Adsorption-desorption noise can be used for improving selectivity

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Abstract

Small chemical sensors are subjected to adsorption-desorption fluctuations which usually considered as noise contaminating useful signal. Based on temporal properties of this noise, it is shown that it can be made useful if proper processed. Namely, the signal, which characterizes the total amount of adsorbed analyte, should be subjected to a kind of amplitude discrimination (or level crossing discrimination) with certain threshold. When the amount is equal or above the threshold, the result of discrimination is standard dc signal, otherwise it is zero. Analytes are applied at low concentration: the mean adsorbed amount is below the threshold. The threshold is achieved from time to time thanking to the fluctuations. The signal after discrimination is averaged over a time window and used as the output of the whole device. Selectivity of this device is compared with that of its primary adsorbing sites, based on explicit description of the threshold-crossing statistics. It is concluded that the whole sensor may have much better selectivity than do its individual adsorbing sites.

Keywords: sensor, fluctuations, noise, adsorption, selectivity, electronic nose

1. Introduction

Detectors of chemical substances are usually based on selective adsorption-desorption (binding-releasing) of analyzed chemicals by specific adsorbing sites (receptor molecules). The receptor molecules are attached to an electronic device able to measure the amount of the analyte adsorbed during the binding-releasing process. The device may be either a MEMS device, such as quartz crystal microbalance \(^1,2\) or vibrating/bending cantilever \(^3\), or field effect transistor \(^4\), or other \(^5\). The device with the receptor molecules is called chemical sensor or detector. In order to be useful, the detector must be able
to discriminate between different chemicals, to be selective. Its selectivity is normally the same as that of its receptor molecules (see Eqs. (9,10)).

The size of industrial sensors has constant tendency to decrease [3]. The power of useful signal produced by a small detector becomes very small. As a result, noise of the detector itself constitutes a substantial portion of its output signal. Depending on its construction, there are several reasons for a small detector to be noisy [6]. One type of noise is due to the fact that the adsorption-desorption process is driven by brownian motion, which is stochastic. As a result, the instantaneous total amount of adsorbed analyte is subjected to irregular fluctuations visible in the output signal. This noise is called the adsorption-desorption noise [7]. It is present in any small detector which is based on binding-releasing of analyte. The adsorption-desorption noise can dominate over all other types of intrinsic noise [8].

In this paper only the adsorption-desorption noise is taken into account. The detector is expected to be a threshold detector (ThD), Fig. 1.

![Figure 1: Schematic picture of threshold detector. A — analyte molecules; R — adsorption sites; PSU — primary sensing unit; ThU — threshold unit; TAU — temporal averaging unit.](image)

Namely, the fluctuating signal characterizing the amount of adsorbed analyte in the primary sensing unit (PSU in Fig. 1) is fed into amplitude discriminator unit (threshold unit, ThU in Fig. 1). The threshold unit is characterized by a certain threshold. It has zero as its output if the adsorbed amount is below the threshold, and it outputs standard dc signal while the adsorbed amount is equal or above the threshold. The output of ThU is averaged over a sliding time-window to have final output practically time-independent. This signal is considered as the output of the ThD.

In this paper, the temporal properties of the binding-releasing stochastic process are utilized to characterize the outputs of ThD if two analytes are separately presented at equal concentrations. This allows to compare selectivity of ThD with that of its receptor molecules. The main conclusion is that the ThD may be much more selective than do its adsorbing sites.
2. Definitions and assumptions

The adsorption-desorption process is described by the following association-dissociation chemical reaction

\[ A + R \rightleftharpoons AR, \]  

(1)

where \( A, R, AR \) denote molecules of analyte, adsorption site or receptor, and analyte-receptor binary complex, respectively. At constant temperature, the rate constants, \( k_+, k_- \) are time-independent. They can be determined either from experimental measurements, or estimated theoretically. Let \( N \) denote the total number of receptor molecules per detector. The analyte is presented at concentration \( c \). The probability \( p \) for any \( R \) to be bound with \( A \) is

\[ p = \frac{k_+ c}{k_+ c + k_-}. \]  

(2)

The adsorption-desorption process is driven by brownian motion. Therefore, instantaneous number of adsorbed molecules, \( n(t) \), changes in time randomly. The mean number of adsorbed molecules, \( \langle n \rangle \), can be calculated as follows:

\[ \langle n \rangle = pN. \]  

(3)

If two different analytes \( A_1, A_2 \) are tested at the same concentration in two separate experiments, either the Eq.(2), or experimental measurements will give two values, \( p_1, p_2 \). We say that the receptor molecule has selectivity with respect to \( A_1, A_2 \), if \( p_1 \neq p_2 \). We expect that

\[ p_1 = p_2 + \Delta p, \quad \Delta p > 0. \]  

(4)

The molecular selectivity, \( \mu \), is defined as

\[ \mu = \frac{\Delta p}{p_1}. \]  

(5)

The primary signal, \( S_0(t) \) in Fig.1 usually increases if the number \( n \) of adsorbed molecules increases:

\[ n > n' \Rightarrow S_0 > S_0', \]  

(6)

where the exact dependence of \( S_0 \) on \( n \) is determined by the sensor construction and the transduction mechanism it employs. For simplicity, it is expected that in the case of gravimetric sensor, \( A_1 \) and \( A_2 \) have equal molecular masses.

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1. See [1], where Eq.(2) is justified.
2. This definition of selectivity differs from one used in the previous version, namely, \( \mu = \ln \frac{p_1}{p_2} \). It can be easily checked that both definitions are equivalent for small selectivities, when \( \Delta p \to 0 \).
In the case of $A_1$ and $A_2$ used in the definition (5) one may expect that for the final output signal ($S$ in Fig.1)

$$S_1 = S_2 + \Delta S, \quad \Delta S > 0,$$

where $S_1, S_2$ are the output levels if either $A_1$, or $A_2$ is applied.

Define selectivity $\delta$ for a whole detector in terms of final output signal as follows:

$$\delta = \frac{\Delta S}{S_1}.$$

Both $S_0(t)$ and $n(t)$ are subjected to adsorption-desorption noise. In a detector without the threshold unit, the final output signal can be made linearly proportional to the mean number of adsorbed molecules:

$$S_i \sim p_i N, \quad i = 1, 2.$$

This is achieved either by temporal averaging, or by choosing large detector with powerful primary signal in which contribution of adsorption-desorption fluctuations is not visible. By using (5), (9) in (8) one obtains for selectivity of a conventional detector

$$\delta = \frac{\Delta p N}{p_1 N} = \mu.$$

Thus, selectivity of detector in which the fluctuations are averaged out, either immediately after the primary sensing unit, or inside it, equals to that of its individual adsorbing sites.

The threshold unit, ThU, rises a threshold which the $S_0$ must overcome in order to make possible further stages of processing. The crossing may happen from time to time thanking to the adsorption-desorption fluctuations. Due to (6), the threshold can be characterized by the number $N_0$ of analyte molecules which must be adsorbed before the nonzero signal appears at the output end of the ThU. It is assumed that the ThU is ideal in a sense that the $N_0$ is the exact value which is not subjected to fluctuations. If $N_0$ is achieved, the ThU has standard constant signal as its output. The signal does not depend on the exact value of $n(t)$ provided it is above or equal to $N_0$.

Denote by $T$ the temporal window over which the averaging is made in the TAU (Fig.1), and by $T_b$, $T_a$ ($T_b + T_a = T$) the total amount of time the $n(t)$ spends below or above the threshold, respectively, when $0 \leq t \leq T$. The final output, $S$ in Fig.1 should be linearly proportional to $T_a/T$. From (4), it is clear that

$$T_{a1} = T_{a2} + \Delta T_a,$$

where $T_{a1}, T_{a2}$ correspond to $A_1, A_2$, respectively. This gives for the selectivity of ThD:

$$\delta = \frac{\Delta T_a}{T_{a1}}.$$ 

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3See footnote 2
3. Estimation of selectivity gain

Here we will introduce a selectivity gain $g$, which evaluates how much better selectivity of threshold detector can be if to compare with that of its individual receptor sites. The gain is defined as follows

$$g = \frac{\delta}{\mu} = \frac{\Delta T_a}{\Delta p T_a}.$$ 

For poor selectivities both $\Delta p$ and $\Delta T_a$ are small. Taking this into account the latter can be rewritten as a derivative:

$$g = \frac{p}{T_a} \frac{d T_a}{d p},$$

(12)

where $T_a$ is the amount of time spent above the threshold during period $T$ for a given binding probability $p$ (we write here $p$ instead of $p_1$ to simplify expressions).

It seems evident that

$$T_a = T \text{Prob}\{n(t) \geq N_0\},$$

(13)

$$\text{Prob}\{n(t) \geq N_0\} = \sum_{N_0 \leq k \leq N} \binom{N}{k} p^k (1 - p)^{N - k}. \quad (14)$$

Eq. 12, after substituting 13 and 14 turns into the following:

$$g(p) = \frac{p}{N_0} \sum_{N_0 \leq k \leq N} \frac{1}{\binom{N - k}{k}} p^{k - 1} (1 - p)^{N - k - 1} (k - Np)$$

$$\sum_{N_0 \leq k \leq N} \frac{1}{\binom{N - k}{k}} p^k (1 - p)^{N - k},$$

which after simplification gives

$$g(p) = \frac{\sum_{N_0 \leq k \leq N} \frac{1}{\binom{N - k}{k}} p^{k - 1} (1 - p)^{N - k - 1} (k - Np)}{\sum_{N_0 \leq k \leq N} \frac{1}{\binom{N - k}{k}} p^k (1 - p)^{N - k}}.$$

(15)

From 15 it can be concluded that

$$g(p) > \frac{N_0 - Np}{1 - p} = N \frac{p_0 - p}{1 - p},$$

(16)

where $p_0 = N_0/N$. Taking into account that the total number of adsorbing sites, $N$, as well as $N_0$ can be very large, it is clear from the estimate 16 that selectivity gain $g$ can be much larger than 1, provided the fraction $(p_0 - p_1)/(1 - p_1)$ is not very small. It must be at least positive, which requires

$$p_0 > p_1, \quad \text{or} \quad p_1 N < N_0.$$

(17)
Taking into account that \( p \) increases with concentration (see Eq. (2)), inequality (17) can be considered as imposing an upper limit on concentration \( c \) at which the effect of selectivity improvement might be expected based on the estimate (16). It is worth to notice that when condition (17) holds, the mean amount of adsorbed analyte is below the threshold one, and threshold crossing may happen only due to fluctuations.

4. Numerical examples

As one can conclude from the estimate (16), the selectivity gain is higher for higher \( N_0 \). On the other hand, one cannot chose the \( N_0 \) as high as desired because the ThU in Fig. 1 is expected to be ideal. If one chose \( N_0 = 100 \) then the ideality means that the threshold level in the ThU is allowed to have less then 1\% jitter. Similarly, if one chose \( N_0 = 10^4 \) then the threshold level must be kept with better than 0.01\% precision. Otherwise, noise in the threshold level should be taken into account in the reasoning of n.3 and this will lead to a less promising estimate. Another conclusion, based on the estimate (16),

| \( k_+ \) | \( k_- \) |
|------|------|
| (1/(s\cdot M)) | (1/s) |
| \( A_1 \) | 1000 | 1000 |
| \( A_2 \) | 1000 | 1050 |

Table 1: The rate constants used in the examples of Table 2 and in Fig. 2

suggests that the smaller is the concentration (smaller \( p \)) of the analytes, the better is discrimination between them. But in this case the threshold will be achieved during small fraction of time spent for measuring. As a result, the output signal will be very small and may be lost in the TAU unit. It is natural to require that the output signal for more affine analyte is higher than the 10\% of the maximal output signal, which is produced if \( n(t) \geq N_0 \) all the time. Two examples satisfying this constraints are shown in the Table 2. Concentration dependencies of \( \mu, \delta, \) and the estimate (16) are shown in Fig. 2. A short segment of the trajectory \( n(t) \) modelled on PC is shown in Fig. 3.

| \( N \) | \( N_0 \) | \( c \) | \( g \) |
|------|------|------|------|
| \( \text{Example 1} \) | \( 10^9 \) | \( 10^3 \) | \( 9.6 \cdot 10^{-5} \) | 72.6 |
| \( \text{Example 2} \) | \( 10^8 \) | \( 10^4 \) | \( 9.9 \cdot 10^{-5} \) | 360.0 |

Table 2: Numerical examples of improved selectivity. The rate constants for the analytes are shown in the Table 1. \( g \) is calculated here by means of the exact expression (15).
Figure 2: Concentration dependences of selectivity for the examples of Table 2. Concentration (x-axis) is given in M. The \( N, N_0 \) values in \( a \) and \( b \) correspond to the first and second rows of Table 2 respectively. The \( \delta_{est} \) corresponds to the right hand side of the inequality (16).

Figure 3: Short segment of the trajectory \( n(t) \) modelled on PC for the Example 1 of Table 2. Time (x-axis) is given in seconds.

5. Conclusions and discussion

In this paper, selectivity of chemical sensor is compared with that of its primary receptors (adsorbing sites). The sensor is expected to be a small one, in which the main source of noise is due to the adsorption-desorption fluctuations. In the sensor considered, the signal from the primary sensing unit is immediately subjected to the amplitude discrimination defined in the Introduction, and obtained piecewise-constant signal \( L(t) \) in Fig 1 is averaged over a time window. The averaged signal \( S \) in Fig 1 is taken as the output of whole sensor.

It is concluded that selectivity of this sensor can be much better than that of its primary receptors. The effect may be expected in a limited range of concentrations of analytes, which depends on the threshold level. For high concentrations the selectivity falls to that of the primary receptors (Fig 2), and for low ones the output signal will be too small even for more affine analyte. The best situation is expected when the mean number of bound receptors is just below the threshold one, and the threshold is frequently crossed due to the presence of fluctuations. Thus, in practical realization a possibility of tuneable threshold should be considered.
Usually, noise in sensory devices is taken as unfavorable factor\textsuperscript{4}. In this consideration, the presence of noise looks like factor improving the sensor performance. But with the ideal threshold unit in hands much can be done even without noise. Expect that the noise is initially averaged out either by spatial averaging (choosing big primary unit with large $N$), or by temporal averaging (interchanging $\text{T}_{\text{AU}}$ with $\text{ThU}$ in Fig.1). The averaged signals for the $A_1$, $A_2$ can be very close (see Eq. 9), but the ideal $\text{ThU}$ with tunable threshold will be able to discriminate perfectly between them. Thus, even if the fluctuations in this sensor are made working, the answer what is better to do first for the practical purposes: the amplitude discrimination, or temporal averaging, depends on physical parameters of the environment in which the sensor operates, and on physical characteristics of the sensor itself, including intensity of noises other than the adsorption-desorption one. Interesting, in natural olfactory systems, a kind of amplitude discrimination is made immediately after the primary reception\textsuperscript{11, 13}. Also in those systems the threshold is tunable due to adaptation of individual neurons.

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\textsuperscript{4}but see\textsuperscript{12}, where some characteristics of noise are employed for discriminating purposes.
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