Chapter 3
Theories and Methods for Soil Nutrient Sensing

Fei Liu, Xiantao He, and Yong He

Abstract Soil provides the essential nutrient elements for plant growth. Soil nutrients include soil macronutrients such as nitrogen, phosphorus, and potassium, as well as soil micronutrients such as calcium, magnesium, sulfur, iron, and boron. Precision agriculture is a technology of applying precise and right amounts of inputs such as water, fertilizer, and pesticides at the right time to the crop for increasing the productivity and maximizing the yields. Therefore, it is necessary to obtain soil nutrient information quickly and accurately. Near-infrared spectroscopy (NIRS) with high-efficiency and nondestructive characteristics has great potential in soil nutrition detection. According to the NIR absorption of the hydrogen bonds, soil total nitrogen content and soil organic matter content can be estimated. Multiple linear regression, partial least square regression (PLSR), and principal component analysis (PCA) are commonly used to establish the estimation models of soil nutrient contents based on NIRS. Moreover, the modern algorithms of wavelet algorithm (WA), genetic algorithm (GA), uninformative variable elimination (UVE), support vector machine (SVM), etc., are used to reduce the multicollinearity of the NIR spectra to improve estimation accuracy. Laser-induced breakdown spectroscopy (LIBS) is a promising spectral detection technology with high sensitivity, fast speed, and the ability to measure multiple elements simultaneously. It can also be used to detect both soil macronutrients and micronutrients. At present, scientists have developed various forms of soil testing instruments based on spectral technology, such as portable, vehicle-mounted, and remote sensing devices. Through these devices, it is convenient to implement comprehensive, full-range, all-weather, and real-time soil sensing for soil and crop precision management.

Keywords Soil nutrients · Soil sensing · Near-infrared spectroscopy (NIRS) · Laser-induced breakdown spectroscopy (LIBS) · Soil sensors

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Soil serves as a medium for nurturing plants, and its nutrients have a great influence on the healthy growth and yield improvement of crops. Precision agriculture is a technology to precisely input right amount of agricultural means of production such as water, fertilizer, and pesticides at the right time to the crop for increasing its productivity and maximizing its yield. To achieve expected crop production, it is necessary to obtain soil information quickly and accurately. Soil nutrients mainly include nitrogen, phosphorus, potassium, and organic matter content, and obtaining the information of those soil nutrients is beneficial to farmland management and decision-making, as well as prediction of crop yields.

Traditional soil sampling technology for acquiring soil information is costly, time-consuming, and poor in real time and is not suitable to large-scale farmland. Thus, it is necessary to detect the characteristic information of the soil rapidly and accurately in large-scale areas. In recent years, a lot of studies have been conducted on the method of rapid nondestructive detection of soil information, and great progress has been made.

3.1 Laboratory Measurement of Soil Nutrients

The traditional chemical analysis method of soil nutrients is to extract a specific element in a soil sample through a specific extraction solution, thereby realizing quantitative detection of the soil nutrient content. In this traditional analysis method, the complex procedures of soil sampling and nutrient extracting and measuring are the main reasons for cost reduction and speed improvement of soil nutrient detection.

3.1.1 Detection of Soil Nitrogen Content in Laboratory

Nitrogen is an important building block of proteins, nucleic acids, and other cellular constituents which are essential for all forms of life. Therefore, soil nitrogen is a key nutrient element for plants so that it warrants careful management. Soil nitrogen absorbed by plants is available nitrogen, which is easily hydrolyzed as a part of the soil solution or the cation exchange complex when applied to moist soils. Available nitrogen is mainly from most of the commonly applied inorganic sources, such as ammonia, ammonium nitrate, ammonium phosphate, ammonium sulfate, calcium nitrate, nitric phosphate, potassium nitrate, and sodium nitrate.

The commonly used method for the determination of soil available nitrogen content is the alkali-nitrogen hydrolysis method. The principle of this method is to use sodium hydroxide of 1 ~ 2 mol/L for hydrolyzing soil samples and to decompose the inorganic nitrogen and easily decomposed organic nitrogen in the soil into ammonia nitrogen, which is absorbed with boric acid and standard acid to titrate. The detailed operation process is as follows: weighing 2 g of soil sample into the outer chamber of the Conway diffusion dish firstly and then adding 2 mL of boric acid solution to the inner chamber of the diffusion dish and 100 mL of 1 mol/L sodium hydroxide to the outer chamber and finally sealing it with Vaseline for 48 hours and titrating it with standard concentration of sulfuric acid at 0.005 mol/L. The end of the titration is when the solution turns purple. The formula for calculating nitrogen content is shown in Eq. 3.1:

$$N = \frac{c \times \left(v - v_0\right) \times 14.0}{m} \times 10^3 \tag{3.1}$$

where N is the available nitrogen (mg/kg), c is the concentration of 0.005 mol/L (1/2 H_2SO_4) standard solution (mol/L), v is the volume of the 0.005 mol/L (1/2 H_2SO_4) standard solution used for sample titration (mL), v_0 is the volume of the 0.005 mol/L (1/2 H_2SO_4) standard solution used in the blank test titration (mL), 14.0 is the molar mass of the nitrogen atom (g/mol), m is the mass of the sample for testing (g), and 10^3 is the conversion factor of mass units.

3.1.2 Detection of Soil Phosphorus Content in Laboratory

There are many methods for determining soil available phosphorus, and the results are inconsistent due to different extraction reagents used. The selection of extractant methods is mainly based on the properties of the soil to be tested. Neutral and calcareous soils are extracted by sodium bicarbonate reagent, while acid paddy soils are extracted by hydrochloric acid, and acid dry soils are extracted by hydrochloric acid-sodium fluoride method.

The hydrochloric acid extraction method for acid paddy soil is specifically introduced here (Fig. 3.1). First, a 2.5 g soil sample is weighed into a 250 mL Erlenmeyer flask, and then a teaspoon of phosphorus-free activated carbon is added for decolorization, and 0.1 mol/L hydrochloric acid is added to the 250 mL scale mark for extracting available phosphorus in soil. After shaking the Erlenmeyer flask for about 30 minutes and then filtering the available phosphorus from the solution, 10 mL of filter solution is taken in a tube, and then 5 mL of molybdate-antimony-scandium color agent is added to maintain constant volume. After the solution stands for 15 min, a colorimetry at 700 nm is used to obtain the absorbance value of the test solution, and then the concentration of available phosphorus is determined by the calibration curve of phosphorus solution, and the content of available phosphorus in soil is calculated by Eq. 3.2:

$$P = \frac{\rho \times V \times T_s \times 1000}{m \times 1000 \times k} \tag{3.2}$$

where P is the available phosphorus (mg/kg), ρ is the concentration of available phosphorus (μg/mL), V is the volume of maintaining constant volume during color

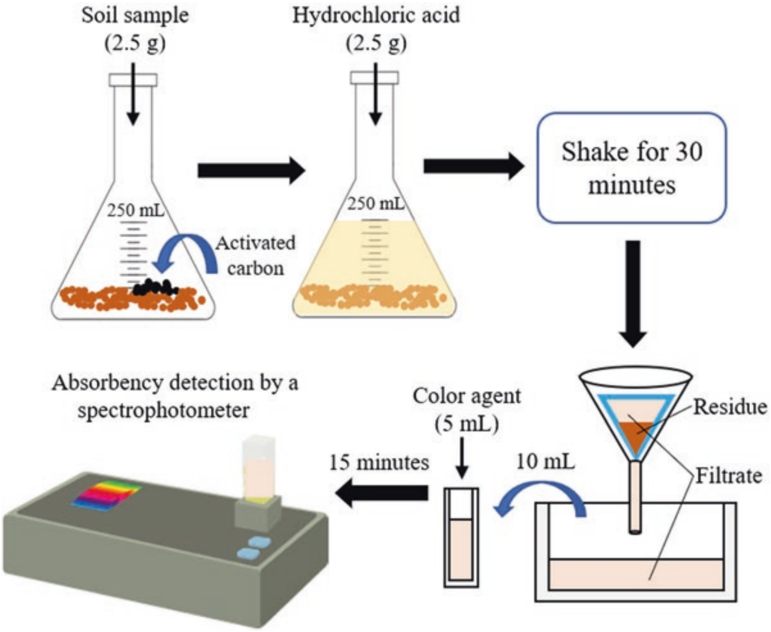


Fig. 3.1 Hydrochloric acid extraction method for detecting phosphorus in soil

rendering (mL), T_s is the ratio of the total volume of the extract solution to the volume of the extract solution absorbed during color rendering, m is the mass value of air-dried soil (g), and k is the mass coefficient of air-dried soil converting into oven-dried soil.

The process of drawing the calibration curve is as follows: accurately take 5 μg/mL phosphorus standard solution of 0, 1, 3, 7, and 10 ml into volumetric flasks, respectively, and add 5 ml molybdate-antimony-scandium color agent in each flask, and then slowly rotate the volumetric flask to shake well and add water to the flasks to obtain standard solutions with phosphorus contents of 0.0, 0.1, 0.3, 0.5, 0.7, and 1.0 μg/mL, respectively. After standing for 30 min, perform colorimetric measurement at a wavelength of 700 nm to obtain the absorbance of the standard solutions, and then draw the calibration curve of the standard phosphorus solution with the phosphorus concentration (μg/mL) as the abscissa and the absorbance (Abs) as the ordinate.

3.1.3 Detection of Soil Kalium Content in Laboratory

Along with nitrogen and phosphorus, kalium is also one of the essential nutrients for crop growth. The kalium in soil can be classified as mineral kalium (insoluble kalium), non-exchangeable kalium (slow-acting kalium), exchangeable kalium, and water-soluble kalium (quick-acting kalium). The kalium that can be absorbed by plants is water-soluble and exchangeable kalium.

The method of chemical determination for available kalium in soil is similar to the method shown in Fig. 3.1. It uses the acetic acid as the extracting solution to extract the available kalium from the soil, and then the content of kalium is determined by flame photometer according to the characteristics of kalium element. The detailed processes are as follows: weighing 5 g of air-dried soil sample into a 100 mL test tube, adding 50 mL of 1 mol/L neutral ammonium acetate solution, and then plugging the tube with a rubber stopper and shaking for 30 minutes, filtering the solution and measuring the filtrate directly on a flame photometer with a 766.5 nm filter, and then recording the galvanometer reading and obtaining the concentration of test solution from a calibration curve of the standard kalium solution. The specific formula for calculating kalium content in soil is shown in Eq. 3.3:

$$K = C \times \frac{v}{m_d} \tag{3.3}$$

where K is the available kalium (mg/kg), v is the volume of acetic acid added, C is the concentration of test solution (μg/mL), and m_d is the mass value of oven-dried soil (g).

3.1.4 Detection of Soil Organic Matter Content in Laboratory

Soil organic matter, as a sign of fertility formation, is an important indicator for identifying soil fertility. The content and composition of organic matter will change regularly with the changes of the climate and biological conditions. Therefore, the detection of organic matter is also an important part in the detection of soil nutrients. The potassium dichromate method is an important method for the determination of soil organic matter in laboratory. The testing principle is to use potassium dichromate-sulfuric acid solution to oxidize organic matter during heating process, and the remaining potassium dichromate is titrated with a standard solution of ferrous sulfate using o-phenanthroline as an indicator, and then the amount of potassium dichromate consumed is used to calculate the carbon content.

The detailed process of detecting soil organic matter by the potassium dichromate method is shown in Fig. 3.2: accurately weighing 0.5 g of soil sample into a 250 mL flask, adding 5 mL of potassium dichromate standard solution and 5 mL of concentrated sulfuric acid into the flask with a pipette, and then carefully shaking the solution to uniform, heating a thermostatic oil bath to 185-degree Celsius, and then placing the flask in the constant temperature oil bath, boiling the solution in the flask for 5 minutes, moving the flask from the oil bath and cool the solution to room temperature, finally adding three drops of o-phenanthroline indicator to the flask, and then titrating it with a 0.1 mol/L standard ferrous sulfate solution. When the

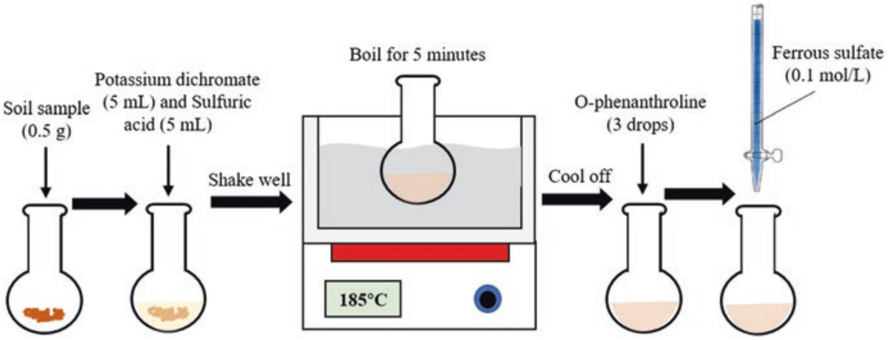


Fig. 3.2 Method of chemical determination for soil organic matter content

color of the solution in the flask changes from orange yellow to green and then mutates to brown red, the titration will be stopped. For each batch of samples, quartz is used instead of soil sample for blank test. The calculation method of carbon content is shown in Eq. 3.4:

$$TC = \frac{c\left(V_0 - V\right) \times 0.003 \times 1.724}{m \times D} \times 100\% \tag{3.4}$$

where TC is the organic carbon content (%), c is the concentration of a standard solution of ferrous sulfate (mol/L), V_0 is the volume of ferrous sulfate used in blank test (mL), V is the volume of sulfuric acid solution consumed during measurement (mL), 0.003 is the molar mass of 1/4 carbon atom (kg/mol), m is the sample mass used for testing (g), and D is the dilution ratio. There is a certain conversion relationship between the organic matter content in the soil and the organic carbon content. The content of organic matter in the soil can be obtained by multiplying the measured organic carbon content with a conversion factor of 1.724: organic matter (%) = TC(%) × 1.724.

3.2 Spectral Technology for Soil Nutrient Sensing

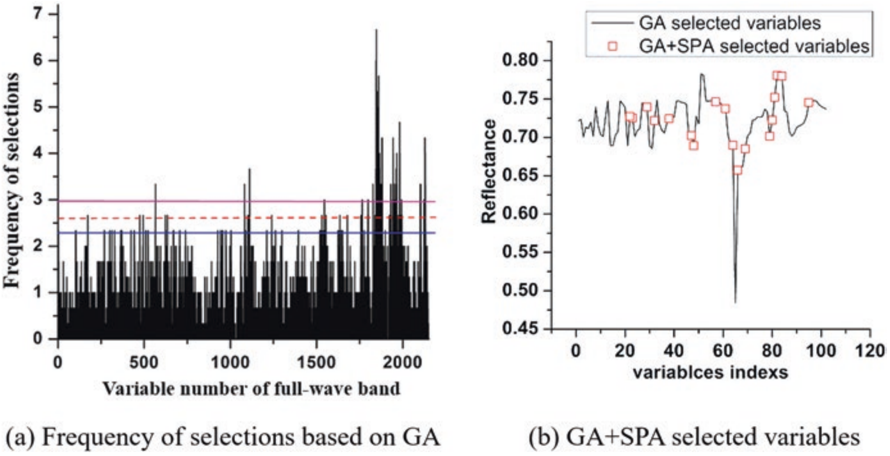
Using laboratory chemical analysis to obtain farmland soil nutrient information can accurately obtain soil nutrient information at a single point in the field, but it is cumbersome, time-consuming, labor-intensive, costly, and poor in real time. Meanwhile, the number of samples is too little to reflect objectively the distributed situation of actual soil nutrients in large areas of farmland. In addition, the method for determining soil nutrient in laboratory will produce chemical waste and cause secondary pollution to the environment. The spectral analysis methods for detecting soil fertility can shorten analysis time, reduce detection costs, and improve testing efficiency. Moreover, the in situ detection for soil fertility based on spectroscopy will help achieve real-time measurement of soil fertility properties, which can facilitate the global application of the technology of on-demand fertilizer management.

3.2.1 Vis/NIR Spectral Sensing Technology for Soil Nutrients

Vis/NIR spectroscopy to sense soil nutrients is a mature technique for detecting soil moisture, organic matter, nitrogen, phosphorus, kalium, etc. Yu et al. (2002) measured total nitrogen, organic matter, and alkali-hydrolyzed nitrogen in soil by near-infrared spectroscopy. The NIR spectra of 2 mm and 0.15 mm air-dried soil were obtained, and a partial least square (PLS) method was used to establish a mathematical model for predicting soil nutrition content. The results showed that NIR spectra had a good correlation for detecting soil organic matter, total nitrogen, and alkali-hydrolyzed nitrogen. Zhu et al. (2008) used near-infrared spectroscopy to detect organic matter in untreated soil. In the experiment, near-infrared spectra in the range of 4000~12,500 cm^{-1} was applied to detect organic matter in the soil that had not been pulverized and sieved, and the quantitative relationship between the spectral absorbance and the organic matter content was established by the methods of first-order differential pretreatment and PLS regression analysis. The experiment has obtained good results. The predicted correlation coefficient of organic matter is 0.818, the standard deviation is 0.069, and the root mean square error is 0.085.

The team from China Agricultural University has been working on the spectroscopic detection methods of soil nutrients since the 2000s (Sun et al. 2006; Sun et al. 2007). The research objects were mainly black soil in Northeast China and Chao (aquic cambisols) soil in North China. The spectral data of soil samples were collected without pretreatment, and then the correlation between soil parameters and spectral characteristics was analyzed and a predictive model for soil nutrient was established. Meanwhile, the effects of soil moisture content and particle size on soil spectrum by using wavelet transform were studied (An et al. 2013). The results showed that the change trend of the soil spectral curve was affected by the soil moisture content, and the instantaneous fluctuation of the spectral curve was mainly caused by the soil particle size. A filtering process was performed to a certain extent, which eliminated high-frequency oscillation of the spectral curve caused by uneven particle size of soil (Li et al. 2013).

The principle of spectral detection of soil nutrition is the multiple frequency absorption of near-infrared spectrum to nutrients in the soil. The mass information of the spectral bands for different substances overlaps heavily, so that the full-band spectrum contains a lot of redundant information and noise data, which affects the prediction accuracy of the model. This is the main reason of low stability and accuracy of spectral measurements for soil nutrition in earlier studies. In order to reduce a large amount of useless information in the full-band spectral information, it is necessary to extract the truly effective bands from the full band to reduce the amount of calculation and increase the speed of detection. The main wavelength extraction methods are wavelet algorithm (WA), genetic algorithm (GA), uninformative



(a) Frequency of selections based on GA

(b) GA+SPA selected variables

Fig. 3.3 Result of spectral feature selection (Zhang 2015) (**a**) Frequency of selections based on GA (**b**) GA + SPA selected variables

variable elimination (UVE), principal component analysis (PCA), successive projection algorithm (SPA), etc. The application of these methods to the spectral detection of soil nutrients combined with advanced modeling methods will greatly improve the speed of spectral determination of nutrients in soil. The result of spectral feature selection for soil organic matter based on GA is shown in Fig. 3.3a (Zhang 2015). There are three horizontal lines in the figure, and the numbers of the wavelengths corresponding to the lines from top to bottom are 64, 102, and 169, with the accumulative contribution rate of 79.51%, 81.99%, and 81.97%, respectively. Therefore, 102 was selected as the number of the wavelengths in the next analysis. A SPA algorithm was used to select 18 characteristic wavelengths from the 102 wavelengths (Fig. 3.3b), and the prediction model was established using PLS. The prediction set achieved a determination coefficient (R^2) of 0.83 and root mean square error (RMSE) of 0.20, while R^2 and RMSE were 0.84 and 0.20, respectively, when using 102 wavelengths for prediction model. It is observed that the prediction accuracy was almost not reduced when the number of wavelengths dropped to 18, indicating that the combination of GA and SPA can greatly simplify the prediction model.

3.2.2 *Mid-infrared Spectral Sensing Technology for Soil Nutrients*

The principle of sensing soil nutrients by mid-infrared (MIR) spectroscopy (2500 ~ 25,000 nm) is absorptions of fundamental frequency related to molecular structures of soil constituents. Different compounds have specific infrared absorption spectra, and the intensity, position, shape, and number of bands are related to the type of compound and its state. Compared with near-infrared spectroscopy, mid-infrared spectroscopy has more specificity in detecting soil nutrients.

Jia et al. (2017) applied diffuse reflectance spectroscopy, including visible and near-infrared (VNIR) and MIR radiation, to rapidly estimate soil organic carbon (SOC). The absorbance spectra in the VNIR and MIR regions at different depths of soil profile of shrub meadow are shown in Fig. 3.4. The SOC concentrations usually decreased with depth, and the absorbance curves reduced overall with increasing soil depths. A comparison of the field-moist intact and air-dried ground spectra in the range of 400 ~ 2450 nm indicated that the soil moisture and structural integrity also affected the soil absorbance spectra. The strong absorptions near 1400 and 1900 nm in the VNIR spectra were caused by the O–H functional group of free water, and the absorptions near 2200 nm were caused by the organic matter. In the MIR region, the spectra information mainly responded to mineral properties, such as quartz, kaolin, and montmorillonite. Preprocessed spectra were used to predict the SOC in the soil cores using partial least square regression (PLSR) and support vector machine (SVM) algorithm. The SVM models (average values of RMSEP and R^2 of 8.31 $g{\cdot}kg^{-1}$ and 0.84, respectively) performed better in predicting the SOC concentration under different land cover types than the PLSR models (average values of RMSEP and R^2 of 12.41 $g{\cdot}kg^{-1}$ and 0.70, respectively). The prediction of forest soil had the highest prediction accuracy, followed by the total dataset and finally the shrub meadow subset.

Janik et al. (2007) applied MIR spectroscopy and partial least square analysis to predict the concentration of soil organic carbon. The PLS calibrations were derived from a standard set of soils that had been analyzed for total organic carbon (TOC), particulate organic carbon (POC), and charcoal carbon (char-C) using physical and chemical means. PLS calibration models from this soil standard set allowed the prediction of TOC, POC, and char-C fractions with a coefficient of determination (R^2) of measured and predicted data ranging between 0.97 and 0.73. For the POC fraction, the coefficient of determination could be improved ($R^2 = 0.94$) by using local calibration sets. The capacity to estimate soil fractions such as char-C rapidly

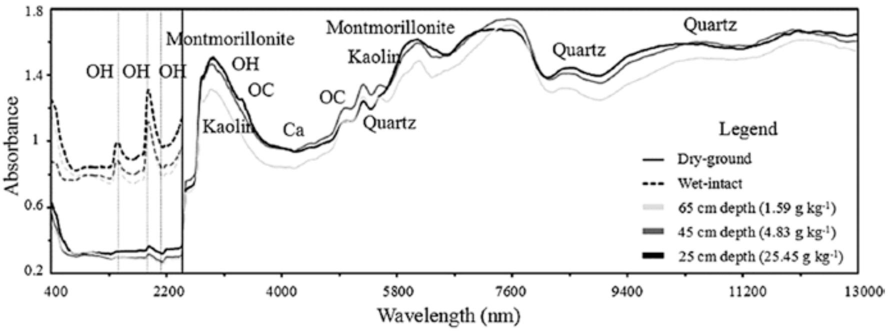


Fig. 3.4 Absorbance spectra at different depths with different contents in one soil core of shrub meadow in the VNIR and MIR regions. (Jia et al. 2017)

and inexpensively makes this approach highly attractive for studies where large numbers of analyses are required. Inclusion of a set of soils from Kenya demonstrated the robustness of the method for total organic carbon and charcoal carbon prediction. Baldock et al. (2013) combined diffuse reflection MIR spectra with PLSR analysis to predict soil carbon content and composition. Total organic and inorganic carbon contents were determined with MIR spectra acquired for 20,495 soil samples collected from 4526 locations from soil depths to 1 m within Australia's agricultural regions. It was found that the degree of soil dryness and grinding of soil samples had a great impact on the test results. Therefore, the grinding time was standardized in the study, and prediction of total carbon, organic carbon, and inorganic carbon was achieved. Compared with the traditional laboratory method, the MIR method provided a faster and more economical method for detecting the soil carbon and total nitrogen content in soil.

3.2.3 LIBS Sensing Technology for Soil Nutrients

1. Working Principle of LIBS.

Laser-induced breakdown spectroscopy (LIBS) is a promising spectral detection technology with high sensitivity, fast speed, and the ability to measure multiple elements simultaneously. As early as 1994, scientists at the International Association for Remote Sensing Science announced that they had successfully detected As, Cd, Cr, Hg, Pb, Zn, and other metal elements in soil using LIBS technology (Alexander et al. 1994). In the soil nutrient detection, it can be used for the detection of metal nutrient elements, such as potassium, calcium, and cuprum. At present, in the process of detecting heavy metals in the soil by LIBS, a single pulsed laser is generally used to excite soil samples to generate plasma, and the detection sensitivity obtained is generally tens of mg/kg, and some metals with high sensitivity can reach several mg/kg.

The working principle of LIBS is to use high-energy laser pulses to directly hit the surface of the sample, forming a high-intensity laser spot (plasma) on the surface of the analysis material and exciting the elements to be tested to a high-energy state. When outer electrons of the element atoms move into the ground state, their characteristic spectra will be emitted and then detected by a spectrometer. By comparing the detected spectrum to elemental spectrograms in the standard spectral library, the content of elements contained in the soil sample can be obtained.

In the calculation process, it is generally considered that the content of each element in the plasma is the same as that in the sample before ablation. The intensity of the radiation spectrum when an atom transitions from the k-level to the i-level (I_{ki}) is

$$I_{ki} = \frac{h\nu_{ki}}{4\pi} N \frac{g_k A_{ki}}{U_S(T)} e^{-E_k/(kT)} \tag{3.5}$$

where *h* is the Planck constant, v_{ki} is the frequency of spectral lines, *N* is the number of excited particles, g_k is the k-level statistical weight, A_{ki} is the probability of atomic transition from *k*-level to *i*-level, $U_s(T)$ is the distribution function of elements at temperature *T*, E_k is the *k*-level potential energy, *K* is the Boltzmann's constant, and *T* is the Calcination temperature. When the characteristic spectral line of the specified element is detected, the v_{ki}, g_k, A_{ki}, *T*, $U_s(T)$, E_k, and *k* have certain values, and the number of excited particles *N* is proportional to the content of the test element in the sample (*C*), so the above formula can be rewritten as

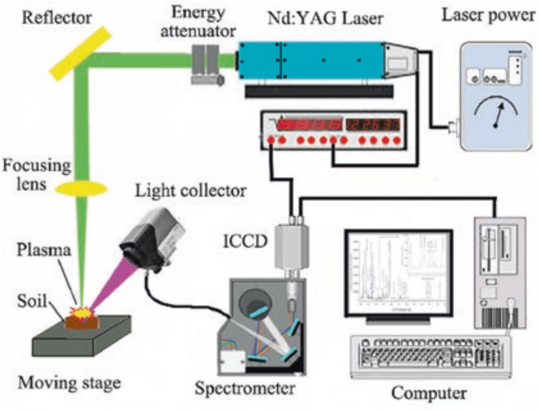
$$I = aC^b \tag{3.6}$$

where *a* is proportionality coefficient and *b* is self-absorption coefficient, which is related to the content of the element to be measured. According to this formula, the element content in the soil sample can be calculated by the intensity of the characteristic line of the element, providing a theoretical basis for the quantitative detection of the element in soil.

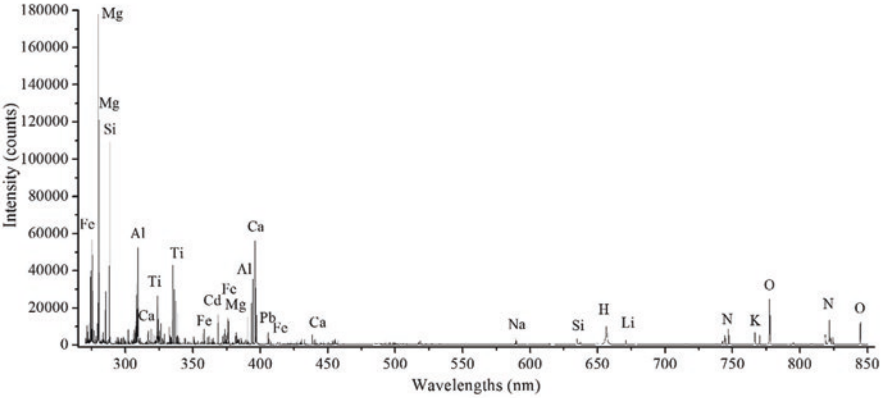
2. Theoretical Basis of Soil Nutrient Detection with LIBS.

A typical experimental platform system for LIBS is mainly composed of a laser, a spectral information acquisition system (a spectrometer and a detector), digital pulse delay generators, and accessory devices (sample stage, energy meter, computer, etc.). Figure 3.5a shows the composition of a typical LIBS system (Yu 2016; Yu et al. 2019). The laser is the energy source of the LIBS system and can provide energy to excite the sample and generate plasma. The acquisition system consisting of a spectrometer and a detector is used to collect the radiation spectrum of laser-induced plasma and perform photoelectric conversion for digital analysis. The digital pulse delay generator is used to control the delay time of the spectrometer detector relative to the laser pulse, and the computer is applied to conduct the setup of working parameters and subsequent data processing of each component. Yu (2016) obtained that a spectral curve of soil added some heavy metals in the range of 270~850 nm by the experiments (Fig. 3.5b). It can be seen that the emission lines of most metal elements are distributed in the range of 270~450 nm. The emission spectrum of elements such as Fe, Mg, Si, Ca, Ti, Al, Pb, Cd, Na, Li, N, K, H, and O can be observed in the entire spectrum, and the wavelengths of the atomic spectrum and the ion spectrum correspond to specific elements, and the spectral signal intensity has a certain quantitative relationship with the corresponding element content. Generally, the same element produces multiple emission lines with different wavelength positions and different intensities. However, the quantitative prediction of an element is mainly based on data analysis in a single band in practical applications, that is, only the intensity data of a certain spectral line needs to be selected to predict the element content in the soil.

In addition, there are also O and N emission lines in the spectrum diagram, some of which are due to the breakdown of a large amount of O_2 and N_2 in the air and others are due to the presence of O and N in the soil. For the low content of elements, although characteristic spectral lines are detected under this test condition,



(a) Representative LIBS analytical system for soil analysis



(b) Spectral curve of soil added some heavy metals in 270-850 nm

Fig. 3.5 Soil analysis based on LIBS analytical system (Yu 2016; Yu et al. 2019) (**a**) Representative LIBS analytical system for soil analysis (**b**) Spectral curve of soil added some heavy metals in 270~850 nm

the signal is weak and unstable at low concentrations. Besides, some trace elements in the soil are below the detection limit of LIBS, and other elements are distributed outside the effective band of the spectrometer, so their stable characteristic lines cannot be detected under these experimental conditions.

3. Applications of LIBS in Soil Sensing.

The common nutrition elements in the soil are C, N, P, K, Si, S, Ca, Mg, etc. These elements promote the healthy growth of plants and are also a basic guarantee for maintaining normal physiological activities of crops. Therefore, the content of these elements determines the level of soil fertility.

(i) Detection of C Content in Soil.

Carbon (C) element is one of the most basic constituent elements of the soil. Its content is directly related to the water-holding capacity of the soil and reflects the fertility and other characteristics of soil. As a fast and nondestructive method of spectrochemical analysis, LIBS technology has attracted the attention of many researchers, letting them use it to analyze and detect carbon in soil.

Cremers et al. (2001) first applied LIBS spectroscopy to measure soil organic carbon content. A 1064 nm laser wavelength was used to detect soil organic matter in some farms and woodlands in Colorado and New Mexico. The detection limit of LIBS is 300 mg·kg^{-1}, and the precision is 4~5%. With further research, Martin et al. (2003, 2010) explored the effect of key detection parameters, including laser wavelength and excitation energy, as well as univariate and multivariate methods on detection accuracy, in order to build a robust calibration model to predict soil organic carbon concentration. The carbon signal of LIBS at 247.8 nm measured on 20 pellets from each homogenized soil sample was shown to be highly correlated (coefficient of determination, $R^2 = 0.962$) with the organic carbon content measured by dry combustion using an elemental analyzer. Glumac et al. (2010) successfully explored a method to avoid the interference of neutral and single ionized Fe lines to the standard detection line of LIBS at 247.8 nm. A low-power Nd:YAG laser with a wavelength of 532 nm was used to optimize the high dispersion of the LIBS signal and time-gating strategy to minimize interference signals and maintain a high signal-to-noise ratio. Martin et al. (2013) used LIBS technology combined with multivariate data analysis methods to distinguish total carbon (TC), inorganic carbon (IC), and organic carbon (OC) in 58 soil samples from 5 places. The results showed that the correlation coefficients of TC, IC, and OC contents predicted by LIBS are 0.91, 0.87, and 0.91, respectively. Izaurralde et al. (2013) used LIBS technology, diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS), and inelastic neutron scattering (INS) methods to determine the carbon content of field soil, and these three methods have achieved ideal measurement results.

(ii) Detection of Kalium Content in Soil.

Kalium (K) is one of the important nutrients in the soil and plays a significant role in plant growth. The nutritional functions of K on plants include promoting the activation of various enzymes in plants; improving photosynthesis, sugar metabolism, and protein synthesis; and enhancing the plant's ability to resist drought, cold, and pests. Dong et al. (2013a, b) analyzed the farmland soil with K content between 8.74 and 34.56 g·kg^{-1} by using the LIBS technique at 766.49 nm spectral line and established a quantitative model for predicting K content in soil. The correlation coefficient of the quantitative model is 0.935, and the predicted standard deviation is 9.26%. Meng et al. (2014) used a pulsed laser with a wavelength of 1046 nm as the excitation light source to study the spectral characteristics of potassium in soil. A spectral line of 769.9 nm was used as the analysis line of potassium. The optimal detection delay was 1 μs and the optimal gate width was 5.2 μs. The prediction curve of the soil K was obtained, and the relative error between the predicted value and the true value was less than 5%. The results of this study provide a theoretical foundation for rapid and on-site quantitative detection of K element in soil.

In order to meet the urgent needs of online detection of soil K nutrients in the field, Zhang et al. (2014) designed a system for online detection of soil nutrients based on LIBS (Fig. 3.6) and carried out an experimental study of rapid determination of soil nutrients. The results showed that the characteristic absorption spectrum of soil potassium was at the wavelengths of 766.49 nm and 769.90 nm. The potassium nutrient content was positively correlated with the intensity of the specific wavelength, but when the mass fraction of potassium was greater than 0.3%, there was a significant self-absorption, and the relationship between potassium content and spectral intensity became nonlinear. The determinate coefficient of the model was 0.9337, the root mean square error was only 0.2761, and the minimum detection limit of soil potassium nutrients was 212 μg/g, which met the requirements for online detection of soil potassium nutrients.

(iii) Detection of Other Elements in Soil.

For other nutritional elements, such as N, P, and Ca, researchers have also obtained rich research findings using LIBS technology. Lu et al. (2013) used the calibration curve method to establish the relationship model between the intensity of LIBS spectrum and the contents of total nitrogen (TN) and total phosphorus (TP) in soil, indicating that there is a close correlation between them: the correlation coefficient of TN is 0.981, and the correlation coefficient of TP is 0.868. Dong et al. (2013a, b) studied the characteristics of N element with LIBS spectrum. The laser energy had an influence on the detection results, and the correlation coefficient between N content and the intensity of LIBS spectral lines is 0.996. Hussain et al. (2007) conducted a study on the distribution of nutrient elements in greenhouse soils using LIBS technology. Using the calibration curve method, the content of Ca,

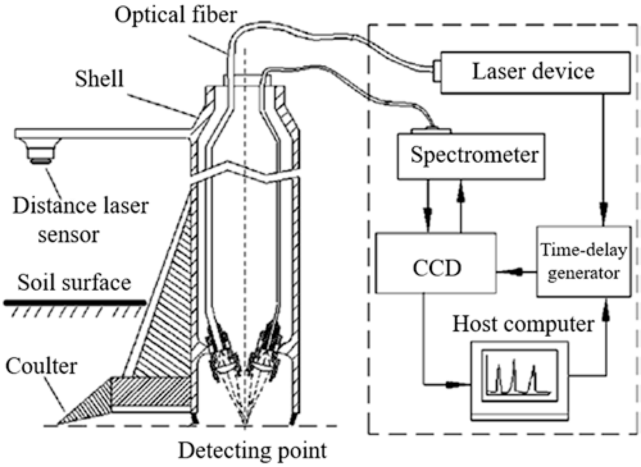


Fig. 3.6 Structure of soil nutrient detection system of LIBS. (Zhang et al. 2014)

K, P, Mg, Fe, S, Ni, and Ba in the soil samples was measured as 12, 9, 7, 9, 7, 10, 8, and 12 mg·kg^{-1}, respectively. Wang et al. (2017) used LIBS technology to quantitatively detect nutrients in soil. An Nd:YAG pulsed laser with an output wavelength of 1064 nm and a pulse width of 5.82 ns was used as the light source. Based on the traditional LIBS system, a beam expander system and a real-time monitoring system were added; as a result, a cage-type LIBS system was developed to optimize the laser focus position of the beam expander system in the cage structure, and an optimal laser focus position of 0.2 cm was obtained. The contents of Cu, Mn, Mg, and K in the soil were quantitatively analyzed. Their detection limits were 0.42×10^{-6}, 13.2×10^{-6}, 38.5×10^{-6}, and 62×10^{-6}, respectively, which was better than that of the traditional LIBS systems. The mass fractions of Cu, Mn, Mg, and K elements in the soil were predicted, and the average relative errors of their predicted values were 9.2%, 9.6%, 8.5%, and 10.9%, respectively.

LIBS method has the advantages of short analysis time, acceptable detection limit and high accuracy, etc. However, the effects of different soil properties, such as texture, carbonate, total soil C, moisture, clay mineralogy, and silicon content on LIBS measurements, should be studied more extensively. In addition, the potential of field portable LIBS instruments to measure soil nutrients in situ and in complete soil profiles should be explored in future studies to expand the applicability of LIBS detection to soil nutrients.

3.2.4 Multispectral and Hyperspectral Imaging Sensing Technology for Soil Nutrients

Vis/NIR spectroscopy has been rapidly popularized to detect soil properties, because it can not only detect the organic components of the soil but also identify the mineral components and the texture of the soil; meanwhile, the detection speed is much faster than traditional methods. However, the spectral analysis technology can only obtain the point spectral information of the sample, and the spectral information acquired is not comprehensive. Hyperspectral imaging technology has the dual advantages of both spectral analysis and image analysis technologies and can obtain the spectral information, planar information, and spatial information of the detection object simultaneously. It can accurately collect information of each pixel at a minimum of nanometer level, and the information obtained is more comprehensive, specific, and accurate.

Sorenson et al. (2018) used a SisuROCK automated hyperspectral imaging system in laboratory to detect soil organic carbon (SOC) and total nitrogen (TN) content in discrete, intact, and unground soil and evaluated the potential of spectral imaging technology to replace traditional chemical analysis for predicting spatial distributions of soil components. After completing the spectral detection, soil samples were analyzed for SOC and TN concentrations by dry combustion. Spatial variation of carbon and nitrogen was determined using Moran's I and comparisons of spatial variations among soil types. The TN in turn showed more aggregation for all soil types and horizons compared to SOC. In this study, imaging spectroscopy was successfully used to measure and characterize the spatial variability of SOC and TN at the soil aggregate scale.

Hyperspectral remote sensing technology has been applied to soil detection due to its extremely high spectral resolution. Qualitative and quantitative detection on soil nutrient using remote sensing technology began in the 1960s. Various components in the soil have characteristic absorptions in the range of the solar reflection spectrum, so the relationship between soil components and absorption spectra can be used to predict the material composition in soil. The development of spectral remote sensing makes it possible to quickly and widely obtain soil physical and chemical information. Zhang et al. (2019a, b) used remote sensing methods to determine spatial distribution of soil total nitrogen (STN). A random forest (RF) model was used to estimate the spatial distribution of STN content by combining 21 prediction factors such as the original band (O), the normal spectral index (S), the red edge index (R), and the environmental variable (E). The results indicated that the best prediction performance can be obtained by combining the RF model with the original band, normal spectral index, red edge index, and environmental variable (O + S + E + R). The RF-based remote sensing method proposed in this research can accurately capture the change of STN, and the performance of the prediction model can be improved by providing appropriate prediction factors. Lu et al. (2018) evaluated the detection method of organic matter (SOC) based on remote sensing imaging from land satellites, and the spatial distribution and dynamic changes of organic matter were analyzed using random forest (RF) and geographic weighted regression (GWR). The results show that the root mean square error of RF was 4.6 g/kg in 2008 and 4.4 g/kg in 2013, which is better than the GWR prediction model.

3.3 Instruments of Soil Nutrient Detection

Applying spectroscopic techniques to detect physical and chemical parameters of soil can not only reduce the time and cost of analysis but also realize the in situ and real-time detection of soil information, which is conducive to promote the application of precision agriculture. At present, scientists engaged in the research of soil fertility management and agricultural information technology have developed various forms of soil testing instruments based on spectral technology, such as portable, vehicle-mounted, and remote sensing devices. Through these devices, it is convenient to implement comprehensive, full-range, all-weather, and real-time monitoring of soils from three spatial dimensions of ground, air, and satellite, providing a prerequisite for intelligent on-demand variable operations and ensuring increased grain production and efficiency.

3.3.1 Portable Instruments of Soil Nutrient Detection

Vis/NIR spectroscopy is efficient to detect the soil temperature, humidity, organic matter, nitrogen, phosphorus, potassium, and other components. Based on the spectroscopy, various portable soil devices have been extensively researched, which can realize an in situ and real-time detection of soil parameters. Sudduth and Hummel (1993) developed a portable real-time soil sensor, which was mainly used to measure the organic matter content in the soil surface. Figure 3.7 shows the structure diagram of the portable instrument, which is mainly composed of three parts: light source, beam splitting, and measurement unit. The light source consists of a light bulb and a focusing lens, where the light bulb is an iodine tungsten lamp and can stably provide light source of Vis/NIR. The main components of the beam splitting are an entrance slit, a focusing lens, a filter disk, an angle sensor, and an optical fiber entrance port. Among them, the key component is the filter disk, which can be rotated by a drive motor to continuously produce rays of 1650~2600 nm, and the

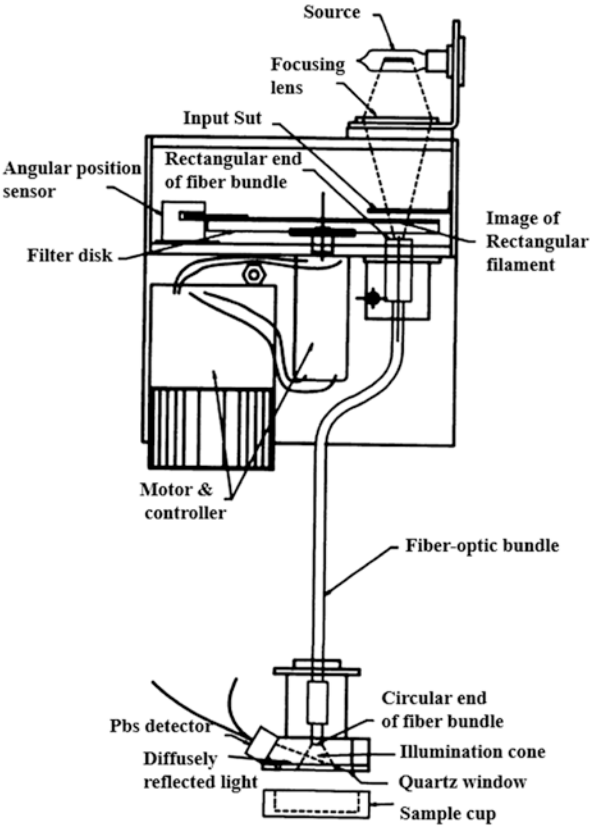


Fig. 3.7 Portable soil sensor. (Sudduth and Hummel 1993)

spectral resolution is below 55 nm. The measurement unit mainly includes an exit port of optical fiber, quartz plates, a sample box, and a photosensor. The photosensor provides stable photoelectric response in a wide spectral range of visible and near infrared, which is used to obtain the soil reflective spectrum and then achieve the prediction of soil organic matter content.

Li et al. (2010) developed a portable device for organic matter measurement, which could detect soil organic matter up to a depth of 30 cm. This measuring instrument was mainly composed of an optical module and an electronic module. The optical module included a light source, an optical signal transmission fiber, and a photoelectric conversion device. The electronic module included a driving circuit of light source, an amplifying circuit, an A/D conversion circuit, a liquid crystal display, a storage circuit of U disk, etc. (Fig. 3.8). The device used 850 nm LED as the light source. In order to minimize the energy consumption of incident and reflected light, a Y-type glass fiber was designed for input and output of the light source. When working, the probe was inserted into the soil to form a closed space, and then the rays from the light source was transmitted to the top of the probe and illuminated the soil around. The diffuse reflection rays from the soil were transmitted to the photoelectric conversion device, and the generated current was sent to the circuit unit for amplification, filtering, and storage. Under the condition of natural soil samples (about 20% moisture content), the coefficient of determination between the spectral absorbance and the content of soil organic matter was 0.950, and as for dry soil samples, the coefficient of determination was 0.982.

Based on the measurement device of soil organic matter above, An et al. (2012) developed a portable soil analyzer to obtain nitrogen content. The number of wavelengths used was increased from 1 to 7 wavelengths: 1550, 1450, 1300, 1200, 1100, 1050, and 940 nm. Its schematic diagram is shown in Fig. 3.9. When it is working, the probe is inserted into the soil and the code disk rotates sequentially to get the soil

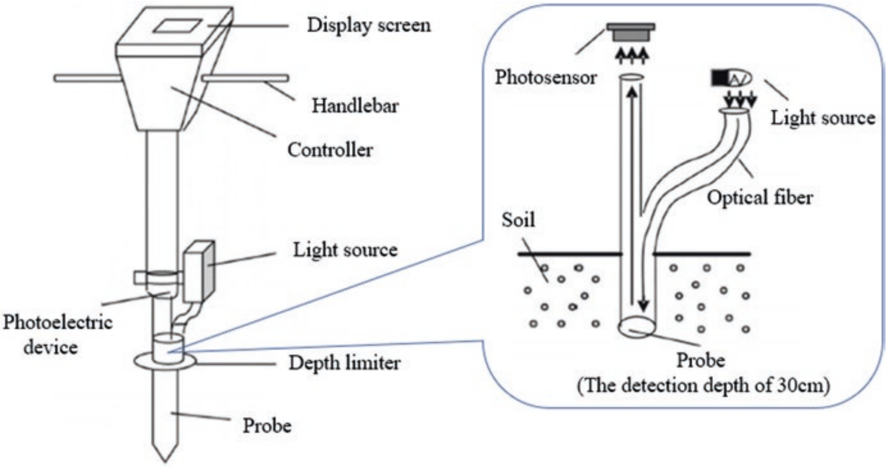


Fig. 3.8 Structure of soil detection device for organic matter. (Li et al. 2010)

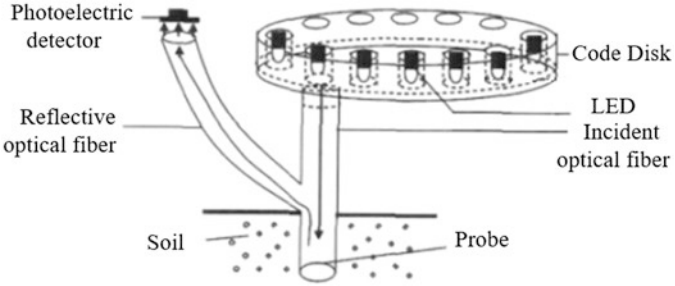


Fig. 3.9 Schematic diagram of portable tester for soil nitrogen content. (An et al. 2012)

Table 3.1 Measurement result using ASD and portable detection equipment. (Zhang 2015)

ASD instrument	Method	Wave number	Modeling set		Prediction set		
	SPA-LS-SVM	5	R^2	RMSEP	R^2	RMSEP	RPD
			0.80	0.0038	0.80	0.0031	2.26
Portable detection equipment	Method	Wave number	Modeling set		Prediction set		
	SPA-LS-SVM	15	R^2	RMSEP	R^2	RMSEP	RPD
			0.63	0.0079	0.62	0.0080	1.57

reflectance at 7 wavelengths, and then the total soil nitrogen content was obtained according to the established prediction model of soil nitrogen. The experimental results showed that the correlation coefficients of calibration and prediction for soil total nitrogen were 0.81 and 0.80, respectively.

Zhang (2015) developed a set of portable detection equipment for soil nutrient using hyperspectral analysis of Vis/NIR. The hardware part of the equipment is composed of the chassis shell, optical fiber, voltage conversion module, light source, drive circuit, integrated development board, power supply, touch screen, etc. The software part consists of the function loading module, spectrum acquisition module, data preservation module, display module, and parameter setting module. The core hardware component of the soil detection device is a USB4000 spectrometer. The optical fiber used for data collection is a Y-shaped optical fiber, which can also be replaced by two independent optical fibers (one for collecting data and one for receiving data). Then, a quantitative prediction model of near-infrared spectrum for soil total nitrogen (STN) content was established based on characteristic wavelengths. The results of portable instrument and ASD instrument to detect STN were shown in Table 3.1. The accuracy of portable instruments is inferior to ASD (350~2500 nm wavelength range) instruments, which is largely due to the size of the core component USB4000 which is only about a quarter of the ASD spectrometer, and the noise of the spectral data collected by the USB4000 spectrum is significantly greater than the spectral data obtained by the ASD.

3.3.2 Airborne Equipment of Soil Nutrient Detection

The UAVs (unmanned aerial vehicles) combined with remote sensing technology can quickly obtain the spectral data of soil and plants and achieve a monitoring of soil nutrients or plant growth information in large scale. UAVs can be classified as multi-rotor drones, fixed-wing drones, and helicopters according to the types of the flying platform (Fig. 3.10a). Multi-rotor drones have the most applications in soil remote sensing due to their simple control, no need for special runways to take off and land, and capability of hovering in the air after takeoff. In the field of consumer drones, the companies such as DJI and Parrot already have mature flight control platforms of multi-rotor drones, which can be conveniently equipped with various airborne cameras for remote sensing of soil nutrients. In addition, the drones gather spectral data by push broom scanning or hovering. In the push broom scanning mode, the drone takes continuous images of the soil while flying. After the acquisition is completed, image stitching and correction are conducted to complete a remote sensing image. In this mode, the data collection efficiency is high, but the data processing is troublesome. Under the hovering mode, the drone hovering in the air obtains a whole spectral image of the soil directly and does not require complex splicing in subsequent research work. However, its image acquisition efficiency is relatively low compared to the drone of push broom scanning (Fig. 3.10b).

In the actual soil information detection, the corresponding airborne equipment should be selected for remote sensing tasks according to the target component of the soil. RGB camera can be used to detect soil texture, type, organic matter, and other components. Vis/NIR camera can detect soil nitrogen, phosphorus, potassium, calcium, magnesium, aluminum, and other components. Thermal infrared camera can detect the surface temperature and humidity of soil, and Lidar can analyze the texture and terrain of the soil in three dimensions. Guo et al. (2019) used Vis/NIR remote sensing technology combined with partial least square regression model to predict the soil organic matter composition and obtained high prediction accuracy.

(a) Platforms and airborne equipment (b) Hovering method and airborne camera

Fig. 3.10 Remote sensing based on UAVs for soil nutrient detection (**a**) Platforms and airborne equipment (**b**) Hovering method and airborne camera

Quebrajo et al. (2018) applied drone thermal infrared remote sensing technology to detect the water content of the soil, demonstrating the technological feasibility for the intelligent irrigation of sugar beets.

3.3.3 Satellite-Based Equipment for Soil Nutrient Detection

A satellite remote sensing system usually consists of satellites in the space and ground stations and client applications in the ground. The satellites are used to collect spectral information from Earth's surface at large scale and send the data to the ground stations. After that, the data are transmitted to the users by the ground station and then are processed and analyzed for obtaining remote sensing images. Satellite-based equipment is a key instrument for sensing soil nutrients. There are many forms of equipment that can be mounted on satellites, such as visible, NIR, and MIR cameras, multispectral scanners, and microwave radiometers. At present, satellite-based sensors are developing in the direction of multi-spectrum, multi-polarization, miniaturization, and high resolution.

Countries around the world have launched their own remote sensing satellites. Typical satellites that can be used for agricultural remote sensing are shown in Table 3.2. These satellites are equipped with Vis/NIR bands that can be used to detect soil nutrients or other soil properties. The spatial resolution is 10~30 m, and the revisit period is 4~44 days, which meets the needs for a wide range of soil monitoring. Zhai (2019) used GF-1 and Landsat 8 satellites to detect the organic content of soil. The results show that the reflectance of remote sensing images in the visible and NIR bands is significantly related to soil organic matter, and remote sensing images from Landsat 8 and GF-1 have similar prediction capabilities for organic matter. However, considering that GF-1 has higher spatial resolution and shorter revisit periods, it can replace the commonly used Landsat 8 to detect soil organic matter content. Zhang et al. (2019a, b) applied five satellites to observe soil moisture, which not only improved the spatial coverage of daily observations but also improved the accuracy of predicting soil moisture: the accuracy of soil moisture detection increased by 57.7% in Anhui Province, China, and 9.1% in Central Tibet, China.

Table 3.2 Parameters of main satellites

Model	Spatial resolution (m)	Waveband (nm)				Revisit period (day)	Country
		Blue	Green	Red	NIR		
GF-1	16	450 ~ 520	520 ~ 590	630 ~ 690	770 ~ 890	4	China
Landsat 8	30	450 ~ 515	525 ~ 600	630 ~ 680	845 ~ 885	16	USA
SPOT-5	10	/	495 ~ 605	617 ~ 687	780 ~ 893	26	France
JERS-1	18	/	520 ~ 660	630 ~ 690	760 ~ 860	44	Japan

Due to the influence of atmospheric conditions, data quality, and applicability of inversion models, it is difficult to achieve a prediction accuracy of more than 90% with only one satellite for the detection of soil parameters. Integrating multiple satellites to detect soil nutrients is one of the methods to improve the detection accuracy. In addition, in the study of satellite remote sensing for soil information, more research should be focused on parameter optimization and calibration methods of inversion models in order to further improve the sensing accuracy of soil by satellites.

3.3.4 Sensors in Internet of Things of Soil Nutrient Detection

Sensors, such as moisture, temperature, and nutrient sensors, are commonly used for monitoring soil characteristics in Internet of Things (IoT). The soil information monitored is transmitted to the cloud via wireless networks of Zigbee, Bluetooth, or WIFI, and then users can remotely retrieve soil data in cloud for obtaining the soil moisture and nutrient content to develop irrigation and fertilization strategies (Fig. 3.11).

In the detection of soil information, there is a requirement for monitoring soil moisture in real time and around the clock. Zhang et al. (2009) used Zigbee to connect soil moisture sensors and meteorological sensors to the network and developed an automatic monitoring and irrigation system for soil management based on fuzzy control algorithm. The wireless sensor network system is shown in Fig. 3.12. The system obtains real-time humidity of the soil and meteorological information such as ambient light, temperature, and wind speed. The established mathematical model calculates the moisture evaporations of soil and farmland, and then the intelligent

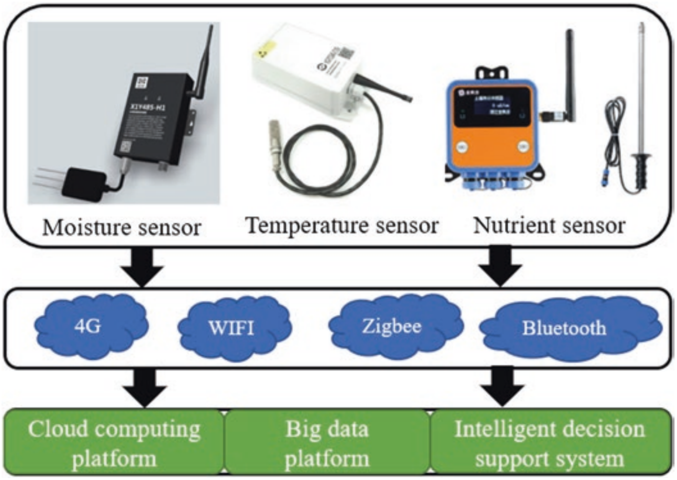


Fig. 3.11 Soil sensors of IoT

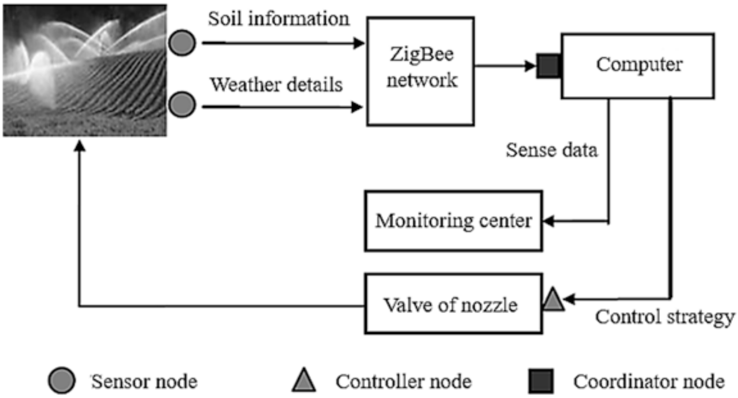


Fig. 3.12 Information flowchart of wireless sensor network system. (Zhang et al. 2009)

decision-making system takes the two evaporation values as the input parameters of irrigation system to spray the crops on demand. Its saving effect of water is significant.

3.4 Summary

The detection method of Vis/NIR spectroscopy has achieved high accuracy for predicting soil nutrients such as nitrogen, phosphorus, potassium, and organic matter content. Therefore, developing portable soil detectors as well as airborne- and satellite-based sensors based on Vis/NIR spectroscopy for rapidly detecting soil nutrients will play an important role in the extension of precision fertilization by soil testing. LIBS has a strong ability of detecting heavy metals in soil and is therefore a promising technique for soil nutrient detection. Revealing the absorption characteristics of LIBS under different soil types, structures, and components is the research focus that needs to be carried out.

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