Optimization of sodium extraction from soil by using a central composite design (CCD) and determination of soil sodium content by ion selective electrodes

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Abstract

Article Info

Rapid determination of sodium (Na) ions in soil samples using ion selective electrodes (ISE) was investigated in this study. The compatibility of ISEs with soil extraction solution is a challenging subject as various effects such as pH, ionic strength and other interferences have to be considered as well as efficiency of the extraction solution. Because almost every type of sodium salt is soluble in water, and the pH of water is suitable for ISE studies, it was chosen as the soil extractant. Firstly, the extraction parameters were optimized by using a central composite design (CCD), secondly thirty agricultural soil samples were extracted with water and the extracts were measured by Na-ISE in a previously developed flow system. The results were compared with ion chromatography (IC) as the reference method, and the regression analysis between IC and ISE results yielded a high correlation (R^2 = 0.9408). It was concluded that, ion selective electrodes can be used with water as an extraction solution for rapid determination of sodium in soil samples.

Introduction

In history, countless civilizations that began in the irrigated agriculture areas became extinct due to soil salinity. Even today, despite the state-of-the-art techniques in soil and farm management, non-agricultural lands have become quite common due to salinity. Today more than ever salinity is one of the most important factors threatening the sustainability of irrigated agriculture. If not brought under control salinity reduces the productivity, and in many cases lands may become entirely non-productive (Kanber and Unlu 2010).

Soil salinity accrues from accumulation of water soluble salts or retention of exchangeable sodium in high levels by adsorption complex in soil. Soils that are exposed to various types and levels of salinity contain salts formed by Na^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, K^+, HCO_3^-, CO_3^{2-}, NO_3^- ions (Eruz, 1979). Sodium is one of the most commonly found elements in nature. It abounds in soil, water and air (Kacar, 2012). Sodium exists as an exchangeable cation (Na^+) held on soil colloids and as a Na^+ ion in the soil solution (Benton and Jones 2001). Even though sodium is not a major plant food nutrient, it has a critical role in soil health. Excessive amounts of sodium ruins the physical structure of soil. The aggregates fragmentize by causing decline in water and air permeability of soil, adversely affecting root development. As structure deteriorates, stickiness of soil increases making cultivation impossible. Sodium content of agricultural soils varies between 0.1 - 1 %, 0.63 % is average. In general, the salinity of the soil in arid and semi-arid regions is higher than the soil in rainy regions (Kacar, 2012). When NaCI content of soil exceeds 0.5 %, salinity, problem shows up (Kanber and

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Unlu, 2010). Sodium content of soil is conventionally determined by flame photometer. However, conventional soil testing methods are costly and time consuming processes, also the number of samples that can be analyzed are limited. Drawbacks in conventional soil analysis methods have led to the investigation of fast in-field monitoring systems. Ion-selective electrode (ISE) technology is a good alternative in this sense as it is an accurate, fast, economic and sensitive method. Above all, ISEs are portable enabling fast and in-situ soil analysis. Many of ISEs are commercially available for use in various matrixes, and significant developments have been made in ISE technology in recent years by development of various ion-selective membranes including NO_3, K, Ca, and Na which are the most important soil nutrients, and also many researches have been working on developing phosphate ion-selective electrodes (Tsukada et al. 1989; Carey and Riggan 1994; Knoll et al. 1994; Xiao et al. 1995; Chen et al. 1997; Wroblewski et al. 2000; Bratovcic et al. 2009; Eren ve ark., 2014).

The selection of a convenient extraction solution is the key point of ISE studies, especially in difficult matrixes like soil. The extraction solution should be compatible with ISEs while extracting the target ions from soil efficiently. Many solutions are available for conventional soil analysis as extractant, but only few of them can be used with ISEs successfully because of their high ionic strength, high acidity or alkali (Wang and Scott, 2001; Wang et al. 2004; Zbiral and Nemec, 2005; Ciesla et al. 2007; Madurapperuma et al. 2008; Matula, 2009; Bortolon and Gianello, 2010; Kahveci and Atalay, 2010; Bortolon et al. 2011). In this study, water was chosen as soil extractant, because almost every sodium salt is soluble in water, and also pH of water is suitable for ISE studies.

The focus of this research was to investigate the applicability of soil sodium content measurement by using ion selective electrode technology. Response surface methodology (RSM) is a group of mathematical and statistical techniques that enables modeling and analysis of problems by assessing influences of each input variable on a particular response and determining optimum values for this response (Montgomery, 1997; Khuri and Mukhopadhyay, 2010). Extraction conditions of soil sodium was optimized by using RSM and Central Composite Design (CCD). The extraction parameters were determined as soil:extractant ratio (w:v), shaking time (min) and shaking speed (rpm). CCD is appropriate for fitting a quadratic mathematical model and it is used to optimize the effective input variables with a minimum number of experiments, also enabling analysis of the interaction between the parameters. In the sequel, Na-ISE measurement results were compared with ion chromatography (IC) results as the reference method.

Material and Methods

Measurement system

Tests of the Na-ISE were conducted with a previously developed flow system (Figure 1) that contains a commercially available all solid state sodium ion selective electrode, a measuring cell into which the electrodes (Na-ISE and reference electrode) were inserted, containers to hold solutions (1 and 2), and a control unit that allows collection of voltage data from Na-ISE measured relative to the reference electrode (R). Each test began with the flow of 0.01 mol/L $CuSO_4$ baseline solution. The desired volume of test solution was fed to the flow line by using 3-way mini valve as shown on the scheme (Figure 1) and measurements consistently continued under computer software control. When the test solution sensed by the detector (Na-ISE), voltage differences occurred by forming peaks with different heights according to the ion concentration. After the system reached equilibrium by baseline solution, each individual test solution was introduced to the flow line. The electrode was first calibrated with 1×10^{-5}, 5×10^{-5}, 2.5×10^{-4}, 1.25×10^{-3}, 6.25×10^{-3} mg/L NaCl solutions prepared in water.

Optimization of extraction parameters

Water, which is compatible with ion selective electrodes, was used to extract Na ions from soil. Extraction was done by adding the extractant into the soil sample and shaking the mixture in an orbital shaker. The parameters that effect the extraction efficiency were determined as soil:extractant ratio, shaking time and shaking speed. CCD was used to optimize the extraction parameters. In order to determine the relationship between the extraction parameters and obtained sodium concentration, the data must be statistically analyzed by using regression equations (Montgomery, 1997). For regression equation, the extraction parameters were coded as shown in Table 1.
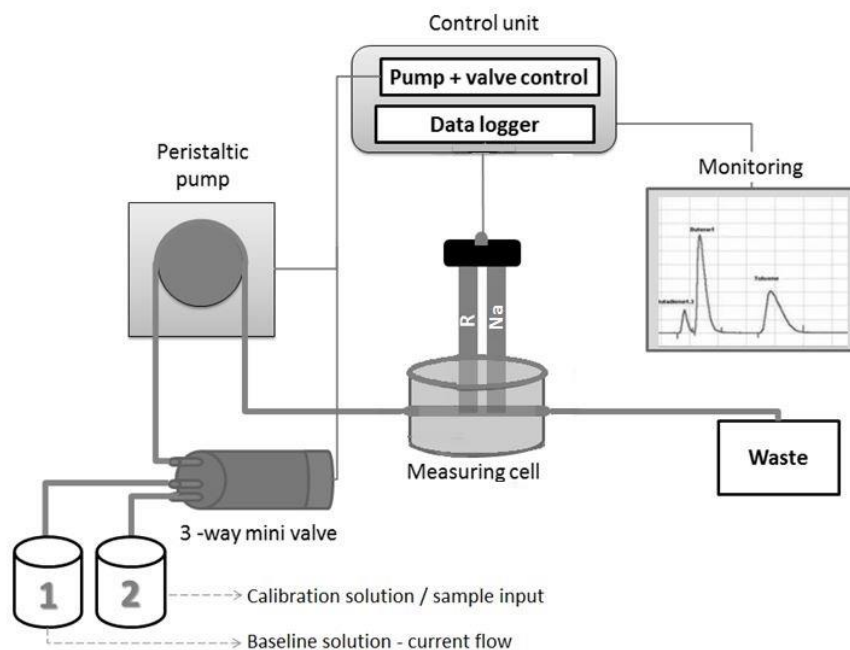
Figure 1. The scheme of the flow system that uses Na ion selective electrode as detector.

Table 1. Coded values of central composite design (CCD) (Liu et al. 2006)

Parameters	Coded Parameters	Coded Levels				
		-2	-1	0	1	2
Soil: Extractant ratio (w/v)	X_1	1:1	1:2	1:3	1:4	1:5
Shaking time (min)	X_2	10	20	30	40	50
Shaking speed (rpm)	X_3	150	180	210	240	270

A central composite design (CCD) with three factors, i.e., soil: extractant ratio (w/v), shaking time (min), and shaking speed (rpm), was adopted in the present study. The experimental design consisted of three variables with five levels i.e., low (-2) and high (+2) with 20 experimental runs. The experimental runs and variables are shown in Table 2. The experiments were randomly conducted in order to reduce the effects of uncontrolled factors. The soil sample which was chosen for optimization experiments had a sandy loam texture (% 63.03 sand, % 21.14 silt, % 15.83 clay) and its pH and EC were 5.80 and 0.13 dS/m (1:1 w/v), respectively.

Sodium extraction parameters (X_1, X_2, X_3) were correlated with the Na-ISE responses according to a quadratic model. Experimental data was analyzed by using analysis of variance (ANOVA) to determine the effects of each variable in quadratic equation. Thus, variables with small effect ($p < 0.05$) were eliminated from the quadratic equation and the final mathematical model was obtained. The process of optimization was performed by validating the mathematical model to obtain maximum Na-ISE response using Mathcad software (Mathcad Prime 3.0). All three dimensional response surface graphs were generated using Statistica software, (Statsoft). All reagents were prepared by using ultrapure water obtained with a Milli Q system (Millipore Direct Q-UV3). All chemicals with analytical grade were purchased from Merck (Merck KGaG, Darmstadt, Germany). Stuart SS11 orbital shaker was used in extraction process.

Comparison of ISE with IC

The new extraction method needed to be tested with a variety of soils to represent the extreme features of agricultural soils in Turkey. For this purpose, thirty soil samples were provided from Soil, Fertilizer and Water Resources Central Research Institute in Ankara. The properties of thirty soil samples are given in Table 3.

Table 2. Central composite design (CCD) (Liu et al. 2006)

Experiment No	Coded Parameters			Actual Parameters		
	X_1	X_2	X_3	Soil: Extractant ratio (w/v), X_1	Shaking time (min), X_2	Shaking speed (rpm), X_3
1	-1	-1	-1	1:2	20	180
2	-1	1	1	1:2	40	240
3	1	-1	1	1:4	20	240
4	1	1	-1	1:4	40	180
5	-1	-1	1	1:2	20	240
6	-1	1	-1	1:2	40	180
7	1	-1	-1	1:4	20	180
8	1	1	1	1:4	40	240
9	-2	0	0	1:1	30	210
10	2	0	0	1:5	30	210
11	0	-2	0	1:3	10	210
12	0	2	0	1:3	50	210
13	0	0	-2	1:3	30	150
14	0	0	2	1:3	30	270
15	0	0	0	1:3	30	210
16	0	0	0	1:3	30	210
17	0	0	0	1:3	30	210
18	0	0	0	1:3	30	210
19	0	0	0	1:3	30	210
20	0	0	0	1:3	30	210

Table 3. Chemical and physical characteristics of 30 soil samples used in this study.

ID	pH	EC, dS/m	Textural class	ID	pH	EC , dS/m	Textural class	ID	pH	EC , dS/m	Textural class
1	8.25	0.43	Heavy Clay	11	8.55	0.29	Sandy	21	7.71	0.49	Loam
2	8.02	0.45	Clay	12	7.85	0.58	Loam	22	7.88	0.41	Loam
3	7.98	0.47	Silty Clay	13	8.22	0.94	Loam	23	6.78	0.36	Loam
4	7.87	0.39	Silty Clay Loam	14	8.17	0.38	Clay Loam	24	7.70	0.33	Clay
5	7.82	0.64	Clay Loam	15	8.05	0.44	-	25	4.82	0.08	Sandy
6	7.85	0.86	Loam	16	8.10	0.51	-	26	6.41	0.40	Clay Loam
7	8.01	0.55	Sandy Clay	17	7.83	0.62	Loam	27	7.32	2.61	Heavy Clay
8	7.96	0.42	Sandy Clay Loam	18	8.00	0.51	Loam	28	7.72	0.41	Loam
9	7.9	0.62	Sandy Loam	19	7.75	0.67	-	29	8.03	0.28	Loam
10	7.33	0.34	Loamy Sand	20	7.6	0.62	Sandy	30	8.14	0.42	Loam

NOTE: pH and EC measurements; 1:1 w/v, 25 ^{0}C.

The soil samples were extracted with water at optimum conditions, which were previously determined by CCD and RSM approach as 1:4.7 soil:extractant ratio (w:v), mixing at 216 rpm for 23 minutes in an orbital shaker. The extracted samples were filtered with Whatman No. 42 filter paper. Every extract was analyzed with Na-ISE in the flow system, and with ion chromatography (IC) as a reference method. The IC analyses were held in Soil Water Laboratory in Atatürk Soil, Water and Agricultural Meteorology Research Station Management.

Results and Discussion

Optimization of extraction parameters

The experimental data of CCD model was analyzed by the response surface regression procedure to fit the quadratic model, providing regression coefficients. The ANOVA for the quadratic model for Na concentration is listed in Table 4.

Table 4. Statistical parameters obtained from the analysis of variances (ANOVA) for Na ions concentration

Regression Statistics	
Multiple R	0.94
R^2	0.89
R^2 adjusted	0.78
Standard Deviation	1.09

The model multiple R observed was 0.94 stating that the model was significant. The quadratic regression model for sodium concentration (Y) can be represented by the following Equation (1):

$$Y = 9.66 + (2.20) \cdot X_1 + (0.4) \cdot X_2 + (0.03) \cdot X_3 + (0.50) \cdot X_1 \cdot X_1 (0.06) \cdot X_2 \cdot X_2 - (0.31) \cdot X_3 \cdot X_3 - (0.26) \cdot X_1 \cdot X_2 - (0.26) \cdot X_1 \cdot X_3 + (0.12) \cdot X_2 \cdot X_3 \quad \text{Equation (1)}$$

Here in this equation the coefficient with second order term shows the quadratic effect. Positive sign in front of the terms indicates that this variable is proportional to Na-ISE response while negative sign means the variable is inversely proportional to Na-ISE response. The model also yielded high correlation with the actual results, $R^2 = 0.94$, shown in Figure 2.
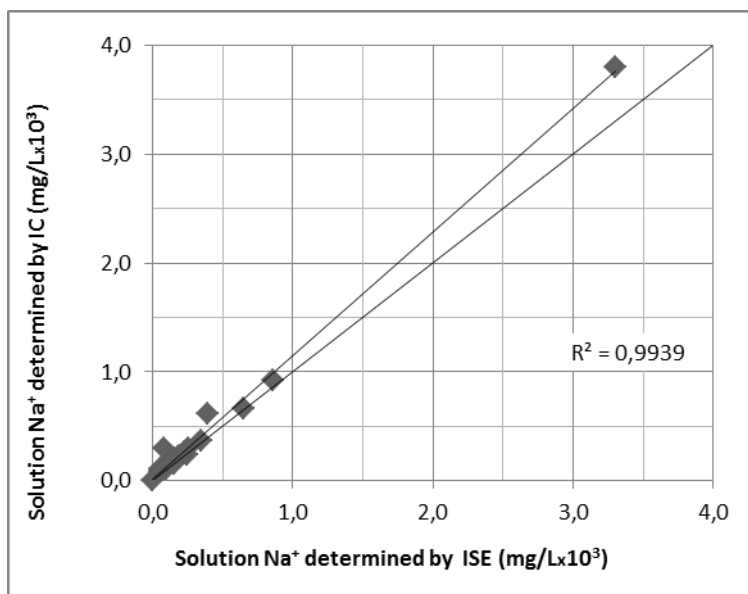

Figure 2. Comparison of the mathematical model with the actual results

The three dimensional response surface graphs that reveal the relation between the extraction parameters and Na^+ concentration were generated by Matlab software, and are shown in Figure 3. Both the graphs and mathematical model indicate that soil:extractant ratio effects Na^+ ion results the most.
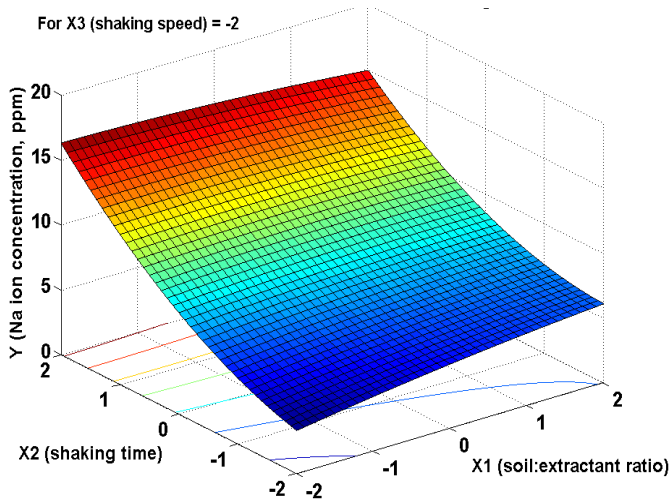
Figure 3. Effects of shaking time and soil:extractant ratio on Na-ISE response while shaking speed is minimum (X3 = -2).
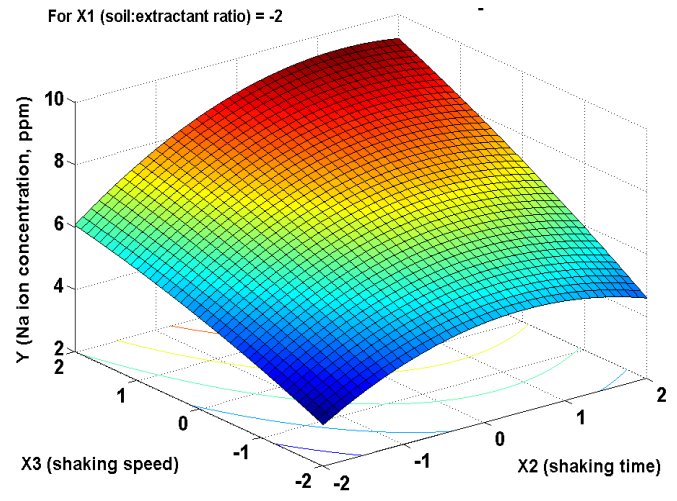
Figure 4. Effects of shaking speed and shaking time on Na-ISE response while soil:extractant ratio is minimum (X1 = -2).
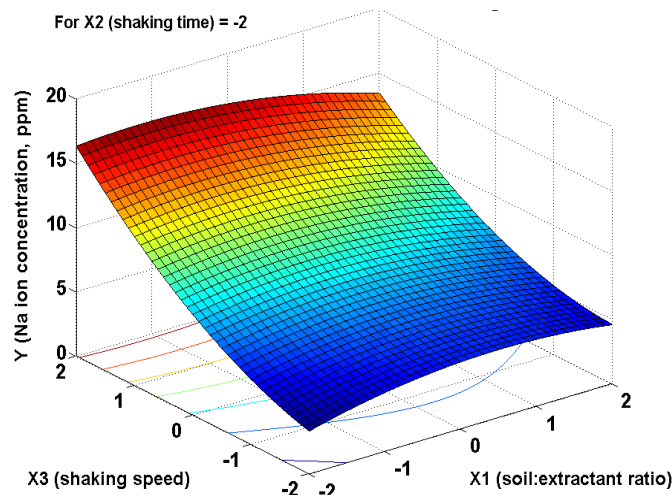

Figure 5. Effects of soil:extractant ratio and shaking speed on Na-ISE response while shaking time is minimum (X2 = -2).

The process parameters were optimized in Mathcad by using the mathematical model and targeting the maximum Na-ISE response. The optimum extraction conditions are listed in Table 6.

Table 5. Optimum extraction conditions determined by Mathcad

Extraction Parameter	Optimum Value
Soil: Extractant ratio (w/v)	1:3
Shaking time (min)	15
Shaking speed (rpm)	260

Comparison of ISE with IC

The primary aim of the research is to develop a sodium ions measuring method based on ion selective electrodes (ISE), so the newly developed soil extraction procedure was applied to the sensor system and the results were compared with those obtained from IC as the reference method. Regression analysis that were applied to ISE and IC results yielded high correlation of $R^2 = 0.9408$ (Figure 3). Na-ISE used with water provided close agreement with IC analysis.
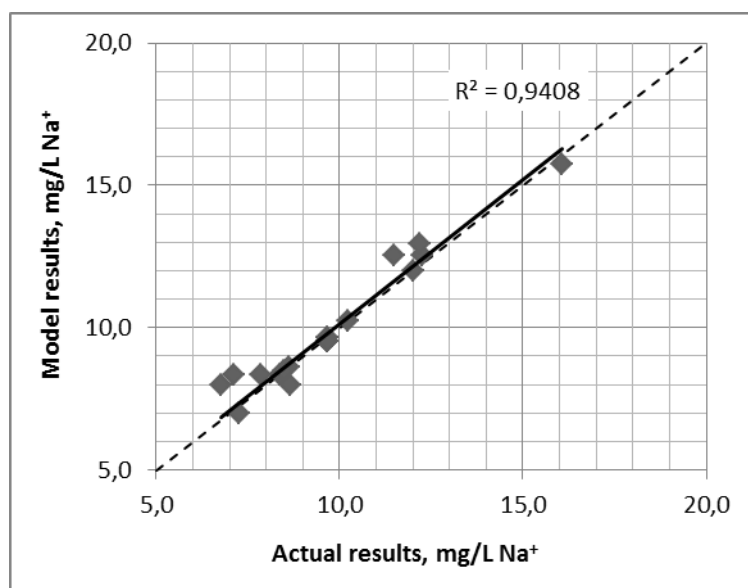
Figure 6. Relationship between soil extract Na+ determined by ISE and IC.

Conclusion

A new analysis method was developed in order to determine Na+ ion concentration in soil extracts. The extraction procedure was determined by optimizing the extraction conditions using central composite design (CCD) and RSM, this new method was tested with 30 different agricultural soil samples from Turkey. The comparison of Na-ISE and IC results yielded high correlation (R^2 = 0.9408) with almost 1:1 relationship, which indicates that Na measurement can be performed by Na-ISE in this flow system together with water extraction, at least for 30 soil samples examined in this study. Additional research and tests with greater number of soil samples are needed to further validate the applicability of these results.

Acknowledgements

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