Chapter 6
Spectral Reflectance of Soils

6.1 Introduction

The intimate knowledge of the spectral behaviour of soils is a key to their identification and characterization using remote sensing techniques. Nearly the entire shortwave solar radiation in the optical domain (from 300 to 2500 nm) incident on soil surface is either absorbed or reflected, and only a little of it is transmitted. The solid phase of the soil, mainly composed of different sized opaque particles covered by organic matter and minerals (mostly clay, iron oxides and calcium carbonate), such as liquid and gas phases, decides the soil reflectance. These physicochemical properties, as well as the direction of the incident radiation and the direction along which the reflected radiation is viewed by a sensor, are considered to be the main influences on the reflectance of a soil sample with disturbed surface under laboratory conditions. Under field conditions the list of these properties must be completed with soil surface roughness that is usually higher and much more variable. Hence, the reflectance of a soil studied under these conditions may not be directly comparable with the reflectance of the same soil analysed under laboratory conditions.

While soil colour provides pedologists with a useful concept for recognizing, characterizing and describing soils, soil colour descriptions are limited by the sensitivity of the human eye and the subjectivity of human perception. Modern spectrometers and radiometers allow us to observe more precisely and objectively the intensity of radiation reflected by soils across the wavelength range of natural solar illumination. These instruments allow us to measure, plot recognize and analyse soil reflectance spectra. A soil reflectance spectrum, set of data or a graphy that provides the relative intensity, is expressed relative to the intensity of the illuminating radiation. Soil reflectance values are often determined, from a practical standpoint, by taking a ratio of the energy reflected by a soil surface to the energy reflected by a bright, diffuse reference material. This approach requires the soil and reference surface to be illuminated and observed in exactly the same manner with

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respect to the positions of the sensor and the Sun or other source of illumination (Palmer 1982; Baumgardner et al. 1985; Jackson et al. 1987).

6.2 Background

To provide a better understanding of soil spectra, in this section we provide background information on the electromagnetic spectrum, radiation interactions with soil and soil attributes that affect their spectral response patterns. This discussion is limited primarily to the region 0.4 through 2.5 μm of the electromagnetic spectrum, which can be separated into three regions; visible (0.4–0.7 μm) near-infrared (0.7–1.1 μm) and shortwave infrared (SWIR; 1.1–2.5 μm) (Gupta 2003).

6.2.1 Energy—Matter Interactions

Characteristics of electromagnetic radiation are altered when radiation interacts with matter (e.g. when radiation is scattered from a soil surface). An understanding of the mechanisms responsible for the alterations requires a quantum mechanical concept of matter at the atomic and molecular levels. The electromagnetic radiation is emitted or absorbed when an atom or molecule makes a transition between energy states. The energy of an emitted or absorbed photon equals the difference between the energy levels. Furthermore, the energy-level transitions must be accompanied either by a redistribution of the electric charge carried by electrons and nucleic protons or by a reorientation of nuclear or electronic spins before a photon is emitted or absorbed (Hunt 1980). The absorption or emission of shortwave radiation usually results from energy-level transitions accompanied by charge redistributions involving either the motion of atomic nuclei or the configuration of electrons in atomic and molecular structures.

6.2.1.1 Vibrational Transitions

A portion of the energy possessed by an atomic or molecular system is by virtue of the transitional, rotational and vibrational motion of the atomic nuclei. Nucleic translations and rotations are restricted in most soil materials and thus do not play a major role in soil interactions with solar radiations. Transitions of vibrational motion, however, significantly affect these interactions. The vibrational motions consist of oscillations in the relative positions of bonded atomic nuclei. The oscillations either stretch molecular bond lengths or bend inter-bond angles. Energy-level transitions that involve nuclear vibrations typically result in the absorption or emission of radiation within the infrared portion of the spectrum (Hunt 1980).

A molecule possesses several modes of vibration, depending on the number and arrangement of atoms in the molecule. A molecule with N atoms that are arranged nonlinearly has 3N—6 normal modes of vibration, but a linear molecule has 3N—5 such modes.

According to the laws of quantum mechanics, only discrete energy levels may be associated with each vibrational model of a molecule. The lowest allowable energy level for each mode is referred to as a ground level. Transitions between the energy levels of each result in the emission or absorption of radiation at specific frequencies. The frequencies/wavelengths associated with transitions between a ground level and the next-highest energy level are called fundamental bands. The absorbed (or emitted) wavelengths are called overtone bands when a vibrational mode transits from one state to a state more than one energy level above (or below) the original state. Combination bands refer to frequencies associated with transitions of more than one vibrational mode. These combined transitions occur when the energy of an absorbed photon is split between more than one mode.

The vibrational transitions corresponding to the fundamental bands are generally more likely to occur than transitions corresponding to the combination and overtone bands. Absorption features in reflectance and transmittance spectra are therefore usually strongest for the fundamental bands. Remote sensing within the solar portion of the spectrum restricts the detection of vibrational transitions in soil materials primarily due to the observation of overtone and combination bands (Hunt 1980).

The vibrational transitions corresponding to the fundamental bands are generally more likely to occur than transitions corresponding to the combination and overtone bands. Absorption features in reflectance and transmittance spectra are therefore usually strongest for the fundamental bands. Infrared spectroscopy is a useful laboratory method for soil analyses because the fundamental bands for most soil minerals occur in the infrared at wavelengths between 2500 and 50,000 nm (White and Roth 1986). Remote sensing within the solar portion of the spectrum restricts the detection of vibrational transitions in soil materials primarily to the observation of overtone and combination bands (Hunt 1980).

6.2.1.2 Electron Transitions

In contrast to the infrared bands associated with vibrational transitions, the bands associated with electron transitions generally occur in the ultraviolet and visible portions of the spectrum. The location of these bands is due to the relatively large gaps between electron energy states. As per principles of quantum mechanics each electron of an atom, ion or molecule can exist in only certain states corresponding to discrete energy levels. Numerous mechanisms have been identified to explain the role of electrons in the absorption and emission of radiation by molecules and crystals. Although not all of the electronic excitations require ultraviolet photons, the mechanisms usually require energy quanta greater than the quanta involved in vibrational transitions.

6.2.1.3 Radiation Interactions with a Volume of Soil

The process of radiation scattering by soils results from a multitude of quantum mechanical interactions with the enormous number and variety of atoms, molecules and crystals in a macroscopic volume of soil. In contrast to certain absorption features, most characteristics of the scattered radiation are not attributable to a specific quantum mechanical interaction. The effects of a particular mechanism often become obscure in the composite effect of all the interactions. The difficulty in accounting for the effects of a large number of complex quantum mechanical interactions often leads to the use of non-quantum mechanical models of electromagnetic radiation.

6.2.1.4 Refractive Indices

The optical properties of a substance are those properties that determine its effect on incident radiation. The fundamental optical properties of a substance are embodied in a wavelength-dependent quantity called the *complex refractive index*

$$n = n_r - \imath n_i, \tag{6.1}$$

where n often represents both the principal quantum number and the complex refractive index by convention. The symbol, n represents the complex refractive index from this point forward.

6.3 Models of Radiation Scattered by Soils

The spectral response pattern of most Earth surfaces including soils are anisotropic with respect to view and illumination angles. The geometry of both illumination and observation irradiance and radiance plays a major role in deriving the soil spectrum. The reflectance from a surface depends upon the direction of incident radiation (and its characteristics), the surface radiative properties and the direction from which the surface is being viewed. The bidirectional reflectance distribution function (BRDF) assumes that the radiation source, the target and the sensor are all points in the measurements space and that the ratio calculated between absolute values of radiance and irradiance is strongly dependent on the geometry of their positions. This phenomenon can be described by the bidirectional reflectance distribution function (BRDF). The BRDF of a particular target represents the reflectance at all possible illumination and sensor view angles. BRDF is defined as the ratio of the radiance L (W m^2 sr^{-1} μm^{-1}) reflected in direction ($\theta_{V,}$ φv) to the incident irradiance E (W m^2 μm^{-1}) from a specific direction ($\theta_{i,}$ φi). Theories and models explaining the BRDF phenomena in relation to soil components are widely discussed and covered in the literature (Liang and Townshend 1966; Hapke 1981a, b, 1984, 1993; Pinty et al. 1989; Jacquemoud et al. 1992). Mathematically BRDF can be expressed as

$$\mathrm{BRDF} = \frac{\mathrm{L}(\theta_V, \phi v)}{\mathrm{E}(\theta i, \phi i)}, \tag{6.2}$$

where θ_V and, ϕv are viewing zenith and azimuth angles, respectively, θi, and ϕi are the zenith and azimuth angles of the irradiance, respectively (Fig. 6.1).

As BRDF is a characteristic of reflectance referring to a monodirectional illumination at all possible angles of collection, it is impossible to measure under natural conditions (Cierniewski and Courault 1993). However, the BRDF of natural surfaces can be estimated by means of the bidirectional reflectance factor (BRF), which is defined as the radiance reflected by the surface to the radiance which would be reflected by a perfect Lambertian panel, both under the same illumination and viewing conditions (Nicodemus et al. 1977).If the soil is homogeneous, a small

$$\mathrm{BRF}(\phi i, \theta i; \phi v, \theta v) = \frac{\mathrm{Lt}(\phi i, \theta i; \phi v, \theta v)}{\mathrm{Lp}(\phi i, \theta i; \phi v, \theta v)}, \tag{6.3}$$

where Lt is the radiance reflected by a target surface and Lp is the radiance reflected by a perfect Lambertian panel.

Whereas the BRDF is better suited for remote sensing applications, in the laboratory, hemispheric and bidirectional reflectance factors are also used (Baumgardner et al. 1985). To reduce the effects of geometry and to eliminate systematic and nonsystematic measurement interferences, reflectance standards such as MgO, $BaSO_4$ and Halon are often used to correct the reflectance spectrum relatively (Tkachuk and Law 1978; Young et al. 1980; Weindner and Hsia 1981).

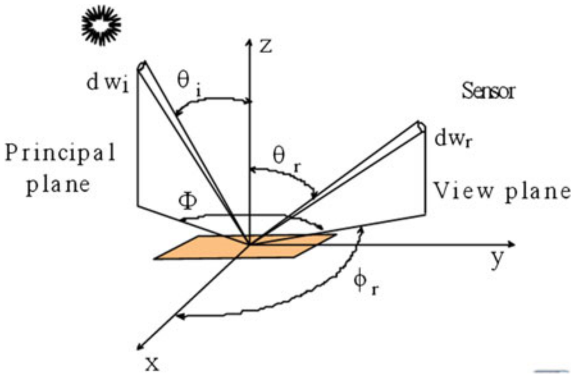

Fig. 6.1 Coordinate system defining geometry of incident and reflected elementary beams: dω (solid angle element), θ (zenith angle), φ (azimuth angle), i (illumination direction), r (viewing direction) and Φ (azimuth relative angle)

Another factor that affects the soil spectra is the sensor's field of view (FOV) and Sun target geometry. If the soil is homogeneous, a small FOV may be sufficient. However, where some variation occurs in the soil, the FOV should be adjusted to cover a representative portion of the soil.

A number of models have been developed that express soil bidirectional reflectance, as a function of illumination and viewing direction [i.e. soil bidirectional reflectance distribution function (BRDF) models]. Several different methods have been applied to the development of these models. The methods include the formulation of empirical functions, the calculation of the relative fraction of illuminated and shadowed surface area on rough surfaces, the use of rough surface scattering theory and the application of radiative transfer theory.

6.4 Spectroscopy

Field spectroscopy pre-dates the development of imaging spectrometry by many years (Milton et al. 2009). Field spectroradiometers were first used to study human colour vision, and in particular the colour of the Earth's surface from the air (Penndorf 1956). Spectroscopy measures light that is emitted, absorbed or scattered by materials and can be used to study, identify and quantify those materials. Spectroscopy is the study of the absorption and emission of light and other radiation by matter, as related to the dependence of these processes on the wavelength of the radiation. More recently, the definition has been expanded to include the study of the interactions between particles such as electrons, protons and ions, as well as their interaction with other particles as a function of their collision energy (http://www.britannica.com/science/spectroscopy Accessed on 25 February 2016). It measures light that is emitted, absorbed or scattered by materials and can be used to study, identify and quantify those materials. Typically two distinctive classes of spectra: *continuous* and *discrete* can be observed. For a continuous spectrum, the light is composed of a wide, continuous range of colours (energies). With discrete spectra, one sees only bright or dark lines at very distinct and sharply defined colours (energies). *Continuous spectra* arise from dense gases or solid objects which radiate their heat away through the production of light. Such objects emit light over a broad range of wavelengths, thus the apparent spectrum seems smooth and continuous. There are two types of discrete spectra, emission (bright line spectra) and *absorption* (dark line spectra). Based on the region of electromagnetic radiation utilized for spectroscopic analysis spectroscopy can be categorized into the following:

Ultraviolet–Visible Spectroscopy: Absorption of this relatively high-energy light causes electronic excitation. The easily accessible part of this region (wavelengths of 200–800 nm) shows absorption only if conjugated pi-electron systems are present.

Visible and infrared diffuse reflectance spectroscopy: In visible and infrared diffuse reflectance spectroscop*y*, radiation in corresponding wavelengths is directed to the sample, and a spectrum is generated. Depending on the constituents present in the soil, the radiation will cause individual molecular bonds to vibrate, either by bending or stretching, and they will absorb light, to various degrees, with a specific energy quantum corresponding to the difference between two energy levels. As the energy quantum is inversely related to wavelength, the resulting absorption spectrum produces a characteristic shape that can be used for analytical purposes (Miller 2001). The frequencies at which light is absorbed appear as a reduced signal of reflected radiation and are displayed in % reflectance (R), which can then be transformed to The wavelengths at which light is absorbed appear as a reduced signal of reflected radiation and are displayed in % reflectance (R), which can then be transformed to apparent absorbance

$$A = \log(1/R). \tag{6.4}$$

The wavelength at which the absorption takes place (i.e. the size of the energy quantum) depends also on the chemical matrix and environmental factors such as neighbouring functional groups and temperature, allowing for the detection of a range of molecules which may contain the same type of bonds.

6.4.1 Infrared Spectroscopy

Infrared spectroscopy is the analysis of infrared light interacting with a molecule. Infrared light striking a molecule causes vibrational and rotational changes. The measurements of vibrations of atoms enable determining the functional groups. Generally, stronger bonds and light atoms will vibrate at a high stretching frequency (wave number). The possible rotations are around the axis of symmetry for a given molecule or either of the two perpendicular axes. Vibrations can be in the form of a bend or a stretch for each bond. This can be analysed by measuring absorption, emission and reflection. Apparatus for infrared spectroscopy can largely be divided into two types. One is *the dispersive IR spectrophotometer* that uses a diffraction grating for wavelength dispersion of an infrared ray for measurement. The other is the *Fourier transform infrared spectrophotometer* (FT–IR) that modulates an infrared light by an interferometer, measures the interference waveform, and subjects it to a Fourier transform to obtain a spectrum. Based on the kind of radiation measured, there are three techniques, viz. *transmission (absorption)*, *reflection* and *emission* methods. For further details you may refer to reviews of IR spectroscopy and its applications in soil science (Du and Zhau 2009; Du et al. 2015; Tiniti et al. 2015).

6.4.1.1 Infrared Transmission Spectroscopy

Transmission (absorption) spectroscopy is the oldest and most straightforward infrared technique. The method of analysis is based on the absorption of the infrared beam by a sample at specific wavelengths or frequencies of light. The infrared beam passing through a sample will produce an infrared spectrum unique to the sample itself. In this way, infrared spectroscopy is used as a qualitative measurement of a sample. The extent of absorption (A) of the infrared beam at a particular frequency or wavelength of light is defined by the Beer-Lambert law.

$$\mathrm{A} = \mathrm{abc}, \tag{6.5}$$

where a is the absorptivity coefficient, b is the path length and c is the concentration. Use of the Beer-Lambert law for infrared data determines how much of a sample is present and hence also provides for a quantitative measurement of a sample. The limitations of IR transmission spectroscopy include (1) possible reaction of the sample with the halide matrix, and (2) scattering and/or total absorption for samples with high concentrations and large particles relative to the infrared wavelengths.

6.4.1.2 Infrared Diffuse Reflectance Spectroscopy

In order to circumvent limitations of the infrared transmission spectroscopy, Nguyen et al. (1991) introduced the use of diffuse reflectance (DRIFT) for soil analysis. His study was qualitative in nature and was confined to band assignments. The subsequent studies (Janik et al. 1995; Janik and Skjemstad 1995) showed that mid-IR DRIFT could be used to quantify various soil components. Since then, the use of mid-IR DRIFT has been investigated in numerous soil studies (Reeves III 2010), and it has been acknowledged as the most commonly used technique for soil analysis.

Upon striking the soil particles, the energy that penetrates one or more particles is reflected in all directions and this component is called *diffuse reflectance*. In the diffuse reflectance (infrared) technique, commonly called Diffused Reflectance Infrared Fourier Transform (DRIFT), the DRIFT cell reflects radiation to the powder and connects the energy reflected back over a large angle. Diffusely scattered light can be collected directly from material in a sampling cup or, alternatively, from material collected by using an abrasive sampling pad. Kubelka and Munk developed a theory describing the diffuse reflectance process for powdered samples which relate the sample concentration to scattered radiation intensity. The Kubelka-Munk equation is as following (Kubelka and Munk 1931):

$$1 - \mathrm{R}^2/2\mathrm{R} = \mathrm{c}/\mathrm{k}, \tag{6.6}$$

where R is the absolute reflectance of the layer, c is the concentration and k is the molar absorption coefficient. An alternative relationship between the concentration and the reflected intensity is widely used in infrared diffuse reflectance spectroscopy, namely

$$\log(1/\mathrm{R}) = \mathrm{k}'\mathrm{c} \tag{6.7}$$

6.4.1.3 Infrared Attenuated Total Reflectance Spectroscopy

In the Attenuated Total Reflectance (ATR) method, the IR radiation propagates through a crystal with a high refractive index that is in contact with the sample. Mirrors are used to direct the IR beam toward the crystal at an angle that exceeds the critical angle for internal reflection, so that the radiation undergoes multiple reflections within the crystal. This critical angle θ_c depends on the refractive indices of the sample and ATR crystal according to (Fig. 6.2)

$$\theta_c = \sin^{-1}(n_2/n_1) \tag{6.8}$$

where n_1 and n_2 are the refractive indices of the crystal and the sample, respectively.

The crystal used in ATR cells are made from materials that have low solubility in water and are of a very high refractive index. Such materials include zinc selenide, germanium and thallium-iodide. Different designs of ATR cells allow both liquid and solid samples to be examined. It is also possible to set up a flow-through ATR cell by including an inlet and outlet in the apparatus. This allows for continuous flow of soil solutions through the cell and permits spectral changes to be monitored with time.

6.4.1.4 Infrared Photoacoustic Spectroscopy

Fourier Transform Infrared Photoacoustic Spectroscopy (FTIR-PAS) is a relatively new infrared technique that is based on photoacoustic theory. The phenomenon of the generation of sound when a material is illuminated with nonstationary (modulated or pulsed) light is called the photoacoustic effect. Photoacoustic spectroscopy differs from conventional optical techniques mainly in that, even though the incident energy is in the form of photons, the interaction of these photons with the

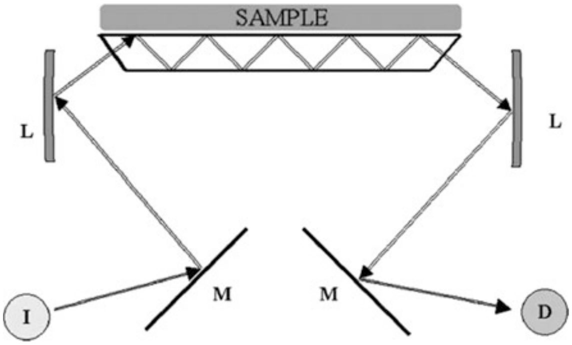

Fig. 6.2 Attenuated total reflectance (ATR) configuration. I denotes the incoming light (from the interferometer), D denotes the detector, L and M are lenses and mirrors (Reproduced from Etzion et al. 2004)

material under investigation is studied not through subsequent detection and analysis of photons after interaction (transmitted, reflected or scattered), but rather through a direct measurement of the effects of the energy absorbed by the material.

In FTIR-PAS the electromagnetic radiation is absorbed by molecules. Relaxation processes (such as collisions with other molecules) lead to local non-radioactive warming of the soil sample matrix. Pressure fluctuations are then generated by thermal expansion, which can be detected by a very sensitive microphone (Fig. 6.3) (Du et al. 2007). The resulting spectrum differs from both equivalent transmission and reflectance spectra (both diffusion reflectance spectrum and total attenuated reflectance spectrum) because the technique detects nonradioactive transitions in the sample. (http://www.nssmc.com/en/tech/report/nsc/pdf/n10014.pdf Accessed on 16 October 2015).

6.4.1.5 Emission Spectroscopy

Infrared emission spectroscopy is a method in which a sample is energized by heating, and the infrared light emitted from the sample is measured to obtain a spectrum (Fig. 6.4). Emission is a transition opposite in direction to absorption. A highly absorptive substance shows a high degree of emittance, and the number of waves in an emission band (peak) is the same as for an absorption peak. In the case of emission, however, the probability of there being an excited state is low and hence, the emission intensity is feeble. The spread of highly sensitive FT-IR has made it possible to measure even these weak emissions (Tasumi 1986; Hiraishi 1991). This method is applicable to rough metallic surfaces, powders including soils because (1) the infrared emission is isotropic and is hardly affected by the surface profile of the base material, and (2) it permits nondestructive, noncontact measurement of the sample and so on (Fig. 6.3).

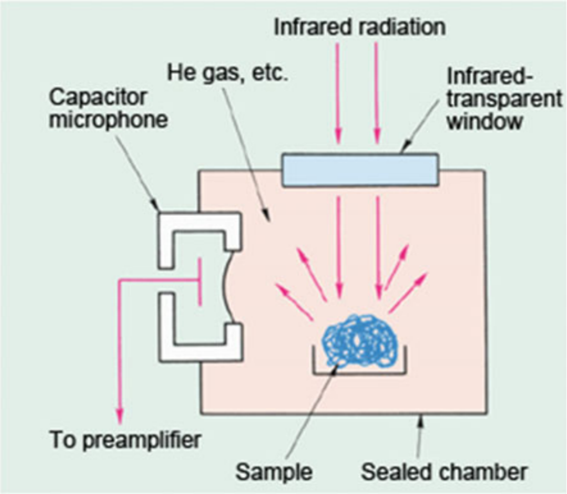

Fig. 6.3 Schematic description of photoacoustic spectroscopy (*Source* http://www.shimadzu.com/an/ftir/support/ftirtalk/talk7/intro.html 22-01-2016)

6.4.2 Fluorescence Spectroscopy

Fluorescence occurs when a fluorescent-capable material (a fluorophore) is excited into a higher electronic state by absorbing an incident photon and cannot return to the ground state except by emitting a photon. The emission usually occurs from the ground vibrational level of the excited electronic state and goes to an excited vibrational state of the ground electronic state. Thus fluorescence signals occur at longer wavelengths than absorbance. The energies and relative intensities of the fluorescence signals provide information about structure and environments of the fluorophores. Depending on the region of the electromagnetic spectrum being used the fluorescence spectroscopy is of two types: *x-ray fluorescence spectroscopy* and *laser-induced fluorescence.*

X-ray fluorescence is a spectroscopic technique for multi-elemental characterization of samples, measuring elemental concentrations directly. In this method, sample material is exposed to x-rays of appropriate energy to excite the elements in the sample, and during relaxation, x-rays of lower energy is emitted. The energy and intensity of the emitted light is characteristic for each element.

The *laser-induced breakdown spectroscopy* (LIBS) is a technique employing a highly focused laser beam to create small plasma on a sample surface. The plasma contains excited atomic and ionic species, which emit light as they relax to lower energy states during cooling of the plasma, which lasts only milliseconds. This light is detected and results in a spectrum with specific emission lines for the various species. By use of certified reference material, the detected spectrum is related to total concentrations of elements. A major advantage of the LIBS technique is that little or no sample preparation is needed.

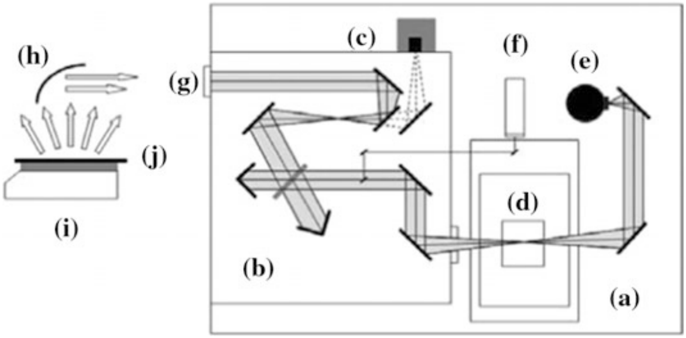

Fig. 6.4 Schematic diagram of infrared emission spectrometer. **a** FTIR, **b** interferometer, **c** light source, **d** sample room, **e** MCT detector, **f** He–Ne laser, **g** external lighting window, **h** condensing mirror, **i** hot plate, **j** sample

6.4.3 Preprocessing and Analysis of Spectroscopic Data

Owing to a large number of spectral bands and resultant overlapping spectral response of plant and soil nutrients the spectroscopic data need to be processed and analysed. A brief on preprocessing and analysis of spectroscopic data is given hereunder

Preprocessing is a very important part in the analysis of spectroscopic data, and is defined as any mathematic manipulation of the spectral data prior to primary analysis. There are a number of techniques available, such as, normalization, baseline corrections, spectrum smoothing and difference spectrum and spectral derivatives, in the pretreatment of spectra data, which are helpful to both the qualitative and quantitative interpretation of spectra (Beebe 1998). The critical point is how to identify single functional group vibrations or the presence of well-defined molecular structures. Normalization, baseline correction and smoothing are the first steps to process a spectrum (Demyan et al. 2012).

Diffuse reflectance spectra of soil in the visible–NIR are largely nonspecific due to the overlapping absorption of soil constituents. This characteristic lack of specificity is compounded by scatter effects caused by soil structure or specific constituents such as quartz. All of these factors result in complex absorption patterns that need to be mathematically extracted from the spectra and correlated with soil properties. Hence, the analyses of soil diffuse reflectance spectra require the use of multivariate calibrations. The most common calibration methods for soil applications are based on linear regressions, namely stepwise multiple linear regressions (SMLR) (Ben-Dor and Banin 1995; Dalal and Henry 1986), principal component regression (PCR) and partial least squares regression (PLSR). The main reason for using SMLR is the inadequacy of more conventional regression techniques such as multiple linear regression (MLR) and lack of awareness among soil scientists of the existence of full spectrum data compression techniques such as PCR and PLSR. Both of these techniques can cope with data containing large numbers of predictor variables that are highly collinear.

PCR and PLSR are related techniques and in most situations their prediction errors are similar. However, PLSR is often preferred by analysts because it relates the response and predictor variables so that the model explains more of the variance in the response with fewer components, it is more interpretable and the algorithm is computationally faster. The use of data mining techniques such as neural networks (NN) (e.g., Daniel et al. 2003; Fidencio et al. 2002), multivariate adaptive regression splines (MARS) (Shepherd and Walsh 2002) and boosted regression trees (Brown et al. 2006) is increasing. Viscarra Rossel (2007) combined PLSR with bootstrap aggregation (bagging-PLSR) to improve the robustness of the PLSR models and produce predictions with uncertainty.

MLR, PCR and PLS are linear models, while the data mining techniques can handle nonlinear data. Viscarra Rossel and Lark (2009) used wavelets combined with polynomial regressions to reduce the spectral data, account for nonlinearity and produce accurate and parsimonious calibrations based on selected wavelet coefficients. Mouazen et al. (2010) compared NN with PCR and PLS for the prediction of selected soil properties. They found combined PLSR-NN models to provide improved predictions as compared to PLSR and PCR. Viscarra Rossel and Behrens (2010) compared the use of PLSR to a number of data mining algorithms and feature selection techniques for predictions of clay, organic carbon and pH. They compared MARS, random forests (RF), boosted trees (BT), support vector machines (SVM), NN and wavelets. Their results suggest that data mining algorithms produce more accurate results than PLSR and that some of the algorithms provide information on the importance of specific wavelength in the models so that they can be used to interpret them.

Analysis Due to the large amount of data generated by spectrometers and hyperspectral sensors (in the laboratory, in situ, air-borne and spaceborne) and due to the complexity of the spectra, it is imperative to use chemometrics procedures to analyse the data. The chemometric techniques, such as partial least squares (PLS), principal components analysis (PCA) and artificial neural networks (ANN), have been applied when a large amount of data generated by FTIR spectrometers has to be processed to estimate the soil properties. PLS and PCA are the most popular procedures for quantitative determination or to predict one or several soil components (D'Acqui et al. 2010); PCA and PLS serve two purposes in regression analysis. First, both techniques are used to convert a set of highly correlated variables to a set of independent variables by using linear transformations; second, both techniques are used for variable reduction. A detailed description of such procedures can be found in various text books such as Brereton (2003).

The *wavelet transform* is a very powerful tool for resolving overlapping bands and separate the bands of interest from the background and interferences since it decomposes the signal into components at different scales. For instance, Jahn et al. (2006) used such an approach to distinguish between the strongly overlapping absorbance bands of nitrate and calcium carbonate in the ATR spectra of calcareous soils.

Spectral subtraction is commonly used when a compound is present in a mixture. If the interaction between the components results in a change in the spectral properties of either one or both of the components, the changes can be observed in the difference spectra.

Second derivative of a spectrum enhances the spectral resolution and amplifies subtle differences in IR spectra. Many differences visible in FTIR spectra such as frequency position, information on the width and the maximum absorption intensity become clearer (Abdulla et al. 2010). For example, the SOM spectra in the 1800–800 cm^{-1} region are very broad and exhibit many shoulders, indicating the presence of overlapping bands close in frequency (Ferrari et al. 2011).

6.5 Spectral Reflectance Pattern of Soils

The laboratory-based measurements enable an understanding of the chemical and physical principles of soil reflectance. Recently, considerable effort has been put into the development, operation, and use for spaceborne image spectrometers. These advances in technology can provide a near-laboratory-quality spectrum of every pixel in the image and very soon will permit remote sensing of soils with high standards. Information about soils from reflectance spectra in the visible/near-infrared (VNIR 0.4–1.1 μm) and shortwave infrared (SWIR 1.1–2.5 μm) spectral regions represent almost all the data that passive solar sensors can provide. Although the thermal infrared regions (3–5 μm, 8–12 μm) also contain diagnostic information about soil materials, the discussion will be confined to the VNIR-SWIR spectral region because it deals with soil reflectance and not emittance.

Soil reflectance data have been acquired in a substantial number of recent remote sensing, field and laboratory studies (Baumgardner et al. 1985). Most of the studies have focused on the spectral distribution of the scattered radiation, but some data on the directional distribution and polarization state of radiation scattered by soils are also available in the literature. The studies generally demonstrate relationships between spectral reflectance data and certain soil properties that correspond to the well-known relationships with soil colour.

6.5.1 Factors Affecting Soil Spectra

As mentioned in Sect. 6.5.1.3, the spectral response pattern of soils varies with soil composition, and terrain and environmental conditions apart from viewing geometry of the sensor. In many cases the spectral response pattern related to a given factor overlap with response pattern of other's and thereby hinder the assessment of the affect of a given factor. Hence it is important to understand the physical activity as well as origin and nature of soil's constituents and terrain and environmental conditions. Soil is composed mainly of minerals—mostly clay and iron oxides, organic matter both living and decomposed, and water in all the three phases, namely solid, liquid and gas phases. These constituents have direct/indirect bearing on soil spectra. In the following sections we focus our discussion primarily on factors affecting soil spectra directly and indirectly.

6.5.1.1 Minerals

Soil minerals are of two types—(i) primary minerals formed at high temperature and inherited from the igneous and metamorphic rocks, sometimes through a sedimentary cycle, and (ii) secondary minerals by reactions at low temperature, and inherited from sedimentary rocks or formed in soil by weathering. Quartz, feldspars, pyroxenes, amphiboles olivine and other accessory minerals of primary origin are some of the important primary minerals. Some of the important secondary minerals in soils include clay minerals, oxides and hydroxides of Si, Al and Fe (haematite, goethite, gibbsite, calcite, dolomite, gypsum and apatite). In this section we discuss and highlight the spectral reflectance of common soil minerals that significantly affect soil spectra.

Clay minerals Clay minerals, also referred to as phyllosilicate minerals, are naturally occurring crystalline minerals found in clay fraction (<2 mm) of soil. Included in the most commonly observed clay minerals are: illite, montmorillonite, chlorite, vermiculite and kaolinite. The spectra of three smectite end members, namely montmorillonite (dioctahedral, aluminous), nontronite (dioctahedra, ferruginous) and hectorite (trioctahedral, manganese) minerals are given in Fig. 6.5. The OH absorption feature of the vOH + OH in combination mode at around 2.2 micron is slightly but significantly shifted for each member (Ben-Dor 2002). In addition to O, OH, Al and Si clay minerals also contain Mg, Fe and K in large amounts. The colour of these minerals range from grey, light yellow and white depending upon their chemical composition. Clays and oxihydrates of iron which form coatings on mineral grains impart shades of yellow, brown and red colour to soils.

The crystal structure of clay minerals consists of two basic units: the Si tetrahedron, which is formed by a Si^{3+} ion surrounded by four 0^{2-} ions in a tetrahedral configuration, and the Al octahedron, formed by an $A1^{4+}$ ion surrounded by four 0^{2-} and two OH^{-} ions in an octahedral configuration. These structural units are joined

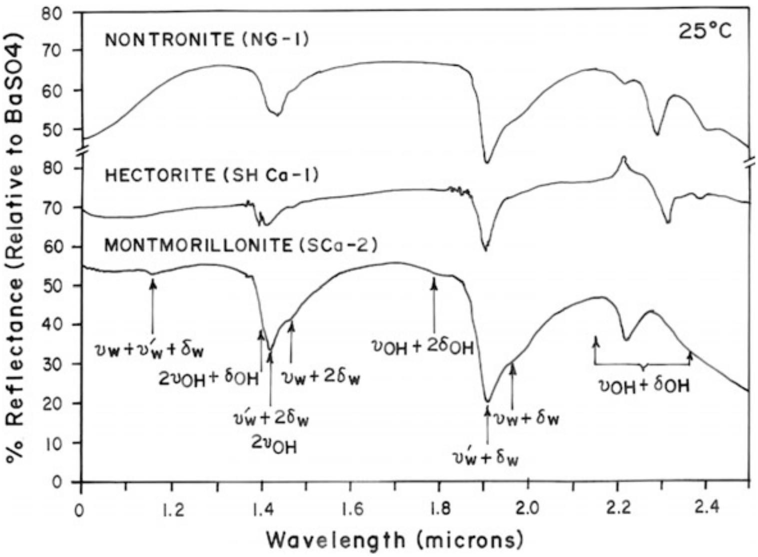

Fig. 6.5 Reflectance spectra of three pure smectite end members at room temperature (25 °C) Also given in the combination and overtone modes for explaining each of the spectral features (After Ben-Dor et al. 1999)

together into tetrahedral and octahedral sheets, respectively, by adjacent Si tetrahedral sharing all three basal corners and by Al octahedrons sharing edges. These sheets, in turn, form the clay mineral layer by sharing the optical 0 of the tetrahedral sheet. Layer silicates are classified into eight groups according to layer type, layer charge and type of inter-layer cations. The layer type designated 1:1 is organized with one octahedral and one tetrahedral sheet, whereas the 2:1 layer type is organized with two octahedral sheet and one tetrahedral sheet (Ben-Dor 2002).

Non Clay Minerals. The minerals are divided into five groups; silicates, phosphates, oxides and hydroxides, carbonates, and sulphides and sulphates. The fraction of each mineral in soils is dependent on the environmental conditions and parent material. In general, the quartz mineral is spectrally inactive in the VNIR-SWIR region and therefore diminishes other spectral features in the soil mixture. Other non clay silicate minerals such as feldspars may have some diagnostic absorption features that make the soil spectrum less monotonous.

Oxide group minerals occur in highly weathered areas such as those associated with slopes, highly leached profiles, or in areas of "mature" soils. Phosphate and sulphate minerals can be found in soils as apatite and gypsum, respectively. Although both minerals have unique spectral features, their occurrence in soils may be relatively rare and even non-detectable, whereas other oxides, such as iron, are strongly spectrally active, mostly in the visible region, because of the crystal field and the charge transfer mechanism. The content of free oxides (both iron and aluminium) is low in young soils but increases gradually as soil ages, just as happens with organic matter. Younis et al. (1997) have studied the influence of weathering process on the reflectance spectra of fresh (nonclay) rocks. They concluded that reflectance differences between the fresh and weathered surfaces are highly significant in the VIS-NIR-SWIR spectral region whereas the iron oxides components play an important role in this effect. The laboratory spectra of biotite and amphibole (nonclay minerals) are given in Fig. 6.6.

6.5.1.2 Organic Matter

The presence of organic matter in a soil causes a marked difference in reflectance throughout the 0.5–1.1 μm wavelength region (Swain and Davis 1978; Latz et al. 1984). Baumgardner et al. (1985) indicated that organic matter content relates to soil reflectance by a curvilinear exponential function (Fig. 6.7). At organic matter contents greater than 2%, the decrease due to organic matter may mask other absorption features in soil spectra (Baumgardner et al. 1970). Furthermore, it is not only the amount of organic matter that affects the spectral response pattern of soils but also its state of decomposition. Baumgardner et al. (1985) demonstrated that three organic soils with different decomposition levels yielded different spectral patterns. With the progress of decomposition from fabric to sapric through humic there has been a conspicuous in the spectral response pattern of organic soils (Fig. 6.8).

39 states into two categories of organic matter (0–2% and more than 2%). Coleman and Montgomery (1987) and used all radiometer bands to develop

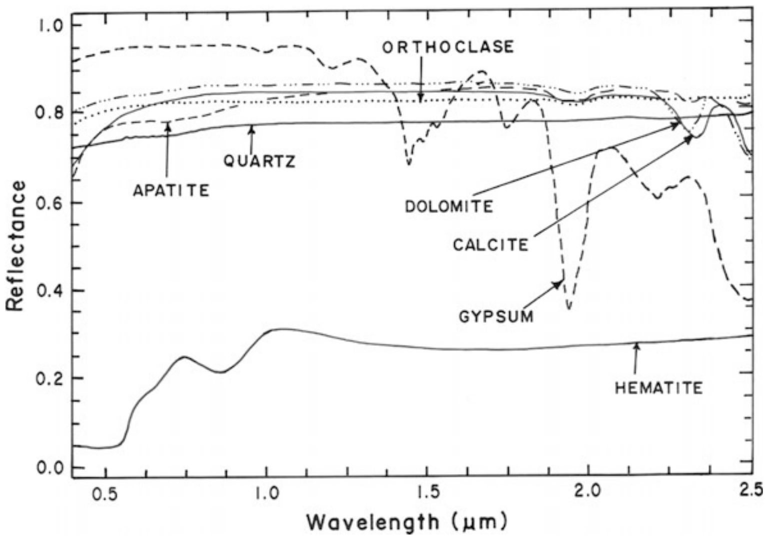

Fig. 6.6 Reflectance spectra of representative pure non-smectite minerals in soils (Adapted from Grove et al. 1992)

spectral relationships for organic matter. Schreier et al. (1988) used colour aerial photographs and spectral measurements to determine rates of change and spatial distribution of organic matter in individual agricultural fields. Frazier and Cheng (1989) used Landsat-TM band ratio to map organic matter levels and TM bands 1, 3, 4 and 5 were found to be most important. Bhatti et al. (1991) and Frazier and Jarvis (1990) evaluated the association between measured soil properties and observed TM reflectance data. The estimated soil surface reflectance measured by Landsat-TM has been found to be potentially accurate and efficient method for estimating surface organic carbon of bare soils (Baumgardner et al. 1985).

Organic matter plays a major role with respect to many chemical and physical processes in the soils and has a strong influence on soil reflectance characteristics. Organic matter has spectral activity throughout the visible and near-infrared short wave infrared (VNIR-SWIR) region. Baumgardner et al. (1970) noted that if the organic matter in soils drops below 2% it has only minimal effect on the reflectance property. Further, Baumgardner et al. (1985) have pointed out that organic matter content relates to soil reflectance by a curvilinear exponential function. Krishnan et al. (1980) used a slope parameter at around 0.8 µm to predict organic matter content. The wide spectral range found by different researchers (Coleman et al. 1991; Hendereson et al. 1992; Chen et al. 2000) to assess organic matter content suggests that organic matter is an important chromophore across the entire spectral region. Hendereson et al. (1992) have found that visible wavelengths (425–695 µm) had a strong correlation with soil organic matter for soils with the same parent material. However, the relationship was sensitive to Fe and Mn- oxides for soils from different parent materials. Dalal and Henry (1986) were able to predict

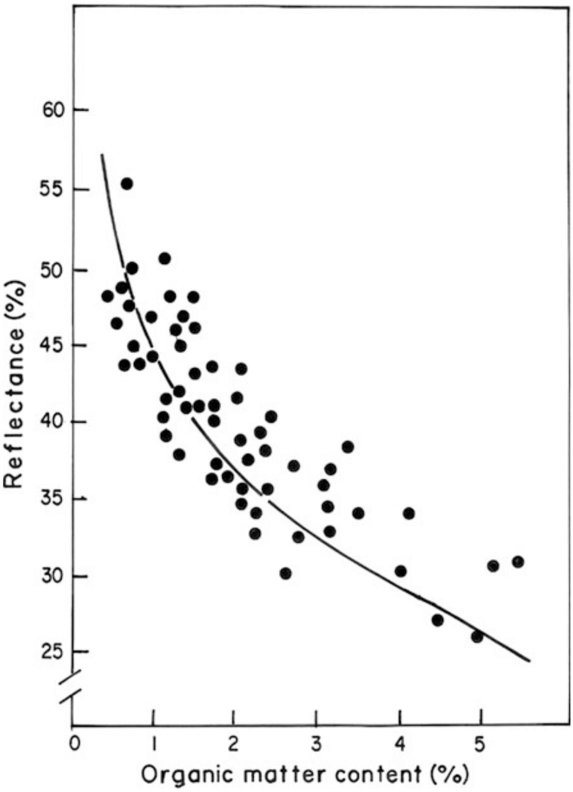

Fig. 6.7 Spectral curves of three organic soils exhibiting different levels of decomposition: **a** fibric, **b** hemic, **c** sapric (Baumgardner et al. 1985)

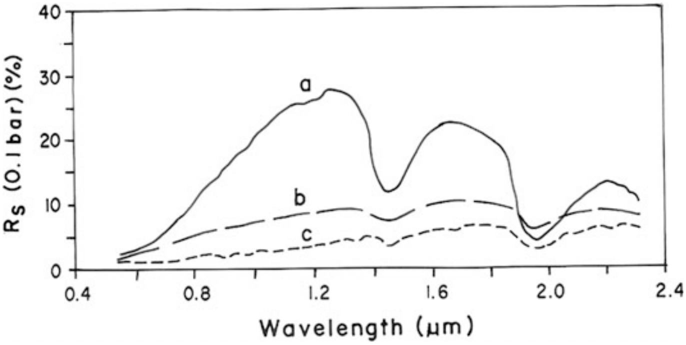

Fig. 6.8 Spectral curves of three organic soils exhibiting different levels of decomposition: **a** fibric, **b** hemic, **c** sapric (After Baumgardner et al. 1985)

the organic matter and total organic nitrogen content in Australian soils using wavelengths in the SWIR (1.702–2.052 µm) in combination with chemical parameters derived from the soils. Morra et al. (1991) showed that the SWIR region is suitable for identification of organic matter composition between 1.726 and 2.426 µm. Leger et al. (1979) and Al-Abbas (1972) have observed that organic matter assessment from soil reflectance properties is related to soil texture, and more likely to soils clay.

6.5.1.3 Soil Colour

While visualizing the soil or taking spectral measurements using various kind of sensors we essentially observe the soil colour. It is, therefore, essential to comprehend soil colour-one of the important soil physical properties in relation to spectral behaviour of soil. Soil scientists have long used soil colour to describe soils, to help classify soils, and to infer soil characteristics. As Baumgardner et al. (1985) stated: ‘Ever since soil science evolved into an important discipline for study and research, colour has been one of the most useful soil variables in characterizing and describing a particular soil’. Certain qualitative relationships between colour and soil properties are well recognized by pedologists on the basis of their collective observations and on a conceptual understanding of the interaction of visible light with soil material. Even though today’s instruments can measure soil reflectance as a function of wavelength, soil colour continues to play a major role in modern soil classification and description.

Soil colour results from the brain’s perception of the eyes’ response to light reflected by soil. The eye responds to electromagnetic energy within the 0.4–0.7 µm portion of the wavelength spectrum (visible or light region) in a ‘sensor like’ sensitivity distribution. Orna (1978) stated that colour provides the perfect link between an easily observed and described property and an underlying theory. Hence for years, soil colour has been used for qualitative assessment of many soil components, such as organic matter, iron oxides and carbonates in both the remote sensing and soil science fields (Escadafal 1993).

Soil Determinants

Soil colour is related to the presence of pigments or chromophores that absorb radiation in different soils are often related to a thin coating matter, water, iron oxides and chemical composition of transition metals in clay minerals are the major components affecting soil colour (Leger et al. 1979; Kondratyev and Fedchenko 1983). In general, the yellow and red colours of soils results from the presence of goethite and hematite, respectively (Karmanova 1981). Torrent et al. (1983) showed the quantitative relationship between soil colour and hematite content. Other iron oxides, such as lepidocrocite (which varies in colour between orange and yellow) and ferrihydrate (which is yellow to brown), can also be identified using the Munsell colour notation (Schwertmann 1988). Soil darkness is governed by the presence of humic substances. Black ped facies in soils are often related to a thin coating layer of manganese oxides. The green-blue related colours often encountered in gleyed soils come from “Green rust” in Fe^{2+} ions, indicating anaerobic soil conditions.

Colour in soils is also related to mineral compositions in the clay mineral lattice. For instance, green illite generally contain more Fe^{3+} than Fe^{2+} ions, both in the octahedral position. Purple colours in illite are relate to the structure of manganese complexes. Most smectites, which contain Fe, have an off-white to green colour, but numerous other colours have been observed, including yellow, yellow-green, apple green, blue-green, blue-grey, olivine-green and brown (Taylor 1982). In kaolinite, Jepson (1988a, b) described colour changes as a result of impurities.

In biotites, Hall (1941) noted that the relationship between iron, manganese and titanium is responsible for the colour sequence, ranging from red to blue-green.

Colour and Soil Properties

Various workers have studied the correlation of Munsell’s notations with different soil components: McKeague et al. (1971) concluded that no general relationship existed between chroma and dithionite extraction of Fe, or between value and organic matter content. Leger et al. (1979) concluded that colour variations in soils are the result of changes throughout the entire range of reflected wavelengths rather than changes in specific wavelength ranges. Da Costa (1979) studied various relationships between soils properties and colour parameters and found that clay, organic carbon cation exchange capacity and water content at different tensions are the most important properties related to value and chroma parameters. Moist and dry values are more correlated with the soil properties (except for organic matter and nitrogen) than is chroma. Silt and sand components are the least important soil properties in determining soil colour. Sand is positively correlated with the soil colour. Where a soil spectrum can be rearranged into a colour space (Berns et al. 1985; Fernandez and Schultz 1987) the spectrum is highly preferable because it contains unique information that might be overlooked when simply determining the colour.

Studies on the relationship between colour and soil environment and mineral composition carried out have indicated a close relationship between soil colour and environmental change. The effect of slope and soil moisture on soil colour is illustrated in Fig. 6.9. As evident from the figure as the slope gradient decreases (from left-hand side to right-hand side) there is an increase in soil moisture resulting thereby darkening in soil colour.

Soil reflectance has a direct relationship with soil colour, as well as to other parameters such as texture, soil moisture and organic matter (Condit 1970). A correlation between Munsell colour and reflectance has been observed by many researchers. A strong correlation between soil colour and particle size of the soil material and spectral reflectance data collected by hand held radiometer or Landsat satellites was observed (Horvath et al.1984).

In most of the earlier studies, soil colour data were employed to model or rebuild-reflectance spectra using simple or multiple regression analysis although some studies have modelled soil colour in terms of reflectance (Escadafal et al. 1989). Escadafal (1993) concluded that for measuring soil colour through remote

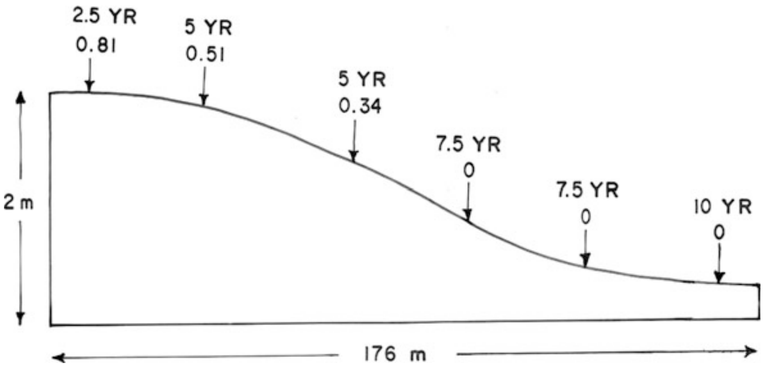

Fig. 6.9 Changes in Munsell colour parameters units with the variations in slope in Oxisols from Brazil (After Curi and Franzmeier 1984)

sensing sensors capable of sensing blue (450–500 nm), green (500–550 nm) and red (650–700 nm) are very important. Mattikalli (1997) developed a method called ‘optimal rotational transformation technique’ to maximize the correlation between soil colour and transformed reflectance.

The wide spectral range found by different workers to assess organic matter content suggests that organic matter is an important chromophore across the entire spectral region. Numerous absorption features exist that relate to the high number of functional groups in the OM. These can all be explained spectrally by combination and Vinogradov (1981) developed an exponential model to predict the humus content in the upper horizon of ploughed forest soils by using reflectance parameters between 0.6 and 0.7 m for two extreme end members (humus-free parent material and humus-enriched soil). Schreier (1977) found an exponential function to account for the organic matter content in soil from reflectance spectra. Al-Abbas et al. (1972) used multispectral scanner with 12 spectral bands covering the range from 0.4 to 2.6 μm from an altitude of 1200 m and showed that a polynomial equation will predict the organic matter content from only five channels. They implemented the equation on a pixel-by-pixel basis to generate an organic matter map of a 25 ha field. Dalal and Henry (1986) were able to predict organic matter and total organic nitrogen content in Australian soils using wavelengths in SWIR region (1.702–2.052 μm) combined with chemical parameters derived from the soils. Morra et al. (1991) showed that the SWIR region is suitable for identification of organic matter composition between 1.726 and 2.426 μm. Al-Abbas et al. (1972) and Leger et al. (1979) have provided the evidence of the dependence of assessment of organic matter from soil reflectance on soil texture and more so on the presence of clay. Organic matter and its stage of decomposition have shown to exercise control on reflectance properties of soils (Aber et al. 1990). Organic soils with different stages of decomposition are shown to yield different spectral pattern (Baumgardner et al. 1985). In a study carried out using controlled decomposition process over more than a year revealed significant changes across the entire VNIR-SWIR region as organic matter aged (Ben-Dor et al. 1997). They have postulated that some of the analysis traditionally used to assess organic matter content in soils from spectral reflectance may be biased by aged factor.

6.5.1.4 Water

The various forms of water in soils are all active in the VNIR-SWIR region and can be classified into three categories: (i) *Hydration water* where it is incorporated into the lattice water of the minerals (e.g. limonite $Fe_2O_3 \cdot 3H_2O$), (ii) *Hygroscopic water* which is adsorbed on soil surface areas as a thin layer, and (iii) *Free water* which occupies soil pores. Each of these categories influences the soil spectra differently, providing the capability of identifying the water condition of the soil. In the infrared region of the spectrum, there exists three basic fundamentals between radiation and water molecule particularly OH group: V_{w1} symmetric stretching; $\delta_{w,}$ bending; and V_{w3}, asymmetric stretching vibrations. Theoretically, in a mixed system of water and minerals, combination mode of these vibrations can yield OH absorption features at around 0.95 μm (very week), 1.2 μm (week), 1.4 μm (strong), 1.9 μm and (very strong) (Ben-Dor 2002).

Hydration Water

The hydration water can be send in minerals such as gypsum as strong absorption features at around 1.4 and 1.9 μm (Hunt and Salisbury 1971).

Hygroscopic Water

The significant spectral changes are related to changes in the adsorbed water molecules on the mineral's surfaces since the hygroscopic water in soil is governed by the atmospheric conditions; It is interesting to note that a similar observation was by Bowers and Hanks (1965) was based on soils that consisted of different moisture values (ranging from 0.8 to 20.2%) (Fig. 6.10). This observation demonstrates that the gas phase (water vapour in this case) in the soil environment plays a major role in the quantitative assessment of both structural and free water OH. Cariati et al. (1983) examined shifts of the OH absorption features at 1.4, 1.9 and 2.2 μm, and found that vibration properties of the adsorbed water depend strongly on the composition of the smectite structure.

In another study, Cariati et al. (1981) pointed out that several kinds of interactions are responsible for the vibration properties of the hygroscopic molecules, where sometimes this may even change with the water content. Because smectite is the most effective clay mineral in the soil environment that affects the reflectance spectrum at the major water absorption features, Cariati's observations may help us to understand the spectral activity of hygroscopic moisture in soils. Further work, however, is still required to implement the results obtained for pure smectite in the complex soil system

Free pore water. Free pore water (wet condition) is water that is not in either the hygroscopic phase or filling the entire pore size (saturated condition). The rate of movement of this water into the plant is governed by water tension or water

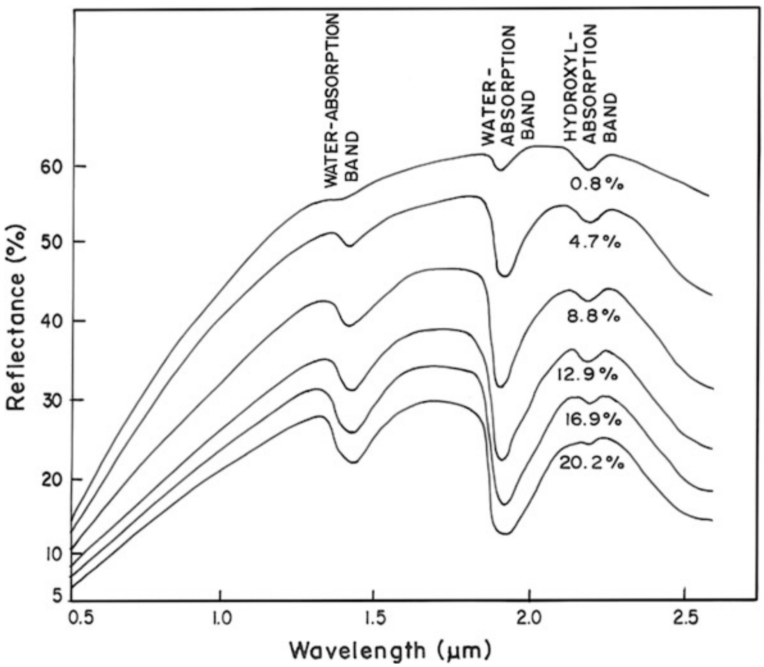

Fig. 6.10 Spectral reflectance curves for Newtonia silt loam at various moisture contents (After Bowers and Hanks 1965)

potential gradients in the plant soil system. Water potential is a measure of the water's ability to do work compared to pure free water, which has zero energy. In soils, water potential is less than that of pure free water, due in part to the presence of dissolved salts and the attraction between soil particles and water. Water flow from areas of high potential to lower potential and hence flow from the soil to the root and up the plant occurs along potential gradients. In agricultural systems plant growth occurs with soil water potentials between 15 and 0.3 bar tension (note these are actually negative water potentials); however, water tensions in desert environments are far greater) studied the reflectance spectra of a representative soil (Typic Hapludalf by the U.S. Department of Agriculture) over various water tensions at 1.4 and 1.9 μm also decreased. Clark (1981) examined the reflectance of montmorillonite at room temperature for two different water conditions and showed that albedo decreased dramatically from dry to wet material. Other changes related to the water and lattice OH can be observed across the entire spectrum as well. Some of these changes are related directly to the total amount of free and adsorbed water and some, to the increase of the spectral reflectance fraction of the soil (wet) surface.

In kaolinite minerals, a similar trend was observed in two moisture conditions; however, the changes around the water OH absorption features were less pronounced than in montmorillonite. In montmorilloinite, adding water to the sample enhanced the water OH features at 0.94, 1.2, 1.4 and 1.9 μm, because of the relatively high surface area and a corresponding high content of adsorbed water. In kaolinite, the relatively low specific surface area obscured a similar response, and hence only small changes are noticeable. Note that in the montmorillonite, the lattice-OH features at 2.2 μm diminished just as happened with Ca-montmorillonite exposed to different humidity conditions, suggesting that the hygroscopic moisture is a major factor affecting the clay minerals' (and soil's) spectra. Clark (1981) also studied a mixture of water in montmorillonite at low temperature that actually simulated a frost situation. In soils where the entire pore size (or more) is filled with water (in saturated conditions, respectively), it is more likely that the soil reflectance consists of more specular than Lambertian components.

6.5.1.5 Surface Roughness

A decrease in roughness results in increased reflectance. Eroded Alfisols were found to have higher spectral reflectance as compared to normal soils because of the exposure of B horizon with higher iron content and low organic matter. Coulson and Reynolds (1971) have observed that the hemispherical reflectance from dry smooth soil to be about 50% higher than the reflectance from soil after disking.

6.5.1.6 Soil Texture

The texture of soil affects the spectral reflectance both because of its influence on moisture holding capacity, and because of the size of soil particles. (If other factors are constant, fine-textured soils show a higher reflectance than coarse-textured soils under in vitro conditions (Fig. 6.11). In one of the studies with increasing particle size from 2200 to 2650 nm, at least an additional 14.6% of the direct solar radiant energy was found to be absorbed (Bowers and Hanks 1965). Further, often the response is strong enough to identify only at surface.

Bidirectional reflectance of particulate soil minerals generally increases and the contrast of absorption feature decreases as particle size decreases. It is interesting to note that the type of clay present in soils also influences the absorption of incident energy thereby affecting the spectral reflectance pattern of soils. Using handheld radiometer, (0.45–0.52 μm), 2(0.52–0.60 μm), (0.63–0.69 μm). Using the relationship between the amplitude of reflection of incident energy in specific regions of spectrum quantitative information on soil separates, i.e. clay silt and sand has been attempted. Coleman et al. (1991) found Landsat-TM bands 1,2,3, and 7 (2.35–2.6 μm) to be key bands for silt content and TM bands-2 (0.52–0.60 μm,- 6 (10.3–12.5 μm) and -7 (2.08–2.35 μm) to be key bands for quantification of clay content.

With increasing particle size from 2200 to 2650 nm, at least an additional 14.6% of the direct solar radiant energy was found to be absorbed (Bowers and Hanks 1965). Generally, clayey soils often appear darker to the eye than sandy soils even though primary clay particles are much smaller than sand grains. Using a handheld

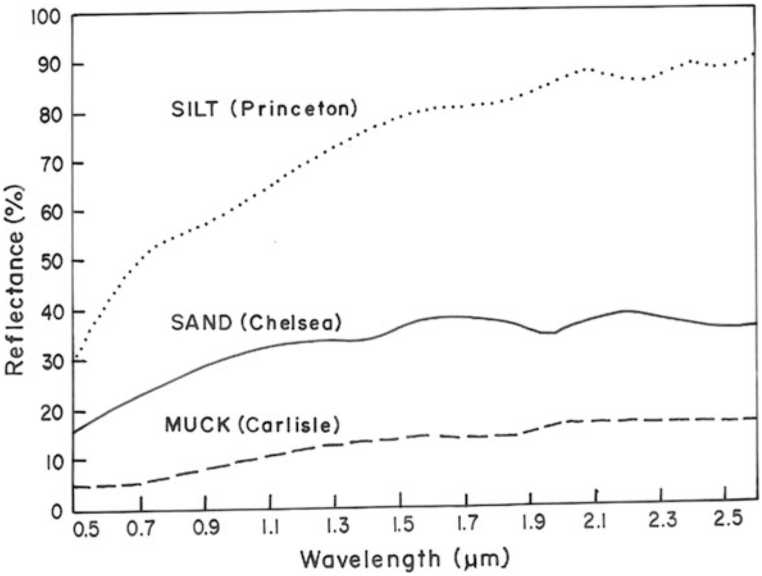

Fig. 6.11 DK—2 spectral reflectance curves for three soil types at low moisture contents (After Hoffer 1976)

radiometer, Coleman et al. (1991) found TM bands 1, 2, 3 and 7 to be key bands for identification of silt content and TM bands 2, 6 and 7 to be key bands for identification of clay content.

Reflectance measurements over tilled fields have been used to develop predictive equations for the fraction of sand, silt and/or clay at the soil surface with varying levels of success (Suliman and Post 1988; Coleman et al. 1991). Experience of various researchers has shown that the dependable relationships are only possible when imagery is acquired over fields with uniform tillage conditions and often the response is only strong enough to identify textural class at the surface (Barnes and Baker 2000). To minimize the effects of soil properties other than texture (e.g. soil moisture, organic matter and minerals other than quartz), Salisbury and D'Aria (1992) used a combination of visible, near-infrared (NIR) and thermal-infrared data.

6.5.1.7 Iron Oxide

Iron is the most abundant element on the Earth as a whole and the fourth most abundant element in the Earth's crust. Major Fe-bearing minerals in the Earth's crust are the mafic silicates, Fe-sulphides, carbonates, oxides and smectite clay minerals. All Fe^{3+} oxides have striking colours ranging among red, yellow and brown due to selective light absorption in the VIS range caused by transitions in the electron shell. The iron's feature assignments in the VIS-NIR region result from the electronic transition of iron cations (3+, 2+), either as the main constituent (as in

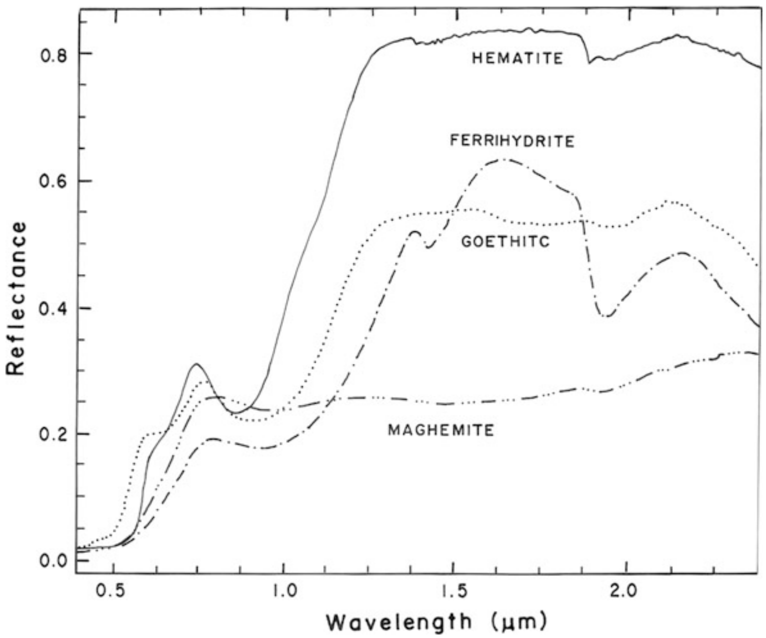

Fig. 6.12 Reflectance spectra of representative iron oxide minerals in soils (From Grove et al. 1992)

iron oxides) or as impurities (as in iron smectite). Hematite and goethite are common iron oxides in soils, and their relative content in soils is strongly controlled by soil temperature, water, organic matter and annual precipitation. Hematitic soils are reddish and goethitic soils are yellowish brown. Hematite (α–Fe_2O_3) has Fe^{3+} ions in octahedral coordination with oxygen. Goethite (α FeOOH) also has Fe^{3+} in octahedral coordination, but different site distortions along with oxygen ligand (OH) provide the main absorption features that appear near 0.9 μm.

Iron oxide, as mentioned earlier, has been found to have profound influence on spectral response pattern of soils. Many of the absorption features in soil reflectance spectra are due to the presence of iron in some form. The steep decrease in reflectance towards the blue and ultraviolet wavelengths is a characteristic of almost all soil reflectance spectra. This decrease is due to a strong iron–oxygen charge transfer band that extends into the ultraviolet region (Hunt 1980). The intensity of reflection from soils in the 0.50–0.64 μm region is inversely proportional to iron content of the soil (Obukov and Orlov 1964). Other absorption bands often occur near 0.7 and 0.87 μm (Stoner et al. 1980). Additional absorption in the middle infrared wavelengths can be attributed to ferrous iron in disordered octahedral sites (Hunt and Salisbury 1970; Mulders 1987).

Many of the absorption features in soil reflectance spectra are due to the presence of iron in some form (Fig. 6.12). The steep decrease in reflectance towards the blue and ultraviolet wavelengths is a characteristic of almost all soil reflectance spectra. This decrease is due to a strong iron–oxygen charge transfer band that extends into the ultraviolet region (Hunt 1980). The intensity of reflection from soils in the 0.50–0.64 μm region is inversely proportional to iron content of the soil (Obukov and Orlov 1964). Other absorption bands often occur near 0.7 and 0.87 μm. Additional absorption in the middle infrared wavelengths can be attributed to ferrous iron in disordered octahedral sites (Hunt and Salisbury 1970; Mulders 1987). Iron absorption in the middle infrared can be strong enough to obliterate the water absorption band at 1.4 μm.

6.5.1.8 Calcium Carbonate Content

The higher the calcium carbonate content of soil samples with their natural surfaces disturbed under laboratory conditions, the higher their reflectance is Lagacherie et al. (2008) found that this substance most strongly absorbs the electromagnetic waves of the 2208 and 2341 nm wavelength (Fig. 6.13a and b) (Clark et al. 2003). The CaCO3 affects the soil reflectance under field conditions weaker than the OM. Białousz (1978) mentioned that the relation becomes directly proportional only if the CaCO3 content is higher than 20%. For a lower content, the relation is inversely proportional and has an indirect character. The substance, since it is conductive to forming of soil aggregates, causes a higher roughness and therefore decreases the soil reflectance.

6.5.1.9 Soil Salinity and/or Alkalinity

The presence of excess amount of salt especially salts of sodium and magnesium lead to the development of salt-affected soils. These soils have salt efflorescence of varying colours ranging from light grey to white on the surface and in many regions in the world are devoid of vegetation. An increase in the spectral response pattern in visible and near IR regions has been observed with and increase in the salt content in the soil (Fig. 6.14). In fact, the spectral response pattern of these soils as observed in the field have enabled researchers to identify three levels of soil salinity and alkalinity in the Indo-Gangetic plains of northern India (Rao et al. 1995). In another study Hick and Russel (1990) studied the spectra of sodium chloride and magnesium chloride mixed with silica. While the spectral curve for sodium chloride exhibited the maximum spectral response with hardly any water/OH absorption features, magnesium chloride and the mixture of sodium and magnesium chloride displayed water and OH absorption features, and recorded lower reflectance as compared to sodium chloride alone (Fig. 6.15).

The modified stepwise principal component analysis of reflectance spectra of salt-affected soils samples measured at 10 nm spectral resolution between 495 and 2395 nm has enabled Csillag et al. (1993) to identify the key spectral ranges in the

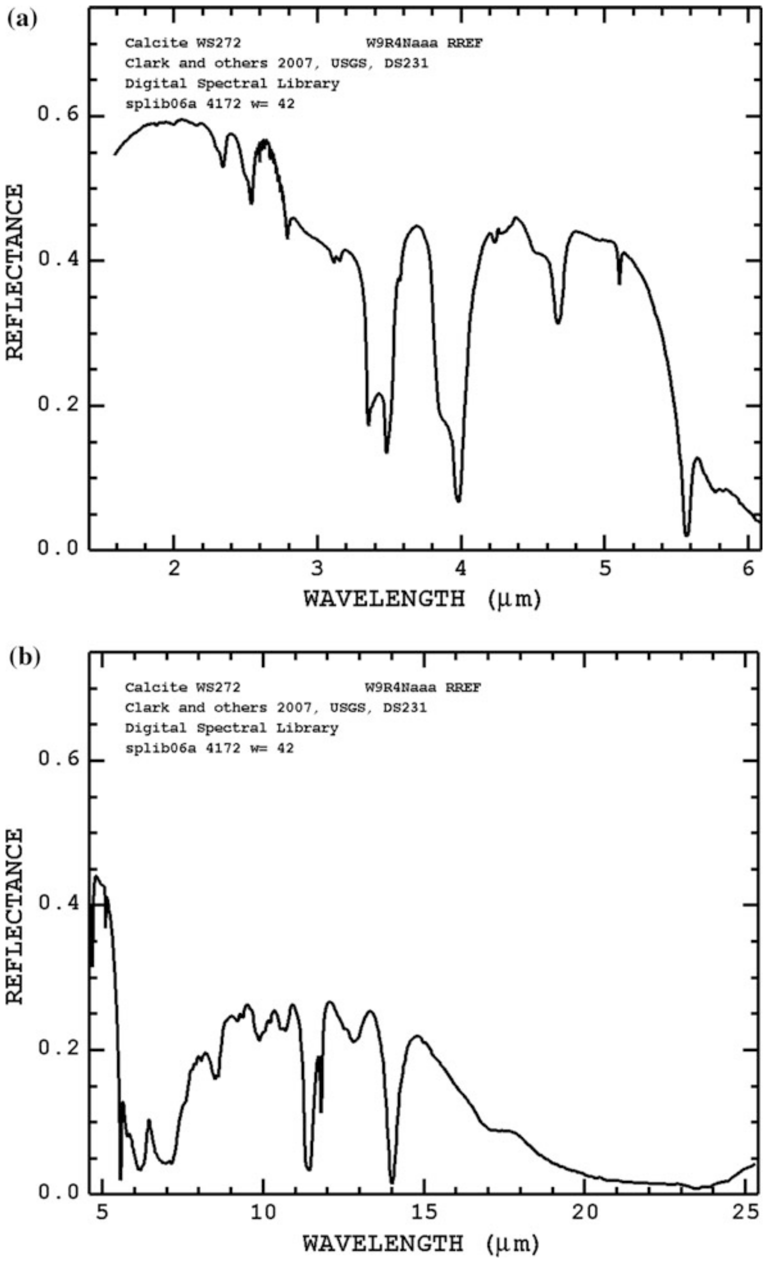

Fig. 6.13 **a** Spectral response pattern of calcite in 0.4–6.0 μm region (Clark et al. 2003). **b** Spectral response pattern of calcite 5.0–25.0 μm region (Clark et al. 2003)

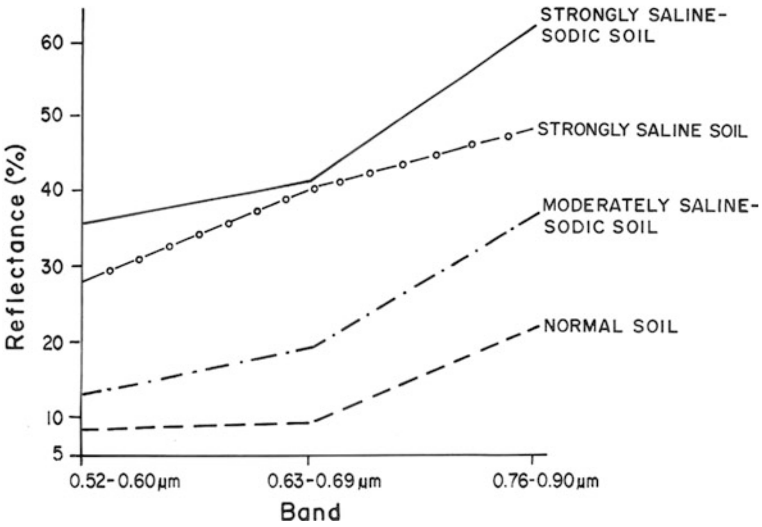

Fig. 6.14 In situ spectral reflectance of saline and saline—sodic soils (Rao et al. 1995)

visible (550–770 nm), near-infrared (900–1030 nm) position of the spectrum at 20, 40 and 80 nm spectral resolution.

Ben-Dor et al. (2002) analysed hyperspectral airborne sensor DAIS-7915 data over Israel valley employing the visible and near informed analysis (VNIRA) approach to demonstrate its potential for quantitative mapping of soil organic matter, soil field moisture, soil saturated moisture and soil salinity.

6.5.1.10 Direction of Illumination and Polarization

Apart from wavelength soil reflectance also depends on the direction of illumination and viewing. It has been observed that the particulate material having low absorption, such as desert sand (gypsum) and beach sand (quartz) strongly scatter in the forward direction (i.e. away from the direction of illumination) with a maximum reflectance at a view zenith angle. Forward scattering was less pronounced and retroreflectance (i.e. backscattering in the anti-illumination direction) was more pronounced in observation of reflectance from highly absorbing materials such as clay and loamy soils (Coulson 1966). While studying the effect of illumination direction and view direction in the field, Coulson and Reynold (1971) observed hemispherical reflectance maxima at solar zenith angles between 70° and 80° (i.e. low solar elevation angle). Using a pointable airborne sensor Irons et al. (1989) found a more strongly light scatter back towards the antisolar direction from a rough recently ploughed bare-soil surface than a smooth soil surface.

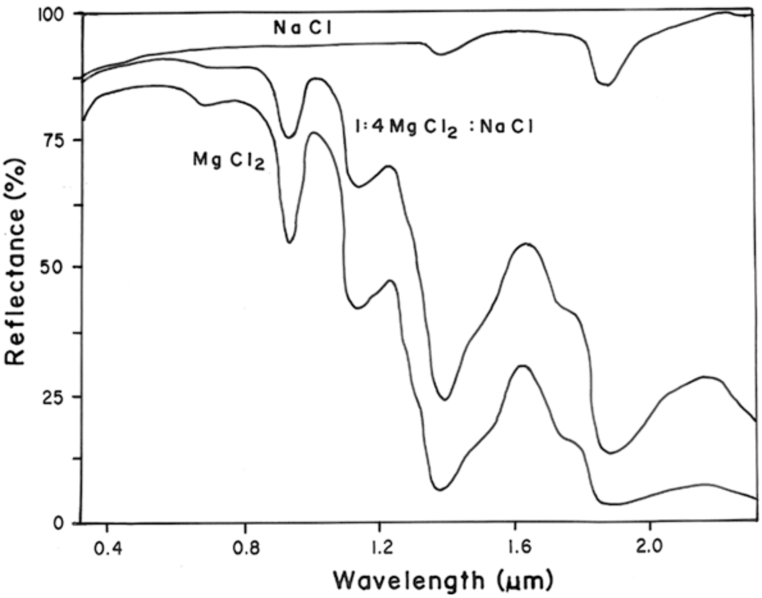

Fig. 6.15 Reflectance spectra of sodium and magnesium chlorides with silica mixtures (After Hick and Russel 1990)

Bidirectional reflectance of transparent particulate soil minerals and silicate minerals generally increases and the contrast of absorption feature decreases as particle size decreases. (Bowers and Hanks 1965; Hunt 1980; Stoner and Baumgardner 1980a). In contrast, the bidirectional reflectances of opaque materials decreases with decreasing particle size (Hunt 1980). Whitelock et al. (1994) studied the narrow band angular reflectance properties of alkali flats at White Sand, New Maxico from helicopter measurement in the 0.4–0.85 µm and concluded that soil moisture causes significant change in surface albedo on the alkali flat region. Increased wetness caused reduced surface albedo values at all wavelengths.

Coulson (1966) studied the degree of polarization of light scattered by soil particulate mineral and observed that darker particulate surfaces such as loamy soils polarized light to a greater degree than did highly reflective surfaces, such as desert sand. In addition, Coulson (1966) also concluded that the phase angle (i.e. the angle formed by the illumination direction and view direction) is the primary geometric variable controlling degree of polarization by soils. Further, he found the degree of polarization by soils to decrease as the observed wavelength increased from 0.4–1.0 µm.

6.6 Epilogue

Soil spectra carry unique and important information about many of the soil properties. Since the soil is a very complex system, for each type of soil, a separate study needs to be carried out to comprehend the intercorrelations between all possible chromophores. In order to be more useful, soil reflectance data must be accompanied by additional detailed information about the sampling site in terms of climate, topography, parent material, age, and if possible, detailed information on chemical and physical properties (Stoners et al. 1980). Although the research carried out so far has shown that soil spectral variation can be captured into a few broad bands, for quantitative information on soil properties, high-spectral resolution data collected using hyperspectral sensor seems to be the only alternative. This is because of the fact that even weak spectral features can carry invaluable information about soil properties and conditions. In many cases, only subtle spectral differences can be the key for classifying soils based on their spectra. In order to exploit full potential of high-spectral resolution data for deriving information on soil properties necessary correction for the effects of relative humidity, water content, slope and aspects, sun angle, shadow and vegetation coverage may be carried out.

Due to the unknown interactions between soil chromophores, it is difficult to assess the most appropriate wavelengths for explaining the composition of a given soil. The complex interactions between components in soils may cause the theoretical models to be impractical, and hence empirical models need to be incorporated. It is true that spectral variability can be explained by relatively small and broad spectral bands, but there is no doubt that additional information will provide a better performance. Development of analytical methods and a synergy between physical and empirical models may be the keys for retrieving quantitative information about soil properties solely from their reflectance spectra. This option should be the focus for today's researchers particularly, as new spectral imaging systems with greater near-laboratory spectral capabilities are emerging and becoming more available.

For soil applications air-and spaceborne imaging spectrometers should consist of a reasonable number of spectral channels across the entire visible–near infrared and shortwave infrared (VNIR-SWIR) region, which will cover the spectrally active regions of all chromophores with a reasonable bandwidth. Price (1991) believes that a relatively low number of spectral channels (15–20) with a bandwidth of 0.04–0.10 nm and high signal/noise ratio are those that promise better remote sensing capabilities of soils. Goetz and Herring (1989) preferred more spectral channels (192) but wider bandwidth (about 10 nm) to permit diagnostic evaluation of specific features across the entire VNIR-SWIR region. However, for quantitative analysis of soil spectra, the optimal bandwidth and number of channels may be strongly dependent on the soil variability and the property to be studied. Furthermore, high signal/noise ratio is a crucial factor in quantitative analysis of soil spectra derived from both air and space measurements.

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