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Optimizing information content in MOF sensor arrays for analyzing methane-air mixtures

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ABSTRACT

In this study, multiple arrays of sensors composed from all possible combinations of nine different metal-organic framework (MOF) materials were evaluated for their methane-in-air sensing performance using molecular simulations. We considered all of the gas mixture compositions of CH_4, N_2, and O_2, varying from 0% to 100% of each component in 1% steps (5151 mixtures in total), in all MOFs. Assuming the mass of adsorbed gas in each MOF can be measured using a microelectromechanical system (MEMS) device such as a surface acoustic wave (SAW) sensor, the expected signal response can be predicted from molecular gas adsorption simulations. By combining predicted signal responses from each MOF sensor element in an array, we are able to determine which sets of MOFs provide the most information about the gas mixture they are exposed to, as measured by the Kullback-Liebler divergence (KLD). The KLD values are then used for ranking array performances. We report results for both binary mixtures of CH_4 and N_2 and ternary mixtures that include O_2. As expected, we found that increasing the number of elements in an array improves overall sensor performance; however, for a given array size, there is a wide disparity in KLD values between the best and worst arrays. This disparity highlights the potential inefficiency of choosing sensing materials for an array by experimental trial-and-error. Instead, we advocate the use of theory to intelligently select the best performing sensor arrays.

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1. Introduction and background

Gas sensor arrays, sometimes called electronic noses, are analogous to mammalian olfactory systems in that they employ multiple sensing elements to analyze complex odors. Electronic noses are already used in industries such as food, drug, and cosmetics for quality control and product monitoring [1]. However, there are many potential applications whose technical requirements are still out of reach for current electronic noses. Detecting hazardous gases as a first responder, for example, is a challenge due to the large number of both target gases and possible interferents [2]. Similarly, detection of various diseases via analysis of patients' breath is beyond the capabilities of existing commercial electronic noses, although impressive progress has been reported recently [3]. A simpler but still challenging problem is the detection of low concentrations of methane in air to detect natural gas leaks. Such leakage is a significant contributor to global climate change and reported measurements may be inaccurate [4,5]. Methane has an explosion limit of about 5%, and current commercial technology cannot accurately read low ppm or ppb methane levels using portable, low-power sensors [6–8]. Efforts to create better natural gas sensors have included metal-oxide catalysts, which are easily poisoned by halogens and do not survive extreme environmental conditions [9,10]; sensors with higher operating temperatures that have a high risk for explosions [5]; and traditional energy-consuming electrochemical sensors, where only minimal success has been achieved in low-cost portable sensor development [11].

This work explores electronic noses that leverage metal-organic frameworks (MOFs). Previous work has found MOFs to be promising sensing materials due to their record high internal surface areas, tunable pore structures, and reproducible synthesis [12]. However, only recently have MOFs been studied as component materials for electronic noses devices. Ellern et al. deposited MOFs onto microcantilever arrays and demonstrated their ability to detect gases [13]. Campbell et al. created an array of chemiresistive sensors, using conductive MOFs, to distinguish various types of volatile organic compounds (VOCs) [14]. An electrically conductive MOF was also tested by Yao et al. for the detection of ammonia [15]. Another example is of ZIF-8, a well-studied MOF known for its stability and small pores, which was employed as a thin film sensing layer on arrays of metal-oxide nanowires to increase sensitivity [16].

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However, a central problem in MOF-based electronic nose design has not yet been addressed: how does one choose an array of MOFs that would maximize device performance? Given that there are thousands of MOFs to choose from, and many millions of possible MOF-array combinations, it is unlikely that one would determine the most effective array by experimental trial-and-error. This work proposes a novel method to computationally screen MOF sensor arrays to determine which ones are best at resolving gas mixtures within a specified composition range. We use atomistic simulations to predict gas mixture adsorption into each of the MOFs considered, which is assumed to cause a detectable mass change measurable by a suitable MEMS device. Then we reverse the process by *assuming* a change in mass is detected, add noise to the signal, and "ask" each MOF sensor element to guess which gas mixture caused that mass change, resulting in a probabilistic distribution of possible gas mixtures. By combining information from multiple MOFs in a candidate array (i.e., joining the probability distributions), we are able to show the estimated gas composition from the eyes of each MOF array considered. Arrays that are able to more precisely resolve the gas mixtures—i.e., whose joint probability distributions have sharper peaks—score higher Kullback-Liebler divergence (KLD) scores, which are a rigorous measure of signal information content. Such a systematic analysis for ranking materials' performances for electronic nose fabrication has not been developed before now.

Our approach differs from other commonly used methods to identify gases from electronic nose data, which are typically based on fingerprints, training data, and pattern recognition [17–20]. Electronic nose performance is often scored based on a sensor's percentage of correct classifications of compounds [17,19]. Common classification techniques include principle component analysis (PCA) or partial least squares-discriminant analysis (PLS-DA) with leave-one-out training, which reduce data dimensionality and group responses. Others have used information theory measurements to statistically quantify the ability of individual elements to discriminate odors and compare to the overall array performance [21]. In contrast, our approach uses a molecular model of gas mixture adsorption instead of fingerprints to convert sensor signals into detailed gas composition information.

2. Methodology

An overview of the methods described in this section can be seen in the flow diagram, Fig. 1. Although our methodology is general with respect to signal transduction mechanisms, we nevertheless assume that a change in mass is measured via a MEMS device. For example, surface acoustic wave (SAW) devices are commonly used MEMS devices to measure small changes in mass and are compatible with MOF materials [12].

2.1. Performing molecular simulations of gas adsorption

Similar to our previous work on analyzing MOF arrays for gas sensing [22], grand canonical Monte Carlo (GCMC) simulations were performed using the RASPA software package [23] to obtain gas mixture adsorption data for a range of MOFs at 298 K and 1 bar. The MOF structures used were IRMOF-1 [24], HKUST-1 [25], NU-125 [26], UiO-66 [27], ZIF-8 [28], MgMOF-74 [29], NU-100 [30], MOF-177 [31], and MOF-801 [32]. We chose these particular MOFs because they are well-studied, have structural and chemical diversity, and are straightforward to synthesize in the lab. Unit cells of these MOFs are shown in Fig. 2. Simulation results of binary mixtures of N_2 and CH_4 are reported, followed by ternary mixtures of CH_4, N_2, and O_2, chosen as a simplified model for methane in air. Mixtures cover a range of 0–1 mole fraction for each component, in steps of 1%, resulting in a total of 5151 mixtures for all ternary mixtures (of which the binary mixtures we refer to are a subset). For each gas mixture-MOF pair, the change in total mass (mg/cm^3) due to adsorption is obtained from the simulation results.

Fig. 1. Flow diagram of analysis described in the Methodology section.

2.2. Choosing "experimental" gas mixtures

To quantify sensor array performance, we performed simulated "experiments," where arrays were exposed to unknown, or "experimental," gas mixtures. Sensor arrays were then ranked on their ability to correctly estimate the composition of these unknown gas mixtures. In this step, we chose a few gas mixtures of interest from our simulated data set generated in Step 1, and removed them from the data set, similar to leave-one-out regression methods. Specifically, we chose four binary mixtures of CH_4 and N_2 and nine ternary mixtures of CH_4, N_2, and O_2, listed in Table 1 and Table 2, respectively. We chose these compositions because we wanted to test

Fig. 2. Unit cells of all MOFs used in this study: a) NU-100, b) HKUST-1, c) IRMOF-1, d) MgMOF-74, e) MOF-801, f) ZIF-8, g) UiO-66, h) MOF-177, and i) NU-125.

sensor array performance over the whole range of concentrations for all gases. For each experimental mixture, we saved only the corresponding total adsorbed mass in each MOF, pretending the detailed compositions of the gas mixtures were unknown to us.

2.3. Simulating sensor element mass measurements

Once gas adsorbs on the MOF sensing material, a MEMS sensor element, such as a SAW device, can measure the corresponding change in mass. In this step, we simulate this mass measurement

Table 1
List of binary experiments tested, with mole fractions of each gas.

Experiment #	Component Mole Fraction	
	CH_4	N_2
1	0.1	0.9
2	0.25	0.75
3	0.5	0.5
4	0.75	0.25

Table 2
List of ternary experiments tested, with mole fractions of each component.

Experiment #	Component Mole Fraction		
	CH_4	O_2	N_2
1	0.1	0.15	0.75
2	0.2	0.2	0.6
3	0.3	0.3	0.4
4	0.4	0.2	0.4
5	0.5	0.2	0.3
6	0.6	0.3	0.1
7	0.7	0.1	0.2
8	0.8	0.1	0.1
9	0.9	0.05	0.05

process by taking the total adsorbed mass calculated from our simulations and adding to it normally distributed noise to represent measurement error with a width equal to that of the device's assumed precision, in this case 0.1 mg/cm^3. Because adsorption always results in a positive mass change, we used a truncated normal distribution (see Supporting Information for details) that always gives a zero probability for any negative values of mass.

Thus, we imagine a MOF sensor element is exposed to an unknown gas mixture, and then we compare its simulated mass measurement to all of the known adsorbed masses from the molecular simulations in Step 1. Intuitively, the gas mixture whose adsorbed mass is the closest to the simulated mass measurement is the most likely composition. However, many other gas mixtures may correspond to similar adsorbed masses that are within the assigned measurement error, resulting in a probabilistic distribution of possible gas compositions.

We obtain these probability distributions for every unknown gas mixture chosen in Step 2, and for every MOF sensor element. Each probability distribution quantifies the likelihood, based on total mass change observed by an individual sensor element, that one of the previously simulated gas mixtures *is* the unknown gas mixture. The result is a set of 5150 (one for each possible gas mixture) *discrete* probabilities for each MOF-unknown mixture combination for all nine MOFs.

2.4. Combining information from sensor elements

We emulate a sensor array by joining the probability distributions of each element, calculated in Step 3. Here, a joint probability is calculated by multiplying *n* discrete probability distributions, for *n* array elements, and then renormalizing so that all of the points add up to one.

Next, we test all possible sensor configurations using the nine MOFs, ranging from single element arrays (of which there are nine configurations) up to nine element arrays (of which there is only one configuration). For every MOF-array, the combined information result is still a list of 5150 probability values, one for each of the possible $CH_4/O_2/N_2$ gas mixtures. We then are able to rank each MOF array's performance by measuring the information content contained in the combined probability distribution.

Fig. 3. Total mass adsorbed (normalized by subtracting a value from each data set so all start at 5 mg/cm^3 for a CH_4 concentration of 0) for nine MOFs vs concentration of CH_4 in various CH_4/N_2 mixtures.

2.5. Ranking sensor arrays

Rather than plotting probability curves and visually comparing MOF arrays, we calculated the amount of information (in *bits*) provided by each array for detecting *a gas component* via the Kullback-Liebler divergence (KLD), as shown in Eq. (1). The probability at each mole fraction is represented by P_i, and a reference probability of Q_i is a probability equivalent to $1/N$ (i.e., a uniform probability distribution), where N is the number of points (mole fractions) we have from 0 to 1 for each gas.

$$KLD = \sum_i^N P_i \log \frac{P_i}{Q_i} \quad (1)$$

This KLD value determines the *information content* of a probability distribution produced by an array, where a higher value is better. Thus, we rank arrays per their KLD values for the various "experimental" gas mixtures chosen in Step 2. A detailed example calculation may be found in the Supporting Information.

3. Results and discussion

3.1. Binary mixtures

We begin by first considering results from binary gas mixtures of N_2 and CH_4. Predicting two-component gas mixtures is simpler, allowing for us to clearly validate our method.

Of the 5151 ternary mixtures, 101 are binary N_2/CH_4 mixtures. The predicted total adsorbed mass for each MOF from the GCMC simulations is shown in Fig. 3. We see that mass adsorption (mg/cm^3) for all MOFs increases linearly with increasing concentration of methane, with some MOFs exhibiting higher slopes, indicating a stronger methane selectivity, particularly for ZIF-8, MgMOF-74, and HKUST-1.

We tested four different experimental binary gas mixtures, as shown above in Table 1. For each mixture, we report the *best* and *worst* performing arrays of each size, per their KLD values, as can be seen in Fig. 4.

Initially, we can see overall KLD increases as array size increases, although more dramatically for the worst arrays, as seen in Fig. 4b. Although MOF configurations differ among experiments with the same array size, particular MOFs stand out as performing consistently well or poor. Moreover, the best one-MOF arrays all contained ZIF-8, and in the majority of the worst one-MOF arrays contained MOF-801. Overall, the best performing MOFs were ZIF-8, HKUST-1, UiO-66, and NU-125 across all array sizes. Conversely, the worst arrays contained MOF-801, NU-100, MOF-177, and IRMOF-1.

Fig. 4. a) KLD vs number of MOFs for the *highest ranked arrays* with respect to all four experiments (bars 1–4, grouped by # MOFs), where MOFs in each array are distinguished by color, b) same as a) but for the *lowest ranked arrays*.

Fig. 5. Average KLD vs number of MOFs in an array for the best (red) and worst (blue) arrays of each size over all four experiments. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

As shown in Fig. 4, arrays that performed well (i.e., had higher KLD values) for one experimental gas mixture were not necessarily the best for other gas mixtures. To find arrays that would perform well over the whole CH_4/N_2 composition range, we took the average of the KLDs over all experiments in Table 1 (see Fig. 5). Assessing the trends in array size by averaging the values allowed us to generalize a "good" vs "bad" KLD value for binary CH_4/N_2 mixtures. In the case of the best arrays, the KLD values were relatively high at just one MOF, at 3.20, and peak at an array of five MOFs, at 3.88. On the other hand, the worst arrays started off at a very low KLD value of 0.79 and showed a steady increase as the MOF array size increased, leading up to 3.88 for nine MOFs.

Focusing on the four-MOF case in Fig. 5, we see that the *best* array performed much better than the *worst*, at KLDs of 3.81 and 1.84, respectively. This disparity in KLD values highlights the benefits of computational array design for gas sensing. From nine possible MOF materials, there are 126 possible configurations of four-MOF arrays. Thus, it is unlikely that the best array would be selected through a trial-and-error process, where synthesis and testing is time consuming; computational screening can significantly expedite the selection process.

As described in the Methodology section (Section 2.3–2.4), we calculated the probability outcomes for each experiment to test whether an array could predict the concentration values. Fig. 6 shows the probability vs methane concentration for the two *best* and two *worst* MOF arrays at each array size. The plots are for experiment #1 only (the mixture most closely related to methane detection in air), where the best MOFs predicted the methane concentration to be around 0.1, the correct result. Furthermore, the trends in average KLD values (Fig. 5) were manifest in the narrowing of the probability distributions as MOFs are added to the array, more apparently so in the worst ranked arrays.

Ultimately, the goal is to be able to choose the array that best fits the needs of a specified application, taking into consideration the time and resources needed to construct larger arrays. A four-MOF array may perform just as well as an eight-MOF array, with the right materials.

3.2. Ternary mixtures

Having shown how the KLD metric can rank MOF arrays for resolving two-component mixtures, we now demonstrate how the same method can be applied to ternary ($CH_4/N_2/O_2$) gas mixtures using the same set of MOF sensor arrays.

GCMC simulations were performed on ternary mixtures of CH_4, N_2, and O_2, for which a subset was particularly relevant to natural gas detection. Fig. 7 shows the mass responses of each MOF to all 5151 gas mixtures.

The adsorption trends in Fig. 7 provide insights into the individual gas behaviors in each MOF. All MOFs we considered exhibited a linear increase in mass with CH_4 concentration, although some gradients were steeper, as for NU-125, UiO-66, ZIF-8, and MgMOF-74. Additionally, we saw higher N_2 concentrations result in a slight linear decrease in mass for MOFs IRMOF-1, HKUST-1, NU-125, UiO-66, and NU-100. Finally, adsorbed mass decreased slightly with increasing O_2 concentration for MOFs UiO-66, ZIF-8, and MgMOF-74. There was essentially no impact of N_2 on the adsorbed mass of MOF-801, as well as for O_2 in IRMOF-1, NU-100, and MOF-177. Per these adsorption trends, we hypothesized that MOF arrays would more accurately resolve concentrations of CH_4 and N_2 in the mixture than O_2, and we prove this to be true in the following analysis.

As in the binary mixture analysis, we analyzed all combinations of the same nine MOFs, but using nine different unknown gas mixtures, as listed above in Table 2. The result of each experiment was a ranking of MOF arrays per their KLD values.

For the ternary mixtures listed in Table 2, we looked at probability distributions of the concentrations of each *component* in the mixture; therefore, we calculated KLD values on a per component basis. Fig. 8a shows KLD values averaged over all nine experiments, where at each array size, the three bars represent the KLD value for each gas component (CH_4, N_2, O_2). For example, the *best* five-MOF array predicted CH_4 with an information content of 2.41, while the *worst* predicted CH_4 at an information content of 0.954. Furthermore, as hypothesized from the mass adsorption trends, the KLD values were highest for CH_4, followed by N_2, and lowest for O_2. In Fig. 8b, we averaged the three component KLD values together for each array size, which allowed us to compare the best and worst arrays' on their overall performance. Similar to the binary case, the best arrays peaked in KLD around five MOFs, at 1.98, and the worst arrays exhibited a steady increase as MOFs were added.

Distinct from the binary case, in the ternary analysis, the arrays that best predicted each component were not always constructed of the same MOFs. For example, the five-MOF array which best predicted CH_4 in experiment #1 was IRMOF-1, HKUST-1, UiO-66, ZIF-8, and MgMOF-75, and for O_2 it was IRMOF-1, HKUST-1, MgMOF-74,

Fig. 6. The probability versus concentration of methane is plotted for the top and bottom two arrays, showing increasing confidence through narrowing peaks as the array size increases.

MOF-177, and NU-100. One advantage of this component-specific information is that we can tune a sensor array for a particular gas if necessary, or optimize one to maximize detection of all components. Thus, if we are designing a sensor array for low concentration methane detection, we can construct an array which maximizes information for CH_4 prediction specifically.

Fig. 9 depicts the abilities of the two best and two worst sensor arrays at predicting individual gas mixture components for experiment #1 as listed in Table 2 (i.e., 0.1 CH_4, 0.75 N_2, and 0.15 O_2). The plots contain probability curves for all three gas components, representing the complete predicted mixture from an array. Because the best and worst arrays differ between the three gases,

Fig. 7. Total mass adsorption (mg/cm^3) vs. mole fraction of various ternary gas mixtures in nine MOFs: a) IRMOF-1, b) HKUST-1, c) NU-125, d) UiO-66, e) ZIF-8, f) MgMOF-74, g) NU-100, h) MOF-801, i) MOF-177. Note: The color bar scales vary between plots. Color represents the total mass of gas adsorbed (mg/cm^3), and each triangle edge is the component mole fraction.

Fig. 8. Averages over nine experiments: a) KLD vs number of MOFs in an array, predicting CH_4 (bar 1), N_2 (bar 2), and O_2 (bar 3). The best array KLD is read at the top of the red and the worst is the blue portion. b) This is the same as a) but averages the KLD over all three gases at each array size. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 9. The probability versus concentration of CH_4, N_2, and O_2 is plotted for the top and bottom two arrays, showing increasing confidence through narrowing peaks as the array size increases. Arrays are ranked by the product of the KLD values as they relate to each gas.

a new KLD metric was used to rank the arrays per their performance over all components. For each array, the *product* of their KLD values for each gas was calculated and listed on each plot in Fig. 9.

As with Fig. 6, we see the probability distributions in Fig. 9 narrow with increasing array size, allowing for clearer resolution of the predicted gas mixture concentration. In agreement with the KLD trends (see Fig. 8), CH_4 and N_2 are better resolved than O_2, with sharper probability peaks. Even with nine MOFs, the mole fraction of O_2 in the mixture is not as well resolved; however, if the other gas concentrations are known, then the O_2 concentration is such that the sum of all mole fractions is one.

Fig. 10. The nine-MOF probability vs concentration plot from Fig. 9 above. Below are the five highest probability gas mixtures for experiment #1 in Table 2, whose concentrations align with the peaks in the plot.

In Fig. 10, we take a closer look at the nine-MOF array plot from Fig. 9, where the predicted concentrations are shown more precisely.

The peak probabilities for each gas occur at 0.1 CH_4, 0.8 N_2, and 0.08 O_2, whereas the experiment values are 0.1 CH_4, 0.75 N_2, and 0.15 O_2. Note that adding the mole fractions associated with each peak does not necessarily have to add to one. However, by looking at specific gas mixtures in the simulation data set, we can list the best matches, for which the mole fractions of the gas components necessarily add to one. In Fig. 10, one can see that the top five best matches have each of their gas component concentrations near the peaks of their corresponding probability distributions.

Although similar KLD values were found for the nine-MOF array and best four-MOF array (Fig. 8b), which might lead one to think they have very similar performances in resolving gas mixtures, we found that even small differences in KLD values can have significant impacts on their associated probability distributions. Looking at Figs. 11 and 12, we can compare the predicted compositions for the nine-MOF array for each experiment, to the corresponding best four-MOF arrays, respectively. Note that, in Figs. 11 and 12, best and worst is defined according to KLD values for CH_4 probability distributions only. Across all nine experiments, the gas mixtures are more sharply resolved for the nine MOF array (Fig. 11) than for the best four MOF arrays (Fig. 12). Thus, the nine-MOF array is clearly better able to narrow down the concentrations of each component, even though its KLD values is only marginally higher than for the best four-MOF arrays.

We see also, in Fig. 12, an example of how the probability distributions are affected by the choice of gas component to maximize KLD values for. Since the data in Fig. 12 are for the best four-MOF arrays, according to KLD values for CH_4, there is a narrower range for possible CH_4 mole fractions, whereas for O_2 and N_2 the ranges are much larger. The red points, which correspond to the highest probabilities, generally cover a greater range of possible N_2 mole fractions, so the precise concentration of N_2 is more difficult to ascertain (at least for the MOFs considered in this study). Similarly, for O_2, the predicted concentrations are spread over a large range in most experiments. If we were interested, instead, in the concentration of one of the other components, then we choose to

Fig. 11. Probability vs concentration for all simulated gas mixtures in the nine-MOF array, a)–i) being experiments 1–9.

Fig. 12. Probability vs concentration for all simulated gas mixtures for the best four-MOF arrays a)–i) being experiments 1–9.

maximize arrays according to the appropriate KLD values. When it is necessary to resolve all mixture components, this KLD ranking system can facilitate making informed trade-off decisions, where greater precision in resolving one component comes at the cost of less precision at detecting another.

4. Conclusion

We have described a method for screening arrays of MOFs via atomistic molecular simulations and ranking them based on concepts from information theory. We applied this method to the full range of gas mixtures composed of CH_4, N_2, and O_2, where individual MOF sensing elements were assumed to only detect total mass adsorption. When considering all of the four-MOF arrays, from a library of nine possible MOFs, of which there were 126 possible configurations, the *best* ones produced significantly more information than the *worst* ones, highlighting the benefit of computational array optimization over trial-and-error. In general, arrays were able to resolve CH_4 concentrations more precisely than for N_2 and O_2. However, if precise detection of either N_2 or O_2 was a desired feature, arrays could be optimized to produce the highest information content for those specific gas components. Alternatively, our method may be used to optimize an array to maximize sensitivity for trace gas detection, which is of critical importance for detect methane leaks in air. Furthermore, we will consider additional components present in air, including CO_2 and water vapor, as their presence will have an impact on MOF behavior. In the future, we intend to consider larger arrays, and larger libraries of MOFs, to explore how much further we can increase the precision of MOF-based sensor arrays.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.snb.2018.04.049.

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