Use of ion-selective electrodes for determination of content of potassium in Egner-Rhiem soil extracts

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Abstract: Potassium is one of the most important nutrients for plants and its content in the soil should be monitored. In the precision agriculture, which is recommended now, the ion selective electrodes are tested to determine chemical properties of the soil. The objective of this work was an evaluation of use of the valinomycin-based ion selective sensors for determination of assimilated potassium in Egner-Rhiem soil extracts. Flame photometry was used as a reference method. Results obtained from potentiometric and photometric methods in soil extracts correlated linearly (R^2 = 0.84). Analysis of soil extracts by the ion selective electrodes is simple and there is not a need for calcium ions precipitation.

Keywords: potassium; ISE (ion selective electrode); Egner-Rhiem soil extract; precision agriculture

Potassium is one of most essential macroelements for the correct growth and development of plants. This nutrient is taken by the root system of plants in form of ions present in soil solution (active potassium) and/or released from the surface of solid phase of the soil (exchangeable potassium). Potassium present in the crystal lattice of soil minerals constitutes a reserve pool of this element.

If the nutrient content in soil is too low, use of fertilizers is needed to obtain a requested crop yield of a good quality (Cermak & Budnakova 2005). Decision on application of fertilization, liming or irrigation should be taken on the base of the results of chemical and physical soil analysis. Because soil properties (including nutrients availability) may considerably vary from place to place the investigation of their spatial variability is one of the most important issues in precision agriculture. This permits proper planning of agricultural operations and reduction of costs, in a consequence (Stafford 2000; Auernhammer 2001; Adamchuk *et al.* 2004). Taking above into consideration, a monitoring of the nutrients content in the soil is necessary.

A number of methods is known for determination of the potassium content in soil (Hesse 1971; Farrell & Scott 1987; Lemos *et al.* 2004; Malinowska 2005). Recently designed and tested modern measuring systems make possible to conduct chemical soil analysis directly in the field. In these systems, the ion selective electrodes are applied as chemical sensors (Davenport & Jabro 2001; Lemos *et al.* 2004; Adamchuk *et al.* 2005).

The results of many works show that ion selective electrodes can be used in determination of exchangeable potassium in soil extracts (Farrell & Scott 1987; Wang & Scott 2001; Grygołowicz-Pawlak *et al.* 2006). In the Chemical-Agricultural Stations, which are specialized agrochemical laboratories in Poland, potassium is determined by flame photometry (PN-R-04022 1996 and Az1/2002).

The aim of this work was to evaluate the possibility of use of ion selective electrodes for determination of easily available potassium in Egner-Rhiem soil extracts.

MATERIALS AND METHODS

The investigations were conducted on 120 samples of soil extracts, obtained from non-carbonaceous mineral soils of Lublin Region (south-east Poland). Very strongly acidic (11% of samples), acidic (29%), slightly acid (47%) and neutral (13%) soils were studied. The majority of the analysed soil material (96%) contained about 21–35 w/w% of silt and clay particles.

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Preparation of Egner-Rhiem extracts and the photometric analysis of potassium (Zeiss flame photometer) were performed in Chemical-Agricultural Station in Lublin. The extracts were obtained by shaking 5 g of the air-dried soil samples with 250 ml of the extractant composed of 0.02M calcium lactate $(CH_3CHOHCOO)_2Ca \times 5H_2O$ (pH = 3.5 ± 0.5), for 1.5 h with 40 shakes per min and filtering. The filtrates were then transferred to 25 ml test-tubes and mixed with 2 ml 10% oxalic acid ($H_2C_2O_4 \times 2H_2O$) to precipitate calcium ions. After overnight sedimentation, the clear supernatant was taken for further analysis.

Calibration of flame photometer was made using the extractant solutions with additions of KCl to reach potassium concentrations equal to: 0.02mM, 0.04mM, 0.06mM, 0.08mM and 0.13mM (which was equal to: 0, 5, 10, 15, 20 and 30 mg K_2O/100 g of dry soil, respectively), before and after precipitation of calcium ions.

The same set of solutions (also without precipitation of calcium ions) was used in calibration of ion selective electrodes. To observe the eventual interfering effect of calcium ions on the electrode signal, additionally the calibration of electrodes was done in set of solutions with potassium concentrations: 10^{-6}, 10^{-5}, 10^{-4}, 10^{-3} and 10^{-2}M, containing 3×10^{-2}M $CaCl_2$ as a background.

Potentiometric determination of potassium was performed using 5 valinomycin-based electrodes in the extracts before and after precipitation of calcium ions. The electrodes were made in the Warsaw University of Technology in a frame of Project No. 2P04G 032 26. The reference electrode was a commercially available Ag/AgCl double-junction electrode with 1M NH_4NO_3 (recommended by the producer) salt bridge. Electrodes were rinsed with distilled water and dried between each measurement. The measuring system consisted of five IS and one RE electrodes connected to multi-channel potentiometer, which was designed and made in the Institute of Agrophysics PAS in Lublin. In calibration solutions and samples the potential was measured during 5 min and recorded with 10 s interval. The concentrations of potassium ions in the soil Egner-Rhiem extracts were calculated from the potentiometrically measured activities using Debye-Huckel approach (Yu & Ji 1993).

The errors in determination of the potassium content by the electrode method were determined using 150 independent measurements of electrode potentials in that same KCl solution of the concentration equal to the average concentration of the soil extracts. The relative standard deviation RSD (%) for the above data was 5.7% and the maximal error noted was 28% of the average.

RESULTS AND DISCUSSION

Exemplary calibration curves (electrode potential vs. ion activity) for the electrode No. 1 are shown in Figure 1.

The curves for the other electrodes were very similar. The clearly distinguished linear parts of the calibration curves were used for calculation of the electrode characteristics in all calibration media, which are shown in Table 1.

The slopes of the calibration curves are slightly lower than theoretical, that can be connected with the electrodes aging. New electrodes respond to the potassium concentration with the slope equal to 59 mV that is in agreement with the Nernst equation.

Table 1. The slope of the calibration curve and limit of detection of the potassium selective electrodes

Factor			Electrode's number				
			1	2	3	4	5
Before Ca^{2+} precipitation	slope (mV/dec)		42.9	43.99	42.97	43.3	44.2
	limit of detection	$\log(a)_{K+}$	–4.99	–5.0	–5.0	–4.99	–4.97
		mg K_2O/100 g of dry soil	1.8	1.8	1.8	1.8	1.9
After Ca^{2+} precipitation	slope (mV/dec)		41.8	43.0	41.8	39.2	36.9
	limit of detection	$\log(a)_{K+}$	–4.94	–5.0	–4.96	–4.9	–4.9
		mg K_2O/100 g of dry soil	2.0	1.8	2.0	2.2	2.2
Calibration KCl + $CaCl_2$	slope (mV/dec)		53.3	54.9	53.4	54.0	53.3
	limit of detection	$\log(a)_{K+}$	–4.96	–4.99	–4.96	–4.99	–4.99
		mg K_2O/100 g of dry soil	2	1.8	2	1.8	1.8

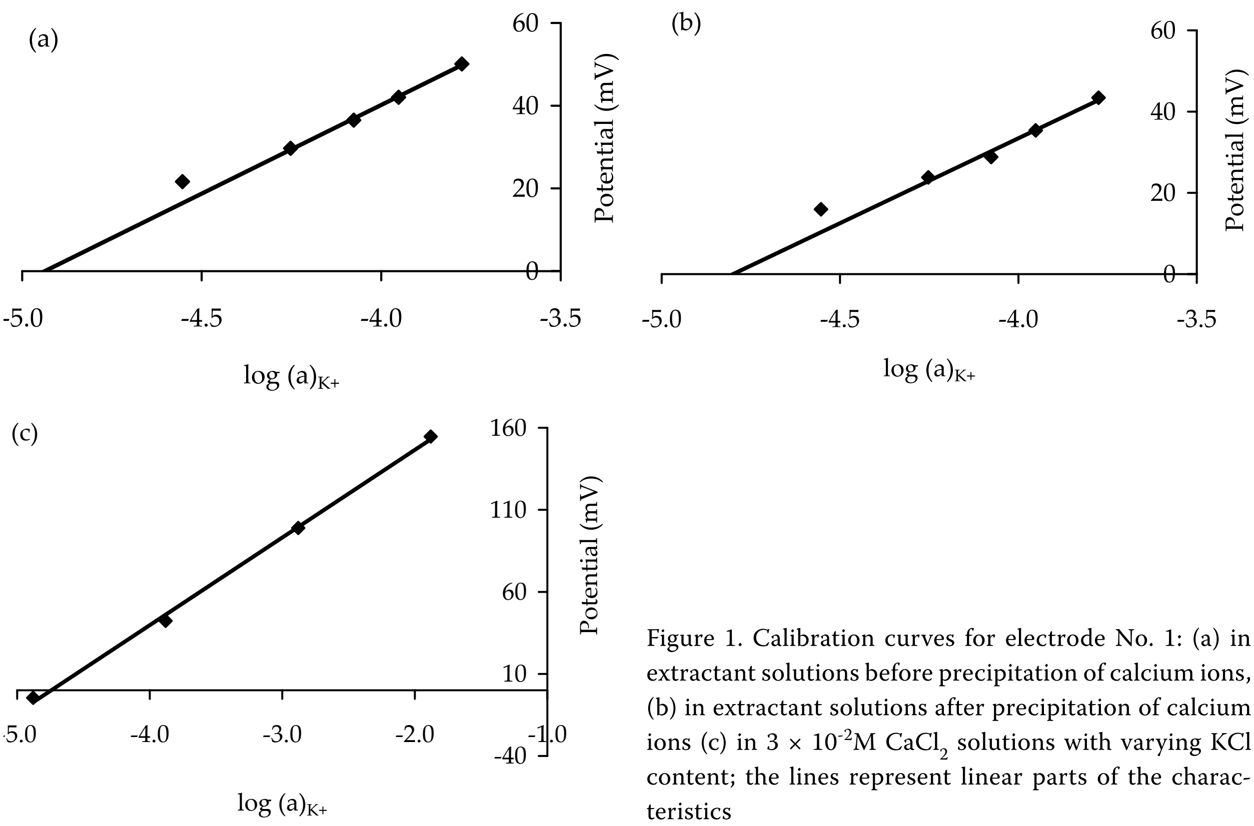

Figure 1. Calibration curves for electrode No. 1: (a) in extractant solutions before precipitation of calcium ions, (b) in extractant solutions after precipitation of calcium ions (c) in 3 × 10^{-2}M $CaCl_2$ solutions with varying KCl content; the lines represent linear parts of the characteristics

In KCl/$CaCl_2$ solution the slope is around 54 mV which is quite satisfactory taking into account that our electrodes were two years old. It suggests rather well persistence of the selectivity of the IS membranes towards the matrix ions. This is necessary to note that using calibration solutions composed from Egner-Rhiem reagents the slope of the calibration curve is markedly lower. This may be due to the effect of lactate anions on the electrode membrane or on potassium activity decrease by e.g. ion pairs formation. The interfering effect of calcium ions on the electrode signal was insignificant. The selectivity coefficient of the valinomycine potassium electrodes towards calcium is equal to $10^{-4,3}$ (Grygołowicz-Pawlak *et al.* 2006).

It should be noticed; that the limit of detection of the electrodes was equal to about 10^{-5}M K^+ (2 mg K_2O per 100 g of dry soil) and the lowest potassium concentration detected by flame photometer in the analysed samples was equal to 6 mg K_2O/100 g of dry soil.

Results obtained from flame photometric and potentiometric methods in soil extracts after precipitation of calcium ions correlated linearly that is illustrated in Figure 2.

The coefficient of determination (R^2) was equal to 0.84. Values of potassium concentration obtained by means of potentiometric method were lower than these measured by the flame photometry that appears like a systematic shift of the results from the 1:1 curve. This is most probably caused by the presence of dissolved organic matter (DOM) in the extracts (humic or fulvic acids), which contain exchangeable potassium in the DDL of the colloidal micelles. This amount of potassium is detected only by flame photometry. Various amounts of DOM extracted from different soils may be one of most important reasons that large variations between the results of both methods is observed (and so the correlation coefficients are smaller than these measured for pure salt solutions).

Results of potentiometric measurements in Egner-Rhiem soil extracts before and after precipitation of calcium ions are presented in Figure 3.

Significant correlation (R^2 = 0.89) is noted between the respective data. This is seen that the potassium concentration measured after calcium precipitation is lower. This may be due to electrostatic adsorption of potassium ions on the calcium oxalate precipitate. To precipitate calcium, the oxalic acid is added to the extract in excess and oxalate anions may be incorporated on the surface of the precipitate forming negative surface charge on which electrostatic adsorption of counterions occurs. This suggests that calcium precipitation is not needed prior to the potentiometric measurements of potassium content in Egner-Rhiem soil extracts and that the IS electrode measurements may give more reliable results than flame photometry.

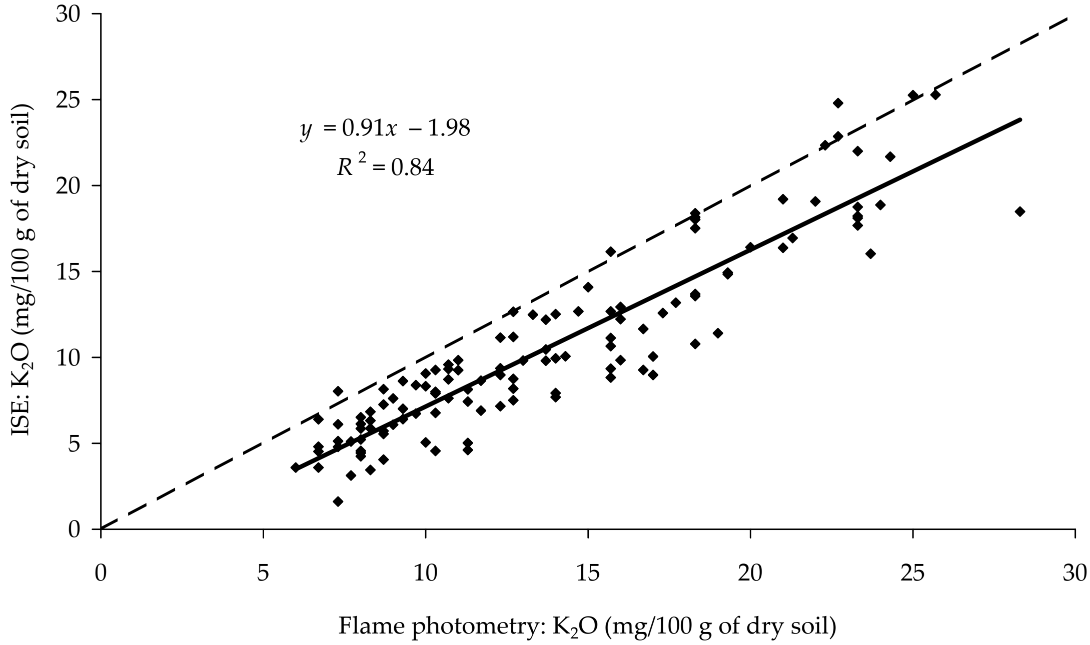

Figure 2. Dependence between results obtained from photometric and potentiometric (the mean value of measurements done by 5 electrodes) analysis of Egner-Rhiem soil extracts; dashed line represents 1:1 relationship

CONCLUSIONS

The obtained results suggest that potentiometric analysis of Egner-Rhiem soil extracts is feasible. It is much cheaper and simpler than photometric method and the calcium ions precipitation is not necessary. The potassium concentration measured by flame photometry in analysed samples was higher than this measured by ISE most probably due to the presence of some amount of exchangeable potassium on soil dissolved organic matter.

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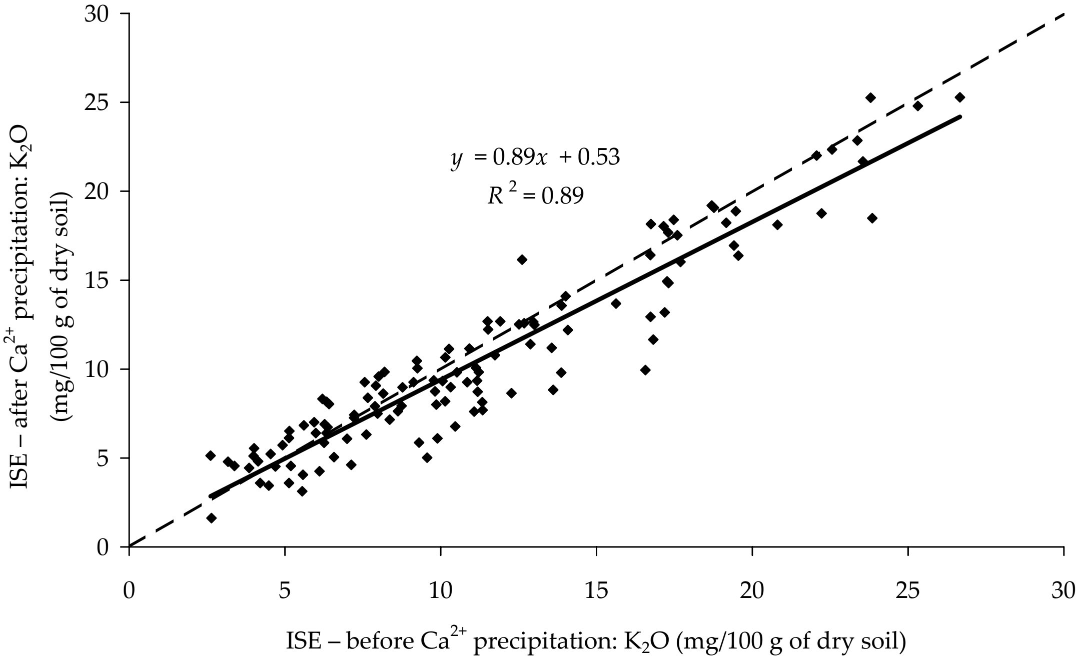

Figure 3. Relationship between results of potentiometric measurements (the mean value of measurements with 5 electrodes) for Egner-Rhiem soil extracts before and after precipitation of calcium ions; dashed line represents 1:1 relationship

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Abstrakt

Cieśla J., Ryżak M., Bieganowski A., Tkaczyk P., Walczak R.T. (2007): **Použití iontově selektivních elektrod ke stanovení draslíku v Egner-Rhiemových extraktech.** Res. Agr. Eng., **53**: 29–33.

Draslík je pro rostliny jednou z nejdůležitějších živin a proto je nutno monitorovat jeho obsah v půdě. V precizním zemědělství, které se nyní doporučuje, se testuje použití iontově selektivních elektrod při stanovení chemických vlastností půdy. Cílem této práce bylo hodnotit použití iontově selektivních senzorů na základě valinomycinu ke stanovení asimilovaného draslíku v Egner-Rhiemových půdních extraktech. Jako kontrolní metoda byla použita plamenová fotometrie. Mezi výsledky získanými v půdních vzorcích potenciometrickou a fotometrickou metodou byla zjištěna lineární korelace ($R^2 = 0,84$). Analýza půdních extraktů pomocí iontově selektivních elektrod je jednoduchá a odpadá při ní potřeba srážení vápníkových iontů.

Klíčová slova: draslík; ISE (iontově selektivní elektroda); Egner-Rhiemův půdní extrakt; precizní zemědělství

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