WeBIOPATR2013

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Proceedings from the
4th WeBIOPATR
Workshop & Conference
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2.-4.10.2013.

Milena Jovašević-Stojanović
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Editors
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Publisher
Public Health Institute of Belgrade
Slobodan Tošović, Director
Boulevar Despota Stefana 54 a
Serbia, 11000 Belgrade

Technical assistance
Dušan B. Topalović

ISBN 978-86-83069-40-8

5.6 FLUCTUATIONS OF THE NUMBER OF ADSORBED MICRO/NANOPARTICLES IN SENSORS FOR MEASUREMENT OF PARTICLE CONCENTRATION IN AIR AND LIQUID ENVIRONMENTS

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ABSTRACT

We present a theoretical model of fluctuations of the number of adsorbed micro/nanoparticles in environmental sensors operating in air and liquids, taking into account the effects of the mass transfer processes of the target particles in a reaction chamber. The presented analysis shows that the transfer processes have a significant influence on the spectrum of fluctuations. The influence is estimated at different values of target particles concentration, functionalization sites density, and adsorption and desorption rates constants. The analysis provides the guidelines for optimization of sensor design and operating conditions in order to decrease the influence of the transport processes, thus decreasing fluctuations and improving the ultimate performance of sensors for particle detection.

1. INTRODUCTION

Detection of micro/nanoparticles in the environment is very significant for environmental protection, public healthcare, agriculture and other fields. Different platforms exist for detection of particles and measurement of their concentration in a sample. The principle of operation of a large group of sensors is based on selective adsorption of target particles on a functionalized sensor surface, occurring in the sensor's reaction chamber and causing a change of some of the measured parameters (mechanical, optical, electrical) (Alvarez 2010, Homola 1999). In this paper we examine micro/nanosensors with a flow-through reaction chamber (e.g. plasmonic, FBAR - thin Film Bulk Acoustic wave Resonators, QCM - Quartz Crystal Microbalance, microcantilever sensors etc. (Anderson 2011, Gervais 2006, Myszka 1998). We also observe the case of reversible adsorption of target particles to the functionalizing surface sites. The value of the sensor's response is determined by the number of adsorbed particles. The response rate depends on the rates of adsorption and desorption, and also on the rates of transport processes (convection and diffusion) of target particles, by which they are moved to (or from) the immediate vicinity of the adsorption sites (Myszka 1998). Unavoidable fluctuations of the number of adsorbed particles cause fluctuations of the sensor's output signal and thus affect the sensor's ultimate performance (noise, minimal detectable signal).

In this paper, a theoretic model of fluctuations of the number of adsorbed micro/nanoparticles in environmental sensors will be presented. The approximations used in the model derivation are applicable for transport-reaction regimes typical for the mentioned types of affinity-based sensors with a flow-through reaction chamber. A characteristic of such regimes is the formation of a thin layer depleted of target particles, adjacent to the functionalized sensor's surface. Based on numerical calculations, the influence of the transport processes on the parameters of the spectral density of the fluctuations of the number of adsorbed particles will be considered, as well as the dependences of that influence on the concentration of target particles, on the surface density of the functionalizing sites and on the affinity of target particles for the adsorption sites on the sensing surface. Since the fluctuations of the number of adsorbed particles directly cause the fluctuations of the sensor's response, theoretic modeling and analysis of fluctuations are important for estimation of the sensor's ultimate performance (e.g. minimal detectable signal) as a function of both the relevant sensor's parameters and the measurement conditions.

2. THEORETICAL DERIVATIONS

In a large group of micro/nanosensors the principle of operation is based on the change of a measured parameter caused by the adsorption of the target particles from the environment. Therefore, the response of such sensors is determined by the number of adsorbed particles, $N(t)$. In the sensor flow-through reaction chamber the following processes occur: adsorption, desorption, convection and diffusion of target particles (Figure 1). Adsorption and desorption processes take place on the functionalized sensor surface. Adsorption can occur when a target particle is transported to the immediate vicinity of a surface adsorption site. A desorbed particle can be adsorbed again or moved away from the adsorption site by diffusion or convection.

The following assumptions are introduced: 1. the adsorption sites surface density is approximately uniform, 2. no more than one target particle can be bound to any adsorption site, 3. all the adsorption sites are equivalent, 4. there is no interaction between target particles.

The typical transport-reaction regime in plasmonic, QCM and FBAR sensors with a flow-through reaction chamber (Anderson 2011, Gervais 2006, Myszka 1998) is such that a thin layer depleted of target particles forms adjacent to the functionalized surface when the process kinetics, $N(t)$, is limited by diffusion (in the case of reaction-limited kinetics the concentration of target particles in a reaction chamber is uniform, so the problem is much simpler for mathematical analysis). In a diffusion-limited case, the distribution of the particle concentration in a reaction chamber can be approximated by a model which assumes the existence of two regions (i.e. compartments). In the first, narrow region adjacent to the sensing surface (the inner compartment), the concentration gradient exists, while in the second, encompassing the rest of the reaction chamber (the outer compartment), the concentration is uniform and equals the particle concentration in the analyzed sample, C (Figure 1). According to the two-compartment model it can be assumed that the imaginary boundary between the two compartments is parallel to the sensor's surface, the concentration at the sensor's surface, C_s, is uniform, and for all the parameters of the adsorption-desorption (AD) and transport processes the values can be used that are obtained by averaging across the surface on which adsorption occurs. The suitability of the model for the analysis of the kinetics of the process of binding of particles to a functionalized surface was experimentally confirmed (Myszka 1998). According to the model, a boundary condition valid for the functionalized surface is defined by the expressions

$$k_m A(C - C_s) = dN/dt \tag{1}$$

$$dN/dt = k_f C_s (N_m - N) - k_r N = a_{eq}(N) - d_{eq}(N). \tag{2}$$

where N_m is the total number of adsorption sites on the functionalized surface of the area A, k_m is the mass transfer coefficient of target particles, while $a_{eq}(N)$ and $d_{eq}(N)$ denote the equivalent rate of the processes that contribute to the increase of the number of adsorbed particles and the equivalent rate of the processes that decrease the number of bound particles, respectively.

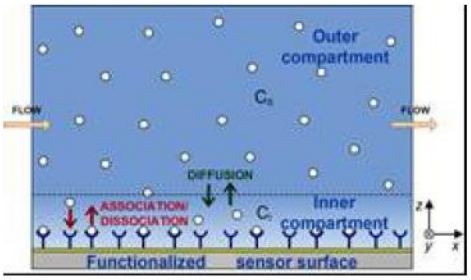

Figure. 1 Illustration of the processes in the sensor's reaction chamber, relevant for the sensor's response. Two regions of characteristic concentrations, according to the Two-compartment model, are also shown.

The number of adsorbed particles on the sensor's functionalized surface, $N(t)$, is a random process because it is a result of stochastic AD processes coupled with transport processes. Let us observe the fluctuations ΔN around the expected equilibrium value, N_e, assuming $\Delta N << N_e$. Based on Eqs. 1 and 2, a nonlinear differential equation is obtained for N. Its linearization around N_e yields the fluctuation equation

$$d(\Delta N)/dt = \left(da_{eq}/dN - dd_{eq}/dN\right)\Big|_{N=N_e} \cdot \Delta N = -\Delta N/\tau, \tag{3}$$

$$\tau = \left(1 + k_f k_r N_m/(k_m A)/(k_r + k_f C)\right)/(k_r + k_f C) \tag{4}$$

$$N_e = N_m k_f C/(k_r + k_f C)\ . \tag{5}$$

Eq. 3 assumes the Langevin form after addition of the stochastic term η on the right side. According to (Jokić 2012), based on the Langevin equation the expression is derived for the single-sided power spectral density of the fluctuation process

$$<\Delta N^2(\omega)> = <\eta^2(\omega)> \tau^2/(1+\omega^2\tau^2) = 4a_{eq}(N_e)\tau^2/(1+\omega^2\tau^2), \tag{6}$$

which is of the Lorenzian type ($\omega=2\pi f$). The spectral density of the number of adsorbed particles equals $<\Delta N^2(f)>^{1/2}$ [1/Hz$^{1/2}$], and the parameters by which it is fully determined are the spectral density for $f\to 0$, the so-called plateau, P, and the frequency at which the spectral density decreases by the factor $2^{1/2}$ (the cut-off frequency). This frequency equals $1/(2\pi\tau)$, where τ is given by Eq. 4. Based on Eq. 6, the plateau is determined by

$$P = \sqrt{4a_{eq}(N_e)\tau^2} = 2\tau\sqrt{k_r N_e} \ . \tag{7}$$

Based on Eqs. 4 and 7 the spectral density of fluctuations of the number of adsorbed particles in micro/nanosensors with a flow-through reaction chamber can be analyzed.

3. RESULTS AND DISCUSSION

The presented theory is applied for the analysis of the influence of transport processes on the plateau value of the fluctuations spectral density of the number of adsorbed particles in sensors. It is used in order to determine how pronounced the influence is at different target particles concentrations, different surface densities of functionalization sites, and different values of adsorption and desorption rate constants. The area of the functionalized surface is typical for microsensors, $A=1\cdot10^{-9}$ m^2. On all of the given 3D diagrams (Figs. 2 a-d), the lower surface (shown in uniform gray) is obtained by assuming that the mass transfer is fast enough that it does not influence the kinetics of the process of binding the particles to the sensor's surface. It is intended for the comparison of the influence of each of the analyzed parameters on the effect the mass transfer has on the fluctuation spectrum.

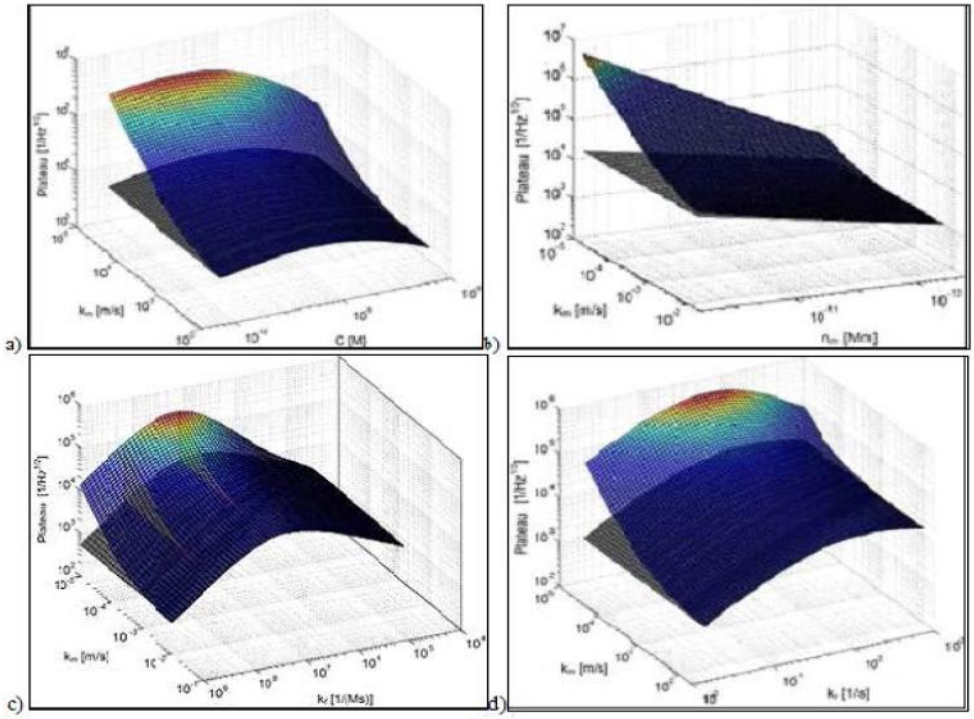

Figure 2. The influence of the transfer process coefficient on the plateau value of the adsorbed particles number fluctuations spectrum for different: analyte concentrations (a), values of the functionalization sites surface density (b), adsorption rate constants (c), and desorption rate constants (d).

Fig. 2a shows the dependence of the spectrum plateau on both the mass transfer coefficient and the target particles concentration at $k_f=5\cdot10^7$ 1/(M·s), $k_r=0.08$ 1/s and $n_m=N_m/A=1\cdot10^{-11}$ M·m. It can be seen that when the mass transfer is slow (i.e. at lower k_m), the influence of the transfer on the plateau magnitude becomes significant. The plateau magnitude can be increased by more than one order of magnitude compared to the case of fast mass transport. Fig. 2b shows the plateau magnitude as a function of both k_m and the surface density of adsorption sites on the sensor's surface ($k_f=8\cdot10^7$ 1/(M·s), $k_r=0.08$ 1/s, $C=5\cdot10^{-10}$ M). In the case of slow mass transfer and high n_m, the plateau magnitude is more than 100 times greater than it is when the mass transport is fast. As the number of functionalized sites decreases, so does the influence of the transport

process speed on the plateau magnitude. In Fig. 2c the influence is shown of both the transfer process speed and the adsorption rate constant on the fluctuation spectrum plateau (k_r=0.02 1/s, C=2·10^{-9} M, n_m=2.5·10^{-11} M·m). At higher binding affinities of the target particles for the sensing surface (i.e. higher k_f), the mass transfer exhibits a higher influence on the fluctuation spectrum in the plateau range, and thus also on the corresponding sensor noise. In order for the analysis to be complete, it is also necessary to consider the dependence of the fluctuations spectrum plateau on both the k_m and the desorption rate constant (the affinity is inversely proportional to k_r). This dependence is shown in Fig. 2d for k_f=5·10^7 1/(M·s), C=2·10^{-10} M and n_m=1·10^{-11} M·m.

4. CONCLUSIONS

We presented the theoretical model of fluctuations of the number of adsorbed micro/nanoparticles in environmental sensors operating in air and liquids, taking into account the effects of the mass transfer processes of the target particles in a reaction chamber. The expression for the fluctuations spectral density, which is of Lorentzian type, yielded expressions for the parameters that determine it completely, i.e. the maximal value of the spectral density (the so-called plateau), and the frequency at which the spectral density reduces to the value $2^{1/2}$ times lower than the plateau (usually called the cut-off frequency).

The presented theory is applied for the analysis of the influence of transport processes on the plateau value of fluctuations spectral density. The analysis shows that transfer processes have a significant influence on the spectrum of fluctuations. It shows how significant this influence can be at different values of target particles concentration, functionalization sites density, and adsorption and desorption rates constants. Significant differences have been observed in the maximal value of the fluctuations of the number of adsorbed particles at different values of these parameters, chosen to correspond to real conditions. The results of the analysis provide the guidelines for optimization of sensor design and operating conditions (the flow rate of the sample through the reaction chamber, the surface density of the functionalization sites etc.) in order to decrease the influence of the transport processes, thus decreasing fluctuations and improving the ultimate performance of sensors for particle detection in the environment.

5. ACKNOWLEDGEMENTS

This work was partially funded by the Serbian Ministry of Education, Science and Technological Development within the Project TR32008 and by the Serbian Academy of Sciences and Arts within the project F150.

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