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Review of approaches and techniques for quantitative and qualitative measurement of soil nutrients.

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ABSTRACT

Soil nutrient testing is carried out through conventional instrumental and chemical extraction techniques. Chromatographic methods for soil analysis have been attempted but with unacceptable levels of variance and inconsistent results with the conventional testing methods for many of the key soil parameters. The purpose of this review paper is to explore the suitability of near infrared spectroscopic techniques for the rapid and accurate evaluation of key soil fertility parameters; and to review the performance of the developed methods in comparison to conventional methods of soil analysis.

Keywords: Spectrophotometry, Near Infrared Spectroscopy, Soil organic matter, Pre-processing, Chemometrics

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INTRODUCTION

Though post green revolution period, there has been a substantial growth in the consumption of fertilizers, their reckless use has been one of the major reasons for declining productivity in recent years. To remain profitable in agriculture under present conditions, every farmer should consider that fertility levels must be measured. In recent years, herbicides have been increasingly identified in surface and ground water, and the general public, as well as food-agricultural producers, have raised concerns with the possible overuse of such chemicals. Assessment of soil and crop health, pest infestation in rural India is usually performed with manual survey and experience without the application of technologies or quantitative/heuristic methods. Manual inspection of vast field round the clock is difficult, tedious and prone to error. The study of soil for agricultural applications has always been of great scientific curiosity due to the high demand for food products to meet the demand. Therefore, the analysis methods should be increasingly accurate in predicting, for example, detection of contaminants or nutrients in soils.

A soil test is a process by which elements (N, P, K, pH, EC, Ca, Mg, S, organic carbon and micronutrients: Zn, Fe, Cu, Mo, Br, Mn) are chemically removed from the soil and measured for their "plant available" content within the sample. The quantity of available nutrients in the sample determines the amount of fertilizer that is recommended by the soil testing services. A soil test also measures soil pH, humic matter and exchangeable acidity. These analyses indicate whether lime is needed and recommendations based on the available quantity.

Effective management of farm resources demands dynamic and accurate characterization of farmlands. This necessitates in-situ collection of quantitative and qualitative information on the soil quality before and during the cultivation of crops to optimize utilization of premium farm resources such as water and soil nutrients.

There exists diverse analytical methods based on chemical analysis or with advanced instrumentation like Atomic Absorption Spectrophotometer, Automated Ion Analyser or Calorimetric Spectrophotometer for the reliable measurement of soil parameters. However, these methods are all expensive, invasive, complex, labour-intensive and time consuming. Moreover, it is very difficult to accurately estimate in large quantities because of the variability associated with testing procedures.

Also there is no single method or instrumentation to measure the various soil nutrients simultaneously. There isn't any universal extractant or chemical available to detect all the fertility parameters. Accurate monitoring of soil nitrate is limited since the soil nitrate levels vary frequently due to leaching and de-nitrification.

Chemical methods for soil analysis are very accurate and widely accepted. However, after obtaining the samples in the field, these methods require a laborious laboratory analysis. The analysis of a single soil sample for all the parameters takes typically upto 30 hours. While the typical turn-around time to completely give results to end user is around 3-4 months taken by leading government agency.

ANALYTICAL METHODS FOR ASAAY OF SOIL FERTILITY PARAMETERS

Table -1: VARIOUS METHODS FOR SOIL ANALYSIS

Soil Nutrient	Assay method
Soil acidity	pH meter
Soil organic matter	Wet chemistry titration
Nitrogen, Phosphorous, Sulphur, Boron	Chemical extraction & UV spectral analysis
Exchangeable Potassium, calcium & magnesium, available Iron, Zinc, Manganese & copper	Chemical extraction followed by atomic absorption spectrophotometer or automated ion analyser or inductively coupled plasma spectrometer analysis

Soil test considerations

Soil colour and reflectance properties are a function of such parameters as moisture, texture, chemical makeup, parent material and soil organic matter. Investigators have taken varying approaches and attained varying degrees of success in developing and implementing electro-optic SOM sensors. Distinctions can be made in terms of:

a. Application (herbicide rate control vs. soil classification)
b. Sensor proximity (close-range sensing vs. remote sensing)
c. Spectral region [near infrared (NIR) vs. visible]
d. Spectral data type (color vs. wide-band reflectance vs. narrow-band reflectance)
e. Spectral data quantity (number of data channels)
f. Calibration development (within a soil landscape vs. large geographic range)

Different Tests performed:

a. Laboratory Test
b. Organic Carbon Calibration Test
c. Organic Carbon Error Analysis
d. Height Variation Tests
e. Moving sample tests
f. Estimation Of Soil Moisture And CEC
g. Instrument Modifications For Field Testing
h. In-Field Estimation Of Organic Carbon

The spectral reflectance has proved to be a powerful tool for such studies in agricultural applications since it allows knowing the chemical and physical state of the soil, providing results in real-time and on-site of interest due to its portability. This method can be adjusted to provide results for more than one soil parameters with a single analysis [5].

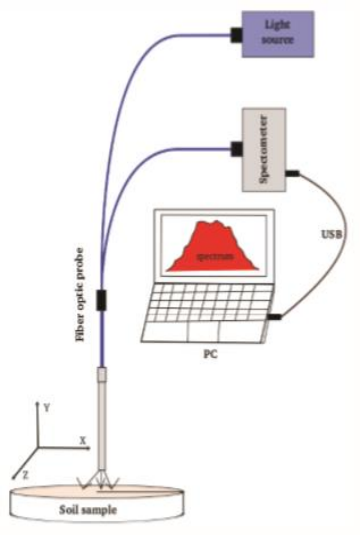

Fig. 1 : Experimental setup for sample testing

Qualitative analyses by near infrared spectroscopy

Qualitative analysis means classification of samples according to their NIR spectra. NIR identifications are based on few pattern recognition methods. Application of patter recognition methodologies within biology, chemistry and food sciences are important. The classification techniques are divided into two categories: the supervised and the unsupervised. Supervised pattern recognition are the technique in which a

prior knowledge, i.e. the category membership of samples, is required to be known. In the unsupervised classification, on the spectra is classified, rest of the samples are classified without a prior knowledge. Thus, the classification model is developed on a training set of samples with known categories. Then the model performance is evaluated by comparing the classification predictions to the true categories of the validation samples.

Quantitative analyses by near infrared spectroscopy

Once the classification of samples has been achieved, more precisely to what extend samples are different is useful information [8]. Therefore, the development of quantitative model quantifies the requisite data. Using a predictive model of the spectra measured, the quantitative values of the attributes can be obtained. The model is based in statistical analysis of the spectrum signal to be able to obtain the information of interest on the soil studied.

Processing of the data to analysis

NIR spectroscopy cannot be considered as a primary technique, therefore to develop a quantitative model it is essential to have a reference method to evaluate the property of samples. The processing steps include the following:

a. Obtain raw reflectance data from the portable spectrophotometer
b. Convert the data to percent reflectance form
c. Develop calibrations for prediction of soil organic matter content
d. Algorithms and software for data collection
e. Multiple scan averaging, baseline correction
f. Wavelength calibration and interpolation
g. Reflectance and optical density calculation is developed

Calibration development and soil property estimation is accomplished with partial least squares regression (PLS) techniques implemented in the PC-based Unscrambler software (CAMO A/S, Trondheim, Norway).

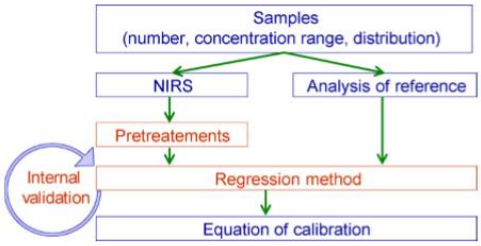

Fig. 2 : Scheme of the construction of a quantitative model

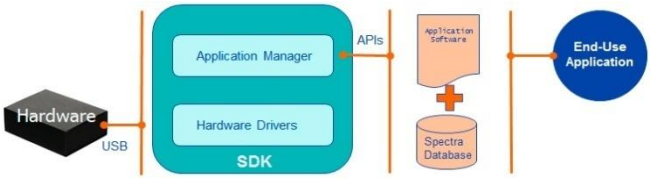

Fig. 3 : Scheme of the construction of a quantitative model

NEAR INFRA-RED SPECTROSCOPY

Near Infra-red Spectroscopy (NIRS) is a rapid and non-destructive analytical method. Associated with chemometrics it becomes a powerful tool for various food-agriculture applications. NIRS covers the transition from visible spectral range(Vis) to the mid infrared region(MIR). In this area of NIR (800-2500nm, respectively

12821-4000 cm-1) mainly vibrations of –OH, –CH, -NH and –SH bonds are observed. Using reflectance spectroscopy in near infrared and the visible of the electromagnetic spectrum (VIS- NIR)(400-1000 nm) can predict the presence of common soil contaminants, such as, heavy metals (Cr, Co, Ni, Cu, Pb). All the absorption bands are the result of overtones or combinations of the fundamental mid infrared region bands. Many literature materials have described the theory of near infrared spectroscopy. It has shown its usefulness in the analysis of agricultural products & foodstuffs, polymers, textiles, pharmaceutical and medical sciences, soil, and petrochemicals (Williams and Norris, 2001; Siesler et al, 2002; Burns and Ciurczak, 2001).

Characterization of soil for vital nutrients using techniques like NIRS offers many potential benefits. Some of them are listed below:

- Easy sample preparation (only drying and crushing necessary)
- Non-destructive analysis where the sample is not exposed to any chemical treatment
- No complex chemical analysis requiring any trained persona
- Measurement and analysis can be done instantaneously
- Several soil parameters can be measured and assessed simultaneously from a single scan
- (Simplicity in Multiplicity)
- Use of different spectroscopic technique which uses different physical phenomenon and provides for complementary information about soil nutrients.

Majorly, the interest in NIR has increased due to the instrument technological advancements and the development of fibre optics field that allow the delocalization of the measurements. Additionally, it has increased due to the development in the computational tools and the development of new mathematical and statistical methods allowing data treatment.

INSTRUMENTATION

[9], [12], [16], [18] and [19] discuss results by using visible/near infrared spectroscopy method to predict soil organic Carbon, N, P and K. [10], [13] and [20] discuss results by using visible near infrared reflection spectroscopy(vis-NIR) and mid-infrared reflection spectroscopy(MIR) to predict vital soil parameters such as Soil water content, texture, soil carbon (C), cation exchange capacity (CEC), calcium and magnesium (exchangeable), total nitrogen (N), pH, concentration of metals, metalloids, microbial size and activity. [11] discusses results by using mid-infrared spectroscopy to predict Sand, clay, pH, total C and N, exchangeable Ca, Mg and effective CEC. [11] and [14] have discussed results to predict organic matter, phosphorus, CEC, clay content, and pH using NIR spectroscopy method.

Successful application of NIR depends on the right choice of instruments and these instruments have evolved significantly in response to the flexibility in adapting to different sample states and the need for speed in analysis. NIR spectrophotometers can be of two types with respect to the wavelength selection, namely discrete wavelength and whole spectrum. The discrete wavelength type is simpler, as they irradiate samples with only a few wavelengths, as a result this is used in specific application with analytes absorbing in specific spectral zones. In discrete-wavelength spectrophotometers, wavelength can be selected by using as light sources filters that allow the passage of variable broad wavelength bands or Light Emitting Diodes (LED) that emits narrow bands.

Broadly there are three approaches to NIRS solution for soil analysis.

1. Using filter based
2. Using (red) Light emitting diode based
3. MEMS FTIR based device

Pitts et al. (1986), successfully predicted the SOM of 30 Illinois soils using an exclusion algorithm and polychromatic (white), green, and red reflected light. The results suggested the width of the prediction range for each soil varied from 1 to 3% organic matter, with an average range width of 1.4% [2]. Gunsaulis et al. (1991), Studied the effect of soil surface structure on reflectance from a red (660 nm) light-emitting diode (LED) source. The results suggested that a maximum r2 of 0.61 was obtained on the test set of 20 Arkansas

soils containing from 0.47 to 2.1% SOM [2]. Shonk and Gaultney (1988), Developed a real-time SOM sensor intended to be recalibrated for each new soil landscape, rather than for the larger geographic area (such as an entire state) attempted by other researchers. Results: Laboratory tests using red (660 nm) LEDs as the light source yielded good correlations (r2 = 0.80 to r2 = 0.98) for soils obtained within a single landscape and prepared to a single moisture content. Noted that below-surface field tests showed a curvilinear relationship between sensor output and SOM (r2 = 0.84 to r2 = 0.95), with new calibrations developed for changes in travel speed or sensing depth (Gaultney et al., 1989) [2].

MEMS FTIR based solutions are a novel approach which solves the challenges faced with the typical lab based setup and is a micro sized device. MEMS interferometer based on the Michelson or Mach-Zehnder architecture are its typical types. MEMS interferometers are gaining increased importance for a wide range of industrial applications. The MEMS technology is the right technique for this objective, as it enables the integration on a single chip using the IC technology & different functions. The challenge is to maintain the high performance required in the different applications while achieving the small integrated scalable spectrometer. In this technique the beam splitter has a very wide spectral range and is robust. The whole structure is aimed to be integrated on a single die which includes two beam splitters, two moving mirrors, and comb actuator. This is an advantage achieved by the MEMS technology which opens the door for more advanced industrial applications.

SoilCares, an initiative aims to improve agricultural and horticultural procedures, by combining the latest agricultural know-how with high quality analytical experience and expertise. SoilCares has developed: The SoilCares Scanner, a handheld device that executes on-the-spot soil tests in order to receive adequate lime and fertilizer recommendations within 30 seconds.

Fig. 4. How the handheld scanner works

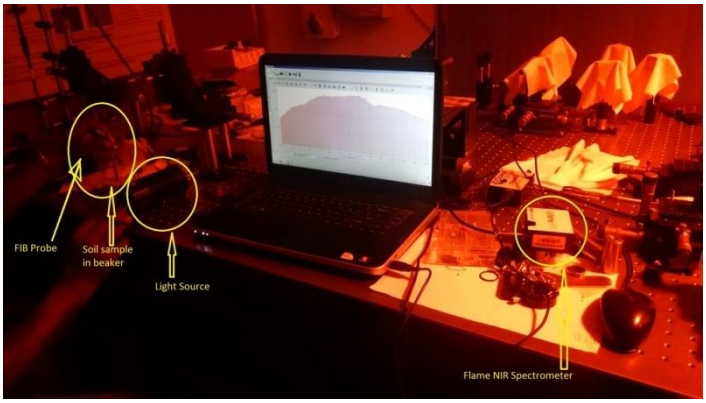

Fig. 5. How the handheld scanner works

DISCUSSIONS

Within the last years NIR imaging systems were developed. A hyper-spectral imaging spectrometer records simultaneously spectral and spatial information of samples. NIR imaging complements NIR spectroscopy and is used when spatial distribution is an important issue of the analyses. This method will be a useful tool in future.

CONCLUSION

The potential power of NIRS in process analytics and quality control is evident. NIRS is a powerful way to discriminate food-agriculture compounds. This method can be used qualitatively to detect, to identify, and to qualify the soil sample. NIRS is a suitable method for classification but also for quantification of soil samples. It is a useful tool for quality control and on-line applications. Near infrared spectroscopy is a potentially precious diagnostic tool in process trouble shooting and can provide a fingerprinting of the agriculture products.

The ability of reflectance spectroscopy is confirmed (using the Vis/NIR) for the evaluation of soil nutrients in soils. Therefore, the VIS-NIR spectroscopy is a good option of evaluation, as its advantages are attributed to being non-destructive analysis method and environment friendly. This spectroscopy can be performed on the raw material, avoiding the sample preparation procedure. It is non-destructive and above all, the measurement is fast.

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