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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. (6) and (7)).

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).

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.

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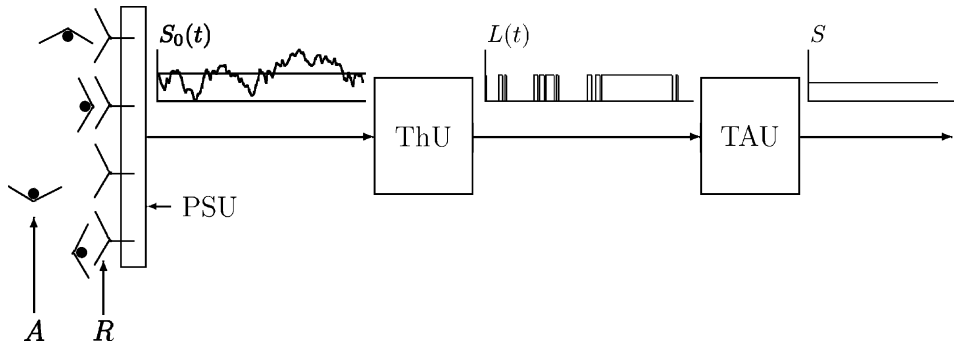

Fig. 1. Schematic picture of ThD. A: analyte molecules; R: adsorption sites; PSU: primary sensing unit; ThU: threshold unit; TAU: temporal averaging unit.

2. Definitions and assumptions

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

$$\mathrm{A} + \mathrm{R} \underset{k_-}{\overset{k_+}{\rightleftharpoons}} \mathrm{AR}, \tag{1}$$

where A, R, and 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 [8]. Let N denotes 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[1]

$$P = \frac{k_+ c}{k_+ c + k_-}. \tag{2}$$

The mean number of adsorbed molecules, $\langle n \rangle$, can be calculated as follows:

$$\langle n \rangle = PN.$$

If two different analytes A_1, A_2 are tested at the same concentration, either 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 $P_1 \neq P_2$ (expect, $P_1 > P_2$). The molecular selectivity, μ, is defined as[2,3]

$$\mu = \ln \frac{P_1}{P_2}. \tag{3}$$

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

$$n > n' \Rightarrow S_0 > S_0', \tag{4}$$

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. Define selectivity δ for a whole detector in terms of final output signal (S in Fig. 1) as follows:

$$\delta = \ln \frac{S_1}{S_2}, \tag{5}$$

where S_1, S_2 are the final outputs for analytes A_1, A_2, respectively.

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:

$$S_i \sim P_i N, \quad i = 1, 2. \tag{6}$$

This is achieved either by temporal averaging, or choosing large detector with powerful primary signal in which contribution of adsorption–desorption fluctuations is not visible. Substituting (6) into (5) one obtains for selectivity of a conventional detector:

$$\delta = \ln \frac{P_1 N}{P_2 N} = \mu. \tag{7}$$

Thus, selectivity of detector in which the fluctuations are averaged out either immediately after the primary sensing unit, or inside it is equal 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 (4), 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

[1] See [9], where Eq. (2) is justified.

[2] If one do not expect that $P_1 > P_2$ than Eq. (3) should be replaced by $\mu = |\ln(P_1/P_2)|$.

[3] This definition of selectivity differs from used in chemistry the specificity of association which is expressed in terms of dissociation constant. For analyte A, the dissociation constant is defined as $[\mathrm{A}]_{1/2} = k_-/k_+$. Eq. (2) can be rewritten using the dissociation constant: $P = 1/(1 + [\mathrm{A}]_{1/2}/c)$. From this equation it is clear that analytes with different dissociation constants have different binding probabilities and vice versa. This proves suitability of both descriptions, even if numerical values of selectivity expressed in terms of dissociation constants, say as $\mu' = \ln([\mathrm{A}_2]_{1/2}/[\mathrm{A}_1]_{1/2})$, will differ from used here. The μ values can be expressed in terms of dissociation constants: $\mu = \ln((c + [\mathrm{A}_2]_{1/2})/(c + [\mathrm{A}_1]_{1/2}))$. The main difference between the μ' and μ is that the latter depends on concentration. This is in accordance with situation in natural olfactory systems where discriminating ability usually depends on concentration [10].

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 during which $n(t)$ is below or above the threshold, respectively, when $0 \le t \le T$. The final output, S in Fig. 1, should be linearly proportional to T_a/T. This gives for the selectivity of ThD:

$$\delta = \ln \frac{T_{a1}}{T_{a2}}, \tag{8}$$

where T_{a1} and T_{a2} correspond to A_1 and A_2, respectively.

3. Estimation of selectivity

In accordance with (8), it is necessary to estimate the total amount of time the $n(t)$ spends above the threshold when $t \in [0; T]$. This can be done by adding together lengths of all separate intervals during which $n(t) \ge N_0$ continuously. Denote by ζ the number of those intervals, and by T_a^k, $1 \le k \le \zeta$ the length of the kth continuous interval. Then

$$T_a = \sum_{1 \le k \le \zeta} T_a^k = \zeta \frac{1}{\zeta} \sum_{1 \le k \le \zeta} T_a^k = T \frac{(1/\zeta) \sum_{1 \le k \le \zeta} T_a^k}{(1/\zeta) \sum_{1 \le k \le \zeta} (T_b^k + T_a^k)},$$

where T_b^k is the length of kth continuous interval during which $n(t) < N_0$. If T together with k_+, c, k_- ensures that ζ is large, then the last expression can be rewritten in the following form:

$$T_a = T \frac{\bar{T}_{ac}}{\bar{T}_{bc} + \bar{T}_{ac}}, \tag{9}$$

where $\bar{T}_{bc}, \bar{T}_{ac}$ are the mean lengths of the continuous intervals. For the $\bar{T}_{bc}, \bar{T}_{ac}$ the following expressions have been obtained [11] based on the Kolmogoroff (or backward Master) equation:

$$\bar{T}_{bc} = \frac{1}{k_- N_0 C_N^{N_0} P^{N_0} (1 - P)^{N - N_0}} \sum_{0 \le l < N_0} C_N^l P^l (1 - P)^{N-l}, \tag{10}$$

$$\bar{T}_{ac} = \frac{1}{k_- N_0 C_N^{N_0} P^{N_0} (1 - P)^{N - N_0}} \sum_{N_0 \le l \le N} C_N^l P^l (1 - P)^{N-l}. \tag{11}$$

If two analytes, A_1, A_2 are considered, then in (10) and (11), k_- and P should be replaced with k_{-i}, P_i, $i = 1, 2$, respectively. Substituting (10) and (11) into Eq. (9) one obtains[4]

$$T_a = T \sum_{N_0 \le l \le N} C_N^l P^l (1 - P)^{N-l}. \tag{12}$$

Considering (12) for two analytes, use it in Eq. (8). This gives

$$\delta = \ln \frac{\sum_{N_0 \le l \le N} C_N^l P_1^l (1 - P_1)^{N-l}}{\sum_{N_0 \le l \le N} C_N^l P_2^l (1 - P_2)^{N-l}}. \tag{13}$$

The last equation can be replaced by a transparent estimate if one use the following inequality:

$$\frac{\sum_{N_0 \le l \le N} C_N^l P_1^l (1 - P_1)^{N-l}}{\sum_{N_0 \le l \le N} C_N^l P_2^l (1 - P_2)^{N-l}} > \left(\frac{P_1}{P_2} \right)^{N((N_0/N - P_1)/(1 - P_1))}, \tag{14}$$

which is proven in [11]. Substitution of (14) into Eq. (13) gives

$$\delta > N \frac{P_0 - P_1}{1 - P_1} \mu, \quad P_0 = \frac{N_0}{N}. \tag{15}$$

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 (15) that δ can be much larger than μ, provided the fraction $(P_0 - P_1)/(1 - P_1)$ is not very small. It must be at least positive, which requires

$$P_0 > P_1 \quad \text{or} \quad P_1 N < N_0. \tag{16}$$

Taking into account that P_1 increases with concentration (see Eq. (2)), inequality (16) can be considered as imposing an upper limit for concentration c at which the effect of selectivity improvement might be expected based on the estimate (15). It is worth to notice that when condition (16) holds, the mean amount of adsorbed analyte is below the threshold one, and threshold crossing may happen only due to fluctuations.

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

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

4. Numerical examples

As one can conclude from the estimate (15), the selectivity improvement is higher for higher N_0. On the other hand, one cannot choose the N_0 as high as desired because the ThU in Fig. 1 is expected to be ideal. If one chose

[4] The following relation is used: $\sum_{0 \le l \le N} C_N^l P^l (1 - P)^{N-l} = 1$. See also [9], where equivalent to (12) conclusion is obtained based on simpler and less rigorous reasoning not using Eqs. (10) and (11).

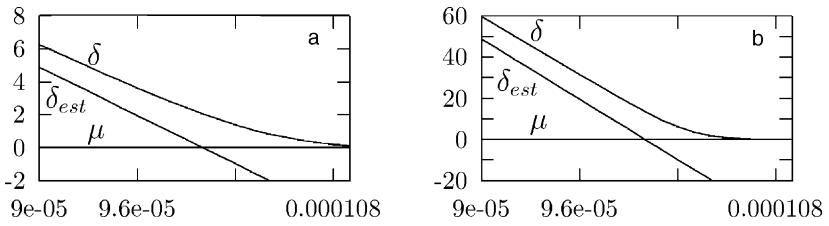

Fig. 2. Concentration dependencies of selectivity for the examples of Table 2. Concentration (x-axis) is given in M. The N, N_0 values in a and b correspond to the first and second rows of Table 2, respectively. The δ_{est} corresponds to the right hand side of the inequality (15).

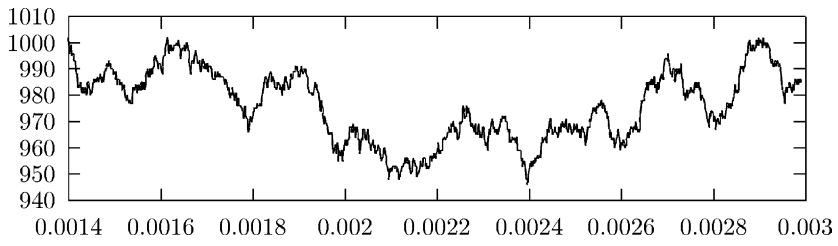

Fig. 3. Short segment of the trajectory $n(t)$ modeled on PC for the Example 1 of Table 2. Time (x-axis) is given in seconds.

$N_0 = 100$ 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 (15), suggests that the smaller is the concentration (smaller P_1) 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. Taking into account Eq. (12) this leads to the following constraint:

$$r_1 = \sum_{N_0 \leq l \leq N} C_N^l P_1^l (1 - P_1)^{N-l} > 0.1. \tag{17}$$

One more constraint comes from assumption of large ζ which is made for derivation of Eq. (9). If the measuring (averaging) time T is to be short enough, say $T = 1$ s, then the mean frequency of crossing the threshold should be high enough in order to have, e.g., $\zeta > 1000$. This could be achieved if the mean durations of being continuously above and below the threshold are short enough. If $\bar{T}_{abc} = \bar{T}_{bc} + \bar{T}_{ac}$, then Eqs. (10) and (11) give

$$\bar{T}_{abc} = (k_- N_0 C_N^{N_0} P^{N_0} (1 - P)^{N-N_0})^{-1}.$$

The $\zeta > 1000$ could be ensured by the following inequality

$$\frac{T}{\bar{T}_{abc}} > 1000,$$

or, choosing $T = 1$ s:

$$\bar{T}_{abc} < 0.001 \text{ s}.$$

Table 2
Numerical examples of improved selectivity[a]

	N	N_0	c (M)	μ	δ	r_1	$\bar{T}_{abc1}$ (s)
Example 1	10^7	10^3	9.6×10^{-5}	0.05	3.63	0.1	1.8×10^{-4}
Example 2	10^8	10^4	9.9×10^{-5}	0.05	18	0.16	4×10^{-5}

[a] The rate constants for the analytes are shown in Table 1. δ is calculated here by means of the exact expression (13), r_1—as shown in Eq. (17).

Two examples satisfying this constraints are shown in Table 2. Concentration dependencies of μ, δ, and the estimate (15) are shown in Fig. 2. A short segment of the trajectory $n(t)$ modeled on PC is shown in Fig. 3.

5. Conclusions

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 Section 1, 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.

The threshold-crossing statistics derived from the exact description of the adsorption–desorption stochastic process is used for estimating selectivity. As a result, 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 tunable threshold should be considered.

6. Discussion

Usually, noise in sensory devices is taken as unfavorable factor.[5] In this consideration, the presence of noise looks like factor improving the sensor's 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 TAU with ThU in Fig. 1). The averaged signals for the A_1, A_2 can be very close, but the ideal 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 [11,13]. Also in those systems the threshold is tunable due to adaptation in individual neurons.

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Biography

Alexander K. Vidybida received his PhD in Mathematical and Theoretical Physics (Kandidat of Physics and Mathematics) in 1975 at the Institute for Theoretical Physics, Kyiv, for his study of the BBGKY hierarchy of equations in nonequilibrium statistical mechanics. He received his DrHab degree in Theoretical Physics (Doktor of Physics and Mathematics) in 2000 at the Institute for Theoretical Physics, Kyiv, for his study of interaction of alternating electromagnetic fields with macromolecular and cooperative systems, including interaction of microwaves with living objects. At present time he works as Leading Scientist in the Institute for Theoretical Physics. Dr. A.K. Vidybida is a Member of Euroscience, IBRO (International Brain Research Organization), EBEA (European Bioelectromagnetic Association). His current research interests are devoted to neurophysics, including formation of high discriminating ability in natural sensory systems, as well as to implementation of basic ideas in technical devices.

[5] But see [12], where some characteristics of noise are employed for discriminating purposes.