

Microelectrode array fabricated in low temperature cofired ceramic (LTCC) technology

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Abstract This work presents the development of a novel construction of an integrated microelectrode array. The device was fabricated on a ceramic support, with the use of low temperature cofired ceramics technology. Model potassium-selective membranes were applied on the surface of PdAg/AgCl electrodes formed on the ceramic substrate. The obtained microsensors exhibited very good repeatability, reproducibility, and sensitivity. The array of microelectrodes covered with polymeric layers of various selectivities was applied as an electronic tongue to differentiate between various diet supplements.

Keywords Electronic tongue · Microelectrode array · LTCC technology

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Introduction

Multisensor devices offer a wide possibility of advanced analytical applications. The fusion of various measurement techniques allows to improve the amount of the information gained in a single act of measurement. In the case of electronic noses and tongues, the combination of sensors based on different transducers provides better characterization of a sample—the chemical image of the sample becomes more complete because wider spectrum of properties is studied [1, 2].

Integration of sensors on a single support can be employed not only in devices mimicking chemical senses [3–6] but also in systems realizing classical analytical procedures. In the case when one kind of sensors is integrated on the same substrate, the accuracy of the measurement can be improved or high density discrete sensing can be performed [6]. When many sensors, selective towards various species, are fabricated on a single platform, the system can be applied in multicomponent analysis [6–11].

Fabrication technology of integrated multisensor devices that can perform several modes of measurement (i.e., electronic nose/tongue, measurements with improved accuracy, and multicomponent determinations) should be carefully chosen. The main feature of that technology should be the possibility of easy formation of transducer structure and spreading of the chemosensitive material on its surface. The device material should be chemically inert and the cost the preparation of the final structure should be relatively low. Moreover, the possibility of scaling down the device would be also advantageous, because it allows to obtain miniaturized total analysis systems [12, 13]. In some cases, the

compatibility of the chosen fabrication technique with the other microsystem technologies should also be considered [14] in order to create appropriate module realizing, e.g., each step in multistage analytical procedure.

All those premises were taken into account in the development of microelectrode array presented in this work. Therefore, the array was chosen to be made on ceramic multilayer substrate manufactured by low temperature cofired ceramics (LTCC) technology. This method is widely used in microelectronics because of its simplicity, low cost, and good properties of the obtained structures [12]. The LTCC ceramic foil is produced by tape casting method from a mixture of glass, ceramics, and organic binder. Thick film inks (conductor, resistor, sensor, etc.) are deposited by screen-printing technique on the separate green ceramic foils. The tapes are then stacked together, laminated, and cofired at 850 °C. The cofired multilayer module consists of ceramic layers, electrical interconnections lines as well as external or internal thick film electronic components. Moreover, channels and cavities can be manufactured inside the 3D multilayer module. LTCC systems are highly chemically inert, which makes them a perfect material for fabrication of sensors [12] or even chemical analysis microsystems, including devices dedicated to PCR, optical detection of bioanalytes, electrophoresis, etc. [12, 15]. LTCC technology was also used to prepare potentiometric integrated system dedicated to the determination of ammonium and nitrate ions [16] and chloride ions [17].

In this paper, the microelectrode array fabricated in LTCC technology was applied to prepare a multisensor system. First experiments were devoted to the development of membrane composition and casting with the use of model membranes selective towards potassium. The final task was to obtain a miniaturized electronic tongue, i.e., LTCC microelectrode structure covered with various polymeric membranes, that could differentiate typical diet supplements commercialized in Poland.

Experimental

The development of LTCC structure

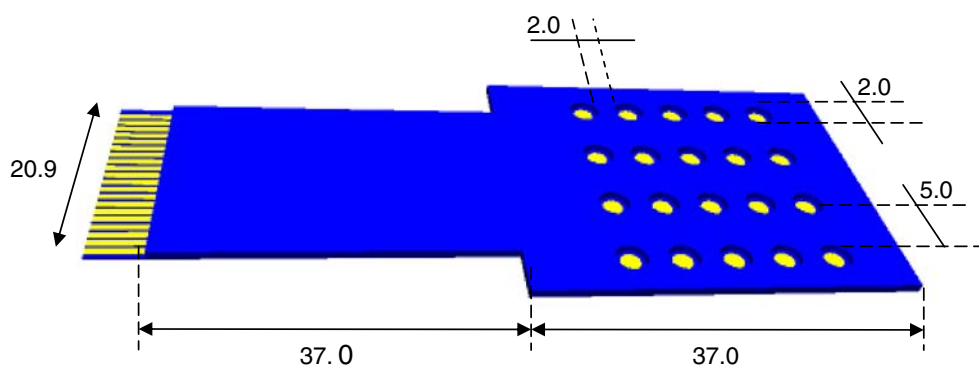
The architecture of LTCC-based microelectrode array is presented in Fig. 1. Seven layers of Du Pont 951A2 ceramic tapes were used. The first layer is only for mechanical support. Standard thick film techniques are used to create electrical interconnections (see the project and LTCC tape with screen-printed paths in Fig. 2). The electric pattern is printed on the second tape layer (Fig. 2b). Conductive films were manufactured using DP6146 (PdAg) paste. The path width was 400 μm . The electrical output dimensions of the tongue are adapted to a standard plug (Fig. 3). The round diameter of PdAg electrode is equal to 600 μm (Fig. 4).

The next five layers of green tape work as a cover and insulator for electric interconnections. The holes are made in these layers to create chambers for ion-selective membranes (see Fig. 4). Among several methods of creation of LTCC shapes, laser beam cutting was chosen. The microelectrode array layers were obtained by the cutting of green tape by Aurel Nd:YAG laser system. The layers were then arranged in a proper order and after that they were laminated in an isostatic press (180 bar, 70 °C, 10 min). The structure was laminated with additional inflexible plate by one side to prevent deformation (such method is necessary for manufacturing continuous conductive paths). Finally, the structure was cofired in 875 °C at a standard for DP951 LTCC tape temperature profile. The final effect of that work was applied to the next experiments.

The modification of the surface of PdAg electrodes

Screen-printed electrodes were fabricated with the use of PdAg paste. The preliminary tests showed that the enrichment of the electrode surface with silver allows to obtain stable potential. Moreover, additional covering with

Fig. 1 Schematic drawing of the microelectrode array



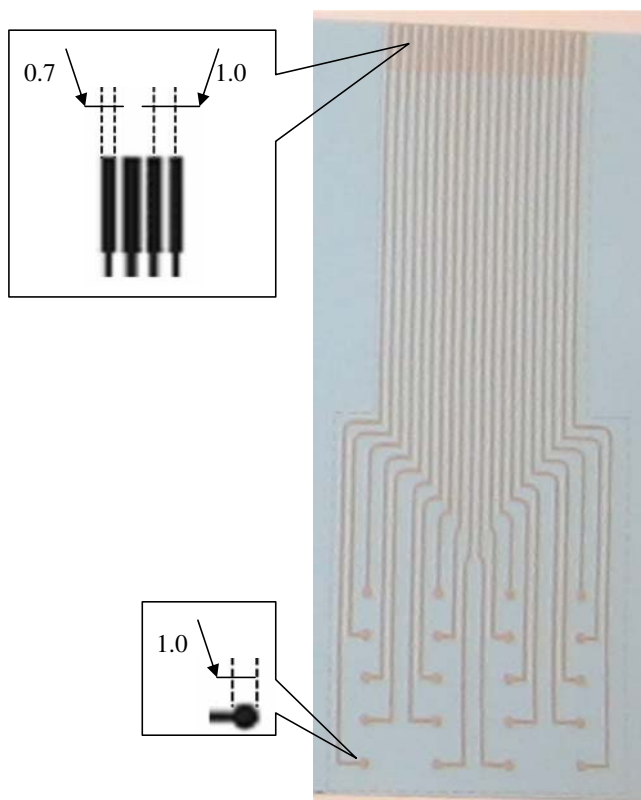


Fig. 2 Green tape with screen-printed electric paths

the layer of AgCl led to better repeatability of the electrode signal.

At the beginning, the surface of the transducers (PdAg paste on ceramic substrate) was cleaned with distilled water and methanol. The additional silver layer was obtained by Tollens reaction. During that reaction, diamminesilver(I) complex, obtained by the reaction of silver nitrate (2% aqueous solution) with concentrated ammonia, is reduced to

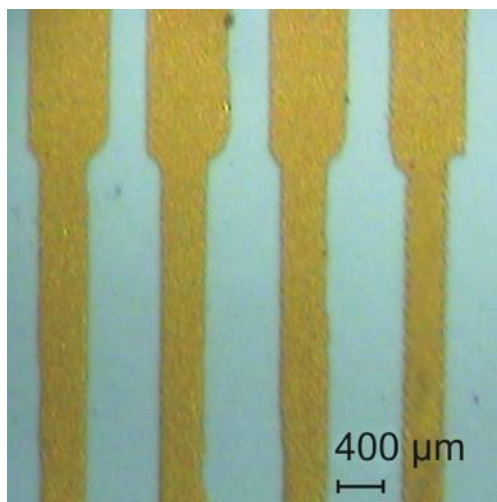


Fig. 3 Close-up view of the contacts printed using standard thick film technique

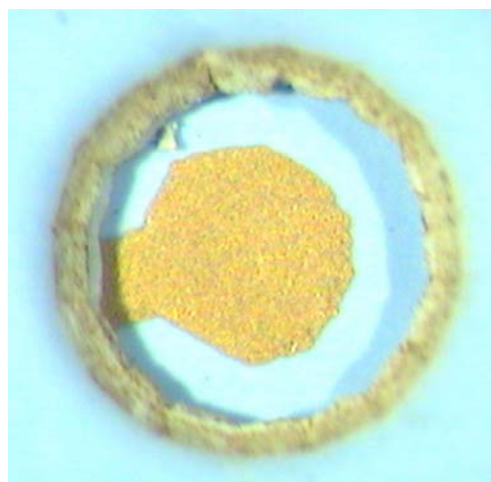


Fig. 4 Metallic electrode printed using standard thick film technique with a chamber for ion-selective membrane

silver metal, which forms a “silver mirror” on the surface of the reaction vessel. The reduction is accompanied by the oxidation of aldehyde group of glucose. Solutions of silver complex and glucose should be prepared just before mixing themselves and casting onto the surface of the screen-printed electrodes (into the chambers fabricated in LTCC structure, see Fig. 4b). After 5 min, the reagents were washed out from the ceramic substrate. Following layer of AgCl was deposited electrochemically in 0.1 mol·dm⁻³ of KCl/HCl solution.

Chemosensitive membranes preparation and deposition

Poly(vinyl chloride) (PVC) or polyurethane (PU) has been applied as polymer matrix of model potassium-selective membranes (Table 1). In both cases, 33 mg of the polymer was weighted together with 66 mg of plasticizer (di(2-ethylhexyl) sebacate, DOS), 2 mg of valinomycin (potassium ionophore), and 1 mg of lipophilic salt (potassium tetrakis [3,5-bis(trifluoromethyl) phenyl] borate, KTFPB). The membrane components were dissolved in 0.5 ml of freshly distilled tetrahydrofuran.

During the measurements of the electronic tongue, only polyurethane membranes were used. Six types of micro-sensors were prepared in the array: calcium-selective (Ca²⁺), ammonium-selective (NH₄⁺), partially selective towards sodium and potassium (Na⁺/K⁺), sensor with general selectivity to cations (CS, cation-selective), sensor with a membrane containing ionic liquid (IL), and chloride-selective sensor (Cl⁻), i.e., PdAg/AgCl electrode without any polymeric membrane. Compositions of Ca²⁺, NH₄⁺, Na⁺/K⁺, CS, and IL membranes are presented in Table 1.

Nine microliters of membrane solution was deposited into the appropriate chamber on the LTCC structure on the surface of PdAg/AgCl electrode. After the membrane solvent evaporation, the obtained ion-sensitive microsensors

Table 1 Membrane components

Electrode type	Plasticizer	Lipophilic salt	Ionophore
Ca ²⁺	<i>o</i> -NPOE	KTFPB	ETH 1001
NH ₄ ⁺	BBPA	KTPCIPB	Nonactine
Na ⁺ /K ⁺	<i>o</i> -NPOE	KTPCIPB	Ionophore X, valinomycin
CS	DOS	KTPFPB	–
Ionic liquid (IL)	DOS	1-dodecyl-3-methyl-imidazolium chloride	–
Cl [−] (Ag/AgCl electrode)	–	–	–

o-NPOE 2-nitrophenyl octyl ether, Fluka; BBPA bis(1-butylpentyl)adipate, Fluka; DOS bis(2-ethylhexyl)sebacate, Fluka; KTFPB potassium tetrakis [3,5-bis(trifluoromethyl)phenyl] borate, Fluka; KTPCIPB potassium tetrakis(4-chlorophenyl)borate, Fluka; TDMAC tridodecylmethylammonium chloride, Fluka; ETH 1001 calcium ionophore I, Fluka; Nonactine ammonium ionophore I, Fluka; Ionophore X 4-*tert*-butylcalix[4] arene-tetraacetic acid tetraethyl ester, Fluka; Valinomycin potassium ionophore I, Fluka; Ionic liquid 1-dodecyl-3-methyl-imidazolium chloride, Solvent Innovation GmbH (Köln); PVC poly(vinyl chloride) high molecular weight, Fluka; PU polyurethane, Fluka

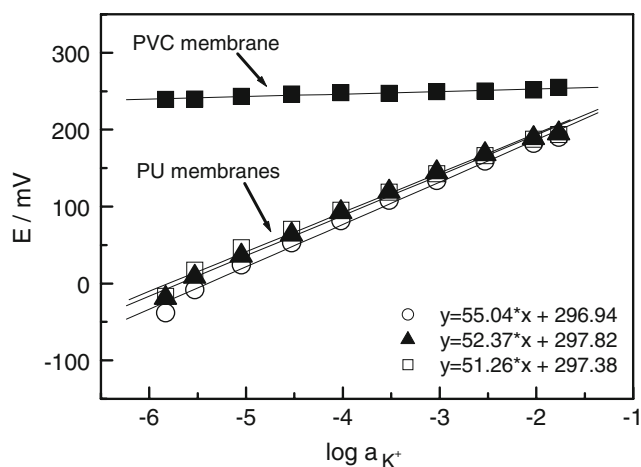
were conditioned for 24 h in 10^{−2} mol·dm^{−3} KCl solution (in the case of K⁺-selective sensors) or in 10^{−3} mol·dm^{−3} KCl, NaCl, and NH₄Cl.

All the experiments were conducted with cells of the following type:

Ag, AgCl; KCl 1 M/CH₃COOLi 1 M/sample solution// polymeric membrane//AgCl, Ag. EMF measurements were carried out using a potentiometric multiplexer (EMF 16 Interface, Lawson Labs Inc., Malvern, USA). Data analysis was performed in MatLab (The MathWorks, Inc., Natick, USA) and Microcal Origin (Microcal Software Inc., Northampton, USA).

Results and discussion

Post-processed tests were performed for the final microelectrode array structures obtained by LTCC technology. The electrical conductance of the paths and a tightness of the platform were examined. When both tests were successful, the PdAg microelectrodes in the array have been used as transducers of microsensors based on ion-sensitive polymeric membrane.

**Fig. 5** Calibration curves for potassium-selective polymeric membranes

The optimization of membrane composition was performed with the use of standard polymeric membranes selective towards potassium ions. Two kinds of polymer matrix were investigated: plasticized poly(vinyl chloride) and polyurethane. In our previous works, PVC-based membranes were applied on miniaturized solid-state electrodes [18, 19] and on integrated array of microelectrodes fabricated on epoxy–glass laminate [3, 4]. However, the adhesion of this polymeric material to the ceramic surface was not good enough (which could be verified by a microscope study), and that was confirmed by potentiometric measurements. Typical calibration curve obtained in the case of sensors with PVC membranes is presented in Fig. 5. Since the sensitivity of such sensors was not acceptable, another polymeric material—plasticized polyurethane—was tested in the preparation of K⁺-selective electrodes. The second type of microsensors exhibited very good sensitivity and very good reproducibility (see the values of response slope and E^0 in Fig. 5) as well as a wide range of linearity.

Coated-wire type electrodes prepared in this work are more prone to drift in comparison to the electrodes with intermediate layer serving as an internal electrolyte solu-

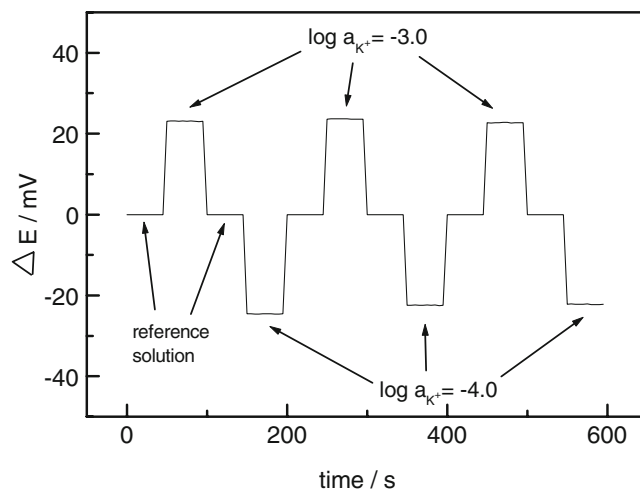
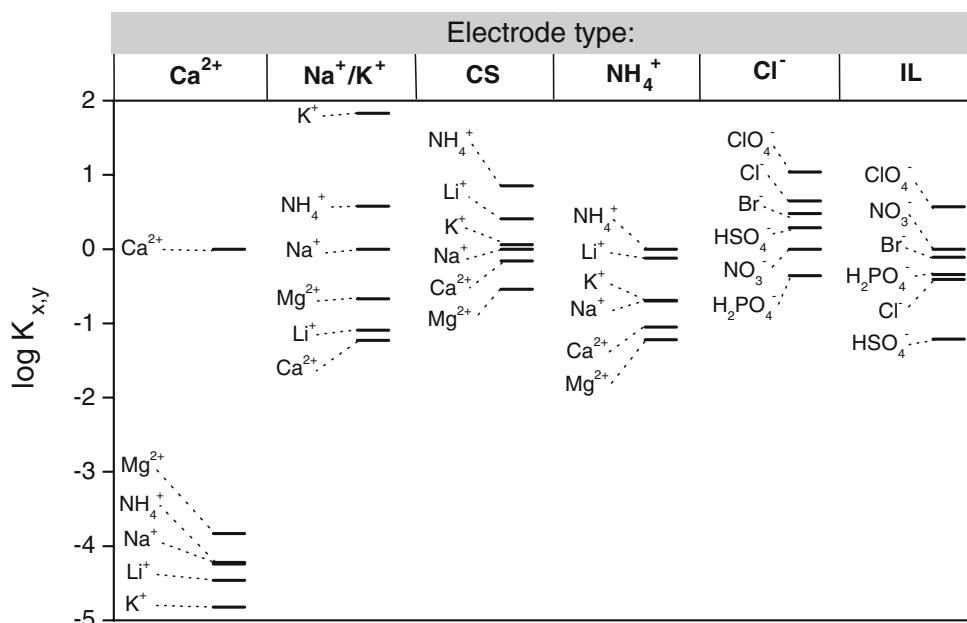
**Fig. 6** Repeatability of the response of K⁺-selective electrode in solutions of various potassium concentrations

Fig. 7 Selectivity patterns of the electrodes used in the LTCC sensor array



tion. Therefore, in order to compensate the eventual sensor drift, the measurement procedure was carried out as follows: firstly, the potential of the microelectrodes in the array was measured for 10 min in the reference solution and then during 10 min in the sample solution. Ten last potential values (collected every 5 s) from each measurement have been used for calculations. The difference of the signal measured in the samples solution and reference solution was the final output of the sensor, according to the formula:

$$\Delta E_{i,j} = E_{i,j} - \frac{\sum_{i=1}^{10} E_{i,j}^{ref}}{10}$$

where:

- $\Delta E_{i,j}$ final output of the j -th sensor in i -th measurement point,
- $E_{i,j}$ signal of the j -th sensor in i -th measurement point, measured in the sample solution,
- $E_{i,j}^{ref}$ signal of the j -th sensor in i -th measurement point measured in the reference solution.

The potential repeatability of the PU-based potassium-selective sensors fabricated on LTCC support was checked during the measurements of their signals in two solutions of various activity of potassium cations at constant background of $0.01 \text{ mol dm}^{-3} \text{ NaNO}_3$. The sensor outputs measured in the reference solution ($10^{-2} \text{ mol dm}^{-3} \text{ NaNO}_3$ and $3 \cdot 10^{-4} \text{ mol dm}^{-3} \text{ KNO}_3$) were applied to calculate the sensor responses depicted in Fig. 6. Signal values obtained in $10^{-3} \text{ mol dm}^{-3} \text{ KNO}_3$ solutions differed only in a range of 1.0 mV (23.10, 23.63, and 22.71 mV; SD=0.46 mV). The results indicated that the proposed approach of drift

compensation guaranteed good stability of the signal of potassium-selective electrodes.

The aim of the further studies was the fabrication of a miniaturized electronic tongue based on LTCC microelectrode array. The composition of the ion-sensitive polymeric membranes were chosen according to our previous results, where the fusion of ion-selective and partially selective materials helped to better characterize many types of foodstuff samples [18, 20] and biological samples [21, 22]. Taking into account the poor adhesion of the PVC-based membranes to the ceramic surface, the membrane matrix was only replaced by plasticized polyurethane. Five types of microelectrodes based on PU ion-sensitive membranes were fabricated: Ca^{2+} , NH_4^+ , Na^+/K^+ , CS, and IL. Chloride-selective sensor (i.e., PdAg/AgCl without polymeric membrane) was also included in the microelectrode

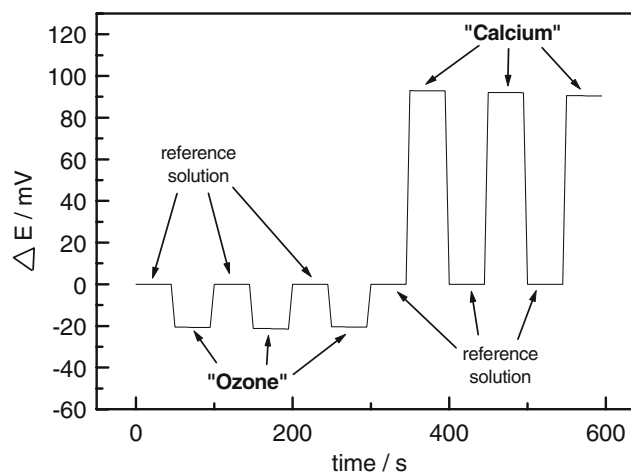
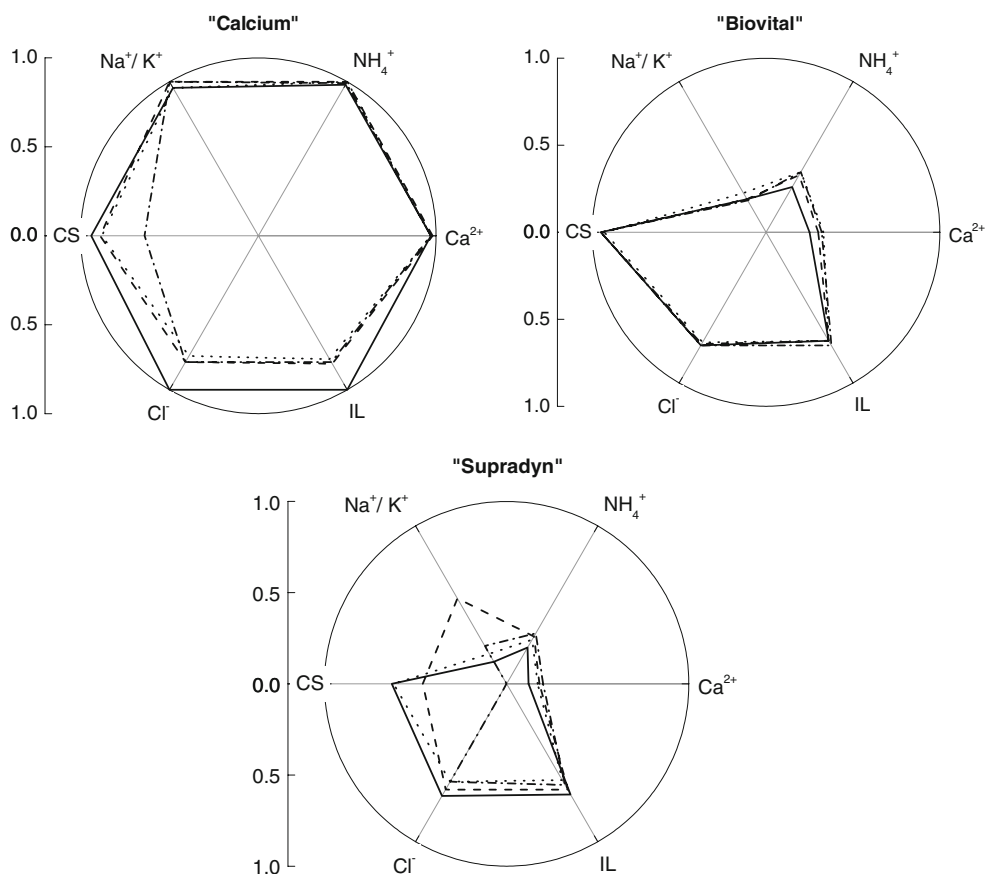


Fig. 8 Repeatability of the response of Na^+/K^+ -selective electrode in solutions of diet supplements: “Calcium” and “Ozone”

Fig. 9 Polar plots representing normalized sensor responses in various diet supplements: "Calcium", "Biovital", and "Supradyn"



array of the electronic tongue. Two specimens of each type of microsensor were prepared on the microelectrode array (12 microsensors in total). The performance of all the electrodes forming an electronic tongue was checked by the investigation of their selectivity patterns, determined by separate solution method. The obtained results (i.e., logarithmic values of selectivity coefficients) showed that the sensors exhibited satisfactory selectivity (see Fig. 7).

Firstly, the repeatability of the potential of ion-sensitive microsensors fabricated on the ceramic platform was tested according to the procedure used above for potassium-selective sensors. The electrode signals were measured in two solutions of diet supplements "Ozone" and "Calcium" and each experimental step was preceded by potential measurement in the reference solution (10^{-3} mol·dm $^{-3}$ KCl, NaCl, and NH $_4$ Cl). Exemplary outputs of Na $^+$ /K $^+$ -selective electrode, calculated according to the proposed formula, are presented in Fig. 8. Comparable electrode signal values have been determined in "Ozone" and "Calcium" solution during three consecutive measurements (−20.66, −21.33, and −20.50 mV in "Ozone"; 92.92, 92.02, and 90.49 mV in "Calcium"; SD=0.44 mV). Other microsensors forming the microelectrode array exhibited similar signal repeatability.

Finally, the constructed electronic tongue was applied in the classification of various diet supplements commercialized in Poland. Seven kinds of pharmaceuticals: "Biovital",

"Calcium", "Plussz", "Ozone", "Supradyn", "Zdrovit Luteoina", and "Zdrovit Zenszen" were in the form of sparkling tablets to be dissolved in 200 ml of water. For each kind of supplement, four sample solutions were prepared and, after intensive mixing (to remove the excess of CO $_2$), they were immediately used in the measurements. The obtained sensor outputs were scaled to <0,1> interval and presented on polar plots in order to visualize the differences in the chemical images obtained for various

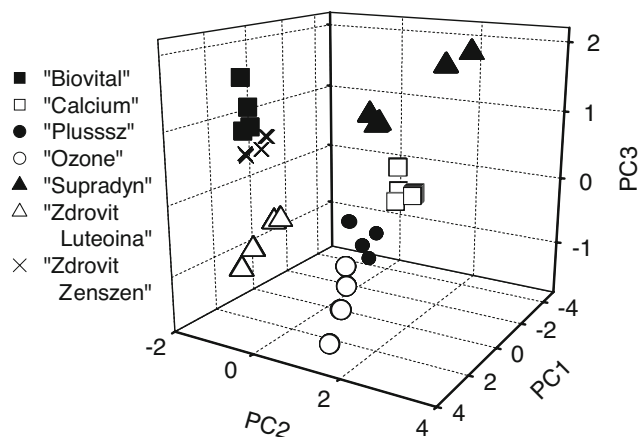


Fig. 10 PCA plot representing the differences between chemical images of various diet supplements obtained with the use of LTCC microelectrode array

samples. The similarity of the same kind of samples and evident differences between various supplements have been noticed. Examples of the chemical image obtained for “Calcium”, “Biovital”, and “Supradyn” samples were depicted in Fig. 9 (the axes are assigned to various kinds of sensors and, for the sake of clarity, the output of only one of each pair of electrodes was presented). The similarity of chemical images of the diet supplements was also examined with the use of principal components analysis (PCA). Distinct clusters of samples of the same brand (see Fig. 10) confirmed the proper performance of the developed device towards the differentiation of examined diet supplements.

Summary

A novel architecture of an integrated microelectrode array was developed using the LTCC technology. PdAg electrodes were screen-printed on ceramic substrate and after the formation of AgCl layer they formed miniaturized transducers for potentiometric microsensors. Preliminary experiments carried out with model potassium-selective membranes showed that the ceramic material is suitable for the fabrication of the ion-sensitive microelectrode array. Further attempts were made to create an electronic tongue based on the array of PdAg/AgCl microelectrodes covered with polymeric membranes of various selectivities. The obtained device exhibited satisfactory differentiation ability in the measurements of diet supplements. The advantageous properties of the designed ceramic microstructures suggest that the LTCC technology can be attractive for the construction of electroanalytical systems based on integrated microelectrode array.

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