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Effect of different modifications of BEA-zeolites on operational characteristics of conductometric biosensor

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ABSTRACT

Effect of different modifications of zeolite Na^+-BEA on working characteristics of urease-based conductometric biosensor was studied. As the biosensor sensitive elements were used bioselective membranes based on urease and various zeolites immobilised with bovine serum albumin on the surface of conductometric transducers. Influence of zeolites on sensitivity of urea biosensor was investigated as well as reproducibility of biosensor signal and reproducibility of activity of the bioselective element after different variants of urease immobilisation on the surface of conductometric transducer. The biosensors based on zeolites (NH_4^+-BEA 30 and H^+-BEA 30) were shown to be the most sensitive. Concentration of these zeolites in the bioselective membrane was optimized. Use of zeolites modified with methyl viologen and silver was ascertained to be of no prospect for urea conductometric biosensors. It was demonstrated that characteristics of urea biosensors can be regulated, varying zeolites modifications and their concentrations in bioselective membranes.

1. Introduction

Biosensor elaboration is one of modern trends in analytical biotechnology. Biosensor methods offer such advantages as high sensitivity and selectivity, low-cost analysis, ease-of-operation [1]. At present, use of new nanosized materials in biosensor design is a promising approach to improve analytical characteristics of the devices.

Zeolites are perspective nanomaterials for biosensor modification [2]. They are inorganic compounds, the structure of which is a crystal lattice consisting of aluminum and silicium bound by oxygen atoms. Inside the lattice there are single atoms of metals or ions of hydrogen, neutralizing negative charge of separate parts of a crystal, and sorbed water. The aluminum–silicium skeleton forms a lot of pores and channels which considerably increases the zeolite surface [3]. Scientists display a keen interest in zeolites due to specific properties of the latter. They are low toxic, chemically, mechanically and thermostable, tolerant to microorganisms [4]. Some zeolite parameters can be controlled in the course of their artificial synthesis. Si/Al ratio can be changed thus varying zeolite charge and hydropathy, number and size of pores. The atoms of alkaline and alkaline-earth metals can be incorporated into a crystal lattice and kept there by coordination bonds [5]. Heat treatment can regulate the amount of surface $-OH$ groups, which are important for immobilisation of zeolite in the bioselective element [6]. The zeolite surface can be also modified with various organic and inorganic groups ($-NH_2$, $-SH$, $-Cl$, $-CN$, $-C_6H_5$, etc.), thus providing different interactions between zeolite, enzyme and transducer [7,8]. Wide range of modifications allows obtaining zeolites with diverse properties potentially helpful in the biosensor development.

Zeolite Beta (BEA) is a large pore zeolite with a three dimensional interconnected channel system with 12-membered openings (7.6×6.4 Å) [9]. Since its discovery in 1967, this particular zeolite type has been of great interest due to the possibility of synthesizing it with a wide range of Si/Al ratios ranging from 5 to ∞. It has received much attention as a potential catalyst in numerous reactions due to its acidic properties as well. Most interestingly for catalytic purposes, BEA-zeolite can be easily modified by different ionic species which may cause to the formation of different acidic and hydrophobic regions on its outer surface. This should enable the investigation of the changing hydrophobic and acidic nature of this material on the biosensor characteristics.

The aim of this work was to verify a potential of versatile modifications of BEA-zeolites for controlled improvement of analytical traits of conductometric urea biosensors. Accordingly, the effect of ammonium

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(NH_4^+) and proton (H^+) ion-exchange, different Si/Al ratio and the modification of same zeolites with methyl viologen on the obtained biosensor characteristics were investigated. Thus, it was aimed to study the influence of ionic properties of zeolites, their hydrophobicity, and pore conductivity on biosensor work. To do this, BEA-zeolite with varying characteristics was added to the bioselective element of the biosensor by mixing zeolite and enzyme solutions and immobilizing the mixture in glutaraldehyde vapor, thus zeolites and enzyme were intimately related. In the current study, influence of zeolites on biosensor calibration curves, biosensor responses, inter-reproducibility and signal reproducibility during a working day were investigated. Finally, optimal zeolite concentration in the bioselective element was selected. Urease was chosen because it is one of the most studied enzymes in biosensoric and biosensors based on this enzyme are widely applied in medicine and potentially can be used in agro-food chemistry and environmental monitoring.

2. Materials and methods

2.1. Materials

Urease (EC 3.5.1.5), activity 66.3 U/mg from "Fluka" (Switzerland); glycerol, bovine serum albumin (BSA) (fraction V), 50% aqueous solution of glutaraldehyde (GA) and urea from "Sigma-Aldrich Chemie" (Germany) were used in experiments. Potassium-phosphate buffer (KH_2PO_4-NaOH) was of domestic manufacture. The rest inorganic substances were of analytical grade.

2.2. Synthesis and ion exchange procedure of zeolite crystals

Zeolite Na^+-BEA samples were hydrothermally synthesized from gel solutions having the compositions of $1{,}92Na_2O{:}Al_2O_3{:}ySiO_2{:}4{,}6(TEA)_2O{:}444H_2O$. The composition was determined according to the changing SiO_2/Al_2O_3 ratio (y = 30, 40, 50, and 60) of the Na^+-BEA samples. Sodium aluminate precursor solution for zeolite BEA was prepared by dissolving NaOH (>97 wt.%, J. T. Baker) and sodium aluminate (50.8 wt.% Al_2O_3, 43.4 wt.% Na_2O, Riedel de Haën) in deionized water (resistivity > 18 MΩ cm). Then tetraethyl ammonium hydroxide solution (TEAOH 35 wt.%, in water, Aldrich), which is the structure directing agent for zeolite BEA synthesis, was added and the prepared precursor solution was stirred thoroughly. Ludox® HS-40 colloidal silica solution (40 wt.% SiO_2 suspension in water, Sigma Aldrich) was added into aluminate precursor and mixed thoroughly before putting into the Teflon lined stainless steel autoclaves. The autoclaves were kept statically at 120 °C in a conventional oven for 7 days. The resulting solid particles were vacuum-filtered, washed with deionized water and dried at room temperature. Ion exchange procedure can be found elsewhere in the literature [10]. NH_4^+ forms of BEA crystals were obtained by ion-exchange with 1 M aqueous ammonium nitrate at 80 °C for 24 h. The acid (H^+) forms were made by calcination of NH_4^+-BEA 30 crystals at 500 °C for 6 h.

The samples were modified with methyl viologen (MV) by stirring 100 mg of MV and 300 mg of zeolite powder in 20 ml distilled water for 24 h at room temperature. Afterwards, the obtained solution was centrifuged twice at 10,000 rpm for 10 min. The resulting particles were dried overnight at 60 °C.

The ion-exchange procedure was applied by stirring 300 mg zeolites with a solution of 120 mg of $AgNO_3$ and 100 ml distilled water for 24 h in a dark environment. The modification of zeolite BEA particles into silver nanoparticle containing ones was carried out by reducing silver ion-exchanged samples in sodium borohydride (60 mM) suspension at room temperature. After each step, the obtained solution was centrifuged twice at 10,000 rpm for 10 min and then the zeolite particles were dried overnight in an oven at 60 °C.

2.3. Characterizations of zeolites

Phase identification of the synthesized zeolites was achieved by powder X-Ray diffraction analysis (XRD) using Ni filtered Cu-Kα radiation (Philips PW 1729). Morphologies of all zeolites were examined by scanning electron microscopy (FE-SEM) (400 Quanta FEI). The energy dispersive X-ray spectroscopy (EDX) analysis of the as-synthesized and ion exchanged samples was carried out utilizing a Phoenix EDAX X-ray analyzer equipped with Sapphire super ultrathin window detector attached to the Hitachi S-4700 FE-SEM. Nitrogen adsorption/desorption isotherms at liquid nitrogen temperature were obtained using a Quantachrome Autosorb-6 analyzer. Prior to the measurements samples were dried at 110 °C for 12 h and outgassed at 300 °C under high vacuum for 3 h. Multi point BET surface areas (S_{BET}) were calculated in the P/P_o range 0.05–0.30.

2.4. Conductometric transducers

Conductometric transducers were produced in V. Lashkaryov Institute of Semiconductor Physics NASU (Kyiv, Ukraine) in accordance with our recommendations. They have dimension 5 mm × 30 mm and consist of two identical pairs of gold interdigitated electrodes deposited onto a ceramized plate. General view of the conductometric transducer was presented in earlier publication [11]. Conductometric transducers were connected to the measuring device Stanford Research Systems Model SR830 DSP Lock-in Amplifier.

2.5. Preparation of bioselective elements

To produce working bioselective membranes, based on urease and zeolites, two mixtures were prepared. The first one is 10% urease, 10% BSA, 10% glycerol in 20 mM phosphate buffer, pH 7.2. The second mixture consisted of zeolites of different concentrations dissolved in the same buffer with 10% glycerol. 20 min before use this solution was dipped into ultrasonic bath with stirring. The prepared solutions were mixed at ratio of 1:1 and then deposited on the transducer surface with Eppendorf microsampler (total volume 0.1–2.5 μl) till complete covering of the working surfaces. The volume of each membrane was about 0.05 μl. The reference membrane was prepared in the mixture consisting of 10% BSA and 10% glycerol dissolved in 20 mM phosphate buffer, pH 7.2. The amounts of protein in both enzyme and reference membranes are the same. After deposition onto transducer surfaces, the membranes were placed into saturated GA vapor for 35 min and then dried in the air at room temperature for 15 min. Next, the transducers were dipped into the working buffer for 20–30 min in order to wash out the unbound enzyme and excess of GA.

2.6. Measurement procedure

Measurement was carried out in 5 mM phosphate buffer, pH 7.2, at room temperature in an open cell of 2 ml volume at continuous stirring. The substrate concentration in the working cell was specified by addition of corresponding aliquot of 500 mM urea solution. Every experiment was repeated at least five times. Nonspecific changes in the output signal associated with fluctuations of temperature, medium pH and electrical noise were avoided due to use of a differential measurement mode.

3. Results and discussion

Urease-based biosensor functions due to the enzymatic reaction that takes place in the membrane on the transducer surface:

$$\text{Urea} + 2H_2O + H^+ \xrightarrow{\text{Urease}} 2NH_4^+ + HCO_3^-$$

Thus, urea is decomposed by urease into ammonium and carbonic acid. Change in ion concentration in the working membrane results

in alteration of the solution conductivity which can be registered by conductometric transducer [12].

Representative XRD patterns of employed BEA samples are shown in Fig. 1. According to Fig. 1, all peaks observed correspond completely to those of the BEA material reported previously [13] and none of the ion exchanged samples showed a change in sample morphology after ion exchange procedure. Moreover, FE-SEM images (Fig. 2) indicated that all BEA samples display truncated square bipyramidal features with a particle diameter of 500 nm.

As shown in Table 1, the BET characterization of as-synthesized zeolite BEA (Na^+-BEA 30) showed that the pore volume, pore size, and surface area were 0.84 cc/g, 0.54 nm, and 260 m^2/g, respectively. The modification of Na^+-BEA 30 to NH_4^+-BEA 30 did not result any significant changes in the results obtained from BET analysis as expected. However, the surface area (S_{BET}, i.e., the total specific surface area), pore size, and pore volume of H^+-BEA 30 were larger than that determined for the as-synthesized material. This increase in the BET surface area is likely due to an increase in the pore volume of zeolite Beta samples owing to the removal of structure directing agent from the pores upon heat treatment [14]. Furthermore, the surface Si/Al ratio of the as-synthesized zeolite BEA was found to be 10 ± 1 as measured by EDX. Ion exchanged and calcined samples prepared from the parent material showed the same value (10 ± 1) (b).

At the first stage of research we studied influence of Na^+-BEA 30 zeolite, added to the bioselective element, on the biosensor response and linear range of measurement. A calibration curve for the biosensor with 5% zeolite was plotted and compared with that without zeolite (Fig. 3). As seen, the presence of Na^+-BEA 30 zeolite had no appreciable effect. A typical method to activate zeolite Beta for catalytic purposes is to change its acidic character through first of all ammonium ion exchange leading to an alteration between the Na^+ ions with NH_4^+ ions in the zeolite framework (NH_4^+-BEA). Next step is to apply a heat treatment procedure to convert those NH_4^+ ions into H^+ ions (H^+-BEA). The ammonium ion exchange is preferred because it reduces the possibility of damaging the zeolite BEA structure during heat treatment, as also shown to be the case in the current study (Fig. 2). Accordingly, in the current study, the Na^+-BEA 30 zeolite was also modified by first transforming Na^+-BEA 30 into NH_4^+-BEA 30 by exchanging the sodium ions for ammonium ions. After that, NH_4^+-BEA 30 was transformed into H^+-BEA 30 by calcination. The obtained calibration curves as a function of this transformation for the biosensors with the modified zeolites can be seen in Fig. 3.

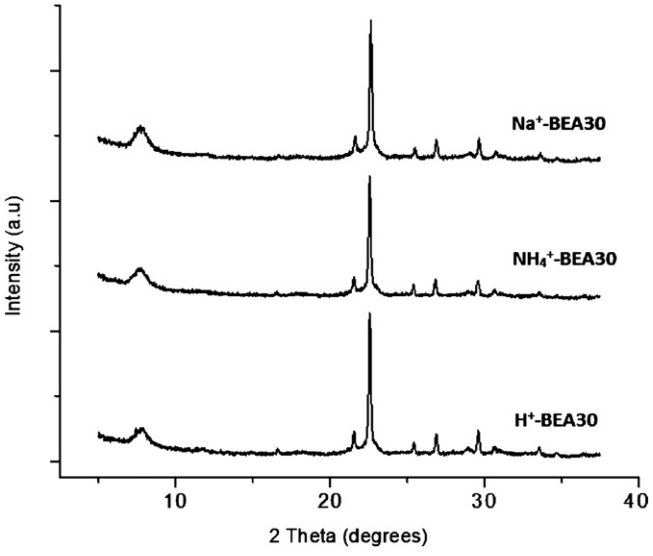

Fig. 1. XRD patterns of as-synthesized and ion exchanged BEA crystals.

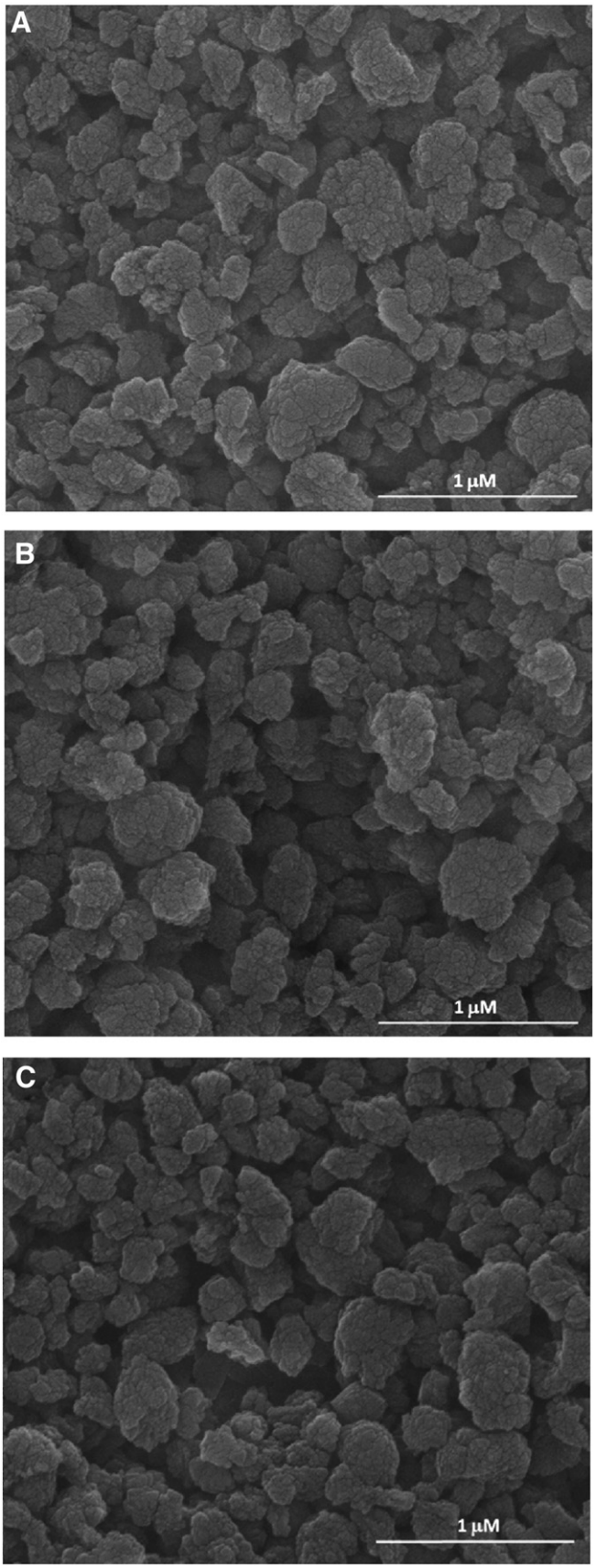

Fig. 2. SEM micrographs of zeolite crystals: Na^+-BEA 30 (A), NH_4^+-BEA 30 (B), H^+-BEA 30 (C).

Table 1
Physicochemical characteristics of employed BEA 30 samples.

Sample name	Si/Al[a]	S_{BET} (m^2/g)[b]	Pore size (nm)[b]	Pore volume (cc/g)[b]
Na^+-BEA30	10 ± 1.0	260	0.54	0.84
NH_4^+-BEA30	10 ± 1.0	279	0.64	0.89
H^+-BEA30	10 ± 1.0	490	0.85	1.3

[a] Si/Al ratio of zeolite crystals were measured by EDX.
[b] Surface area, pore size, and pore volume of zeolite BEA crystals were measured by BET.

As shown in Fig. 3, the presence of modified zeolites in the membrane substantially affected the signal value and, thus, the biosensor sensitivity while the measurement linear range changed insignificantly. This is why, to demonstrate the zeolite effect more obviously, the biosensor responses to 6 mM urea (which is a saturating final concentration) are presented as a diagram in Fig. 4 as a function of the type of modified zeolites. The response of biosensor based on urease only, without any zeolite, was taken as 100%. The results showed that the biosensors with zeolites NH_4^+-BEA 30 and H^+-BEA 30 were the most sensitive.

Thus, zeolites NH_4^+-BEA 30 and H^+-BEA 30 in the composition of bioselective elements were shown to raise the biosensor sensitivity to the substrate. One recognized method to alter the acidic properties of zeolites is to change the Na^+ ions within the framework of zeolites. Since the Si/Al ratio was kept constant at 10 ± 1 during ion-exchange, the observed increase in the biosensor sensitivities can be due to the increasing acidic properties related with the changing surface groups of zeolite BEA. It is known that ammonium exchange of zeolite BEA boosts its acidic character leading to a significant increase in the concentration of Brønsted acid sites and thus the concentration of H^+ ions linked to the tetrahedrally coordinated Al-OH-Si groups in the zeolite framework [15]. It was also shown that it is possible that the relative boost of the acidity with further conversion of NH_4^+-BEA to H^+-BEA can be practically constant. This fact is in line with the nature of the reaction of urea catalysis, which was an example of a hydrolysis system that requires proton as a reactant. Thus, it was shown that increasing acidic character of zeolite BEA stimulates the urease reaction as a result of increasing proton donor sites of the zeolite network. However, it is also important to check whether the zeolites have some negative effect on the signal reproducibility. For this purpose, the biosensor responses to 6 mM urease were measured during working day with 20-min intervals of which were kept in the working buffer at room temperature. The errors of measurement (Sd) were about the same (2%) for biosensors both with and without zeolites.

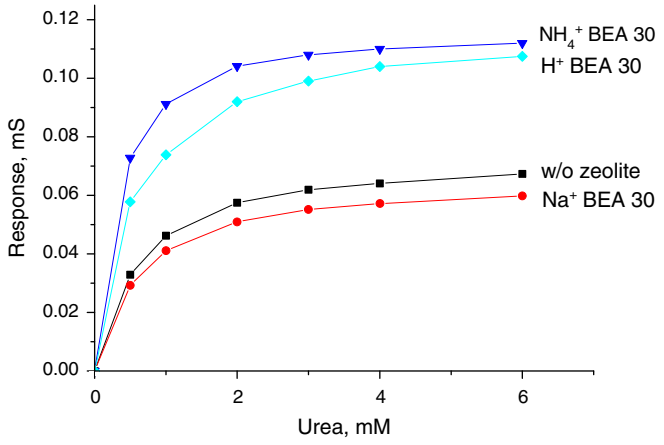

Fig. 3. Influence of zeolites on the calibration curves of urea biosensors. Urease was co-immobilised with zeolites Na^+-BEA 30, NH_4^+-BEA 30 and H^+-BEA 30; urease immobilisation without zeolites is used for comparison. Zeolite concentration in bioselective element of biosensor – 5%. Measurements in 5 mM phosphate buffer, pH 7.2.

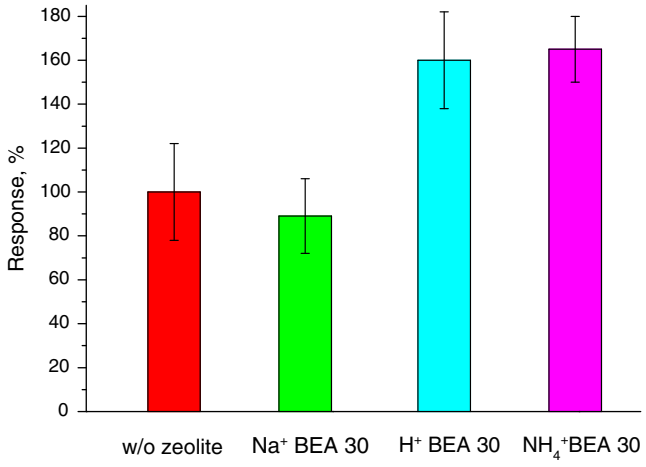

Fig. 4. Biosensor responses to 6 mM urea without zeolites in bioselective element and with zeolites Na^+-BEA 30, H^+-BEA 30, NH_4^+-BEA 30. Zeolite concentration – 5%. Measurements in 5 mM phosphate buffer, pH 7.2.

One more parameter to be investigated is reproducibility of the biosensor activity after immobilisation by different methods, so-called biosensor inter-reproducibility (inter-assay). The biosensors with 5% concentration of zeolites NH_4^+-BEA 30 and H^+-BEA 30 were tested along with control membranes without zeolite. As seen in Fig. 5, addition of zeolite NH_4^+-BEA 30 with a concentration of 5% lead to an improved inter-reproducibility, however the addition of H^+-BEA 30 with a concentration of 5% did not cause any change. Upon increasing the concentration of NH_4^+-BEA 30 from 5 to 15% resulted in a larger Sd and thus worse inter-reproducibility (reason of this effect is explained in the next paragraph).

At the next stage, optimization of zeolite concentration in the membrane was carried out. Zeolites NH_4^+-BEA 30 and H^+-BEA 30 (the presence of which the concentration of 5% zeolite addition was shown to increase the biosensor responses significantly; Fig. 5) were added to the membrane composition in different amounts. As seen in Fig. 6, optimum zeolite concentrations were found to be 15% and 7.5% for NH_4^+-BEA 30 and H^+-BEA 30 respectively. Probably, the observed decrease in the response for H^+-BEA 30 using concentrations higher than 7.5% (Fig. 6-B) as well as worse inter-reproducibility observed upon using 15% NH_4^+-BEA 30 (Fig. 5) is probably due to the incompatibility and poor mixing character of the enzyme-zeolite mixture deposited on

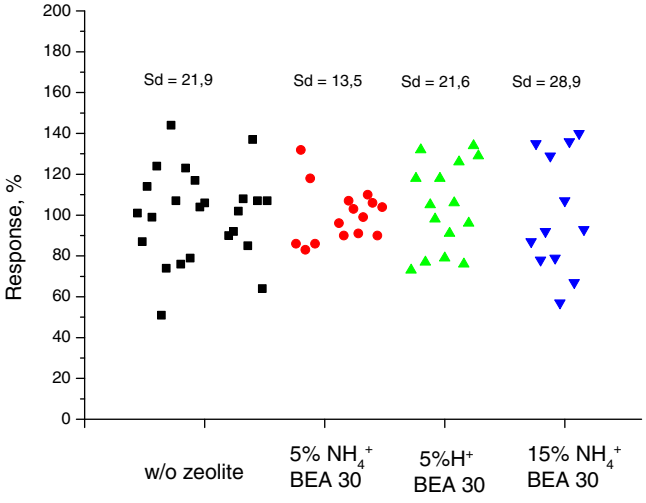

Fig. 5. Influence of zeolites on biosensor inter-reproducibility. Urease was co-immobilised with zeolites: 5% NH_4^+-BEA 30, 5% H^+-BEA 30, 15% NH_4^+-BEA 30; urease immobilisation without any zeolites is used for comparison. Urea concentration in cell – 6 mM. Measurements in 5 mM phosphate buffer, pH 7.2.

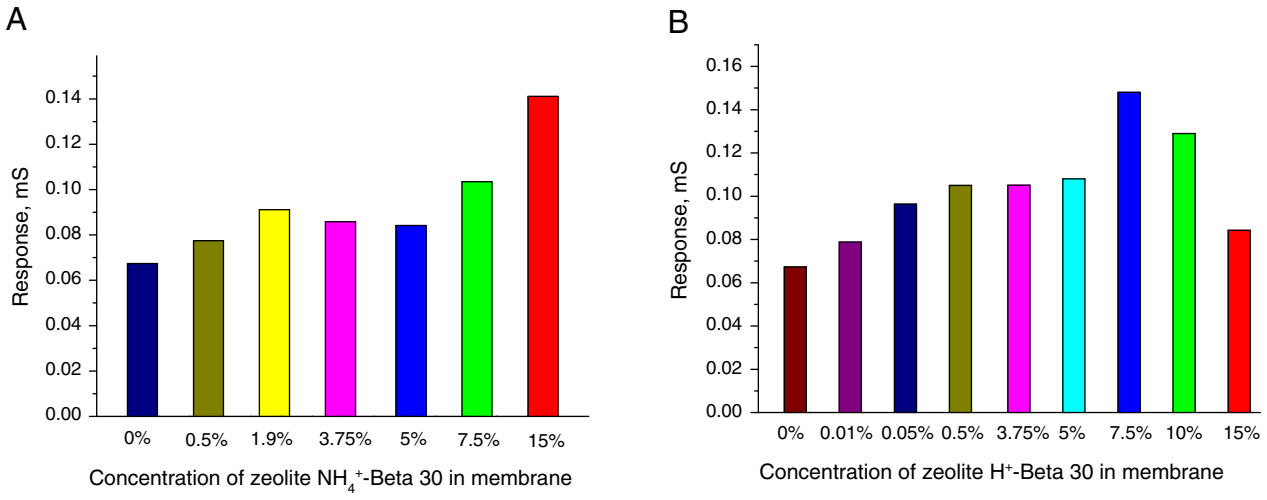

Fig. 6. Dependence of responses of urea biosensors on zeolite concentration in bioselective element. Substrate concentration – 6 mM. Measurements in 5 mM phosphate buffer, pH 7.2.

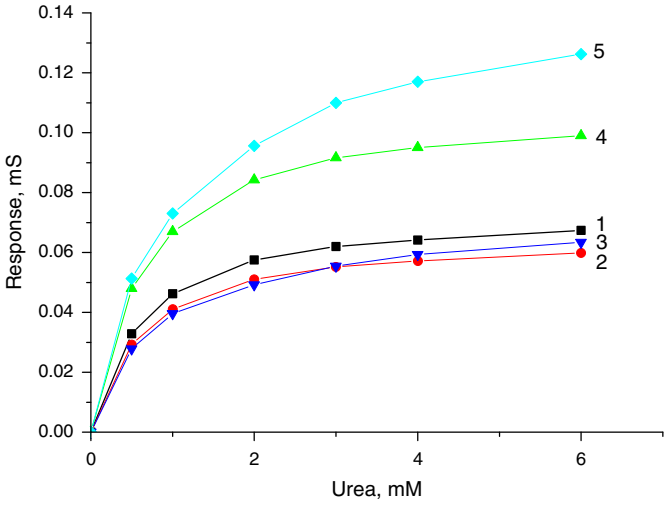

Fig. 7. Calibration curves of biosensors based on urease immobilised without zeolites (1) and with zeolites: Na^+-BEA 30 (2), Na^+-BEA 40 (3), Na^+-BEA 50 (4), Na^+-BEA 60 (5). Zeolite concentration in membrane – 5%. Measurements in 5 mM phosphate buffer, pH 7.2.

the transducer, which resulted in poor quality of immobilisation of the bioselective element.

Thus, it is possible to attain the highest biosensor sensitivity (Fig. 6-A) or to improve inter-reproducibility of biosensor (see Fig. 5) by varying the NH_4^+-BEA 30 zeolite concentration in bioactive element.

The silicon to aluminum ratio (Si/Al) is an important characteristic of zeolites. It is known that zeolites with higher amount of aluminum have greater hydrophilic properties [16]. Hydrophobicity of zeolite obviously has influence on the interactions between the enzyme molecules and zeolite crystals. Therefore the effect of Si/Al ratios (i.e., 30, 40, 50, and 60) of zeolite Na^+-BEA was also studied. As seen in Fig. 7, decrease in Si/Al ratio is accompanied with a decrease in response values. This phenomenon can be a result of decreased hydrophobic interactions between the enzyme molecules and zeolite crystals. Accordingly, using zeolites with high Si/Al ratio can be a promising approach for further improvement of biosensor characteristics.

Furthermore, the effect of adding zeolites that were modified with methyl viologen and silver ions were also investigated. First, zeolite Na^+-BEA 40, 50 and 60 were modified by integration of methyl viologen (MV) in their pores. Methyl viologen was expected to change pore conductivity; however, no increase in responses of the biosensors were observed as compared with the biosensors containing non-modified zeolites (Table 2). Thus, use of zeolites modified with methyl viologen in conductometric biosensors has no sense. Also in order to change the ionic properties of zeolite Na^+-BEA 40, 50 and 60, silver ions were exchanged with sodium ions (Na^+) that are already present in the as-synthesized zeolites. It was observed that silver ion exchanged and silver nanoparticle including zeolites didn't give any responses until 5 mM urea injection. The reason can be the urease inhibition due to the silver ions, which is slowly released out of the zeolite.

Table 2
Influence of zeolite modification with methyl viologen on biosensor responses. Biosensors are based on urease, co-immobilised with non-modified Na^+-BEA zeolites and urease, co-immobilised with Na^+-BEA zeolites, modified with methyl viologen.

Biosensor response, %					
Urease + non-modified zeolites			Urease + zeolites, modified with methyl viologen		
Na^+-BEA 40	Na^+-BEA 50	Na^+-BEA 60[a]	Na^+-BEA 40	Na^+-BEA 50	Na^+-BEA 60
52.6	78.1	100	46.7	68.5	97.6

[a] The responses were normalized to the results obtained from biosensor with non-modified Na^+-BEA 60.

4. Conclusion

Effect of different modifications of BEA-zeolites on operation of conductometric urea biosensor is studied. Immobilisation of zeolites NH_4^+-BEA 30 and H^+-BEA 30 together with urease results in increasing biosensor response, the signal reproducibility being unchanged. Inter-assay of biosensor responses after immobilisation by different procedures was tested and shown to be the best when NH_4^+-BEA 30 zeolite is used as a component of the bioselective element. The biosensors with zeolites having greater Si/Al ratio were characterized by increased activity. Use of zeolites modified with methyl viologen and silver had no positive effect.

The presented results allow us to state that use of different modifications of zeolites at enzyme immobilisation makes it possible to improve operational characteristics of urea conductometric biosensor in required way.

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References

[1] F.R.R. Teles, L.P. Fonseca, Mater. Sci. Eng. C 28 (2008) 1530–1543.
[2] M. Granda Valdes, A.I. Perez-Cordoves, M.E. Dıaz-Garcıa, Trends Anal. Chem. 25 (2006) 24–30.
[3] W.M. Meier, D.H. Olsen, Atlas of Zeolite Structure Types, Wiley-Interscience, New York, USA, 1974.
[4] Adalgisa Tavolaro, Palmira Tavolaro, Enrico Drioli, Colloids Surf. B 55 (2007) 67–76.
[5] Baohong Liu, Fang Yan, Jilie Kong, Jiaqi Deng, Anal. Chim. Acta 386 (1999) 31–39.
[6] S. Öztürk, B. Akata, Microporous Mesoporous Mater. 126 (2009) 228–233.
[7] A.M. Liu, K. Hidajat, S. Kawi, D.Y. Zhao, Chem. Commun. 13 (2000) 1145–1146.
[8] Humphrey H.P. Yiu, Paul A. Wright, Nigel P. Botting, J. Mol. Catal. B: Enzym. 15 (2001) 81–92.
[9] J.B. Higgins, R.B. LaPierre, J.L. Schlenker, A.C. Rohrman, J.D. Wood, G.T. Kerr, W.J. Rohrbaugh, Zeolites 8 (1988) 446–452.
[10] E.J. Creyghton, S.D. Ganeshie, R.S. Downing, H. van Bekkum, J. Mol. Catal. A: Chem. 115 (1997) 457–472.
[11] O.O. Soldatkin, V.M. Peshkova, S.V. Dzyadevych, A.P. Soldatkin, N. Jaffrezic-Renault, A.V. El'skaya, Mater. Sci. Eng. C 28 (2008) 959–964.
[12] N. Jaffrezic-Renault, S.V. Dzyadevych, Sensors 8 (2008) 2569–2588.
[13] K. Narasimharao, M. Hartmann, H.H. Thiel, S. Ernst, Microporous Mesoporous Mater. 90 (2006) 377.
[14] M.A. Camblor, A. Corma, S. Valencia, Microporous Mesoporous Mater. 25 (1998) 59–74.
[15] G.H. Kuehl, H.K.C. Timken, Microporous Mesoporous Mater. 35–36 (2000) 521–532.
[16] Eng-Poh Ng, S. Mintova, Microporous Mesoporous Mater. 114 (2008) 1–26.