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OPTIMIZATION OF THE CONDITIONS OF NITROHYDROCARBON DETERMINATION IN AIR

The method of piezoquartz microweighing was applied for the study of the properties of piezosensors modified with nitrocellulose, nitrostarch, triton X–100, carbowas 20M, triethanolamine: aliphatic and aromatic nitrohydrocarbons were used as adsorbates. Piezosensor selectivity relative to adsorbates was studied. Change of the output analytical signal of the electrodes in the piezosensor was investigated as a function of the nature of the modifies, gas flow rate, detection temperature. The most sensitive surface modifies relaive to nitrohydrocarbons were chosen for piezosensors.

The necessity of determining nitrohydrocarbons in air is due to their high toxicity. Nitroalkanes are poisons with a common irritative effect and they are present in air effluents of industries producing organic solvents, dyes and synthesizing nitroalcohols. When aromatic nitrohydrocarbons enter the human body, they oxidize haemoglobin of the blood into chemoglobin and they are also liver toxicants. The maximum allowed concentrations (MAC) for aliphatic nitroalkanes in the air of cities and industrial zones are ~ 0.03 $\mu g/dm^3$, and the order of 0.06–0.08 $\mu g/dm^3$ for aromatic nitrohydrocarbons [1]. The elaboration of sensitive and proximate methods for determining microamounts of nitrohydrocarbons in the air is of analytical and ecological inportance. To solve this problem we applied the method of piezoquartz microweighing wich is characterized by a low detection limit, simple equipment and proximaty to the source of emission [2, 3]. The method is based on the conversion of the initial vibration frequency of a sensor F_0 (MHz) into a measured analytical signal ΔF (Hz). A piezoquartz sensor is used to proviede the selectivity relative to nitrohydrocarbons. The deposition of sorbent sensitive films on the sensor extends the possibilities of nitrohydrocarbon determination in air. The mass of the determined substance adsorbed on the surface of the piezosensor Δm (μg) was calculated by the equation:

$$-\Delta F = k\,\Delta m,$$

where k is a constant regarding the nature of the quartz. In order to determine nitrohydrocarbons in air, we applied a quartz piezosensor with an aluminium electrode modified with nitrocellulose, nitrostarch, triton X–100, carbowax 20 M and triethanol amine. The choice of a sensor with an aluminium electrode is related to the formation of an oxide film on its surface promoting relatively strong binding of the functional groups of the modifier.

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EXPERIMENTAL

Adsorbents

Samples of long – chain nitrocellulose (LNC) and short – chain nitrocellulose (SNC), as well of nitrostarch (NS) were obtained by a known technique [3] for further application as modifies of the piezosensor electrode. Unlike of the known technique [3–5], this method involves the application of a mixture of concentrated sulphuric (d ≈ 1.84) and nitric (d ≈ 1.50) acids in the composition of the nitration mixture. Carbowax 20 M (CW), triton X – 100 (TN), triethanol amine (TEA) were also applied as piezosensor modifies. The duration and temperature of nitration considerably affect the properties of the obtained adsorbents. Variation of the duration and temperature of nitration results in obtaining nitrocellulose samples with different properties.

Equipment

A previously described unit was used [6, 7]. The unit includes a microcompressor for air sampling. The air then passes through a drying system. The detection cell is rinsed with dried air. After that a two–way cock is switched into the position for passing air through the system of sample inut. Here the air is saturated with vapours of the detected substance. The sample is supplied by a gas main into a cell where the modified piezosensor is located. To measure the output signal ΔF, a universal oscillation frequency meter was applied. Quartz crystals with a nominal frequency of F_0 = 9 MHz, produced in Russia, were used. The surface area of the electrodes was 0.2 cm^2, quartz density ρ_k = 2600 kg/m^3. Air was used as the gas–carrier and the gas flow rate varied in the range 25–75 cm^3/min. The detection temperature was 10–50°C. Modifiers in the form of acetone solutions were deposited on the surface of the

Table 1. Some properties of the detected compounds [1]

Nitrohydrocarbons	Molar mass g/mol	Boiling temperature, ^{o}C	Partial pressure (n · 133.32), Pa	Concentration mmol/dm^3
Nitromethane	78.1	102.4	5.41	4.10
Nitroethane	86.2	115.4	2.30	1.20
1–Nitropropane	101.3	120.6	0.98	0.893
2–Nitropropane	101.3	118.5	0.98	0.893
Nitrobenzene	123.1	210.8	0.24	0.013
o–Nitrotoluene	137.1	220.4	0.161	0.009
m–Nitrotoluene	137.1	230.5	0.161	0.009

piezosensor electrode with a microinjector of 10 µl capacity (10 µl = 10 µg).

Adsorbates

The subject of the investigations werealiphatic (nitromethane, nitroethane, 1– and 2–nitropropanes) and aromatic (nitrobenzene, 0– and m–nitrotoluenes) nitrohydrocarbons (Table 1).

RESULTS

The obtained results for –ΔF allow the estimation of the specificity of the surface of the modified aluminium electrode of the piezosensor relative to nitrohydrocarbons. Variations of the resonance frequency (–ΔF) and sensitivity (S_m) of the quartz piezosensor modified with LNC, SNC and NS are presented in Table 2, while those for the piezosensor modified with CW, TN and TEA are given m Table 3.

DISCUSSION

The values of –ΔF and S_m for the piezosensor modified with LNC are larges than those obtained modified with SNC or NS. Such differences are explained by the more complex structure of NS which prevent. The formation of molecular bonds between the adsorbed compounds and modifier. This results in less effective adosrption. Therefore, more nitrohydrocarbons are adsorbed on the surface of the piezosensor modified with SNC than on the one modified with LNC. The parameters –ΔF and S_m for the piezosensor modified with TEA are larger that those obtained for the sensor modified with triton X–100 or carbowax 20 M (due to the

Table 2. Some parameters of modified piezosensors. Mass of coating was 10 µg

Adsorbates	–ΔF, Hz			S_m, Hz · dm^3/mmol		
	LNC	SNC	NS	LNC	SNC	NS
Nitromethane	5310	6100	3280	3490	4010	2150
Nitroethane	4520	5300	2500	5290	6200	2930
1–Nitropropane	3120	3850	1600	7590	9360	3890
2–Nitropropane	3500	4200	1750	4910	5910	2460
Nitrobenzene	920	1400	562	115000	175000	70250
o–Nitrotoluene	1760	2130	985	293000	355000	164000
m–Nitrotoluene	1690	2000	762	281700	333000	127000

Table 3. Some parameters of modified piezosensors

Adsorbates	–ΔF, Hz			S_m, Hz · dm^3/mmol		
	CW	TN	TEA	CW	TN	TEA
Nitromethane	890	1125	2120	220	250	360
Nitroethane	780	950	1260	210	260	290
1–Nitropropane	690	810	980	760	940	390
2–Nitropropane	705	875	1100	490	590	245
Nitrobenzene	185	280	365	115	175	700
o–Nitrotoluene	215	230	285	130	600	740

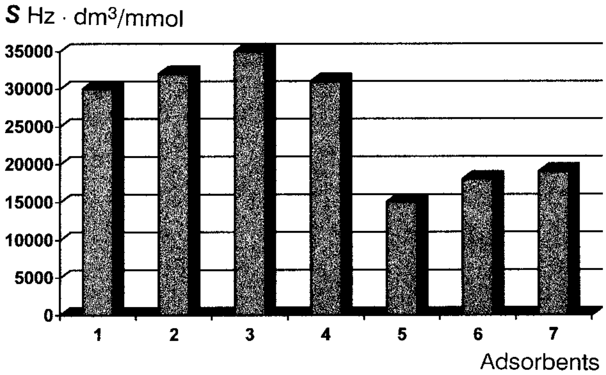

Figure 1. Histogram of piezosensor sensitivity, S, modified with SNC relative to nitromethane (1), nitroeghane (2), 1–nitropropane (3), 2–nitropropane (4), nitrobenzene (5), o–nitrotoluene (6), m–nitrotoluene (7)

lower affinity of triton X–100 and carbowax 20 M relative to the detected compounds. Thus, more nitrohydrocarbons are adsorbed on the surface of the sensor modified with triethanol amine than on those modified with triton X–100 or carbowax 20M.

The histogram of sensitivity is presented in Fig. 1. The maximum affinity to the most effective modifier (SNC) is characteristic of nitromethane. This is connected with its low boiling temperature and a high partial pressure of this adsorbate.

The obtained dependences of the change of the analytical signal $-\Delta F$ of the piezosensor modified with SNC on the gas–carrier flow rate and the detection temperature allow one to make the following conclusions. When detection temperature changes in the range 10–50 °C only a slight increase of the analytical signal is observed. Thus, it seems inefficient from the economic viewpoint to detect nitrohydrocarbons at temperatures exceeding 20–30 °C. With an increase of the gas flow rate up to 50 cm^3/min, the analytical signal becomes stronger. However, with further increase of the gas flow rate up to 75 cm^3/min, the analytical signal is reduced. This is related to the partial removal of the modifier from the surface of the piezosensor.

CONCLUSION

The adsorption of nitrohydrocarbons on modified quartz resonators was investigated by piezoquartz microweighing. The optimum modifier for the electrode surface of the piezosensor proved to be short–chain nitrocellulose (a high specificity relative to the investigated adsorbates). The sensitivity of the sensor modified with 10 µg of SNC was 3500 Hz dm^3/mmol for nitropropane. The detection tempoerature was 20 °C, gas–carrier (air) flow rate 50 cm^3/min, aluminium was taken as the material for the electrodes of the quartz resonators.

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IZVOD

OPTIMIZACIJA USLOVA ZA ODREĐIVANJE NITROUGLJOVODNIKA U VAZDUHU

(Naučni rad)

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Određivanjem promene mase (mikrometodom) piezokvarcnog senzora, koji je modifikovan sa nitrocelulozom, tritenom X–100, karbovaksom 20 M i trietanolaminom identifikovana je adsorpcija nitrougljovodonika (alifatičnih i aromatičnih) na ovako pripremljenim senzorima. Ispitivana je selektivna adsorpcija pojedinih nitrougljovodonika na ovako pripremljenim senzorima u zavisnosti od tipa senzora, jedinjenja kojima je modifikovan piezokvarcni senzor, protoka gasa (vazduh) i temperature. Pokazano je da je optimalni modifikator piezokvarcnog senzora nitroceluloza sa kratkim molekulskim lancima (SNC). Osetljivost senzora koji je modifikovan sa 10 µg SNC je bila 3500 Hz · dm^3/mmol za nitropropn na 20°C, pri protoku vazduha od 50 cm^3/min, kada je za izradu elektrode kvarcnog rezonatora upotrebljen aluminijum.

Key words: Nitrohydrocarbons • Determination • In air • Piezoquartz senzor •
Ključne reči: nitrougljovodonici • određivanje • u vazduhu • piezokvarcni senzor •