On predicting responses to mixtures in quartz microbalance sensors

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Abstract

A fundamental question in studying odor patterns in electronic noses is how to estimate the response to a mixture, given the response curves of the pure chemicals. We study this question by proposing two mixture-predicting models, and verify them against real data collected using quartz microbalance sensors. We find that a simple additive law explains fairly well the measured response patterns of binary mixtures, but that a slightly more complicated mixing model is required in order to produce good estimations of the response patterns of mixtures that are comprised of more than two compounds.
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1. Introduction

Electronic noses (eNoses) were not designed to do mixture analysis. Rather, they were designed with the intention of forming devices that are capable of discriminating between different odor samples. In this regard, an odor sample is any specific headspace content, comprised of a single pure chemical or of a mixture of chemicals. Exactly the same methodology should be used in order to train an eNose to discriminate between methanol and ethanol [1], or to discriminate between different types of olive oils [2]. Indeed, by merely observing a measured signal, one cannot tell whether the sample was a pure chemical or a mixture.

Nevertheless, eNoses are sometimes used for some form of mixture analysis. If two mixtures contain the same ingredients but with different mixing ratios, they would generally produce distinct response patterns. This fact leads to the possibility of designing algorithms that estimate mixing ratios in a mixture whose ingredients are known [3].

Our group is interested in using eNoses for a completely different kind of mixture analysis. Several years ago we sketched the building blocks of a visionary odor communication system that enables an output device—the *whiffer*—to release an imitation of an odorant read in by an input device—the *sniffer*—upon command. We have suggested to use eNoses as the sniffers, and are currently heavily involved in research to advance and implement this scheme; see [4].

Such an odor communication system will not be feasible unless it is supported by an algorithm that determines what mixture to emit from the whiffer on any specific occasion. Implementing such an algorithm—which in [4] we term the *mix-to-mimic* (MTM) *algorithm*—is as yet beyond our reach, but in [4] we suggested to devise it by gradually constructing three sub algorithms, each adding a further complication. Upon the completion of the third, the full MTM will be available. The first of these sub algorithms—the *MTM1 algorithm*—is aimed at "fooling" an eNose. That is, given any pattern measured with an eNose, it should calculate that mixture from a given set of odorants, whose pattern, when measured with the same eNose, best mimics the original pattern.

Developing MTM1 necessitates the understanding of how patterns of mixtures are related to those of the individual ingredients. Consequently, it seems reasonable to precede the construction of MTM1 by formulating a model—the *law of mixing*—that would do the following:

> Given a known mixture composition, predict its response pattern based on knowledge of the response patterns of the mixture's ingredients.

In this paper, we suggest two alternative laws of mixing and examine them against measured data. We show that the response of binary mixtures is fairly well approximated using a simple additive law, but it fails on richer mixtures. We then propose a more general law of mixing, and show

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that it enables excellent response predictions for any number of ingredients in the mixture.

We are aware of only one group—the laboratory of Moriizumi and Nakamoto—whose work is similar; see, e.g. [5,6]. However, they adopted a hardware solution to the problem, based on what they call an active odor system. However, it appears that their solution works best if we have a prior information on the identity of the mixture ingredients (but not on their mixing ratios).

In Section 2 we describe our two laws of mixing. Section 3 describes the experimental setup and the datasets used for validation. Our result are described in Section 4, followed by a discussion in Section 5.

2. Two laws for mixing

Despite the similarity in the signal shape, there is a fundamental difference between the response of an eNose to a pure chemical and to a mixture. In the former case, the concentration-dependent response curves of the sensors (hereinafter, the *response curves*) completely characterize the system behavior. That is, given the stimulus concentration, the response pattern can be predicted straightforwardly from these curves. For mixtures, however, things become more complicated. In general, the response curve of a given stimulus is modified in the presence of other stimuli, and even if the mixture composition is known exactly, the response pattern might be difficult to predict. In the rest of this section we describe two models that try to quantify the response of eNose sensors when chemicals are mixed.

Let $r(o; c)$ denote the response of the eNose to an odorant o in concentration c, and let $r(o_1, o_2, \ldots, o_n; c_1, c_2, \ldots, c_n)$ stand for the response to the mixture of $o_1, o_2, \ldots, o_n$ in concentrations $c_1, c_2, \ldots, c_n$, respectively. We define the *additive law of mixing* to be:

$$r(o_1, o_2, \ldots, o_n; c_1, c_2, \ldots, c_n)$$
$$= r(o_1; c_1) + r(o_2; c_2) + \cdots + r(o_n; c_n). \tag{1}$$

This is the simplest mixing model, and it holds if the sensor responds to each component as if the others did not exist. In general, this is not the case. First, the components in the mixture might interact among themselves. Second, the sensor capacity is limited, and different components are expected to "fight" for their place on the sensor's active surface. Still, if we choose non-interacting components (as we have tried to do in our experiments), and keep the concentrations low enough so that the sensors are well below their saturation level, we expect this law to be a reasonable approximation.

We may generalize this model and introduce the *linear law of mixing*:

$$r(o_1, o_2, \ldots, o_n; c_1, c_2, \ldots, c_n)$$
$$= \alpha_1 \cdot r(o_1; c_1) + \alpha_2 \cdot r(o_2; c_2) + \cdots + \alpha_n \cdot r(o_n; c_n). \tag{2}$$

which assumes mixture specific coefficients (to be denoted by the *mixing coefficients*), $\alpha_1, \alpha_2, \ldots, \alpha_n$, that reflect the relative influence of each component on the total mixture response. Note that the additive law is subsumed by the linear law, as the special case $\alpha_1 = \alpha_2 = \cdots = 1$.

3. Experimental

The algorithm was tested against data we collected using a MOSESII eNose [7] with eight quartz microbalance (QMB) sensors. The samples were put in 20-ml vials in an HP7694 headspace sampler, which heated them to 40 °C and injected the headspace content into the electronic nose in a flow of 25 ml/min. The injection lasted for 20 s, and was followed by a 15 min purging stage using synthetic air. Each stimulus was measured in batches, with a single batch containing several successive measurements.

In a single measurement, a sensor produces a signal over time. Hereinafter, we define the response of a sensor in the traditional way by taking the difference between the maximum of the signal and its baseline. We collected two different datasets:

- The *pure chemicals dataset* was constructed from 10 pure chemicals, each measured in six different concentrations.[1] The chemicals and their concentrations were chosen so that they all have comparable ranges of response. Each sample was diluted in polyethylenglycol 400 (PEG-400), and the concentrations were measured in molar fractions (i.e., the ratio between the number of moles of the sample and the total number of moles in the solution). The chemicals and their measured concentrations are listed in Table 1. A chemical in a certain concentration was measured in batches of at least four successive measurements. In total, this dataset consists of 269 measurements.
- The *mixtures dataset* was used to test the performance of the two laws of mixing. It consisted of binary, trinary, quaternary and quinary mixtures of the above pure chemicals, as listed in Tables 2 and 3. Each of the mixtures was diluted in PEG-400 to obtain six different total concentrations for the same mixing ratios (not shown in tables). Each specific mixture dilution was measured in batches of about seven successive measurements. All in all, there were 27 binary mixtures (1095 measurements), 10 trinary mixtures (409 measurements), 11 quaternary mixtures (452 measurements), and 1 quinary mixture (42 measurements). In total, there were 49 different mixtures (each in six different total concentrations) and 1998 measurements.

We measured concentrations as molar fractions in PEG-400 solution. However, for each compound this number is

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[1] Except for 2,3-butanedione, which was measured only in four concentrations, and butyl butyrate, which was measured in five concentrations.

Table 1
The pure chemicals and their concentrations

Chemical	Abbreviation	Concentrations measured (molar fraction)					
1-Methylpyrrole	M	0.0908	0.1665	0.2306	0.2855	0.3331	0.3747
1-Propanol	P	0.1055	0.1909	0.2614	0.3206	0.3710	0.4144
2,3-Butanedione	B	0.0918	0.1316	0.1681	0.2016	–	–
2,6-Dimethylpyridine	D	0.0711	0.1328	0.1867	0.2344	0.2768	0.3147
2-Methyl-2-pentenal	MP	0.0721	0.1345	0.1890	0.2371	0.2797	0.3179
4-Methylanisole	MA	0.0657	0.1233	0.1742	0.2195	0.2601	0.2967
Amyl formate	A	0.0632	0.0919	0.1189	0.1443	0.1683	0.1910
Butyl butyrate	BB	–	0.0983	0.1406	0.1791	0.2142	0.2465
Isoamyl formate	I	0.0633	0.0920	0.1190	0.1445	0.1685	0.1912
Toluene	T	0.0770	0.1112	0.1430	0.1726	0.2002	0.2260

Molar fractions are measured in PEG-400 solution. The abbreviated names are used extensively throughout the paper.

Table 2
The Binary mixtures

Mixture	Mixing ratios (v/v)				
A:T	1:1	2:1	6:1	1:3	–
M:D	1:1	1:2	1:6	–	–
B:I	1:1	2:1	1:3	–	–
M:P	1:1	1:2	1:6	3:1	–
B:A	1:1	2:1	6:1	1:3	–
D:BB	1:1	2:1	6:1	1:3	3:7
I:T	1:1	2:1	6:1	1:3	–

Mixing ratios are given in liquid-phase volume-to-volume (v/v).

Table 3
Trinary, quaternary and quinary mixtures

Mixture	Mixing ratio	Mixture	Mixing ratio
P:D:MA	1:1:1	M:P:MP:A	1:1:1:1
P:D:T	1:1:1	P:D:MA:BB	1:1:1:1, 1:2:1:2, 1:2:3:1, 2:1:2:1, 3:1:1:2
B:A:T	1:1:1	P:MA:I:T	1:1:1:1
B:I:T	1:1:1	MA:A:BB:I	1:1:1:1
P:D:BB	1:1:1	P:D:A:T	1:1:1:1
P:MA:BB	1:1:1	M:MP:I:T	1:2:1:2
D:MA:BB	1:1:1	D:A:BB:I	2:2:1:1
MA:A:BB	1:1:1	P:MA:A:I:T	1:1:1:1:1
D:A:I	1:1:1		
A:I:T	1:1:1		

Mixing ratios are given in liquid-phase volume ratios.

proportional to its headspace concentration, as we explain in detail in Appendix A.

4. Results

4.1. Response curves of the pure chemicals

The response curves for the pure chemicals were reconstructed from the measured points using three different techniques:

1. *The slope model*: The response curve is assumed to be $r(o; c) = ac$ with a being some coefficient.
2. *The linear model*: The response curve is assumed to be $r(o; c) = ac + b$, with a and b being some coefficients.

3. *The spline model*: The response curve is interpolated from the measured points using cubic spline interpolation (forced to go through the origin of the coordinates, $r(o; 0) = 0$).

Fig. 1 shows two examples of spline response curves. Clearly, when linearity is not so good (as in Fig. 1b), the spline is superior to the other two models. Whatever model is used, the resulting monotonic response curve enables us to calculate $r(o; c)$ for an arbitrary c.

4.2. Measures of the prediction quality

Let $r_0(o_1, \ldots, o_n; c_1, \ldots, c_n)$ be the measured response, and let $r(o_1, \ldots, o_n; c_1, \ldots, c_n)$ be the one calculated from either (1) or (2). We define three measures for the closeness of such two patterns:

1. *Length deviation* is the relative deviation in the length of the vectors, $||r_0| - |r|| / |r_0|$. The closer it is to zero, the better the overall response magnitude prediction.
2. *Angle* is the angle between the vectors. The closer it is to zero, the smaller the deviation in the predicted direction of the response vector.
3. *Distance ratio* is the ratio $|r_0 - r| / |r_0|$. The closer it is to zero, the smaller the overall difference between the measured vector and the predicted one.

4.3. Estimating the mixing coefficients

Let m be the length of the response vector, so that $r(o_i; c_i) \in \mathbb{R}^m$ is an m-dimensional vector. We may rearrange (2) in the matrix form:

$$R \cdot \alpha = r_{\text{mix}}.$$

where $R \in \mathbb{R}^{m \times n}$ matrix whose columns are $r(o_1; c_1), \ldots, r(o_n; c_n)$, $\alpha = (\alpha_1, \ldots, \alpha_n)^{\text{T}} \in \mathbb{R}^n$, and $r_{\text{mix}} = r(o_1, \ldots, o_n; c_1, \ldots, c_n) \in \mathbb{R}^m$. If $r_0(o_1, \ldots, o_n; c_1, \ldots, c_n)$ is the measured mixture response, we can find α as the least-squares minimizer of
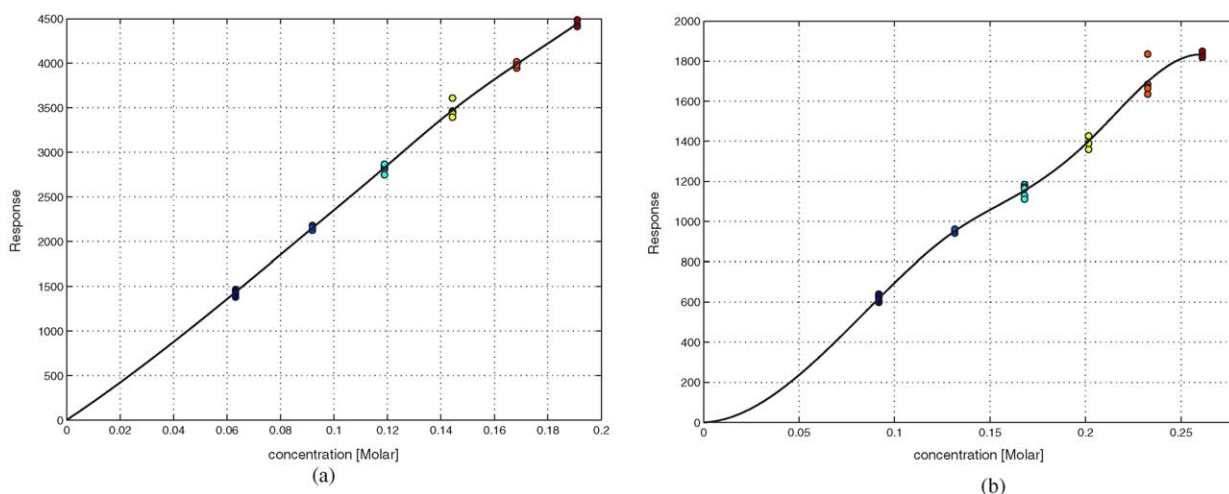
$$R \cdot \alpha = r_0. \tag{3}$$

Fig. 1. Two examples of response curves (spline): (a) amyl formate; (b) 2,3-butanedione. Molar fractions are measured in PEG-400 solution.

Table 4
Comparing the three response curve models (med. is median and avg. is average)

Mixture	Curve model	Mixture law	α_1	α_2	Length deviation		Angle (°)		Distance ratio	
					Med.	Avg.	Med.	Avg.	Med.	Avg.
A:T	Slope	Additive			0.022	0.03	0.85	1.1	0.03	0.037
		Linear	0.9958	1.035	0.022	0.026	0.82	1	0.031	0.034
	Linear	Additive			0.02	0.025	1.6	2.1	0.038	0.048
		Linear	1.005	1.006	0.023	0.025	1.6	2.1	0.041	0.049
	Spline	Additive			0.028	0.034	0.96	1	0.035	0.041
		Linear	0.9726	1.05	0.02	0.027	0.94	0.97	0.028	0.034
M:D	Slope	Additive			0.19	0.21	2.3	2.8	0.2	0.21
		Linear	0.717	1.02	0.024	0.049	1.9	2.3	0.045	0.069
	Linear	Additive			0.27	0.3	13	43	0.34	0.75
		Linear	0.5954	1.477	0.12	0.18	72	33	0.21	0.51
	Spline	Additive			0.067	0.069	1.8	1.9	0.074	0.08
		Linear	0.8388	1.123	0.023	0.04	1.8	1.8	0.04	0.055
B:I	Slope	Additive			0.062	0.064	1.4	1.5	0.065	0.071
		Linear	0.9664	0.8889	0.017	0.026	1.3	1.4	0.027	0.038
	Linear	Additive			0.092	0.1	2	2.5	0.098	0.11
		Linear	0.9583	0.8223	0.021	0.035	2.2	2.7	0.047	0.062
	Spline	Additive			0.048	0.062	1.2	1.1	0.05	0.067
		Linear	0.9694	0.9127	0.031	0.053	1.2	1.1	0.037	0.059

If we use the same ingredients to form various mixtures (say p of them) by changing the mixing ratios or the total concentrations (as we do in our experiments), then we have many equations of the form (3), $R^1 \cdot \alpha = r_0^1, \ldots, R^p \cdot \alpha = r_0^p$ for the same set of mixing coefficients α. We may now form a "super" matrix equation by defining $\mathfrak{R} = ((R^1)^T, \ldots, (R^p)^T)^T \in \mathbb{R}^{mp \times n}$ (putting the R^i's on top of each other[2]), $\tau_0 = ((r_0^1)^T, \ldots, (r_0^p)^T)^T \in \mathbb{R}^{mp}$ (putting the r_0^i's on top of each other), and defining α as the least squares

minimizer of

$$\mathfrak{R} \cdot \alpha = \tau_0. \tag{4}$$

4.4. Comparing the response curve models

We have used the mixings A:T, M:D and B:I (see Table 2) to compare between the three possible response curve models. The results are summarized in Table 4. Clearly, the spline model stands out as the most powerful, always producing good predictions. This is not very surprising, since, unlike the two other models, the spline model does not try to fit

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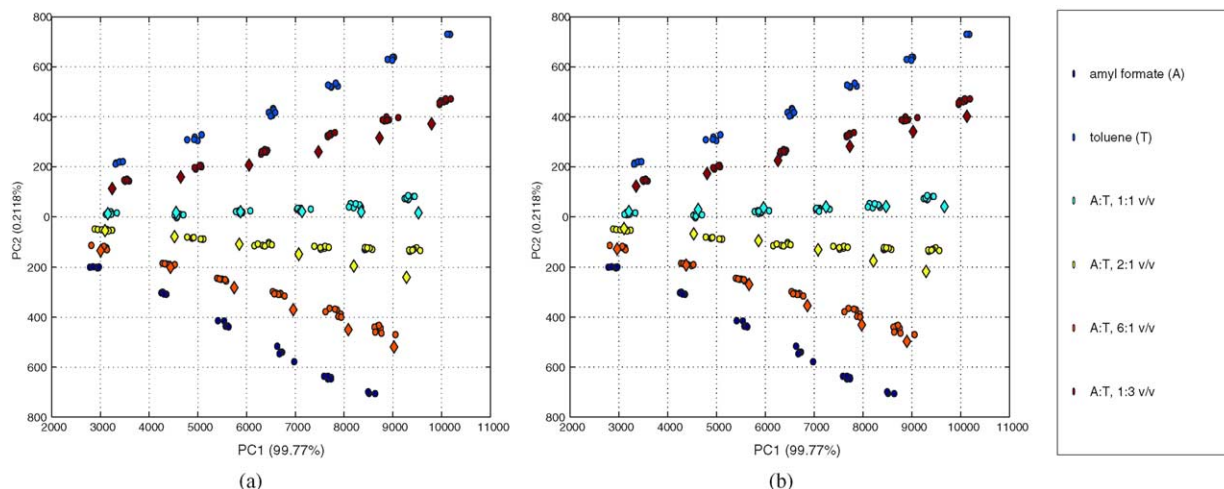[2] The symbol T stands for matrix transpose.

Fig. 2. Measured (dots) vs. predicted (diamonds) points: (a) the additive law of mixing; (b) the linear law of mixing.

Table 5
Summary of the binary mixtures results (med. is median and avg. is average)

Mixture	Mixture law	α_1	α_2	Length deviation		Angle (°)		Distance ratio	
				Med.	Avg.	Med.	Avg.	Med.	Avg.
A:T	Additive			0.028	0.034	0.96	1	0.035	0.041
	Linear	0.9726	1.05	0.02	0.027	0.94	0.97	0.028	0.034
M:D	Additive			0.067	0.069	1.8	1.9	0.074	0.08
	Linear	0.8388	1.123	0.023	0.04	1.8	1.8	0.04	0.055
B:I	Additive			0.048	0.062	1.2	1.1	0.05	0.067
	Linear	0.9694	0.9127	0.031	0.053	1.2	1.1	0.037	0.059
M:P	Additive			0.034	0.046	1.5	1.6	0.045	0.057
	Linear	0.9816	1.038	0.035	0.049	1.6	1.7	0.047	0.062
B:A	Additive			0.036	0.091	1.8	2.1	0.051	0.1
	Linear	0.8248	1.049	0.033	0.057	1.4	1.5	0.039	0.067
D:BB	Additive			0.069	0.084	1.5	1.6	0.073	0.092
	Linear	0.7689	1.009	0.058	0.06	1.7	1.7	0.065	0.07
I:T	Additive			0.057	0.052	0.99	1.1	0.062	0.057
	Linear	0.9025	1.031	0.023	0.024	1.1	1.1	0.031	0.033

The slope curve model was used.

a predefined model to the data, but rather interpolates the actual measured points. Consequently, we shall hereinafter always use the spline model for the response curve.

4.5. Analysis of binary mixtures

In the first step of the analysis we assumed additive law of mixing, and calculated the predicted response pattern of each of the 27 binary mixtures. In the second step we assumed the linear law of mixing, and found the optimal mixing coefficients α_1 and α_2 by solving the least-squares problem (4).

We can get a feeling for the prediction quality by using PCA to visualize the prediction versus the measured response in a two-dimensional space. An example is shown in Fig. 2, which plots both the predictions of the additive law of mixtures (Fig. 2a) and the linear law of mixtures (Fig. 2b). Both figures shows good prediction, but a closer look reveals that those produced by the linear law of mixing

are slightly better (closer to the measured points). Notice that in the figure the first two principal components capture nearly 100% of the variability in the data, indicating that the two pure chemicals and their binary mixtures span almost perfectly a two-dimensional subspace of the feature space.

4.6. Analysis of mixtures with more than two compounds

We have worked along similar lines as for the previous subsection, and the results are summarized in Table 6.

5. Discussion

Comparison of the three response curve models shows, as expected, that the spline model is always to be preferred; see Table 4.

Table 6
Summary of the results for mixtures with more than two compounds (med. is median and avg. is average)

Mixture	Mixture law	α	Length deviation		Angle (°)		Distance ratio	
			Med.	Avg.	Med.	Avg.	Med.	Avg.
P:D:MA	Additive		0.22	0.2	3.8	3.7	0.23	0.21
	Linear	$(1.08, -0.63, 1.80)^T$	0.059	0.08	3.2	3.1	0.078	0.1
P:D:T	Additive		0.041	0.062	1.9	1.8	0.054	0.074
	Linear	$(0.72, 1.55, 0.96)^T$	0.035	0.059	1.9	1.8	0.052	0.074
B:A:T	Additive		0.06	0.057	3	2.8	0.076	0.077
	Linear	$(0.07, 1.13, 1.03)^T$	0.011	0.016	0.84	0.82	0.018	0.023
B:I:T	Additive		0.12	0.11	2.7	2.6	0.13	0.12
	Linear	$(0.14, 0.90, 1.08)^T$	0.0091	0.015	0.97	1	0.02	0.024
B:D:BB	Additive		0.15	0.15	2.8	2.6	0.16	0.16
	Linear	$(0.56, 0.91, 0.98)^T$	0.021	0.033	2.4	2.3	0.049	0.058
P:MA:BB	Additive		0.45	0.47	3.1	3	0.46	0.47
	Linear	$(0.33, 0.60, 0.83)^T$	0.013	0.011	2.3	2.3	0.041	0.041
D:MA:BB	Additive		0.17	0.18	2.5	2.4	0.17	0.19
	Linear	$(-0.26, 1.31, 1.01)^T$	0.023	0.029	2.4	2.4	0.046	0.052
MA:A:BB	Additive		0.3	0.33	2.3	2.1	0.3	0.33
	Linear	$(-0.16, 0.46, 1.21)^T$	0.053	0.051	2.8	2.7	0.071	0.072
D:A:I	Additive		0.048	0.05	1.8	1.8	0.057	0.061
	Linear	$(-0.11, 2.93, -0.36)^T$	0.022	0.024	2.2	2.3	0.046	0.048
A:I:T	Additive		0.031	0.038	1.6	1.6	0.041	0.051
	Linear	$(1.95, 0.15, 1.09)^T$	0.022	0.021	1.6	1.6	0.034	0.037
M:P:MP:A	Additive		0.12	0.11	3.1	3	0.13	0.12
	Linear	$(1.23, 0.30, -0.003, 1.8)^T$	0.053	0.062	2.5	2.4	0.068	0.078
P:D:MA:BB	Additive		0.65	0.62	2.7	2.7	0.65	0.62
	Linear	$(0.36, 0.77, 0.24, 0.80)^T$	0.072	0.083	2.6	2.5	0.084	0.097
P:MA:I:T	Additive		0.16	0.15	1.3	1.4	0.16	0.15
	Linear	$(0.67, 0.70, 0.8, 1.05)^T$	0.0072	0.0093	1.1	1.3	0.02	0.025
MA:A:BB:I	Additive		0.32	0.34	2.4	2.2	0.32	0.34
	Linear	$(-1.15, 2.51, 1.07, -0.63)^T$	0.037	0.037	2.9	2.7	0.062	0.061
P:D:A:T	Additive		0.042	0.063	2.1	2.1	0.059	0.081
	Linear	$(0.06, 2.37, 0.63, 1.17)^T$	0.03	0.056	1.6	1.6	0.043	0.068
M:MP:I:T	Additive		0.15	0.15	2.9	2.9	0.15	0.16
	Linear	$(0.35, 0.85, -0.15, 1.46)^T$	0.018	0.014	2.3	2.5	0.044	0.048
D:A:BB:I	Additive		0.39	0.4	2.2	21	0.4	0.4
	Linear	$(-0.05, 1.58, 0.72, -0.47)^T$	0.029	0.025	2	2	0.044	0.045
P:MA:A:I:T	Additive		0.14	0.13	1.8	1.8	0.14	0.13
	Linear	$(0.33, 2.18, 0.43, 1.27, 0.71)^T$	0.018	0.022	1.3	1.3	0.03	0.033

The slope curve model was used.

For binary mixtures measured with QMB sensors, the additive law of mixing holds fairly well; see Table 5. The calculated mixing coefficients of the linear law, α_1 and α_2, are very close to 1 (recall that $\alpha_1 = \alpha_2 = 1$ indicates an additive law of mixing), with the maximal deviation from this value being 23.11% (0.7689). The additive law of mixing is a special case of the linear law of mixing and is therefore necessarily suboptimal and inferior in the overall prediction accuracy. In most cases, however, the improvement achieved by using the linear law for binary mixtures is not that dramatic, as can be seen in Fig. 2.

However, when examining mixtures with more than two components, the additive law of mixing seems much less promising; see Table 6. At first sight, we see length deviations and distance ratios as high as 65%, but closer inspection reveals that these high values appear whenever butyl butyrate (BB) and 4-methylanisole (MA) are part of the mixture. A possible explanation may be that this non-additive behavior arises due to mutual interaction between these two chemicals. However, this explanation should be rejected when we notice that relatively high length deviations and distance ratios are observed also when the mixture contains either one

of MA or BB; see, e.g., P:D:MA and D:A:BB:I. Hence, it seems more likely that these two chemicals interact with the sensors in a way that results in a non-additive behavior whenever they are mixed with other chemicals, and also with one another. If we restrict ourselves to mixtures that do not contain either BB or MA, then the length deviations and distance ratios are much smaller, with a maximum of ~16%; see, e.g., M:MP:I:T.

Length deviations and distance ratios above 10% may be acceptable for certain applications, but are nevertheless undesirable. A further look at Table 6 reveals that using the linear law of mixing gives excellent response predictions, never above 10%, even when MA and BB are present together in the mixture. Notice, for example, that the quinary mixture is predicted with a precision of ~3% in the distance ratio, and ~2% in the length deviation. Actually, the table shows that using the linear law of mixing reduces the prediction errors approximately by an order of magnitude. For example, the length deviations and distance ratios for the mixture P:D:MA:BB when using the additive law of mixing are about 65%, and they are less than 10% when using the linear law of mixing. Another example is the mixture B:I:T, whose length deviations were reduced from 12% to less than 1% using the linear law of mixing.

Looking at the α_i values in Table 6 reveals two interesting observations. First, not even a single mixture has all its compounds having $\alpha_i \approx 1$. This explains that vast improvement in the prediction achieved by the linear law compared to the additive one. Second, the highly non additive behavior of the mixtures is further demonstrated by α_i values which are close to zero or even negative. For example, the trinary mixture B:A:T behaves almost as if it was the binary mixture A:T, with B influencing only slightly on the combined response pattern ($0.07 \ll 1.13, 1.03$). Another example is the quaternary mixture MA:A:BB:I, which has two ingredients (A and BB) with positive contribution to the combined response pattern, and two ingredients (MA and I) with a negative contribution.

We may conclude that an MTM1 algorithm should model eNose mixing with a linear law of mixing. The core component of the whiffer in an odor communication system, is a palette of odorants that the system can mix accurately in order to mimic desired odor perceptions; see [4]. Therefore, using the palette to perform the MTM1 algorithm necessitates a preprocessing stage, during which the mixing coefficients of the palette odorants will be studied by mixing experiments.

Appendix A. Headspace mixing ratios versus solution mixing ratios

We shall calculate the concentrations of the mixture compounds in our autosampler sample loop. Let $(V_1, V_2, \ldots, V_n)$ be the volumes of the n compounds (including the solvent), prepared at room temperature T_0 and at room pressure P_0,

inside a vial of a total volume V_{vial}. Let the oven be heated to a temperature T_{oven}, and let the over pressure supplied by the headspace sampler be ΔP. When the vial is sealed, the ambient air takes a volume of $V_{\text{air}} = V_{\text{vial}} - \sum_i V_i$. By the gas equation, the number of moles of air in the vial, N_{air}^0 is simply

$$N_{\text{air}}^0 = \frac{P_0 V_{\text{air}}}{RT_0}.$$

When the vial is heated to a temperature T_{oven}, the air pressure in the vial increases to the value

$$P^{\text{air}} = \frac{N_{\text{air}}^0 RT_{\text{oven}}}{V_{\text{air}}} = P_0 \frac{T_{\text{oven}}}{T_0}.$$

After the over pressure is applied, the number of moles of air changes to

$$N_{\text{air}} = \frac{(P^{\text{air}} + \Delta P)V_{\text{air}}}{RT_{\text{oven}}} = N_{\text{air}}^0 + \frac{\Delta P V_{\text{air}}}{RT_{\text{oven}}}$$
$$= \frac{V_{\text{air}}}{R}\left(\frac{P_0}{T_0} + \frac{\Delta P}{T_{\text{oven}}}\right). \tag{A.1}$$

The number of moles in the liquid phase of each of the mixture compounds is simply

$$N_i^{\text{liq}} = \frac{\rho_i V_i}{W_i} = a_i V_i,$$

where ρ_i is the density of the ith compound, V_i is its volume and W_i is its molecular weight. Therefore, the molar fraction of this compound in the liquid is

$$\chi_i = \frac{N_i^{\text{liq}}}{\sum_i N_i^{\text{liq}}} = \frac{a_i V_i}{\sum_i a_i V_i}.$$

By Raoult law, the compound's partial pressure in the oven is

$$P_i^{\text{par}} = \chi_i P_i^{\text{gas}}(T_{\text{oven}}),$$

where $P_i^{\text{gas}}(T)$ is its equilibrium gas pressure in temperature T. Therefore, the number of moles of this compound in the gas phase is

$$N_i^{\text{gas}} = \frac{P_i^{\text{par}} V_{\text{air}}}{RT_{\text{oven}}}. \tag{A.2}$$

One of the compounds here, say i_0, must be the solvent, for which we assume $P_{i_0}^{\text{par}} = 0$. The concentration of compound i in the vial after over pressurizing is therefore

$$C_i = 10^6 \times \frac{N_i^{\text{gas}}}{N_{\text{air}}} \text{ (ppm)}. \tag{A.3}$$

Substituting the results (A.2) and (A.1) in (A.3) we obtain

$$C_i = 10^6 \times \frac{T_0 P_{\text{gas}}^i(T_{\text{oven}})}{T_{\text{oven}} P_0 + T_0 \Delta P} \times \chi_i. \tag{A.4}$$

This equation tells us that the concentration of a compound in the headspace during a measurement is proportional to its molar fraction in the solution.

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