are typically in powder form and require a scaffold for containment. The unintended agglomeration of the powder adsorbent material may occur during operation, resulting in a reduction of the active surface area. The agglomeration problem has been addressed by utilizing structured materials like carbon nanotube (CNT) foam [34] and metal-organic framework embedded metal foam (MOFM) [9]. Some preconcentrators have been developed with micro-machined silicon as the concentrating material without a filler to detect the mixture of VOCs [1, 19]. Advances in the fabrication process for silicon substrates have enabled the production of miniaturized devices to meet the growing demand for small gas sensors. Adsorbent materials with higher specific surface area or larger porosity tend to have larger adsorption capacity toward analyte gas. Polymer-based preconcentrators have mostly focused on poly (2,6-diphenylene-oxide) (Tenax-TA) for its high chemical stability and surface area. However, the preconcentration factor is not solely dependent on the specific surface area but also relies on the analytes and the associated adsorption and desorption mechanisms. Other important factors include the interaction between gas molecules and the preconcentrator surface, as well as the

<table>
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<tr>
<th>Preconcentrator structure</th>
<th>Work Schematic</th>
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<tbody>
<tr>
<td>Cavity layout</td>
<td><img src="image1" alt="Cavity layout" /></td>
</tr>
<tr>
<td>Tube type</td>
<td><img src="image2" alt="Tube type" /></td>
</tr>
<tr>
<td>Planar coating</td>
<td><img src="image3" alt="Planar coating" /></td>
</tr>
<tr>
<td>Three-dimensional (3D) structures</td>
<td><img src="image4" alt="3D structures" /></td>
</tr>
</tbody>
</table>
ability to heat the adsorbent for gas desorption rapidly [8]. Table 1 provides a summary of recent developments in preconcentrators for VOCs.

The sensor array. Based on the interactions between VOC gas molecules and sensing active site, various materials have been used to design VOC sensors, such as electrochemical sensors [40], semiconductor sensors [41], optical sensors [42], micro-gravimetric sensors [26] and colorimetric sensors [4]. The ability to detect the targeted signals precisely and reliably in complex environments is one of the most intricate challenges in VOC sensing. Many VOC sensors, especially modern commercial ones, fail to meet the requirements for drastic (real-world) working conditions owing to their cross-reactivity (i.e., similar responses to different signals) and instability. Moreover, the complexity of the real environment, characterized by intricate and dynamic mixtures of chemical and physical signals, further complicates the challenge [40]. Using a single sensor is inadequate for distinguishing multiple gases due to gas cross-sensitivity and low selectivity, especially for those with similar chemical structures. Therefore, some researchers consider using sensor arrays that integrate multiple sensors to realize the detection of multi-component gas mixtures [43].

Research using sensor arrays can be categorized into two groups. The first category uses the same type of sensors to correct and identify VOC concentrations according to the response mode between VOC and multiple sensors. Li et al. [24] proposed a virtual sensor array (VSA) by depositing a sensing layer of graphene oxide film onto a piezoelectric cantilever with five groups of top electrodes to identify various VOCs. The frequency shifts of multiple resonant modes and changes of impedance values are taken as responses of the proposed VSA to VOCs, and these multidimensional responses generate a unique fingerprint for each VOC that can accurately identify different types of VOCs and mixtures with accuracies of 95.8% and 87.5%, respectively. The second category of sensor arrays involves combining sensors with different principles, and each type of sensor measures its corresponding pollutants. Yang et al. [23] developed an intelligent chip that incorporates various detection units working on the physisorption or chemisorption mechanism to detect VOCs simultaneously. Utilizing these different detection units allows the chip to identify mixing gases of aromatic compounds, aldehydes, ketones and sulfides with high sensitivity (ppb level), selectivity, and robustness (error ~8%).

In recent years, significant progress has been made in the development of new materials and microelectronic technology, which has led to the miniaturization, digitization, intelligence and systematization of micro/mano electrode array sensors. These advancements have enabled the sensors to be widely used in diverse fields, including environmental monitoring, medical and health care [44]. Sensor arrays may have broader applications in the future and contribute to multi-component online monitoring and analysis.

2.2. Characteristics and challenges of the sensing system

Fig. 3 illuminates the characteristics of the three key steps in the sensing system shown in Fig. 1. There are cohesive connections among each step to achieve a better detection effect of low-concentration pollutants.

**Step 1: Adsorption.** In this step, the preconcentrator must absorb the inflow components as much as possible to meet the enrichment requirement and not penetrate at typical concentrations. The inflow concentration at the inlet of the preconcentrator \( C_{in} \) is usually lower than the LOD of sensors \( C_{LOD} \). The blue breakthrough curve in Fig. 3a represents the outlet concentration of the preconcentrator \( C_{out} \) over time during adsorption. At the early stage, \( C_{out} \) will be much lower than \( C_{in} \) or close to zero due to the presence of adsorbent. The time taken to observe the concentration at the outlet is signified as breakthrough time \( t_b \). The accumulation of VOCs, \( M_{ad} \), is the integral of the difference of inlet and outlet concentrations over the adsorption time \( t_1 \). It can be considered proportional to the total mass of pollutants flowing through the preconcentrator \( M_{total} \). The \( M_{ad} \) should be large enough to meet the LOD of the sensor, while the adsorption time \( t_1 \) should be less than \( t_b \). Otherwise, it will lose the significance of instant detection. Therefore, the primary requirements for the adsorption step include excellent adsorption capacity, controllable adsorption time and good moisture resistance. The relationships of the key parameters in Step 1 can be described by Eq. (1) – (3).

\[
M_{ad} = \int_0^{t_1} Q_{ad} \cdot C_{ad} \, dt \tag{1}
\]

\[
M_{ad} = \int_0^t Q_{ad} \cdot (C_{in} - C_{out}) \, dt = \eta_{ad} M_{total} \tag{2}
\]

\[
t_1 < t_b \tag{3}
\]

where, \( Q_{ad} \) is the airflow rate in the adsorption step (mL/min); \( \eta_{ad} \) is the adsorption efficiency, which is the coefficient between the actual adsorption mass \( M_{ad} \) and the total pollutant mass \( M_{total} \).

\( \eta_{ad} \) is the key parameter in evaluating the adsorption stage and is mainly related to the adsorbent material. The adsorbent material in the preconcentrator plays a vital role in its performance. An ideal adsorbent material must have a strong selectivity toward VOCs, large porosity, and large adsorption capacity. Especially for multi-VOC mixtures, high selectivity is desired for some applications. Adsorption materials used in preconcentration to enlarge the adsorption capacity include granular activated carbon, polymers, metal-organic framework (MOF), silicon-based and metal-based materials, etc. Some research also attached adsorbent material onto a substrate to reduce flow resistance and increase the contact between gas and adsorbent. Good binding between the adsorbent and substrate is vital to minimize the chance of the adsorbent being carried away in the gas flow. Considering the extremely low concentrations (ppb or sub-ppm) of VOCs in indoor air, the adsorption amount in each preconcentration cycle will be relatively small. Therefore, it can be assumed that the adsorption performance will not decrease significantly with the increase of adsorption amount and detection time. However, in cases where the preconcentrator is used for extended periods or exposed to high contaminant concentrations, it is crucial to rinse the adsorbent until the sensor detection response returns to the initial baseline. This step ensures that all VOCs have completely left the adsorbent, thereby preventing a decline in adsorption performance.

No matter which adsorbent is used, pollutants need to reach the adsorbent surface from the fluid to be adsorbed. The adsorption process is mainly affected by three factors: the convective mass transfer coefficient \( h_m \) (m/s) [45], the mass transfer area \( A \) (m²), and the partition coefficient of VOC \( K \), which represents the adsorption affinity between gas and adsorbent. \( h_m \) and \( A \) constitute the mass transfer rate \( h_m A \), which represents the mass transfer process of pollutants from the fluid to the material surface. To improve the adsorption performance, on the one hand, it is necessary to enhance the mass transfer rate, such as designing the microporous flow channel to enhance the convection contact between the gas flow and the adsorbent. On the other hand, it is necessary to improve the adsorption performance of materials or increase the specific surface area, change the morphology and structure of materials, etc. [46]. Therefore, the essential problem is the material structure and design to enhance the mass transfer of pollutants at the gas-solid interface.

**Step 2: Desorption.** In this step, it is necessary to ensure that the preconcentrator can desorb the enriched VOCs as completely and quickly as possible to form a signal spike, as illustrated in Fig. 3b. The desorption amount of VOC, \( M_{ds} \), is the integral product of the desorbed airflow rate \( Q_{ds} \) and the desorbed concentration \( C_d \) over the
<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Assembly structure</th>
<th>Adsorption</th>
<th>Desorption</th>
<th>Analyte</th>
<th>PF</th>
<th>LOD</th>
<th>Ref.</th>
</tr>
</thead>
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<tr>
<td>Carbotrap, 80 mg</td>
<td>Carbon-based Tubular</td>
<td>10 min</td>
<td>50 Wound with heating wire</td>
<td>Benzene-toluene-xylene mixture, Heptane Toluene</td>
<td>–</td>
<td>20 ppb</td>
<td>[37]</td>
</tr>
<tr>
<td>Carbotrap and Tenax, 1 mg</td>
<td>Carbon-based Tubular 1/2/10 min</td>
<td>667/1000 Wound with foil micro hotplate</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>[35]</td>
</tr>
<tr>
<td>Carbotrap, 2.0 mg and Carbotrap X, 2.3 mg</td>
<td>Carbon-based Cavity layout 1 min</td>
<td>5 In-film Ti/Pt resistive heaters</td>
<td>225 °C –</td>
<td>9</td>
<td>9 VOC</td>
<td>–</td>
<td>16–600 ppb</td>
</tr>
<tr>
<td>Quinoidal bridging cavitand (QxCav) functionalized silica nanoparticles, 100 mg</td>
<td>Carbon-based Micro GC column 300 s @ 25 °C</td>
<td>250 Platinum thin film</td>
<td>110 °C – 40 s + 140 s (separation)</td>
<td>BTEX, 3 ppb</td>
<td>10(B), 4(T), 2.4 (E), 1.6(X)</td>
<td>–</td>
<td>[18]</td>
</tr>
<tr>
<td>Carbotrap B, 5 mg</td>
<td>Carbon-based Cavity layout 60–600 s @ R.T.</td>
<td>5 Ceramic heaters</td>
<td>330 °C 75 s (injection time) – 2.5</td>
<td>BTEX mixture</td>
<td>–</td>
<td>0.06–0.4 ppb (BTEX)</td>
<td>[36]</td>
</tr>
<tr>
<td>Carboxen 1000, 4.5 mg</td>
<td>Carbon-based Chamber with micro-channels 15 min @ R.T.</td>
<td>50 Cr layer microheater</td>
<td>320 °C 1.25 min 100</td>
<td>BTEX and Trichloroethylene</td>
<td>–</td>
<td>0.834 ppb (B), 0.654 ppb (T), 0.385 ppb (E), 0.665 ppb (X)</td>
<td>[27]</td>
</tr>
<tr>
<td>Restek ResSil-B, 75 mg</td>
<td>Polymer-based Tubular 5–40 min @ 5–15 °C</td>
<td>100–300 Cartridge heater</td>
<td>180 °C 5–20 min 0.8–2.2</td>
<td>VOCs mixture</td>
<td>–</td>
<td>2–43 ppt</td>
<td>[16]</td>
</tr>
<tr>
<td>Nanoporous silica</td>
<td>Oxide-based Electrochemically etched on planar</td>
<td>365 s @ 5 °C</td>
<td>100 Peltier thermoelectric module</td>
<td>Isopropyl alcohol and 1-octene</td>
<td>–</td>
<td>10 ppb</td>
<td>[1]</td>
</tr>
<tr>
<td>Modified Tenax TA-coated silica nanoparticles</td>
<td>Polymer-based Cavity layout 30 °C 1</td>
<td>Ceramic heater</td>
<td>250 °C – 30 s 1.5</td>
<td>Chloroform, isopropanol, propionaldehyde, tetrachloroethylene, chlorobenzene, ethylbenzene and p-xylene</td>
<td>–</td>
<td>–</td>
<td>[33]</td>
</tr>
<tr>
<td>MOF-5 embedded on nickel foam, 90 mg</td>
<td>MOF-based Cavity layout with micro-channel 10 min</td>
<td>5 Pt heater</td>
<td>150 °C 10 s 0.3</td>
<td>BTEX mixture</td>
<td>144</td>
<td>–</td>
<td>[9]</td>
</tr>
<tr>
<td>Tenax TA</td>
<td>MOF-based Cavity layout with micro-posts 10 min</td>
<td>1 Cr/Ni stack</td>
<td>200 °C 10–12 s 2.5</td>
<td>Benzene, toluene, tetrachloroethylene, chlorobenzene, ethylbenzene, and p-xylene</td>
<td>–</td>
<td>1 ng</td>
<td>[39]</td>
</tr>
</tbody>
</table>

Notes: BTEX is the abbreviation of benzene, toluene, ethylbenzene, and xylene. R.T. is the abbreviation of room temperature.
gas desorption. Thus, the response value will have a certain coefficient relationship with the actual desorbed mass. The relationship of key parameters in Step 3 can be described by Eqs. (6) and (7).

\[
M_t = \eta_t \cdot M_{ad} = \eta_t \cdot \int_0^{t_f} Q_{de} \cdot C_{de} dt 
\]

(6)

\[
t_f < t_d 
\]

(7)

where, \(M_t\) is the detected mass obtained by sensors (µg); \(\eta_t\) is the coefficient between \(M_t\) and the actual desorption mass \(M_{ad}\).

Fig. 3. Characteristic of the three key steps in the sensing system.

**Step 3: Sensing.** In this step, when the concentration switches from 0 to \(C_{gas}\), the sensor detection response time \(t_{r1}\) should be as short as possible and far less than the desorption time \(t_d\) to detect the peak signal of the desorption process. The time-lag behavior also exists in the sensor, as presented by the recovery time \(t_{r2}\) (Fig. 3d). In Fig. 3c, the orange curve represents the concentration of the desorbed gas, while the purple curve represents the response value of the sensor. Due to the time-lag behavior, the peak of the response value will shift to the right overall compared with the actual concentration curve of gas desorption. Thus, the response value will have a certain coefficient relationship with the actual desorbed mass. The relationship of key parameters in Step 3 can be described by Eqs. (8) – (10). Therefore, the actual concentration value can be obtained by decoupling the measured values of multiple sensors (\(S_I\), \(S_{II}\), \(S_{III}\)).

\[
S_I = \omega_{1A} \cdot X_A + \omega_{1B} \cdot X_B + \omega_{1C} \cdot X_C \\
S_{II} = \omega_{2A} \cdot X_A + \omega_{2B} \cdot X_B + \omega_{2C} \cdot X_C \\
S_{III} = \omega_{3A} \cdot X_A + \omega_{3B} \cdot X_B + \omega_{3C} \cdot X_C 
\]

(8)

\[
\begin{bmatrix} S_I \\ S_{II} \\ S_{III} \end{bmatrix} = \begin{bmatrix} \omega_{1A} & \omega_{1B} & \omega_{1C} \\ \omega_{2A} & \omega_{2B} & \omega_{2C} \\ \omega_{3A} & \omega_{3B} & \omega_{3C} \end{bmatrix} \begin{bmatrix} X_A \\ X_B \\ X_C \end{bmatrix} 
\]

(9)

\[
y = Wx 
\]

(10)
where, $S_1 - S_{III}$ are the signal values detected by Sensor I – III, respectively; $X_A$, $X_B$ and $X_C$ are the actual concentrations of Components A, B and C, respectively; $\omega_{1A}$, $\omega_{1B}$ and $\omega_{1C}$ are the detection coefficients related to the $i$th sensor and the Components A, B and C, respectively. The detection coefficient constitutes the matrix of sensor detection coefficient $W$, and the $x$ and $y$ column vectors are the actual values of the components and the measured values of the sensing unit, respectively.

The principle behind this method is to obtain the contribution of each VOC towards the sensor’s response value by using different specific sensors. Nonetheless, the disadvantage of this method is that it cannot separate VOCs having similar responses or those pollutants for which detection coefficients are unknown. A unique solution is achieved when the group fraction is less than or equal to the number of sensors. Even so, the sensor array can still be used to calibrate and boost sensor accuracy through algorithms, primarily when current commercial sensors fail to provide adequate specificity.

Currently, most studies are carried out according to problem-oriented thinking, which is analyzed case by case. The adsorption material is first selected, the preconcentration device is further designed, and experiments are conducted to test the enhancement effect. However, this problem-oriented approach is not feasible for field applications where the requirements might be insufficient and harsher than the laboratory.

Zhang et al. [48] proposed a novel inverse-problem-based approach (so-called goal-oriented approach) for solving building energy and environmental problems. The objective of an inverse problem is to find the most suitable model parameters to obtain model results that are the most expected (those that tend to be maximal or minimal). Various inverse problem methods have been used to address some built environment problems and have produced exciting results [49,50]. Therefore, this study aims to propose a goal-oriented, sequential, inverse problem optimization method to guide the design and improvement of the sensing system with a preconcentrator, clarify its principle, and demonstrate its advantages through an illustrative example.

3. Goal-oriented, sequential, inverse design method for accurate sensing system of indoor VOCs

3.1. Inverse problem optimization method principle

The performance of the proposed sensing system relies on the functional integration of these system components, whereby the analytical burden is distributed among the preconcentrator, rapid separation with tunable and programmable heating, and detector module comprising an array of sensors. The ultimate goal is to develop the capability to sample and analyze mixtures of VOCs of arbitrary composition at concentrations as low as sub-ppm within a specific duration and to use response patterns from the sensor array to identify and quantify the vapors.

When designing a sensor with a preconcentrator suitable for detecting low-concentration VOCs, the coordination of all parts in the sensing process should be considered. The design of the intermittent fast response detecting system should comprehensively consider the detection requirements, the sensor’s performance, the detection error and other factors to make the design more directional. Therefore, a goal-oriented, sequential, inverse design process of the preconcentrator is proposed in this study, as shown in Fig. 5. The design process can be divided into the following four parts: (I) determine the detection target or demand; (II) Sensor selection; (III) Determine the requirements for preconcentration; (IV) Design the material and structure of the preconcentrator.

As illustrated in Fig. 5, the detection goal or requirements should be clear first in the goal-oriented design process, including what components need to be detected ($n$), what the concentration level is ($\omega_i^s$), and how fast the detection speed needs to be ($t_d$). Then, the appropriate sensors according to the detection target are selected. Once the sensor selection has been finalized, the detection limit ($C_{LOD}$) and response times ($t_{d1}$, $t_{d2}$) of the sensor are then defined. The requirements for the preconcentration can be follow-up established, including the $PF$ and requirements for adsorption and desorption. These decisions are then passed to the material selection or design. Thus, the decisions at the preconcentrator and material design are influenced by the decisions made at the sensor selection stage, thereby making this an inverse design scheme based on end goals.

3.2. Coupling principles between the preconcentrator and sensor

Following the inverse design method for the sensing system, it should first clarify the requirements or objectives of detection in practical applications, such as the type of components expected to be detected, the range of concentrations, and the acceptable detection duration. These parameters are summarized in Table 2, which describes the detection requirements. A general model will be developed for the sensing system with a preconcentrator.

The following assumptions are made to simplify the analysis: (1) The inflow concentration at the inlet of the preconcentrator $C_{in}$ is lower than the LOD of sensors $C_{LOD}$ and remains the same during adsorption; when the detection limit of the sensor is unknown or lower than the sensor’s resolution, it is necessary to set the detection limit as equal to the resolution. This is because the sensor is incapable of measuring a value smaller than its resolution. (2) the outflow concentration of the preconcentrator $C_{out}$ can be treated as constant before the adsorbent penetrates; (3) the mass of pollutants desorbed by heating is close to that of the accumulated adsorption and can be described by a coefficient. Thus, for the preconcentrator in the sensing system, the accumulated adsorption mass during adsorption time $t_1$ and the desorption amount over desorption time $t_2$ can be expressed as Eqs. (11) and (12), respectively.

![Fig. 4. Schematic diagram of sensor detection array.](image-url)
respectively.

\[
M_{ad} = \int_{t_1}^{t_2} Q_{ad} \cdot (C_m - C_{out})dt = Q_{ad} \cdot (C_m - C_{out}) \cdot t_2 - Q_{ad} \cdot (C_m - C_{out}) \cdot t_1
\]  

\[
M_{de} = \int_{0}^{t} Q_{de} \cdot C_{de} dt = \eta_{de} \cdot Q_{ad} \cdot (C_m - C_{out}) \cdot t_1
\]

For the detector part, the sensor detection response time \(t_{d1}\) should be far less than the desorption time \(t_2\). Meanwhile, the integrated area of the sensor detection limit should be far less than the total peak integrated area of the response value. That is, the area of the yellow region in Fig. 3c only accounts for a small part of the purple region to ensure the effect of pre-enrichment. Therefore, the relationship between the sensor and the preconcentrator can be described by the following Eqs. (13) and (14).

\[
t_{d1} \ll t_2
\]

\[
M_{e} = \eta_{e} \cdot M_{ad} = \eta_{e} \cdot \eta_{de} \cdot Q_{ad} \cdot (C_m - C_{out}) \cdot t_1 \gg Q_{ad} \cdot C_{LOD} \cdot t_2
\]

Therefore, there is a specific range of desorption time \(t_2\) which can neither be too long nor too short.

\[
t_{d1} \ll t_2 \ll \frac{\eta_{de} Q_{ad} \cdot (C_m - C_{out}) \cdot t_1}{Q_{ad} \cdot C_{LOD}}
\]

The desorption efficiency will vary with the desorption temperature, flow rate, vapor volatility, mass of adsorbent and vapor-adsorbent affinity.

When considering the sensor detection response time \(t_{d1}\), the shorter the response time is, the more accurate the detection of the preconcentration signal will be. Although we have given a range of desorption times in this paper, the purpose is not to limit the duration of desorption. Instead, the preconcentrator should meet the enrichment requirements required by the target within this limited desorption time range. Otherwise, it loses the significance of preconcentration for near real-time sensing, such as long-time desorption, by sacrificing single cycle time to achieve enrichment requirements.

### 3.3. Material requirements based on the preconcentrator selection

Once the desorption time, flow rate and preconcentration factor have been determined for the preconcentration process, the next step involves screening candidate adsorbent materials based on these requirements. In this screening process, it is crucial to consider the physicochemical properties of the adsorbent. Properties such as thermal stability, surface area and polarity play a significant role in determining the long-term efficiency, maximum adsorption capacity, and strength and nature of adsorbate-adsorbent interactions [51]. Specifically, relatively strong interactions are required between the adsorbent and the pollutants to capture pollutants at room temperature effectively [52]. However, this process should be reversed when the temperature increases [17]. Therefore, in the selection of preconcentrated materials, three properties should be taken into consideration.

**Adsorption Efficiency.** The vapor adsorption capacity is the overriding performance parameter since the removal of gaseous contaminants from the sample stream is desired for quantitative analysis of VOC concentrations. The adsorption process within the preconcentrator includes external convection, inner diffusion and inner surface sorption, which were influenced by the external mass transfer coefficient \((h_{en})\), the diffusion coefficient of target VOC in the adsorbent \((D)\), the surface area of the adsorbent \((A)\) and the partition coefficient \((K)\), respectively [53]. In general, the optimization of mass transfer and internal diffusion mainly lies in the design of the preconcentration structure. Many efforts have been made to enlarge the specific surface area of the materials to seek higher adsorption capacity and mass transfer rate [54]. Some researchers developed a hierarchical porous structure to improve the adsorption capacity [55]. Research on the Top-Down method to enlarge the pore size distribution of adsorbent has increased the adsorption capacity of VOCs [56-58]. Li et al. [13] produced a hierarchical porous carbon framework from MOF, exhibiting a strong adsorption capacity of toluene (208.5 mg/g). Chowdhury et al. [8] reviewed the reported preconcentrator materials with their surface areas and preconcentration factors. The selective adsorption/desorption of specific VOCs present a great potential for significant advantages, such as reduced detector cost and size, and reduced interference from non-desirable compounds [59].

In the past decades, the strengthening technologies of VOC adsorbent materials have developed rapidly. However, the selective adsorption and sensing of VOCs in complex environments are still crucial problems in science and engineering to address.

**Desorption Bandwidth.** When thermal desorption is performed to release the enriched gas, the preconcentrator needs to achieve rapid heat transfer within the material. To achieve high desorption efficiency, that is, to seek high \(h_{en}\), the adsorbent material used for preconcentration needs to have a suitable desorption activation energy, and an effective heat transfer from the heaters to the adsorbent is desired to promote the fast desorption of analytes. Therefore, a low heat capacity and a minimal thermal mass are paramount to allow a fast temperature ramp. Meanwhile, the material should have good mass transfer performance to make the desorbed gas quickly escape and be carried downstream by the airflow to provide very sharp desorption peaks for the sensor. The
corresponding apparent parameter is desorption bandwidth, which will vary with the desorption temperature, flow rate, vapor volatility, and vapor-adsorbent affinity. Research has suggested that materials with larger specific areas and lower maximum temperatures will have larger desorption bandwidth. Meanwhile, the larger average pore size will promote gas escape and reduce the desorption bandwidth [47].

In terms of thermal conductivity, which is desirable for thermal desorption, metal-based preconcentrator materials are better due to their higher thermal conductivity relative to low thermal conductivity materials such as MOFs, polymers, and oxides.

**Breakthrough Volumes.** In addition to having good adsorption efficiency, the material should also have a large adsorption capacity to avoid premature penetration. The selection of adsorption materials in the preconcentrator with good adsorption capacity is primarily based on analyzing performance parameters such as breakthrough time $t_b$ and breakthrough volume $V_b$. These parameters are measured by the modified Wheeler equation [60], as shown in Eqs. (16) and (17).

$$t_b = \frac{\rho_b W_b}{C_0} \left[ 1 - \frac{1}{k_1} \ln \left( \frac{C_b}{C_0} \right) \right]$$  \hspace{1cm} (16)

$$V_b = \frac{W_b W_0}{C_0} \left[ 1 - \frac{1}{k_2} \ln \left( \frac{C_b}{C_0} \right) \right]$$  \hspace{1cm} (17)

where, $t_b$ is the breakthrough time (min), $\rho_b$ is the packed-bed density (g/cm$^3$), $W_b$ is the kinetic adsorption capacity (g/g), $\tau = W_b/(Q/3600)$ is the bed residence time (min), $Q$ is the volumetric flow rate (cm$^3$/min), $W_b$ is the bed mass (g), $k_1$ is the kinetic rate constant (min$^{-1}$), $C_0$ is the inlet concentration (g/cm$^3$), and $C_b$ is the outlet concentration (g/cm$^3$). The variables $W_b$ and $k_1$ vary directly with $C_0$ and can be determined by different approaches.

Granular adsorbents generally have larger adsorption capacities than other adsorbents due to their compact packing, which allows them to occupy almost all the available volume inside the preconcentrator [17]. However, the complete filling of the microfluidic channel usually results in large pressure drops. On the contrary, thin-film adsorbents exhibit low pressure drop as only the surface of the preconcentrators is covered with the adsorbent. However, the adsorption capacity of thin-film adsorbents is limited due to the small amount of adsorbents. The new generation of foam adsorbents tends to reduce the pressure drop while keeping a relatively high adsorption capacity [9]. Moreover, some of these foams exhibit high thermal conductivity, which improves heat transfer from the adsorbent to the adsorbates, facilitating desorption and reducing power consumption.

4. Application, limitations, and further study

We presented the following two examples and used data from the reported research literature [9,35] to demonstrate the applications of the goal-oriented inverse design method for the novel sensing system.

4.1. Illustrative example 1 – single-component gas detection

As one of the typical organic compounds indoors, toluene is selected as the target pollutant with a concentration set as 50 ppb, which is the average concentration observed in Chinese urban residences [61,62]. We chose a commercial photoionization sensor (4R-PID, Winsensor, China) to detect toluene. The sensor has a response time ($t_{res}$) of less than 5 s, and when the range is selected from 0 to 10 ppm, the sensitivity is 40 mV/ppm. Since the sensor’s zero voltage is 20 mV, the minimum detection limit is about 500 ppb. So, the detection limit should be at least 500 ppb to obtain an accurate quantitative signal. Therefore, the pre-concentration factor (PF) is determined as 10. We screened out two response sensor selected above. In Lee et al. [9] developed a preconcentrator using metal organic framework embedded metal foam (MOFM) as the adsorbent. The MOFM was synthesized using MOF-5 (white cubical crystal-shaped), combined with nickel foam as the metal backbone. The designs of the adsorption chamber, microheater, and resistive temperature sensor were transferred onto silicon wafers via standard photolithography techniques and fabricated using several conventional micromachining processes. This approach achieved a PF value of 144 for BTEX mixture gas.

By applying the same toluene concentration ($C_{in}$ is 50 ppb) and employing the sensor selected above ($C_{LOD}$ is 500 ppb), the desorption time $t_2$ can be estimated to be greater than 5 s and less than 13.5 min by using Eq. (15). The data presented in Fig. 7 demonstrates that the desorption time $t_2$ of the MOFM – BTEX mixture is about 15 s and meet the time limit under the selected sensor. Moreover, this preconcentrator design exhibits a distinctive narrow peak and is ideally suited for the fast response sensor selected above.

![Fig. 6. Preconcentration obtained from the foil gas preconcentrator filled with 1 mg Carbopack B when exposed to 250 ppb of toluene at 1 L/min and desorbed at 200 °C with a flow rate of 67 mL/min. Reproduced with permission [35]. Copyright 2016, Elsevier. (Legend: Sensor response.]

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4.2. Illustrative example II – multi-component gas detection

In addition to toluene, formaldehyde is also a typical indoor volatile organic pollutant [63,64]. Furthermore, formaldehyde and toluene often interfere with each other’s sensors. In this example, toluene and formaldehyde were selected as the target detection components and a corresponding sensing system was designed. The concentration of toluene was set at 50 ppb, the same as in Example I, while the concentration of formaldehyde was set at 46 ppb, which is the corresponding mean formaldehyde concentration in Chinese residences [65].

Based on the components and concentrations to be measured, we chose two commercial electrochemistry sensors (ME3-C\(_{8}\) and ME3-\(\text{CH}_2\text{O}\), Winsen, China) to constitute the sensor array. The specific detection information is listed in Table 3.

Considering the extremely low concentrations (ppb or sub-ppm) of VOCs in indoor air, it is commonly assumed that the response of most sensors remains linear across different concentrations [1,10,15]. Hence, for this example, we have employed the linear assumption of concentration, where the response value is directly proportional to the concentration. It is worth noting that this assumption is based on the response curve provided in the product manual of the selected sensors. By following the methods described in Section 2.2, the sensor detection coefficient matrix \(W\) can be obtained. Then, the actual gas concentration can be calculated by decoupling the response values of multiple sensors.

In this example, the measured values obtained from the two sensors are 2.1 and 1 ppm, respectively. The matrix can be formulated and solved to obtain the actual concentrations of toluene \(X_T\) and formaldehyde \(X_F\), which are 0.804 and 0.060 ppm, respectively.

\[
\begin{pmatrix}
1 & 0.046 \\
21.6 & 1
\end{pmatrix}
\begin{pmatrix}
X_T \\
X_F
\end{pmatrix}
=
\begin{pmatrix}
2.1 \\
1
\end{pmatrix}
\]

We conducted a comparison between the actual values of the multi-components, corrected by the matrix, and the values measured by sensors, as presented in Table 4. Our findings reveal a significant deviation (up to nearly 1567%) in the concentration of formaldehyde due to severe interference. This indicates that the matrix decoupling method holds promise in rectifying the error caused by interfering components. It suggests that the sensor array has excellent potential to obtain the actual value of the multi-component gases, which can mitigate the considerable deviation caused by the interfering components. Measurement of the multi-component gas with common commercial sensors will be possible with this method, rather than relying on the development of sophisticated sensors.

4.3. Limitation and future study

The proposed system is an intermittently responsive detection system designed to address the trade-off challenge associated with indoor volatile organic compounds (VOCs) sensing. It consists of a preconcentrator module in the front section and a sensor array. This combination allows for the selective identification of complex atmospheres under low concentration, thereby enhancing the detection efficiency of the sensors. However, it should be noted that this system does sacrifice a certain degree of response speed in order to achieve the objective of detecting multiple components under low concentration. The adoption of this systematic approach results in a larger volume for the detection system compared to a single sensor setup. Additionally, the signal reading and parsing between different sensors introduce a longer response time.

Future research should focus on developing a preconcentrator that offers both a high preconcentration factor and a short desorption time. Additionally, there is a need to enhance the data extraction and analysis algorithm used with the sensor array. It is important to explore an on-site detection method that combines the advantages of preconcentration with different types of sensors. Moreover, features related to robustness, stability, durability, and reuse under different environmental conditions (temperature [28], pressure, humidity) should also be improved for long-term and real applications [68]. Through continuous innovation and improvement, it is expected that an accurate and sensitive analysis method can be developed, capable of proving near real-time results. Such a method could serve as a non-invasive approach and realize its broad application in building environment monitoring, early diagnosis of severe diseases and practical application at an industrial scale [69].

5. Conclusions

This study proposed a novel design strategy for sensing systems toward indoor VOC detection at low concentrations. The proposed system incorporates a preconcentrator and a sensor array comprising commercially available VOC sensors to enable selective detection of different VOCs at sub-ppm levels. A goal-oriented, sequential, inverse design method is further introduced to guide the design and improvement of the sensing system. Throughout the design process, we provide comprehensive insights into the sensing system’s construction, characteristics, and challenges. Further, we propose that the desorption time of

<table>
<thead>
<tr>
<th>Component</th>
<th>Measured values (ppm)</th>
<th>Corrected values (ppm)</th>
<th>Relative deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{C}_8\text{H}_8)</td>
<td>2.1</td>
<td>0.804</td>
<td>161.2%</td>
</tr>
<tr>
<td>(\text{CH}_2\text{O})</td>
<td>1</td>
<td>0.060</td>
<td>1566.7%</td>
</tr>
</tbody>
</table>
the system preconcentration module should be limited by the sensor parameters selected by the system, which points out the development strategy of the system in practical application and the improvement direction of the pre-concentrated module.

Furthermore, it is recommended that future research should be extended to a broader view of constructing a cohesive system with the cooperation of the preconcentrator and sensor array. A study of the construction and design of novel sensing systems toward low-concentration pollutants holds the potential to deepen the understanding of preconcentration techniques and unearth novel applications. Integrating preconcentrators and sensor arrays composed of low-cost, low-cost gas detectors can unlock fresh opportunities and applications in indoor VOC monitoring and control.

CRediT authorship contribution statement


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.

Data availability

No data was used for the research described in the article.

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