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## SYSTEM FOR THE DETECTION OF ANILINE WITH AN OPEN INPUT BASED ON A PIEZOQUARTZ RESONATOR

*The kinetics of aniline sorption on poly(ethylene glycol succinate) films were studied by piezoquartz microweighing in a system with an open input under isothermal conditions. The optimum mass of poly(ethylene glycol succinate) film was experimentally determined in order to detect aniline in the air. Isothermal sorption curves were obtained and the detection condition were also optimized. The mechanism of aniline sorption under steady state conditions was determined for various aniline concentrations. The sensor sensitivity of the sensor modified with poly(ethylene glycol succinate) was estimated relative to aniline, o- and m-nitroanilines.*

Control of the condition and ecological safety of the atmosphere is performed in two possible ways – flow-type (dynamic) and stationary (static). Choice of the type of measurement is determined by the level of deterioration and the nature of the detected compound. Along with the necessity of determining major organic pollutants in the air at the maximally allowed levels and even lower concentrations, estimation of the total level of air pollution in the epicentre of local effluents (overspreads, locations of waste recycling, emergency locations) proves to be very important. The modern method of gas analysis is based on the application of piezosensors with selective liquid or solid coatings (electrode modifiers) [1, 2].

The goal of the investigation was to optimize the conditions of applying bulk-acoustic wave sensors (BAW-sensors) based on poly(ethylene glycol succinate) (PEGS) for the determination of aniline in the air under steady state conditions (detection system with an open input). The optimization parameters were as follows – mass of the film ( $m_{\text{film}}$ ,  $\mu\text{g}$ ), a range of aniline concentrations providing sensor response ( $\Delta F$ ) adequate to the load ( $\Delta m$ ); calculation of the time parameters of signal measurements and regeneration of the sorbent at different aniline concentrations.

### EXPERIMENT

Piezoquartz resonators (PQR) of AT-cut-off and silver electrodes [3, 4] with a natural vibration frequency of  $F_0 = 8000 \pm 5$  kHz were applied in the experimental unit.

The modifier solution was deposited on the surface of the PQR electrodes with subsequent drying at  $120^\circ \pm 5$  °C which corresponds to the limit of the temperature stability of the sorbent. Complete solvent

evaporation from the modifier film was estimated by the absence of drift of the baseline ( $\Delta F_0 = \pm 5$  Hz).

The quartz resonator was placed into a thermostatic isolated detection cell. The quartz vibration frequency was measured by a frequency meter in the time range of 15 sec. The sorption temperature was  $18^\circ \pm 1$  °C.

### RESULTS

The influence of the mass of PEGS film on the efficiency of aniline sorption was studied in this investigation. The optimum mass of the film was found to be 8 – 15  $\mu\text{g}$ . The kinetics of sorption under isothermal conditions were studied for different aniline concentrations in the detection cell. The shape of the kinetic curves implies one-stage sorption and the absence of chemical transformations of aniline on the surface of the modifier (Fig. 1).

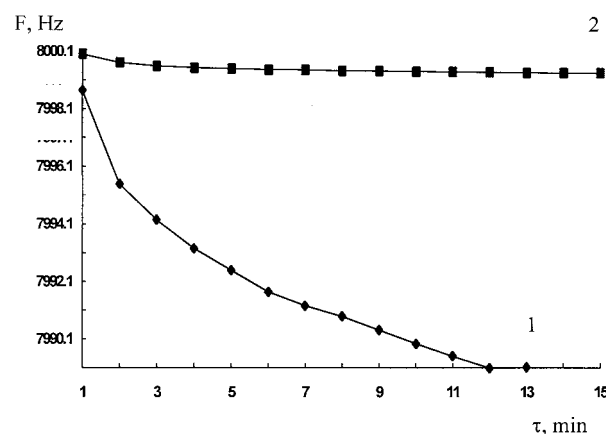


Figure 1. Kinetic curves of aniline sorption on PEGS film for  $C_{\text{aniline}} = 2.65 \text{ mol/m}^3$  (1) and  $C_{\text{aniline}} = 4.9 \cdot 10^{-2} \text{ mol/m}^3$  (2)

The isothermal curve of aniline sorption on PEGS film under the optimum conditions (Fig. 2) at low aniline concentration ( $C_{\text{aniline}} = (2.6 - 11) \cdot 10^{-2} \text{ mol/m}^3$ ) is linear. At  $C_{\text{aniline}} > 0.15 \text{ mol/m}^3$  a pseudo-liquid phase is

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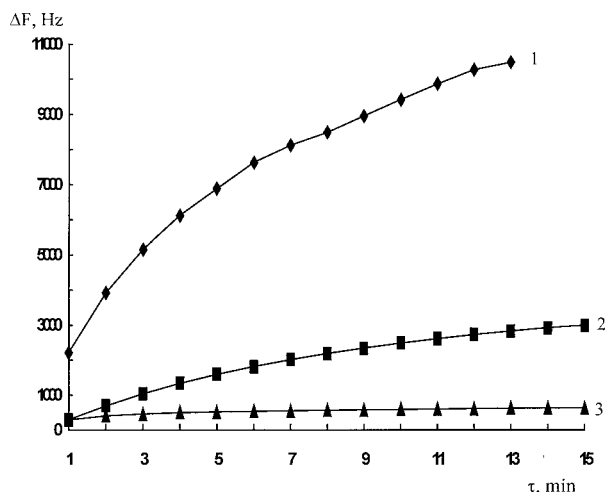


Figure 2. Kinetics of aniline sorption on PEGS film for different  $C_{\text{aniline}}$  concentrations: 1 –  $2.6 \text{ mol/m}^3$ ; 2 –  $1.5 \cdot 10^{-1} \text{ mol/m}^3$ ; 3 –  $4.9 \cdot 10^{-2} \text{ mol/m}^3$ .

formed on the PEGS film (multilayer sorption), thus resulting in an abrupt increase of the sorbent affinity to the sorbate.

The sensitivity of the sensor modified with PEGS relative to aniline lies in the range of  $1.2 \cdot 10^4 - 3.9 \cdot 10^4 \text{ Hz} \cdot \text{m}^3/\text{mol}$ .

## DISCUSSION

The response time of the sensor ( $\tau$ , s) depends on the sorption capacity, mass of the film, dependability of the auto-vibration generator for the crystal and the aniline affinity to PEGS.

The amount of aniline adsorbed at the established equilibrium depends on the adsorbent nature, the value of the specific surface, the sorption capacity of the modifier film, the composition of the gas mixture and on temperature.

The shape of the isothermal curves is determined by the mechanism of aniline sorption on PEGS film. With

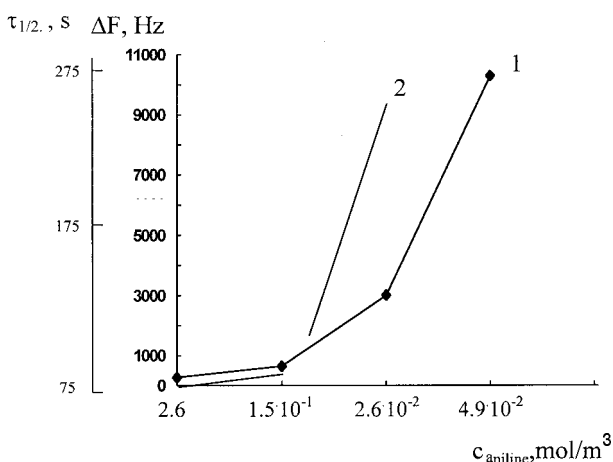


Figure 3. Dependence of the efficiency (1) and time of half-sorption (2) on the aniline concentration in the air

an increase of aniline pressure in the detection cell, the equilibrium limit of adsorption and the time of half-sorption ( $\tau_{1/2}$ ) both vary. This can be explained by the desorption of aniline from the PEGS film in the process of sorption and the activation energy of adsorption and the heat of adsorption change in a similar way (Fig.3).

The rate of aniline sorption under steady state conditions is determined by the rates of the two main processes – diffusion towards the film surface and the interaction with PEGS ( $v = v_{\text{dif}} + v_{\text{sorpt}}$ ):

$$v_{\text{dif}} = k_{\text{dif}} \cdot C_{\text{a}}^*, \quad v_{\text{sorpt}} = k_{\text{sorpt}} \cdot C_{\text{a}}$$

where  $v_{\text{dif}}$ ,  $v_{\text{sorpt}}$  are the rates of aniline diffusion towards the surface of the film and the interaction with PEGS,  $k_{\text{dif}}$ ,  $k_{\text{sorpt}}$  are the constants of diffusion and sorption rates,  $\text{m}^3/\text{mol}$ ;  $C_{\text{a}}^*$ ,  $C_{\text{a}}$  are the concentrations of aniline above the liquid and close to the PQR ( $C_{\text{a}} < C_{\text{a}}^*$ ).

In the first moment of time (the system is far from the equilibrium state) sorption is limited by diffusion ( $C_{\text{a}}$  is small). This is confirmed by the angular coefficients of the straight lines  $\lg \Delta F = f(\lg \tau)$  obtained for different  $v$  values of  $C_{\text{a}}^*$  (Table 1).

Table 1. Bilogarithmic dependences of the analytical signal ( $\Delta F$ , Hz) on the time of aniline sorption ( $\tau$ , min) for different concentrations and multiplicity of sorption

$C_{\text{a}}$ , mol/m <sup>3</sup>	$\lg \Delta F = f(\lg \tau)$	Sorption multiplicity
2.6	$\lg \Delta F = 1.86 + 0.83 \lg \tau$ $\lg \Delta F = 1.95 + 0.92 \lg \tau$	initial secondary
$1.5 \cdot 10^{-1}$	$\lg \Delta F = 0.35 + 1.58 \lg \tau$ $\lg \Delta F = 0.21 + 1.97 \lg \tau$	initial secondary
$4.9 \cdot 10^{-2}$	$\lg \Delta F = 1.86 + 0.36 \lg \tau$ $\lg \Delta F = 0.39 + 0.85 \lg \tau$	initial secondary
$2.6 \cdot 10^{-2}$	$\lg \Delta F = 1.62 + 0.40 \lg \tau$ $\lg \Delta F = 0.51 + 0.81 \lg \tau$	initial secondary

According to the theory of activated sorption [5], the linearity of the bilogarithmic kinetic function  $\lg \Delta F = f(\lg \tau)$  is explained by the consistent interaction of the sorbate and sorbent in the sections with increasing activation energy. Sorption on PEGS corresponds to the exponential type of aniline distribution in the system air – film which can be described by the equation  $\Delta F = a e^b$ . For  $b > 0.5$  sorption is determined by diffusion, while for  $b < 0.5$  sorption is limited by the reaction on the surface of the film.

At low values of  $C_{\text{a}}$  the limiting stage proves to be the interaction of aniline with the sorbent. For high  $C_{\text{a}}$  the fraction of the diffusion component in the total sorption kinetics is maximum.

Under repeated sorption on regenerated sorbent film parameter  $b$  increases. The conditions of the reactions are constant and the rate of diffusion does therefore not change, the total increase of the sorption

Table 2. Metrological parameters of aniline detection

$C_a$ , mol/m <sup>3</sup>	$\Delta F$ , Hz	$\Delta F \pm \Delta x$	s
2.6	10282	$10286 \pm 3$	1.0
	10392		
	10184		
$1.5 \cdot 10^{-1}$	3002	$2712 \pm 32$	10.7
	2421		
$4.9 \cdot 10^{-2}$	640	$668 \pm 17$	5.8
	695		
$2.6 \cdot 10^{-2}$	271	$304 \pm 60$	19.7
	373		
	268		

rate of aniline is explained by the change of the rate of the process proceeding in the sorbent. The activation energy of the separate parts of the surface under repeated sorption is reduced due to changes in the film structure. These variations are due to incomplete aniline desorption (the difference of the initial signal for new and aged films is 150 Hz). Aniline is strongly bound to PEGS and thus forms parts with a lower activation energy where sorption presumably proceeds in the initial period of time.

For optimum conditions of sorption, metrological parameters of aniline detection were estimated. The confidence interval ( $\Delta F \pm \Delta x$ ) including the standard deviation, s, of the values obtained in the concentration range of  $10^{-2} - 10^{-4}$  mol/m<sup>3</sup> is presented in Table 2. The largest detection error corresponds to low aniline concentrations.

The sensitivity of the PEGS coating relative to o- and m-nitroanilines was estimated for the optimum sorption conditions (Table 3).

Aniline and m-nitroaniline were found to be sorbed simultaneously with a similar intensity of sorption

Table 3. Sensitivity of PEGS coating to nitroanilines

Analyte	$a \cdot 10^2$	$\tau_{1/2}$ min	$S \cdot 10^{-7}$ , Hz · dm <sup>3</sup> /mol
aniline	1.846	9.15	49.26
o-nitroaniline	0.943	5.45	16.51
m-nitroaniline	1.076	9.15	43.37

(Sensitivity,  $S = \Delta F_{\text{sorpt}}/C_a$  is given in Hz · dm<sup>3</sup>/mol); o-nitroaniline is sorbed at a considerably higher rate.

The determination of aniline when applying this sorption system is prevented in the presence of m-nitroaniline, while the o-isomer does not hinder the determination.

## CONCLUSIONS

Using piezoquartz microweighing were studied the kinetics of aniline sorption on poly(ethylene glycol succinate) films. The optimum detection conditions were found – sorbent mass and the concentration flow rate of aniline. The mechanism of static sorption were investigated for different concentrations of aniline in the air. Isothermal sorption curves were obtained and the sensitivity of the piezoquartz sensor based on poly(ethylene glycol succinate) was estimated.

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## REZIME

### PRIMENA PIEZOKVARNOG REZONATORA ZA ODREĐIVANJE ANILINA U VAZDUHU

(Naučni rad)

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U radu je ispitivana kinetika sorpcije anilina na filmu od poli (etilenglikol sukcinata) kojim je prevučeni piezokvarcni rezonator. U senzorski element sa piezokvarcni rezonatorom ulazi gasovita faza (vazduh), a detekcija anilina u vazduhu se ostvaruje praćenjem promene mase rezonatora (u mikrogramima) u izotermnim uslovima. U cilju određivanja odgovarajuće koncentracije anilina u vazduhu, odnosno definisanja osetljivosti senzora, definisana je i eksperimentalno utvrđena optimalna masa poli (etilenglikol sukcinata) kojim je prevučeni piezokvarcni rezonator. Definisan je mehanizam sorpcije anilina u stacionarnom stanju za različite koncentracije anilina u vazduhu. Utvrđena je realtivna osetljivost senzora (piezokvarcnog rezonatora presvučenog filmom poli (etilenglikol sukcinatom)) u odnosu na anilin, o- i m-nitroanilin.

Key words: Anilene • Determination in air • Piezoquartz resonator • Poly (ethylene glycol succinate) • Sorption • Kinetic •  
Ključne reči: Anilin • Određivanje u vazduhu • Piezokvarcni rezonator • Poli (etilenglikol sukcinat) Sorpcija • Kinetika •

