International Journal of Emerging Engineering Research and Technology
Volume 2, Issue 2, May 2014, PP 198-204

Primary Nutrients Determination in the Soil Using UV Spectroscopy

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Abstract: *Objective of our research is to analyze soil properties for accurately mapping various primary nutrients in the soil. Various soil samples were taken from cultivated farms at the agriculture college , Pune A multi-parametric analytical system for measuring primary nutrients contents in cultivated soil is developed for on field analysis using the techniques as UV Spectroscopy. This paper gives review of sensor technology used for sensing of primary nutrients in the and demonstrate fundamental results of UV Spectroscopy method for on the go soil sensor***.**

Keywords: *Primary nutrients, NPK, sensor technology, Spectroscopy*

1. INTRODUCTION

Precision Agriculture (PA) can be define as a process of managing crop production input such as fertilizer, herbicide, insecticide, seed, etc. to reduce waste, increase profits, and maintain the quality of the environment using information technology and electronics. It is an integrated crop management system that attempts to match the kind and amount of inputs with the actual crop needs for small areas within a farm. [1].

Farmers usually are aware that their fields have variable yields across the landscape. These variations can be traced to management practices, soil properties and environmental characteristics. Soil properties that affect yields include texture, structure, moisture, organic matter, nutrient status and environmental characteristics include weather, weeds, insects and diseases technologies for precision farming [2].

The vast array of tools for PA includes hardware, software and the best management practices. The most used techniques in precision agriculture are Global Positioning System (GPS) receivers, yield monitoring, grid soil sampling & mapping, Variable rate fertilizer (VRT) application, Remote Sensing(RS) and Crop scouting

Research in precision agriculture has shown the high degree of spatial and temporal variability in primary nutrients content in the soil. Variability in the soil properties can be sense by two methods as on field sensing and remote sensing[3]. In the remote sensing sensed data is monitored as well as control action is taken via satellite .It was found that a large array of agriculturally important soil properties were quantified with RS successfully to the various extents.

On field sensors are of two types, on- the- go soil sample and intensive grid sampling. On-the-go sensors have the advantage of providing non-destructive and rapid quantification of soil variability to enable precision soil nutrient management and monitoring. Intensive grid sampling is generally regarded as one of mapping the variability of crop and soil attributes in PA. However, intensive grid sampling is laborious, time consuming expensive and thus impractical for implementation in large scale [4]. On-the-go soil sensor technologies that can serve as a rapid method for measuring soil mechanical, physical and chemical properties are steadily developing.

Table 1 shows different types of sensor that can be used to sense various properties of soil

Table 1. *On-the-go soil sensor types and their applications [4-6].*

Sensor type	Example applications
Electrochemical	Soil pH, nitrate, potassium
Electrical and electromagnetic	Soil texture (sand, silt, clay), soil moisture content soil depth variability cation exchange capacity

Optical and radiometric	Soil organic matter, soil moisture
Acoustic	Soil texture (sand, silt, clay), soil bulk density (compaction) soil depth variability (depth of topsoil, depth to hardpan)
Mechanical	Soil compaction, compacted soil layers

From the Table 1 it can be seen that there are three methods to sense primary nutrients which are Nitrogen, Phosphorous and Potassium (NPK) in the soil. These methods are conductivity measurement, optical method, and electrochemical methods to analyse concentration of primary nutrients.

Conductivity can be measured using various electrodes such as steel, silver, platinum and graphit, copper. To measure electrical conductivity two or three electrodes of same material are immersed in samples. An A.C. voltage is applied to electrodes in sample. Another electrode is connected to Multimeter to measure the current changes. The A.C. voltage results in movements of ion which in turn results in variability of current of soil sample. Use of A.C. voltage avoids neutralization of ions. Varying current gives varying conductivity. Variability between electrical conductivity and concentration N, P, and K are observed. As concentrations increases, variability in electrical conductivity increases [7].

Electrochemical sensors constitute Ion Selective Electrode (ISE) and Ion Selective Field Effective Transistor (ISFET). ISE and ISFET selects particular ion from samples using sensor cocktail. ISEs/ISFETs uses different membranes, extraction solutions, and a multi-target system with coated wire field-effect transistor [8].

CW/FET type of electrochemical sensor uses a platinum wire coated with PVC which acts as the membrane matrix and it uses the cationic glass electrode (CGE) and the valinomycin-based selective electrode (VKE) for detection of exchangeable potassium in extracts from 30 soils [9].

All-solid-state sensors were built by Aleix Parra et al.[10]. They have applyed ion-selective polymeric membranes over an inner solid contact prepared with graphite-epoxy composites using a copper plate as a reference electrode. Nitrogen is found in the form of NH_4^+, NO_3^{2-} NO_2^- Thus various ammonia sensor can helps in detection of nitrogen. Ammonia determination can be done using dodecylbenzenesulfonate (DBSA) doped polypyrrole film [11].

The last type for soil sensor technology is optical sensor. Principal of optical techniques is based on the interaction between incident light and soil surface properties, such that the characteristics of the reflected light vary due to the soil physical and chemical properties

Laser Induced Florescence Spectroscopy(LIFS) is optical technique in which analyte in the molecule absorbs radiation at a certain wavelength (usually UV and visible regions). The electrons of the analyte are excited to higher energy states from ground state, but soon relaxation occurs from higher vibrational states to the lower vibrational state of the excited electronic state. Following this relaxation, the electrons return back to their ground state by emitting a photon [12-13]

Near InfraRed spectroscopy (NIR) technique is very widely used for experimental as well as commercial purpose. NIR is a spectrophotometric method that deals with the interactions of near infrared radiation with the sample under investigation. It is based on the absorption of electromagnetic radiation at wavelengths in the range of 780-2500 nm. The absorption of infrared radiation depends on the net change in dipole moment of the molecule as a consequence of its vibrational motion. When the vibrations are accompanied by a change in dipole moment, and when the frequency of vibration matches the frequency of infrared radiation, a transfer of net energy from the radiation to the molecule will be observed. This results in a change in amplitude of the molecular vibration. That is, the vibration absorbs the infrared radiation and the molecule is excited to a higher energy level. This energy transmission can be measured as the plot of energy [14] (reflectance, absorption or transmittance) versus wavelength, which is called as a spectrum).

NIR experimental setup by Burns,D.A., Ciurczak, E.W[15]was then modifiec by Alanso,[12], C.D. Christy, P. Drummond, E. Lund [16] and Peter Scharf [5] is shown in Figure 1

Tungsten-halogen lamps are the most common sources with quartz windows, which are capable of working in the visible and near infrared region. Sample cells vary

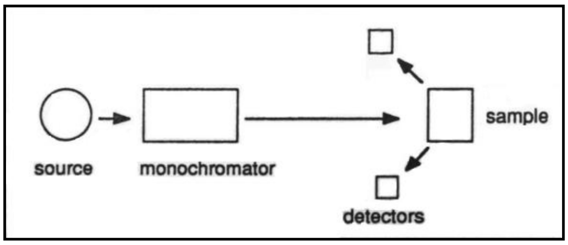


Figure 1. *NIR Spectroscopy[15]*

from 0.1 to10 cm and are made up of quartz or fused silica. The optical configure rations of dispersive instruments depend on the employed monochromator type, which is used for the selection of desired wavelengths. Some of these employ interference filters to provide radiation in a narrow range. And, some use grating monochromators, which are suitable for transmittance or reflectance measurements. In addition, infrared-emitting diodes can also be employed as both the wavelength selection system and the light source (400-1700 nm). The detectors used are generally silicon detectors covering the range 400-1100 nm, Indium gallium arsenide (800-1700 nm), lead sulfide (PbS) (1100- 2500 nm), or lead selenide (PbSe) (1000-5000 nm). In this case, the diffusely reflected radiation (R) is the ratio of the intensity of the radiation reflected from the sample to that of the standard reflector, such as a ceramic disk and it is converted to absorbance by the expression log 1/R. It depends on the concentration (c) of the analyte in the sample based on the Beer’s law $-\log R = \log (1/R) = k \times c$ 4.10

k is the factor of both absorptivity and path length

A study of soil samples was done to determine the concentration of the available phosphate, nitrate and sulfate at different depths using color detection by Samira A. etal [17]. Sulfate and nitrate were extracted in water with ratio of (1:1), while phosphate was extracted with sodium bicarbonate solution at pH of 8.5. Phosphate was determined as available phosphorus by Spectrophotometric method in which the ammonium phosphomolybdate complex, which was formed first, was reduced by ascorbic acid in presence of antimony to give a distinct blue color which was measured at 880nm. The available nitrate was determined by phenoldisulphonic acid to give a yellow color which was measured spectrophotometrically at 410nm. Sulfate was analyzed by adding excess barium chloride to precipitate barium sulfate which be then determined by turbidimetry method and was measured at 420nm [17-18].

2. METHODOLOGY

In this section experimental setup and results of UV spectroscopic methods are discussed.

2.1 Optical Method with UV Sensor

In optical method UV spectroscopy module is used. This deals with the interactions of ultraviolet radiation with the sample under investigation. It is based on the absorption of electromagnetic radiation at wavelengths in the range of 200-400 nm. Molecules containing π-electrons or non-bonding electrons (n-electrons) can absorb the energy in the form of ultraviolet or visible light to excite these electrons to higher anti-bonding molecular orbitals. The more easily excited the electrons (i.e. lower energy gap between the HOMO and the LUMO), the longer the wavelength of light it can absorb. UV spectroscopy follows Beer-Lamberts law. The Beer-Lambert law states that the absorbance of a solution is directly proportional to the concentration of the absorbing species in the solution and the path length. Thus, for a fixed path length, UV spectroscopy can be used to determine the concentration of the absorber in a solution. It is necessary to know how quickly the absorbance changes with concentration. This can be taken from references (tables of molar extinction coefficients), or more accurately, determined from a calibration curve. This energy transmission can be measured as the plot of energy (reflectance, absorption or transmittance) versus wavelength, which is called as a spectrum.

2.2 UV Reflectance Analyses

The instrument used in ultraviolet-visible spectroscopy is called a UV spectrophotometer. It measures the intensity of light passing through a sample (I), and compares it to the intensity of light before it passes through the sample (I_0). The ratio (I/I_0) is called the transmittance, and is usually expressed as a percentage (%T).The absorbance can be given as $A = (-\log T)$

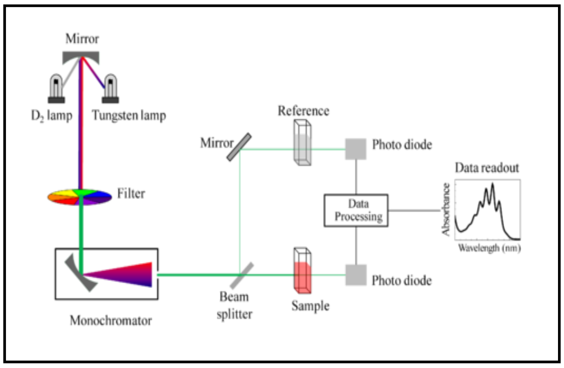


Figure 2. *UV Spectroscopy [19]*

2.3 Preparation of Soil Samples and Experimentation

Soil samples were collected from Mahatma Phule Agriculture College, Pune, Maharashtra. Seven samples were collected from different agricultural plot which are already ploughed up. Soil samples were transferred to plastic bags and were labeled as sample number 1, 2, 3 respectively. In the lab, the samples were air-dried; grass and any external objects were removed.

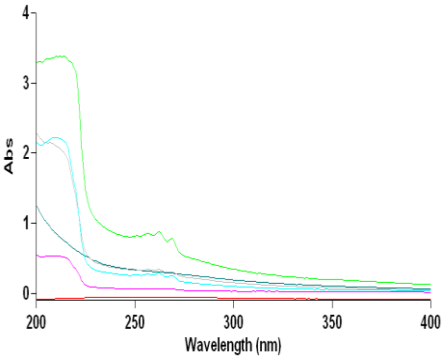
For experimentation aqueous solution of soil residue with varying ion concentration were prepared. For each sample 150gm of soil is added with 350 ml of distilled water. Different chemical solutions were prepared by adding KCl, ZnNO3, Single Super Phosphate (SSP) and Urea. For Each added element we prepared 3 different solutions with different concentration as Sample 1: 100 gm of ion, Sample 2 : 200 gm of ion and Sample 3 : 400gm of ion

These soil samples were analyzed using Varian 100 Cary Spectrophotometer. Result is obtain using UV Scan software

3. RESULT AND ANALYSIS

3.1 Phosphorous Determination in the Soil

Soil is mixed with distilled water and SSP is added to it. SSP represents Phosphorous ion in the form of phosphate as found in soil. For the first sample 150gm of soil is added with 350 ml of distilled water and 100 gm of Phosphorous ion is added. For second sample 150gm of soil is added with 350 ml of distilled water and 200 gm of phosphorous ion is added and for third sample 150gm of soil is added with 350 ml of distilled water and 400 gm of phosphorous ion is added. These samples were given to Varian 100 Carry spectrophotometer and the results spectrum obtained is as shown in Figure 3.



Green: (S1) Soil+ Water+ 400 Gm of SSP

Blue : (S2) Soil+ Water+ 200 Gm of SSP

Silver : (S3) Soil+ Water+ 100 Gm of SSP

Pink: Sample 0

Figure 3. *Wavelength Vs Abs for SSP*

Green curve is of (S1) higher concentration as 400 Gm of SSP is used. (S1) gives its peak absorption at 220 nm. As (S1) has maximum numbers of ions it gives highest reflectance and maximum absorbance.

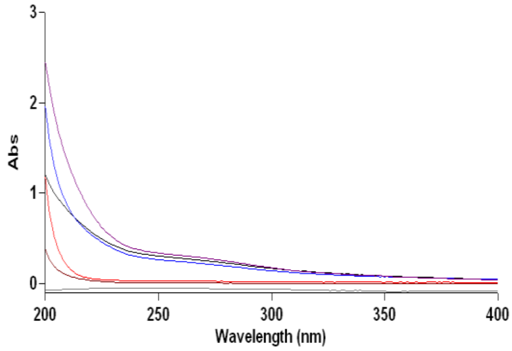
Blue curve is of (S2) medium Concentration as 200 Gm of SSP is used. (S2) gives its peak absorption at 220 nm. As (S2) has optimum numbers of ions it gives medium reflectance and optimum absorbance. Silver curve is of (S3) lowest Concentration as 100 Gm of

SSP is used. (S3) gives its peak absorption at 220 nm. As (S3) has very low numbers of ions it gives less reflectance and lowest absorbance.

Pink curve is spectrum of distilled water which acts as a is reference

3.2 Potassium Determination in the Soil

Soil is mixed with Distilled water and KCl solution is added to it as potassium is found in soil as K^+ ion. For the first sample 150gm of soil is added with 350 ml of distilled water and 100 gm of Potassium ion is added. For second sample 150gm of soil is added with 350 ml of distilled water and 200 gm of Potassium ion is added and for third sample 150gm of soil is added with 350 ml of distilled water and 400 gm Potassium ion is added. These samples were given to Varian 100 Carry spectrophotometer and the results spectrum obtained results spectrum is as in Figure 4.



Purple: (S1) Soil+ Water+ 400 Gm of KCl

Blue : (S2) Soil+ Water+ 200 Gm of KCl

Black: (S3) Soil+ Water+ 100 Gm of KCl

Brown: Distilled water

Red: Sample 0

Figure 4: wavelength Vs Abs for KCl

Purple curve is of (S1) higher concentration as 400 Gm of KCl is used. (S1) gives its peak absorption at 200 nm. As (S1) has maximum numbers of ions it gives highest reflectance and maximum absorbance.

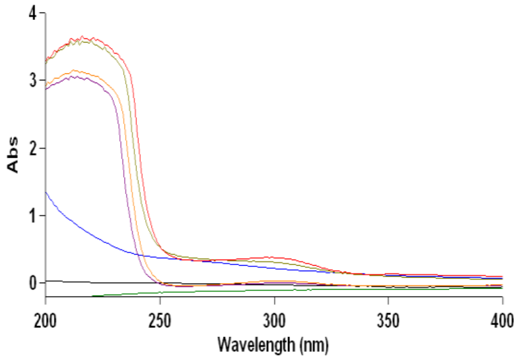
Blue curve is of (S2) medium Concentration as 200 Gm of KCl is used. (S2) gives its peak absorption at 200 nm. As (S2) has optimum numbers of ions it gives medium reflectance and optimum absorbance.

Black curve is of (S3) lowest Concentration as 100 Gm of KCl is used. (S3) gives its peak absorption at 200 nm. As (S3) has very low numbers of ions it gives less reflectance and lowest absorbance.

Brown curve is spectrum of distilled water which acts as a reference

3.3 Nitrogen Determination in the Soil

Soil and distilled water are mixed with $ZnNO_3$. $ZnNO_3$ represents Nitrogen ion in the form of Nitrate as found in soil. For the first sample 150gm of soil is added with 350 ml of distilled water and 100 gm of Nitrogen ion is added. For second sample 150gm of soil is added with 350 ml of distilled water and 200 gm of Nitrogen ion is added and for third sample 150gm of soil is added with 350 ml of distilled water and 400 gm of Nitrogen ion is added. These samples were given to Varian 100 Carry spectrophotometer and the results spectrum obtained results spectrum is as shown in spectrum is as in Figure 5.



Red: (S1) Soil+ Water+ 400 Gm of $ZnNO_3$

Green : (S2) Soil+ Water+ 200 Gm of $ZnNO_3$

Orange: (S3) Soil+ Water+ 100 Gm of ZnNO3

Purple: Sample 0

Distilled Water: Distilled water

Figure 5. *Wavelength Vs Abs for* $ZnNO_3$

Red curve is of (S1) higher concentration as 400 Gm of $ZnNO_3$ is used. (S1) gives its peak absorption at 240 nm. As (S1) has maximum numbers of ions it gives highest reflectance and maximum absorbance.

Green curve is of (S2) medium Concentration as 200 Gm of $ZnNO_3$ is used. (S2) gives its peak absorption at 240 nm. As (S2) has optimum numbers of ions it gives medium reflectance and optimum absorbance.

Orange curve is of (S3) lowest Concentration as 100 Gm of $ZnNO_3$ is used. (S3) gives its peak absorption at 240 nm. As (S3) has very low numbers of ions it gives less reflectance and lowest absorbance.

Purple curve is spectrum of distilled water which acts as a reference

It can be seen that maximum absorbance of sample varies with respect to concentration of NPK in the soil sample

The difference in the spectral features of NPK fertilizer and samples is obvious however it is difficult to interpret accurately the fertilizer concentrations from the sample spectra as they have similar spectral characteristics though the samples contain diverse amounts of nutrients.

4. CONCLUSION

Paper gives review of sensor technology for determination of primary nutrients in the soil. Also results of UV spectroscopy for primary nutrient determination are discussed in the paper. Brief review of remote sensing and on field sensing is also described in the paper.

It can be observed from the experiments that UV spectrophotometer can sense the various Primary nutrients in the soil. As the concentration of the primary nutrients (N, P, K) varies the maximum absorbance of soil sample also varies. Nitrogen gives its peak absorbance at 240 nm wavelength. Potassium gives its peak absorbance at 200 nm wavelength and Phosphorous gives its peak absorbance at 220 nm wavelength. Hence by observing wavelength and absorbance primary nutrients can be differentiated and concentration of the primary nutrients can be determined

ACKNOWLEDGEMENT

1. Mahatma Phule Krishi Vidyapeeth, Narveer TanajiWadi, Shivaji Nagar, Pune, Maharashtra For giving permission to collect various soil sampls
2. Maharashtra Institue of Pharmacy ,Kothrud , Pune,Maharashtra for

providing facility to work on UV spectrophotometer and other instruments

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