Towards miniaturized sensors for determination of exchangeable potassium in soil samples

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Abstract. The sensors for determination of potassium in soil are examined: i) medium-size ion-selective electrodes with plasticized PVC-based ion-selective membranes, hydroxyethylcellulose-based gel as inner electrolyte and silver/silver chloride inner electrode and ii) back-side contact miniaturized sensors with gold inner electrode, polyacrylate-based ionselective membrane and redox-active Self-Assembled Monolayer as an intermediate phase. The selectivity of sensors to potassium ion was achieved by introduction of valinomycin as ionophore into the membrane phase. Preliminary potentiometric characterization of the examined sensors confirmed their good working parameters. The sensors were applied for the analysis of soil extracts. Results revealed good reproducibility and accuracy of proposed sensors, indicating their successful usage for this purpose.

Keywords: potentiometric electrodes, soil analysis, miniaturization, BSC-sensors

INTRODUCTION

Standard methods are applied to measure nutrient levels in soil. Atomic absorption spectroscopy (AAS), flame emission spectroscopy (FES), inductively coupled plasma-mass spectrometry (ICP-MS) and UV-Vis spectrometry (UV-Vis) are the most commonly used methods. Recently, the increasing interest in the application of potentiometric sensors in soil analysis has been observed (Adamchuk et al., 2004). Contrary to classical analytical methods listed above, potentiometric sensors enable fast, relatively inexpensive, direct determination of electrolytes in such a complex matrix as soil.

From the agricultural point of view, potassium is one of the most important soil components because of its connection with water movement, nutrients, and carbohydrates in plant tissue. Recently, the batch treatment of soil with BaCl₂ replacing salt solution and further determination of potassium with valinomycin-based K⁺-selective electrode directly in soil extracts has been reported as a method for determination of exchangeable K⁺ in soils (Wang and Scott, 2001). It has also been shown that ISEs can be applied in suspensions, so that a filtration of sample solutions is not necessary and the total time of the analytical method can be shortened.

Potentiometric sensors, including ion-selective electrodes (ISEs), are capable of fast and very selective recognition of a chosen analyte in a mixture of components without its earlier pre-treatment. These properties, considered in the design of new methods for on-the-go soil mapping (Adamchuk et al., 2004), are very important from the perspective of a real time measurements and continuous monitoring of time-dependent changes in analyte concentration. Both: classical ISEs integrated with automatic extraction systems and small size Ion-Selective Field Effect Transistors (ISFETs) have been thoroughly studied for this purpose. Initially, ISFETs have been applied only for pH measurements, but the modification of the FETs with an appropriate polymeric membrane allows to achieve ISFETs selective for other ions. Most papers focused on ions present in soil in large amounts eg potassium, nitrate and calcium (Artigas et al., 2001).

In this work, two types of sensors: miniaturized back-side contact (BSC) and medium-size have been fabricated and applied for an exchangeable potassium analysis. The goal of the studies was to check whether miniaturized versions of electrodes are able to maintain appropriate response characteristics despite of changes in the size of sensors, the type of polymeric matrix used for membrane preparation (in the case of BSC sensors) as well as the type of an intermediate layers (hydrogel in medium size sensors and solid ion/electron conducting phase in BSC sensors).

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MATERIALS AND METHODS

Reagents

The preparation of the examined ferrocene (Fc) terminated disulfide (S-C$_6$H$_4$-NHCO-Fc)$_2$ is described in Sek et al. (2004). The nonelectroactive thiol, CH$_3$(CH$_2$)$_5$SH, was obtained from Aldrich. 2,2’-Dimethoxy-2-phenylacetophenone (DMAP), potassium tetrakis [3,5-bis(trifluoromethyl)phenyl]borate (KTFPB), potassium tetrakis(4-chlorophenyl)borate (KTPCIPB), bis(2-ethylhexyl)sebacate (DOS), poly(vinyl chloride) (PVC), Valinomycin (potassium ionophore), hexanediol diacrylate (HDDA), tetrahydrofuran (THF) were purchased from Fluka (Ronkonkoma, NY). Acetone, methanol, isodecyl acrylate (IDA), acrylonitrile (ACN) were purchased from Aldrich Chemical Company (Milwaukee, WI) and hydroxyethylcellulose (HEC) from Polyscience, I.N.C. (Warington). IDA was freshly distilled before use. All chemicals were reagent grade. All aqueous solutions were prepared with salts of the highest purity available using water passed through the MilliQ system. All experiments were performed at ambient temperature.

Preparation of ISE electrodes

Potassium-selective membrane, consisting of: 33 wt.% of PVC, 66 wt.% of DOS, 1 wt.% of ionophore (valinomycin) and 30 mol% (relative to the ionophore) of KTPCIPB was glued to the tube separating the inner electrolyte from sample solution. The proposed medium-size electrodes contained gel as an inner electrolyte. It was obtained by dissolving hydroxyethylcellulose (HEC) in 10$^{-2}$ M KCl solution (final concentration of HEC was 25 g l$^{-1}$), followed by the solution heating for 5 min in the temperature of about 75°C. The obtained gel was incorporated to the plasticized PVC tube (5 cm length and 5 mm of diameter). Silver/silver chloride wire serving as an internal electrode was immersed into the gel. The pictures of ready-made electrodes and measuring set-up are presented in Fig. 1 a and b.

Preparation of BSC electrodes

The details of silicon chips fabrication and their chemical modification were described earlier (Sek et al., 2004; Wygl¹dacz et al., 2002; Grygo³owicz-Pawlak et al., 2005). The polyacylate-based potassium-selective membranes were obtained by photopolymerization process directly on silylated surface of the chips. Such membranes contained: 2 wt.% ionophore (valinomycin), 40 mol% (relative to the ionophore) of KTFPB, 0.2 wt.% of the cross-linked agent hexanediol diacrylate (HDDA), monomers isodecyl acrylate (IDA) and acrylonitrile (ACN) (in the molar ratio 2/3). Pictures of BSC silicon transducer (modified with polyacylate membrane and non-modified ones) and applied flow-through system are presented in Fig. 1b.

Potentiometric measurements

The EMF values were measured using the 16-channel electrode monitor (Lawson Labs, Inc), interfaced with personal computer. The potentiometric properties of K$^+$-ISEs were evaluated by immersing the electrodes into calibrating solutions, while in the case of K$^+$-BSC sensors were placed in a flow cell (for details of the cell construction see Chudy et al., 2001). Calibrations were carried out in a flow regime. The potentials of the examined sensors were measured vs. liquid junction Ag/AgCl|3M KCl||1M CH$_3$COOLi reference electrode.

The potentiometric selectivity coefficients, log $K_{pot}$, were determined by fixed interference method (FIM) (Umezawa et al., 1995). The measurements were carried out over 10$^{-6}$-21 0 -1 M potassium concentration range. The background solutions, consisting of 10$^{-1}$ M CaCl$_2$, MgCl$_2$ or NaCl as well as 5 10$^{-1}$ M BaCl$_2$ as interfering species, were used for this purpose.

Fig. 1. Potassium sensors applied in work: a – medium-size ISEs, b – measuring set-up applying medium-size ISE, c – potassium-selective BSC sensor (on the left) and BSC silicon chip without polymeric membrane (on the right) and d – flow-through system applying BSC sensors.
Preparation of soil extracts

The soil of the characteristics shown in Table 1 were applied for the studies (Witkowska-Walczak, 2003). The extraction was carried out according to Polish Standards (PN-ISO 13536, 2002): 3 g of soil sample and 30 ml of extractant solution (0.5 M BaCl$_2$ and 0.04 M N(EtOH)$_3$, pH = 8.1) were shaked for an hour with 560 r.p.m. speed and obtained mixture was centrifuged for 10 min with the speed of 3000 r.p.m. Finally, the extracts were decanted. Whole procedure was repeated twice. The obtained extracts were collected in 100 ml volumetric flask and filtrated before measurements.

Determination of potassium in extracts

The obtained samples of soil extracts were studied using Standard Curve Method. Medium K$^{+}$-ISEs were applied by dipping them in a sample solution, while in the case of K$^{+}$-BSC sensors, samples were passed through the flow system. Each series of samples was preceded and followed by three alternating calibration solutions (marked as 1, 2 and 3) containing $10^{-4}$, $3 \times 10^{-4}$ and $3 \times 10^{-5}$ M KCl in extractant solution, respectively. Potentiometric results were compared with those obtained by atomic absorption spectrometry (AAS) using GBC Avanta spectrometer with flame atomisation. Absorbance measurements were carried out at 766.5 nm wavelength, applying air-acetylene flame.

RESULTS AND DISCUSSION

The goal of this paper was to develop the method of exchangeable potassium determination using potentiometric method for potassium detection instead of spectroscopic method. For this purpose, ion-selective electrodes depicting high selectivity towards potassium over barium ions were applied. Moreover, the presence of other ions eg calcium, magnesium or sodium present in soils in large amounts need to be considered before analysis.

In these studies, two types of potassium-selective electrodes were applied for potassium determination in soil extracts: medium-size ISE with PVC-based membrane, hydroxyethylcellulose (HEC)-based gel as inner electrolyte and silver/silver chloride inner electrode and polyacrylate membrane-based back-side contact (BSC) sensors with gold inner electrode and redox-active Self-Assembled Monolayer (SAM) as solid phase. Valinomycin was used as the ionophore in both cases. The results obtained from the analysis of soil extracts were compared with these obtained using atomic absorption spectroscopy (AAS) as a reference method.

Potentiometric characterization of K$^{+}$-selective sensors

In this part of our studies, both types of sensors modified with potassium-selective membranes were systematically examined in terms of their application for soil extract analysis. For this reason, potentiometric characteristics of five sensors of each type have been examined. Calculated values of the selectivity coefficients, slope and range of the linear response were summarized in Table 2.

Figures 2a and b present typical calibration curves and dynamic responses for the studied sensors. Sensors exhibited near-Nernstian calibration slopes (Table 2) in wide ($10^{-2}$-$10^{-1}$ M) potassium concentration range. Moreover, as illustrated by insets, both types of sensors showed a fast (t$_{95}$<12s) response to changes in potassium concentration. All parameters remained stable for over 2 months in case of BSC sensors and over 6 months for medium-size ISE.

The selectivity coefficients ($\log K_{pot}$) towards potassium over calcium, barium, magnesium and sodium ions were found to be smaller than -4.0. The value $\log K_{pot}$ = -1.8 obtained for ammonium ion seems to be sufficiently low for the potassium determination in soil samples. Considering usual concentration of the examined ions in soils as well as concentration of barium in extracting solution, studied electrodes may be applied for soil analysis.

Potentiometric analysis of soil extracts

During the potentiometric analysis, sample measurements were preceded and followed by calibrations, which allowed to control stability of electrodes parameters. The results of the experiment are presented in Figs 3 and 4. Both types of electrodes appeared to work with very good repeatability. The content of the potassium in soil was evaluated according to the standard curve. As it is seen from Table 3, the obtained results are comparable, indicating similar analytical properties of BSC and medium-size potassium sensors.

### Table 1. Basic properties of the soil (Mollic Gleysol) applied for the studies

<table>
<thead>
<tr>
<th>Grain size distribution (%), dia in mm</th>
<th>CaCO$_3$ (%)</th>
<th>Fe$_2$O$_3$ (%)</th>
<th>C$_{org}$ (%)</th>
<th>Specific surface area (H$_2$O) (m$^2$ g$^{-1}$)</th>
<th>pH$_{KCl}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0+0.1</td>
<td>0.1+0.02</td>
<td>&lt; 0.02</td>
<td>41</td>
<td>36</td>
<td>23</td>
</tr>
</tbody>
</table>
**Comparative AAS analysis**

Besides good precision, analytical method should also depict good accuracy. Potentiometry is known for its unique ability to measure changes of the potential in function of activity instead of concentration. However, when stable ionic strength is ensured, it is possible to use concentration dependence. In this study, high concentration of extractant solution components allow to keep ionic strength of sample and calibration solutions at constant level. To confirm good accuracy of the proposed potentiometric method, it was necessary to compare the obtained results of the analysis of soil extracts with method recommended for this purpose. The results obtained by the use of both analytical methods mentioned are listed in Table 3. As it is shown in the table, the results obtained during potentiometric analysis using both types of the examined electrodes agree with those obtained by AAS. Differences between them were smaller than standard deviation of these analytical methods.

### Table 2. Potentiometric characteristics of K⁺-selective medium-size ISE and BSC sensors (5 sensors of each type were measured)

| Electrode type | Interfering ions | Slope (mV dec⁻¹) | Selectivity coefficients (log K⁻⁺⁻⁺⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻ær³⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻ᵃ⁻⁻⁻⁻⁻⁻⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻ᵃ⁻⁻الةniej

Fig. 2. Potentiometric response to changes in potassium concentration observed in 0.5 M BaCl₂ solutions for: a – medium-size K⁺-ISE and b – miniaturized K⁺-BSC sensors.
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CONCLUSIONS

1. Potassium selective medium-size ISE and BSC sensors were found to work with good selectivity over calcium, magnesium and sodium ions present in soils in large amounts. Also, BaCl₂ applied to extract potassium from soil samples did not affect potassium response in a wide concentration range. This makes developed sensors suitable for practical application.

2. The obtained results of the analysis of soil extracts indicate good reproducibility of the extracting procedure as well as good precision of the applied detection method.

REFERENCES


Table 3. Results of exchangeable K⁺ determination in the chosen soil based on the extraction procedure using 0.5 M BaCl₂ solution and potentiometric or AAS method (the number of samples: n=8)

<table>
<thead>
<tr>
<th>Detection</th>
<th>Potassium content (μg g⁻¹ of soil)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Medium-size ISE</td>
<td>146 ± 2</td>
</tr>
<tr>
<td>BSC sensors</td>
<td>145 ± 2</td>
</tr>
<tr>
<td>AAS</td>
<td>146 ± 3</td>
</tr>
</tbody>
</table>

Fig. 3. Response behaviour of medium-size K⁺-ISE in soil extracts (A-H) and calibrating solutions (1, 2, 3).

Fig. 4. Response behaviour of miniaturized K⁺-BSC sensors in soil extracts (A-H) and calibrating solutions (1, 2, 3).