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# Ion Selective Electrodes As Analytical Tools For Rapid Analysis of Soil Nutrients

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## ABSTRACT

*Sustainable agriculture depends on the support of land resources, one of which is the soil as the primary medium growth of various agricultural commodities. Identification and evaluation of agricultural soil is absolutely necessary in order to be optimally utilized and maintained at the right time and right location, for sustaining the agricultural productivity. Development of analytical methods for soil parameters is also an effort to initiate the concept of precision agriculture. This paper is describing an on going work as an effort for implementing a rapid analytical method for some major soil nutrients (nitrate, ammonium, potassium and sodium) that responsible for plant growing, by using potentiometric analysis based on utilization of ion selective electrodes (ISE). At the beginning it is targeted to obtain the most effective extractant solution for extracting nutrient from the soil prior measurement. It was found that ammonium acetate, potassium chloride and nitric acid were not suitable for extractant solutions when the corresponding nutrient ions measured by ISE method. Promising candidate of the extractant solutions for this purpose were distilled water and calcium chloride. Validation of the proposed ISE method against standard spectrophotometric method is still necessary will be carried in near future.*

**Keywords :** *Ion selective electrode, agriculture, soil nutrient, soil analysis*

## 1. INTRODUCTION

Implementation of variable rate technology (VRT), a part of precision agriculture concept, is important for optimizing crop production and reducing the environmental impact of agricultural activities. In VRT adaptation, the application for soil treatment or remediation depend on previous information of physical and chemical soil condition. More precise and accurate the application to the soil both spatially and temporally may reduce that so called over or under application, hence ensuring optimum productivity for any given land area. The VRT concept requires the collection of high resolution soil chemical and physical information, which is impossible to be fulfilled by conventional sampling and laboratory-based measurement methods. Ion selective electrode (ISE) technology has proven its capability for measuring some soil anion or cation as reported by some researcher[1-3]. Unlike optical based measurement that need a clear solution for its measuring object, ISE can be used in unfiltered soil extract or slurries, making them attractive options for proximal soil sensing, in addition they are small, economical and require little supporting hardware[4]. Initially the ISE techniques has been employed for measurement some cation and anion on three naturally moist soil samples[5], although it have experienced limited success. Extraction is still considered as a vital pre-measurement step in ISE application. This reported work is a part of a research work dealing with development of a measurement system for nutrient in agriculture soil based on the ISE technology. The system is aimed for having several capabilities over the standard measurement methods, namely rapid, inexpensive, robust and capable of repeatable measurements in field. A preliminary result dealing with some extracting solution will be presented in this paper.

## 2. MATERIALS AND METHOD

Main goal of the overall work is producing a direct in field measurement system for  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  in agricultural soil based on the ISE technology. The initial experiment has been carried out obtaining extracting solution (extractant) for the selected nutrient soil ions above. Some commonly used extracting solutions, namely KCl,  $\text{CaSO}_4$ , (for  $\text{NO}_3^-$  and  $\text{NH}_4^+$ ) and  $\text{HNO}_3$ , HCl,  $\text{CH}_3\text{COONH}_4$  (for  $\text{K}^+$  and  $\text{Na}^+$ ) have been evaluated based on their ability to stimulate the ISE in producing corresponding potential response. In addition the distilled water and  $\text{CaCl}_2$  were also applied to both groups of nutrient ions. All the chemicals are purris grade and obtained from respected producer (Sigma-Aldrich, Merck and JT Baker). investigations were conducted on 3 soil samples

collected from different location at Tegalboto regency, Jember East Java. Preparation of the extracts and the potentiometric analysis of the ions using corresponding ISE were performed in Analytical Chemistry Laboratory, Department of Chemistry, University of Jember. The extracts were obtained by stirring 40 g of the air-dried soil samples with 100 ml of the extractant for 45 minutes. A 50 filtrates were then transferred to 100ml beaker-glass and mixed with 2 ml 10% appropriate ionic strength adjuster (ISA) solutions as recommended by the ISE producer. Three sample of each location was then extracted and measured potentiometrically.

Calibration of ISE potentiometric was made by measuring the appropriate standard solution for each ion in concentration range of 0 – 120 ppm for  $\text{Na}^+$  and  $\text{K}^+$ , 0-60 ppm for  $\text{NO}_3^-$ , and 0-5 ppm for  $\text{NH}_4^+$ . To observe the eventual interfering effect of the extractant on the electrode signal, additionally the calibration of electrodes was done in set of the standard solutions containing the corresponding extractant solution as a background.

Potentiometric determination of the soil nutrient ions was performed using the commercially available ISE ELIT brand (Nico 2000 Middlesex, UK). The reference electrodes (RE) were also a commercially available ELIT Ag/AgCl (Nico 2000 Middlesex, UK) double-junction electrode with 0.1M  $\text{CH}_3\text{COOLi}$  as outer solution for  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{K}^+$ , and single junction electrode with AgCl solution as outer solution for  $\text{Na}^+$ . Electrodes were rinsed with distilled water and dried between each measurement. The ISE and RE were then connected to pH/mV meter (Jenway), the potentials generated were then recorded when the reading relatively stable.

### 3. RESULTS AND DISCUSSION

Investigation of several prospective extractant solutions used for extracting nutrient ions from soil, as shown in Table 1, has indicated that ammonium acetate was not suitable as extractant for potassium and sodium ions when used in conjunction with ISE as measuring device. Similar property was also found for potassium chloride as extractant for ammonium and nitrate ions. Both extractant has resulted overestimated ISE potential response hence the concentration of the corresponding ions were higher than predicted actual values. Although both extractants have been widely used as soil extractant, however the extractants were commonly used for optical detection method, i.e. molecular or atomic visible spectrophotometric methods. Overresponse of the ISE was also found when nitric acid used for extracting sodium ion, meanwhile hydrochloride acid has indicated lowering the ISE response for potassium ion. Overall picture of all investigated extractants can be seen on Figure 1.

Table 1: The calculated nutrient concentration extracted by several extractants

Nutrient	Calculated [Nutrient] extracted by the corresponding extractant/ppm						
	D.Water	HCl	$\text{HNO}_3$	$\text{NH}_4\text{-Ace}$	$\text{CaCl}_2$	KCl	$\text{CaSO}_4$
Sodium	8.10	6.08	160.31	768.61	8.10	-	-
Potassium	3.05	0.00	1.51	219.19	3.57	-	-
Nitrate	12.32	-	-	-	21.45	482.38	17.50
Ammonium	0.08	-	-	-	0.19	524.44	0.14

According to the Table 1 and Figure 2, it is clearly indicated that only two remaining extractants solution, distilled water and calcium chloride, that having prospective capabilities for both extracting ions from soil and suitable for used in ISE detection method. Meanwhile calcium sulphate, although it worked quite well for extracting nitrate and ammonium ions, it has not been tested for sodium and potassium ions.

Because of all the extractant tested in this work are commonly used for extracting corresponding ions, hence their ability for extracting ions is not questionable. The drawback of ammonium acetate, potassium chloride, and nitric acid in this work was found due to selectivity or interference effect of the extractant to the working mechanism of the corresponding ISE in sensing the target ions. Potential responses of the ISE for ammonium, potassium and sodium have not responding proportionally to the standard solutions when the corresponding extractant were added the standard solution replacing the distilled water as solvent.

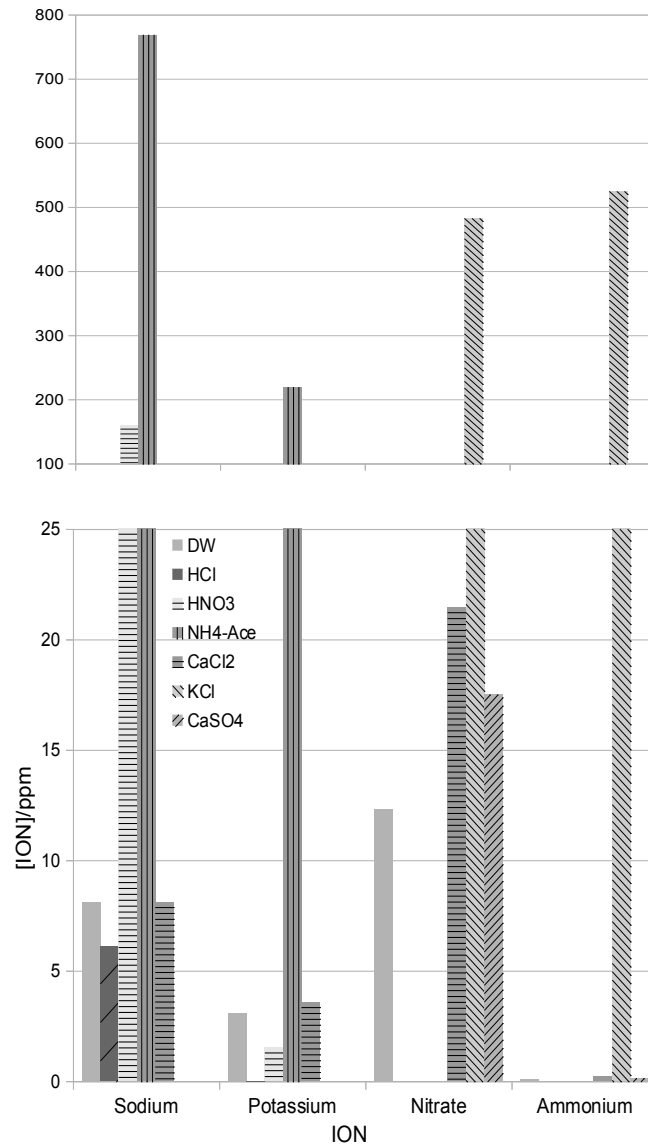


Figure 1: Histogram of sodium, potassium, nitrate and ammonium ions concentration calculated based on corresponding potential response of the ISE after extracted by using several extractant solution.

#### 4. CONCLUSION

The extractants, solutions that responsible for extracting ions from soil sample, are important factor for successful assessment of nutrient ion content in agricultural soil. In addition, selectivity factor and interference effect of the extractant have to be investigated when using ISE as measuring device. This work has shown that ammonium acetate and nitric acid were not suitable as extractant for potassium and sodium ions when ISE was going to be used as measuring device, in addition potassium chloride was also have similar drawback when used as extractant for nitrate and ammonium ions. Distilled water and calcium chloride have shown their role as promising extractant in ISE method for ammonium, nitrate, potassium and sodium ions. Comparative investigation between ISE method and standard spectrophotometric method has to be carried out to clarify the performance of the ISE method as alternative measurement technique for rapid assessment of soil nutrients.

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