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# Can mid infrared diffuse reflectance analysis replace soil extractions?

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**Summary.** Recent developments in infrared spectroscopy and computer software, together with decreasing spectrometer costs, have resulted in an increase in the potential for soil analysis. Infrared spectroscopy in both the near and mid infrared ranges allows rapid acquisition of soil information at quantitative and qualitative, or indicator, levels for use in agriculture and environmental monitoring. In this paper, we describe how mid infrared diffuse reflectance analysis can provide results comparable in accuracy

with many traditional extractive and digestion laboratory methods in soil studies, with the possibility of either replacing or enhancing them. Examples are given for estimation of lime requirement, organic carbon, exchangeable cations, air-dry moisture, clay content and biological indicators. Infrared methodology appears to have advantages in facilitating some soil analyses that are otherwise very time-consuming or expensive, or where spatially dense data is required.

## Introduction

Soil extraction procedures have played a vital role in the characterisation of soils, particularly in analysis of the soil solution, surface chemistry and soil organic matter (Theng 1974; Theng and Tate 1989). However, extraction procedures are relatively slow and expensive, and Peverill (1993) has commented that although chemical measurements are amongst the most common made on soils in Australia, their intensity of use is low. Before the introduction of precision and prescription farming, and because of cost constraints, agronomically significant soil attributes were generally characterised by a single measurement on a combined set of surface soil samples at the field or farm scale. Relatively few analyses, and especially few subsoil samples, were used to describe, often inadequately, the soils for a given site. A consequence of inadequate sampling and analysis, however, is that it can lead to an inefficient use of valuable resources such as water, fertilisers and herbicides.

Soils are rarely homogeneous, either laterally or with depth, and the notion of homogeneity has been questioned following the increasing use of precision and prescription farming (McBratney *et al.* 1996). With a growing need for the accurate representation of the continuous spatial and temporal variation in soil properties for scientific study and where more spatially dense analyses are required, for example in soil property mapping, soil extraction procedures alone may

not meet these needs. Furthermore, although instrumental techniques for soil tests are becoming more sensitive and sophisticated, this often comes at an ever-increasing expense.

Implications are that the speed, number, quality and relevance of soil analysis must be improved to satisfy the demand for use in site-specific information, as well as to improve the utility of traditional approaches to routine soil testing. Of particular importance is the need to efficiently determine the soil fertility parameters as well as, for example, the variation in clay type and content, moisture, organic matter, and a number of sorption and buffering measurements. If these can be precisely and cheaply determined, the data can then also be incorporated in various conceptual and management models.

This review will discuss the application of the mid infrared (MIR) diffuse reflectance technique, in combination with chemometrics, for soil analysis as a surrogate for extractive or digestive laboratory techniques.

## Background

For more than 100 years, soil chemists have developed a range of methodologies, many based on the soil solutions from extractive procedures, such as those presented in Australia by Piper (1944) and, more recently, by Rayment and Higginson (1992). Modern methods that are commonly used to analyse the soil

solution can involve, for example, inductively coupled plasma emission spectroscopy, gas chromatography, injection flow analysis and ion-selective electrochemistry. Schnitzer *et al.* (1991) also used pyrolysis-field ionisation mass spectrometry to analyse the organic matter extracted from soils using water at high temperature and pressures. The techniques have benefited from new technology with ever-increasing sensitivity, computer and database compatibility, reliability and throughput, but they generally require extensive (and expensive) laboratory infrastructure and resources. Soil characteristics and properties can often be predicted from simple equations involving pedotransfer functions, for example for water-holding capacity or pH buffer capacity, but the cost depends on the individual costs of the predictive component analyses.

In order to reduce the need for extractions, other analytical techniques using the solid soil matrix or its separations are being used as alternatives to provide fundamental information about the mineralogy and total organic composition of the soil. These methods are often spectroscopic in nature, for example, mass spectroscopy (MS), X-ray diffraction (XRD), differential thermal analysis (DTA), nuclear magnetic resonance (NMR), MIR and near infrared (NIR) spectroscopy and thermogravimetric analysis (TGA). It is expected that technology will continue to evolve these techniques with increasing sensitivity, versatility and reduced cost.

Soil is a non-ideal system, and is chemically and mineralogically more complex than the 'pure' systems often studied using traditional laboratory procedures. Mechanisms of soil processes are difficult to fully understand and the fundamental link between measured soil chemistry and particular soil attributes or properties may be complex, tenuous and ambiguous. Chemical extraction, used in the characterisation of soils, may in fact further complicate the interpretation. Soil chemical extraction procedures can change the equilibrium between solid and solution phases and the analyte as a result of the extractant interactions at the solution and solution-particle interface. For this reason, there is increasing tendency towards the development of techniques that preserve the basic integrity of the soil system.

### Mid infrared methods

Infrared methods have a particular advantage over many other techniques for soil analysis due to their sensitivity to both the organic and inorganic phases. The fundamental molecular frequencies are generally in the MIR 2500–25 000 nm wavelength ( $4000\text{--}250\text{ cm}^{-1}$ ) range and have overtone and combination modes both in the 700–2500 nm NIR region, as well as in the MIR. The infrared spectra result from the complex vibrational stretching and deformation modes of groups of atoms forming molecular structures and crystals, the

frequencies of which are basically dependent on the number and masses of the atoms, the bonding forces between them and the symmetry of the molecular unit cells (Colthup *et al.* 1990).

The vibrational frequencies can be modified by factors relating to the molecular environment and result in a large number of peaks, often broad and with considerable overlap in soils. Further complexity is added for soil spectra due to the large number of coexisting and often poorly defined or unknown components, sometimes with chemical interactions (Theng 1974; Theng and Tate 1989), each contributing partly to the observed spectra. This contrasts with the infrared spectra of pure minerals in which the peaks are generally well characterised, assigned and resolved (Farmer 1974; Van der Marel and Beutelspacher 1976).

The broadness and high overlap of infrared peaks for soils has, until recently, restricted the use of infrared analysis to qualitative and semiquantitative studies. Improvements in technology are, however, making the infrared method more amenable for more widespread use. Advantages of modern Fourier-transform spectrometers, for example, the very high energy throughput (multiplex advantage), speed, high wavelength precision and accuracy make energy-deficient techniques viable. Techniques such as infrared microscopy, diffuse reflectance, infrared-photoacoustic spectroscopy and internal reflection become practical options for soil studies, and spectral data is stored in the computer in a digital form suitable for routine multivariate analysis.

Of these techniques, only 2 have received major attention for soils: the pressed halide disk and the diffuse reflectance infrared Fourier-transform (DRIFT) method. The KBr disk method has been traditionally used for solid mineral analyses by MIR spectroscopy since the 1950s (Farmer 1957, 1974; White 1964; Fridmann 1967; MacCarthy and Rice 1986), and has been the most commonly used technique for chemically extracted soil components such as humic and fulvic acids (Schnitzer 1965, 1978; Chen *et al.* 1978; Skjemstad and Dalal 1987; Schnitzer and Schuppili 1989) or separated organic matter (Parfitt *et al.* 1997). It relies on dispersing about 1 mg of sample in about 200–300 mg dry KBr powder and pressing the mixture into a clear disk. Although this method gives excellent spectra, with a high degree of intensity, linearity and with few distortions, there is a chance that the KBr matrix may react with the soil sample by ion exchange (Duyckaerts 1959; Ketelaar and van der Elksen 1959; White 1964). Furthermore, the technique is slow, since each sample is small and must be accurately weighed, dispersed and pressed, and any water which is absorbed into the hygroscopic KBr can interfere (Stevenson and Goh 1974; Nguyen *et al.* 1991).

Many of the problems associated with the KBr disk method are overcome using the DRIFT technique in both the MIR and NIR. MIR-DRIFT, in particular, has been shown to be an ideal technique for the quantitative analysis of solid powdered samples (Fredericks *et al.* 1985, 1987) and in soils (Nguyen *et al.* 1991; Niemeyer *et al.* 1992; Piccolo 1994; Capriel *et al.* 1995; Wander and Traina 1996; Hazel *et al.* 1997), in that it reduces sample preparation to a minimum, reduces interference by absorbed matrix hydration, and maintains high sensitivity; thereby speeding up the collection of spectra. The use of relatively large samples also provides a better representation of heterogeneity in soil materials (Niemeyer *et al.* 1992). It does suffer from relatively low energy and considerable distortion compared with the pressed KBr disk technique.

Diffuse reflectance is the non-mirror, or volume, reflectance after incident radiation has been scattered from a powdered sample (Vincent and Hunt 1968; Griffiths 1983; Brimmer and Griffiths 1988). An excellent treatment of diffuse reflectance from loosely packed powders has been presented by Mandelis *et al.* (1991) for particles both smaller and larger than the incident wavelength. In essence, DRIFT is associated with reflection phenomena involving 2 optical constants: the refractive index, and the absorption index. Strong peaks can become distorted by a rapidly changing refractive index through the peak maxima, sometimes even inverting due to total mirror reflection (the Reststrahlen effect), and weaker peaks which become relatively more intense (Baes and Bloom 1992; Niemeyer *et al.* 1992). Peak intensities in DRIFT spectra are non-linear with respect to sample component concentration, with peaks for low concentrations becoming relatively stronger compared with the peaks for higher concentrations. The enhancement of weak peaks, however, may be advantageous since a number of very weak overtone-combinational peaks can thus be easily observed.

In ideal situations, where the sample particles are large and very highly reflective, the specular component dominates the DRIFT spectrum and the resulting distortion or inversions reduced by applying the Kramers–Kronig relationship (Krishnan and Hill 1990). If the diffuse component completely dominates, the non-linearity can be reduced by use of the Kubelka–Munk function (Griffiths 1983; Brimmer and Griffiths 1988). In most real applications, however, there is a mixed contribution from specular and diffuse reflectance components which is difficult to transform correctly with either function. For qualitative predictions, these samples are generally diluted with powdered KBr to reduce the spectral intensity and the Kubelka–Munk function then used to linearise the spectral intensities (Griffiths 1983; Brimmer and Griffiths 1988), although Baes and Bloom

(1992) imply that correct ratios between strong and weak peaks are still difficult to obtain. The distortions are considerably reduced in the NIR due to the much lower spectral intensities and consequently less effect of the surface refractive index. Alternatively, quantification can be achieved using multivariate methods, without the need for prior sample dilution or Kubelka–Munk linearisation of the spectral intensities (Fredericks *et al.* 1985, 1987; Haaland and Thomas 1988; Reeves and Delwiche 1997), in spite of reservations by Piccolo (1994). This can be particularly advantageous for undiluted samples by reducing sample preparation time and improving sensitivity.

For neat samples, by using the DRIFT method, samples need only to be air-dry and ground to a consistent particle size for reproducible diffuse reflectance to be measured. Subsamples do not need to be weighed (thereby eliminating weighing errors), there are no matrix effects to cause ion exchange (Piccolo and Stevenson 1982; Bell *et al.* 1991), interference from water adsorbed onto the KBr matrix is eliminated (Baes and Bloom 1992), and the samples can be completely recovered after the spectra have been recorded. Furthermore, very weak peaks are often sufficiently strong to be easily observed without excessive noise.

Many soils are high in sand (quartz), low in organic matter and contain varying amounts of clay (usually as kaolinite, illite, smectite, mica and gibbsite) and iron oxides. It is therefore expected that the very intense fundamental quartz O–Si–O stretching peaks near 1100–1000  $\text{cm}^{-1}$  (9091–10 000 nm) in the MIR would dominate the spectra of soils. The quartz peaks are in fact so intense that total reflection occurs with DRIFT (Nguyen *et al.* 1991), and the normally very weak overtone-combination peaks become strong enough to effectively mask most other peaks, for example, for organic matter below 2000  $\text{cm}^{-1}$  (5000 nm). Quartz does not show peaks with DRIFT above 2000  $\text{cm}^{-1}$  (except for very weak bands in the –OH stretching region near 3600–3400  $\text{cm}^{-1}$ ). Implications are that clay and organic matter –OH and –CH peaks remain clear of interference from quartz in the higher frequency half of the MIR and throughout the entire NIR range. In essence therefore, MIR with DRIFT should be an effective surrogate for traditional laboratory techniques where sensitivity to both organic and inorganic components is important (Wander and Traina 1996).

### Quantitative infrared analysis

In recent years, the low cost and high speed of NIR spectroscopy has led to its widespread use in remote sensing applications, and as a viable surrogate for routine laboratory ‘wet chemistry’ methods in grain analysis for protein (Tkachuk 1987; Reeves and Delwiche 1997), soil analysis, for example, water,

carbonate, clay and organic matter content (Sudduth and Hummel 1991, 1993; Morra *et al.* 1991; Henderson *et al.* 1992; Capriel *et al.* 1995; Ben-Dor and Banin 1995a; Wander and Traina 1996), biomass (Palmborg and Nordgren 1993, 1996; Fritze *et al.* 1994; Bååth *et al.* 1995), pesticide retention (Bengtsson *et al.* 1996), hydrocarbon contamination (Hazel *et al.* 1997), and in the classification of soil organic matter (Henderson *et al.* 1989; Stenberg *et al.* 1995).

Quantitative analysis of soils by MIR has not been as widely reported and has generally been restricted to simple correlations between selected infrared peak intensities of humic substances and their chemistry (Inbar *et al.* 1989, 1991; Johnson *et al.* 1994). Such methods rely on the inherent linear intensity–concentration ratios, common for pressed KBr disks, an observation which does not normally occur in MIR-DRIFT spectra.

Pioneering work of Fredericks *et al.* (1985, 1987, 1988) and Haaland and Thomas (1988) demonstrated that simple, univariate methods of analysis could be replaced by much more effective multivariate methods such as principal components regression (PCR) and partial least-squares analysis (PLS), mathematical techniques which are based on principal components analysis (PCA). Fredericks *et al.* (1985, 1987, 1988), in particular, demonstrated the effectiveness of PCR for the rapid, commercial analysis of powdered minerals by predicting coal, diesel fuel, iron ore, bauxite, and manganese ore properties from MIR spectra.

Since then, the number of publications reporting the use of MIR-PLS and MIR-PCA for property prediction has grown enormously, but surprisingly its use in soils and agricultural applications has not been taken up so rapidly. MIR-PCA has been shown to determine wheat protein almost as well as the NIR method (Reeves and Delwiche 1997), and it has been used to classify soil organic matter (Tao *et al.* 1994). Few applications for the MIR-PLS analysis of soils and soil organic matter have been reported. These include a MIR-PLS analysis for the prediction of organic carbon, nitrogen and other properties of peats (Holmgren and Nordén 1988), hydrocarbon contamination in wet soils (Hazel *et al.* 1997) and 2 recent reports using MIR-DRIFT on undiluted soils (Janik and Skjemstad 1995; Janik *et al.* 1995) for a range of soil properties such as elemental mineralogical analysis, organic carbon, nitrogen, carbonate, air-dry moisture and cation exchange capacity. Standard PLS methods are now common add-ons in most commercial infrared systems, providing a rapid and simple means of analysing soils. In terms of spectral information, the MIR range should be more appropriate and useful than the NIR for characterising soil components.

The PLS analyses reported in this paper, using the

Galactic PLS-PLUS computer program, are based on a method described in detail by Haaland and Thomas (1988). In very simple terms, the PLS method reduces a spectroscopic calibration data set into a much smaller set of eigenspectra (loadings), taking account of the spectral variance and the predetermined property values of each of the samples in the calibration set. Principal components regression differs in this regard by having a separate spectral reduction and property regression procedure. The PLS loading weights are somewhat similar to ‘spectra’ of the pure soil components in that the peaks correspond to the spectral signatures of those soil components which are related to the property being determined. Spectra of the unknowns are fitted with the same loadings as the calibration set and the properties predicted from the regression coefficients of the PLS loading scaling terms (scores). These PLS methods circumvent the need for peak-intensity linearisation through sample dilution by using additional factors to account for non-linearity.

The mechanisms or relationships between the predicted properties and soil components can often be derived by close inspection of the PLS loading weights (Haaland and Thomas 1988; Holmgren and Nordén 1988; Janik and Skjemstad 1995; Janik *et al.* 1995; Janik and Keeling 1996). In PLS analysis, a separate set of loadings, weights and scores are calculated for each property although many properties can be calibrated and predicted simultaneously. The PLS IR method therefore offers a great advantage over single analysis, laboratory-based extraction techniques in being able to rapidly determine a great many properties from a single infrared spectrum.

For mapping and spatial variability studies, it is therefore simple to map the PLS-predicted values, or even sometimes just plot the first few factor scores for each sample, to produce a 2-dimensional map. Very large data sets can therefore be analysed for composition heterogeneity from their infrared spectra, such as is used for remote imaging, but also taking into account the inherent chemical relationship between the loadings and the property values.

For many soil properties, there is a high correlation ( $R^2 > 0.90$ ) of the predicted property with laboratory data. The residual error may be due either to an inability of the infrared method to completely model the data, or to the lack of precision of the primary laboratory method rather than the PLS method. For analyses where the correlation is lower, but still reasonable, for example for  $R^2 = 0.90$ – $0.70$ , there may still be a case for the use of infrared as a surrogate in variability studies, particularly where the primary method is very time-consuming or costly, or where a large set of analyses are required. In some cases, qualitative data may still be derived from the infrared spectra for even lower  $R^2$  values.



**Table 1. Examples of soil properties for various calibration sets, where MIR-PLS prediction  $R^2$  exceeds 0.50**All regressions are significant at  $P < 0.0001$ 

Soil property	$R^2$	Range	$n$	Soil property	$R^2$	Range	$n$
Air-dry moisture (%)	0.70	0–16	303	Total organic carbon (%)	0.93	1.1–8.0	188
Moisture content (%)				Aromatic NMR OC (%)	0.86	0–1.3	61
@ 10 kPa	0.83	21–34	23	GC-FAME ECL16 peak area	0.88	22 000–82 000	16
@ 30 kPa	0.90	11–21	23	Biomass (g/kg)	0.69	20–70	23
Particle size composition (%)				Lime requirement (t/ha.pH unit)	0.86	0.7–5.0	188
Sand	0.94	21–96	88	P capacity (mg/kg)	0.87	50–900	47
Silt	0.84	0–44	88	Atrazine absorption (L/kg)	0.69	0–4.6	31
Clay	0.79	2–49	88	Fe DTPA (mg/kg)	0.55	17–540	183
Field texture (arbitrary unit)	0.54	1–18	88	Mn DTPA (mg/kg)	0.57	0–181	183
XRF analysis (%)				pH CaCl <sub>2</sub> (1 : 5 w/v)	0.67	3.8–6.0	183
Al <sub>2</sub> O <sub>3</sub>	0.92	0–30	298	pH water (1 : 5 w/v)	0.56	4.9–6.6	183
CaO	0.70	0–4.5	298	Cation exchange capacity (cmol/kg)	0.88	26–224	183
Fe <sub>2</sub> O <sub>3</sub>	0.93	0–23	298	Sum of cations (cmol/kg)	0.84	0–96	298
K <sub>2</sub> O	0.63	0–3	298	CaCl <sub>2</sub> -extractable Al (cmol/kg)	0.53	0–7.6	183
MgO	0.80	0–6	298	CaCl <sub>2</sub> -extractable Mn (cmol/kg)	0.60	0.2–35	183
P <sub>2</sub> O <sub>5</sub>	0.60	0–0.8	298	Exchangeable Ca (cmol/kg)	0.89	11–160	183
SiO <sub>2</sub>	0.97	10–100	298	Exchangeable Mg (cmol/kg)	0.76	1.5–70	183
TiO	0.78	0–7	298	KCl-exchangeable Al (cmol/kg)	0.64	0–17	183
Total organic nitrogen (%)	0.86	0.0–0.7	188	KCl-exchangeable Mn (cmol/kg)	0.66	0–4	183

It is usually accepted that the infrared predicted data can never be better than the original laboratory values. However, if the sources of laboratory error can be identified, the infrared method may in fact be a better tool for interpretation than the ‘appropriate’ chemical analysis. New statistical techniques can, in some instances, reduce calibration errors by correcting for measurement error (Faber and Kowalski 1997).

Quantification, from the infrared viewpoint, depends on the ability to detect the spectral signatures of the soil components responsible for the property of interest. If these are below the detection limits, then quantification may not be valid. Such a situation can occur when the soil property involves transitory aqueous phases between soil particles or some rather subtle ionic properties of the soil surfaces. Aqueous or surface phases may thus only represent a very small part of the observed spectrum and thus may be undetectable.

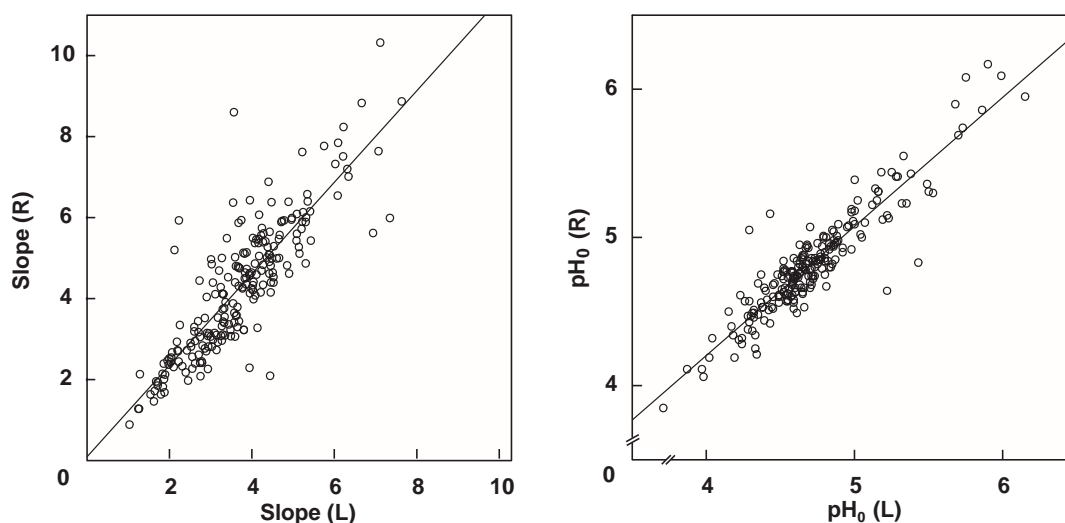
The above factors must be taken into consideration where the suitability of the infrared method for the proposed analysis is being tested. For instance, of the laboratory chemical methods described by Rayment and Higginson (1992), the following could be expected to depend on the chemistry of the soil matrix and thus be predictable by infrared (and often more effectively so by MIR); air-dry moisture content, total organic carbon, total nitrogen, some phosphate, pesticide, herbicide and dissolved organic carbon sorption/retention

characteristics, some extractable iron, aluminium, silicon and ion exchange properties, lime requirement, particle size and soil carbonates. Examples for a number of such soil properties from MIR-PLS analysis are listed in Table 1.

Infrared is unlikely to provide quantitative data where the property being predicted is unrelated to soil chemistry, or for soil solution chemistry where concentrations are low or ephemeral and temporal changes are important, for example, soil nitrate and ammonia nitrogen. This is illustrated in Table 2 for analyses where very low correlations have been obtained. A number of specific examples where infrared

**Table 2. Soil properties where prediction is less reliable ( $R^2 < 0.50$ )**Significant regressions are indicated as: \*  $P < 0.0005$ ; \*\*  $P < 0.0001$ 

Soil property	$R^2$	$n$
Electrical conductivity (1 : 5)	0.23**	88
K available (bicarbonate extract)	0.34**	186
P available (bicarbonate extract)	0.07*	186
P buffer	0.34**	39
DTPA-extractable Zn	0.24**	183
DTPA-extractable Cu	0.20**	183
CaCl <sub>2</sub> -extractable B	0.30**	183
Exchangeable Na	0.33**	183
Exchangeable K	0.33**	183



**Figure 1.** Replication of laboratory-determined lime requirement slopes and  $\text{pH}_0$  intercepts for data from 2 independent experiments (R and L), but using the same incubation procedure. The equations of the regression lines are:

$$\begin{aligned}\text{Slopes: } Y &= 1.13X + 0.09 \quad (R^2 = 0.728, n = 224), \\ \text{pH}_0: Y &= 0.87X + 0.72 \quad (R^2 = 0.850, n = 224).\end{aligned}$$

methodology has been found useful as a surrogate are presented below.

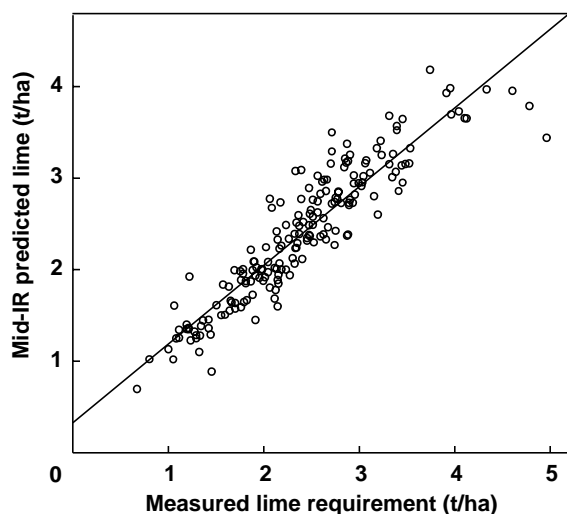
### Specific examples of mid infrared analytical capability

#### Lime requirement

Soil acidity develops from mineralogical sources, such as proton-rich clays, aluminium oxyhydroxide minerals and sulfides, oxidisable ammonium and organic

nitrogen (as amides), and organic acids (carboxylic acids and phenols). The lime required to neutralise these sources is dependent on properties of the soil matrix and therefore should be predictable from MIR analysis. Lime requirements for Australian soils (t/ha of  $\text{CaCO}_3$  to raise the pH of the surface 10 cm by 1 pH unit) have been evaluated using lengthy incubation procedures lasting days to months (Helyar and Porter 1989; Richards 1992; Aitken and Moody 1994) but alternative faster buffer solution methods are also often used in testing laboratories. The laboratory method used for the calibrations reported here (Richards 1992) was based on a 14-day equilibration, and was known to have the usual errors associated with the slopes and intercepts of the  $\text{pH}/\text{Ca}(\text{OH})_2$  regressions (see Fig. 1). These errors often occurred for soils where excessively high pH values resulted from the  $\text{Ca}(\text{OH})_2$  equilibrations and may have been exacerbated by the relatively low soil to solution ratios used for the laboratory measurements.

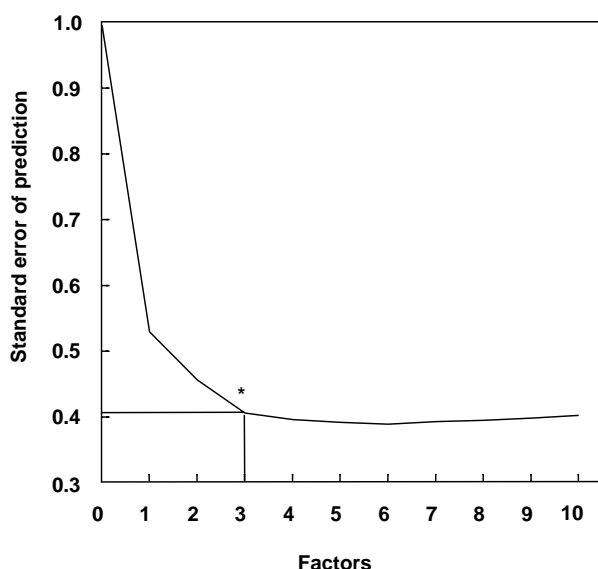
In a detailed MIR study on a set of 188 soils from southern South Australia, Merry *et al.* (1997) assessed the applicability of the infrared-PLS method as a surrogate of a large number of soil properties, including lime requirement, in place of the more lengthy laboratory procedures. For lime requirement determinations in 2 completely separate laboratory runs, replication of laboratory data, illustrated in Figure 1, resulted in  $R^2 = 0.728$  for the slope and  $R^2 = 0.850$  for the starting pH ( $\text{pH}_0$ ). The relatively poor  $R^2$  values for these replications suggested that most of the error associated with subsequent prediction from PLS could



**Figure 2.** MIR-PLS predicted lime requirement versus laboratory-determined incubation data (L data). The equation of the regression line is:

$$Y = 0.86X + 0.33 \quad (R^2 = 0.850, n = 188).$$





**Figure 3.** Standard error of prediction for lime requirement from FT-MIR PLS cross-validation for increasing number of factors. Minimum significant standard error of prediction is indicated (\*) for 3 factors.

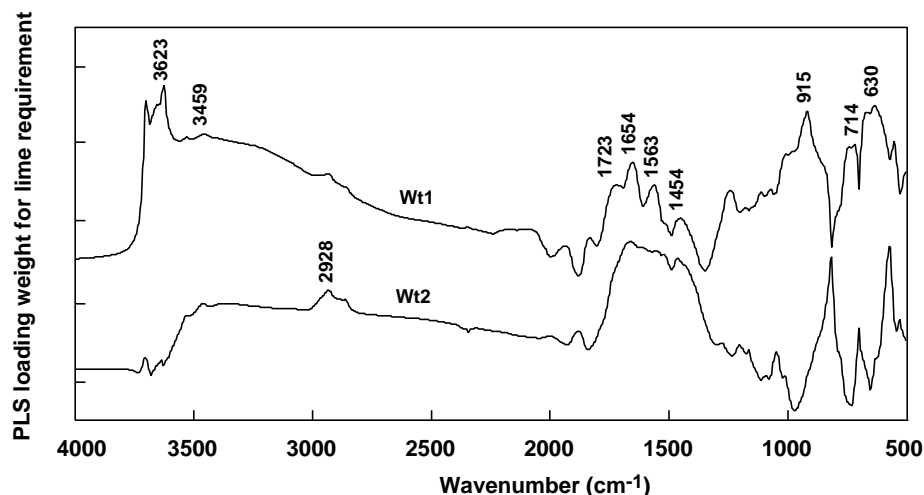
be attributed to high variance in the laboratory determined lime requirement data, rather than an inherent inability to predict lime requirement from the infrared viewpoint.

A plot of the regression between lime requirement from Merry *et al.* (1997), predicted from infrared-PLS, and the laboratory incubation data is presented in Figure 2. An excellent prediction was achieved, with

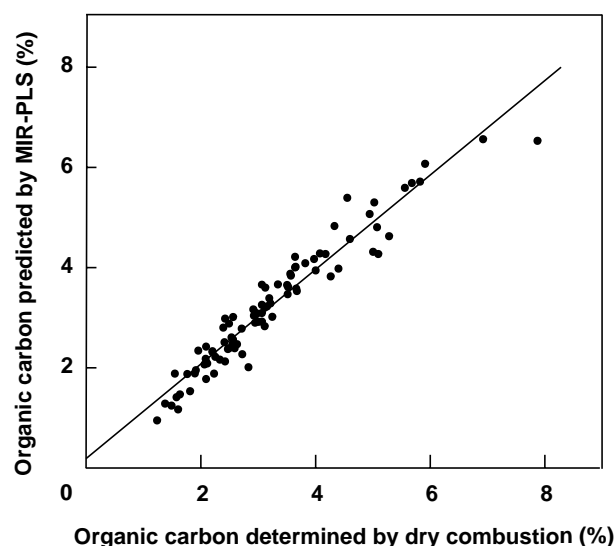
$R^2 = 0.85$ ; better in fact than the original laboratory replication error discussed above. The robustness of the prediction was confirmed by the rapid convergence of the prediction standard error (SEP), as illustrated in Figure 3, suggesting that just 3 loadings (i.e. major soil components) were sufficient to model nearly all the explained prediction variance.

Important qualitative information could also be derived from this study, confirming the link between soil chemistry and acidity. Plots in Figure 4 clearly show the major spectral features which are associated with the first 2 (most important) loading weights. As stated earlier, the loading weights can be considered as indicators for the 'correlations' between the property of interest and the infrared frequencies. The first factor weight shows peaks due to the major components contributing to lime requirement [i.e. smectite clay and gibbsite ( $3631\text{--}3000\text{ cm}^{-1}$ ) and organic matter ( $2929\text{--}2855$  and  $1750\text{--}1449\text{ cm}^{-1}$ )]. A negative contribution due to quartz, as sand, is observed in the region  $1992\text{--}1850\text{ cm}^{-1}$ . Peaks below  $1300\text{ cm}^{-1}$  can generally be attributed to kaolinite and quartz. The second factor exhibits more subtle variations in soil chemistry correlating with lime requirement. In this case, soil organic matter is the dominant component, with strong alkyl ( $2929\text{--}2855$  and  $1449\text{ cm}^{-1}$ ) peaks and strong, broad bands due to carboxylic-protein-aromatic species near  $1750\text{--}1449\text{ cm}^{-1}$ . A strong negative band (negative correlation) due to kaolinite is observed near  $3705\text{ cm}^{-1}$  for the second weight.

As a comparison, lime requirement predictions using the NIR regions from both an extended range Fourier-transform (FT)-MIR spectrometer and also from a field-



**Figure 4.** FT-MIR PLS loading weights 1 (Wt1) and 2 (Wt2) for predicted lime requirements. Weight values range from 0.10 to  $-0.10$ , but are offset for Wt1 and Wt2 for clarity.



**Figure 5.** Organic carbon predicted from FT-MIR PLS analysis versus organic carbon determined by Leco dry combustion. The equation of the regression line is:

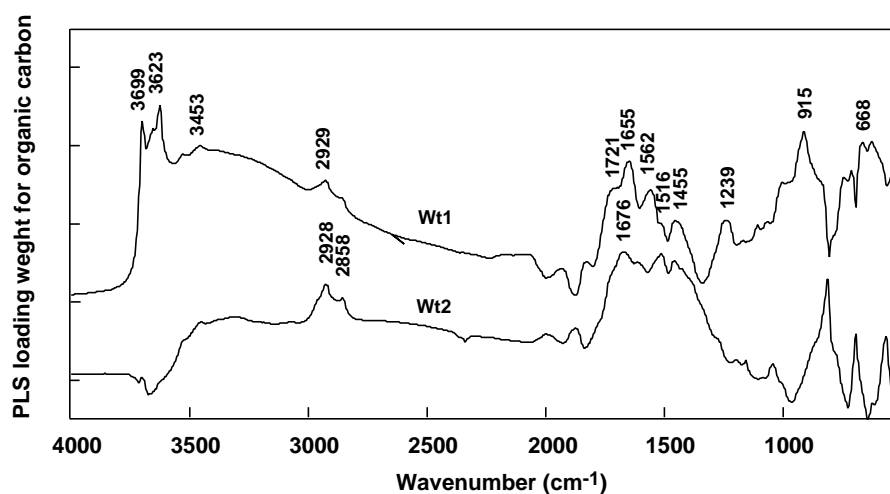
$$Y = 0.94X + 0.19 \quad (R^2 = 0.930, n = 188).$$

portable dispersive (FPD) NIR spectrometer, were examined. The precision of the NIR analyses did not match those of FT-MIR, resulting in  $R^2$  values of only 0.73 and 0.70 for the FT and FPD instruments, respectively, consistent with the reduced spectral information in the NIR compared with the MIR range, and the reduced photometric stability of the FPD spectrometer.

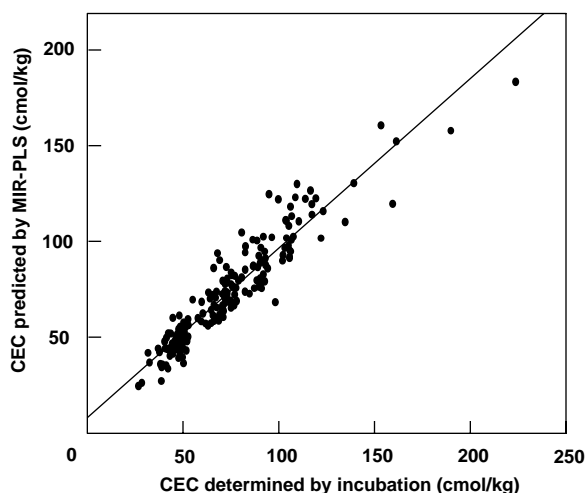
### Soil organic carbon

Soil organic carbon has been regarded as a useful indicator of sustainability and has implications in global warming, soil structure and plant nutrition. In Australia, organic carbon shows a rapid drop in the surface soil after clearing native vegetation, and thereafter declining to a level often less than one third of the initial organic carbon after many years of agricultural production (Skjemstad *et al.* 1996b).

Total soil organic matter is a complex mixture of plant debris, humic substances and inert or recalcitrant material (Theng *et al.* 1992; Theng and Tate 1989; Jenkinson and Coleman 1994; Parfitt *et al.* 1997). It typically contains varying proportions of chemical groups such as  $H_2O$ ,  $-CH_2-$  and  $-CH_3$  (alkyl),  $C-OH$  (carbohydrate),  $-COO-$  and  $-COOH$  (carboxyl),  $-NH$  and  $-CNO$  (amide),  $-C=O$  (carbonyl), and aromatic  $-C=C-$  and  $-CH$  (Van der Marel and Beutelspacher 1976; Skjemstad and Dalal 1987; Bracewell *et al.* 1989; Janik and Skjemstad 1995; Parfitt *et al.* 1997). The chemical groups comprising soil organic matter are nearly all infrared active, with peaks in very specific spectral regions (some groups are also pH dependent e.g.  $-COO-$  and  $-COOH$ ). The intensities and distribution of the infrared peaks can thus be used to characterise the chemistry of soil organic matter (Schnitzer 1965; Piccolo *et al.* 1989; Skjemstad and Dalal 1987). Unfortunately the peaks are often highly overlapped making measurements difficult. In order to separate or resolve the organic matter peaks in soils, computer subtraction of the ignited soil matrix from the spectra of the whole soils has been used to remove the interference from the overlapping soil peaks, thus



**Figure 6.** FT-MIR PLS loading weights 1 (Wt1) and 2 (Wt2) for the PLS analysis of soils for predicted organic carbon. Weight values range from 0.10 to  $-0.10$ , but are offset for Wt1 and Wt2 for clarity.



**Figure 7.** Regression between cation exchange capacity (CEC) predicted from MIR-PLS versus values determined in the laboratory by direct exchange of ammonium. The equation of the regression line is:

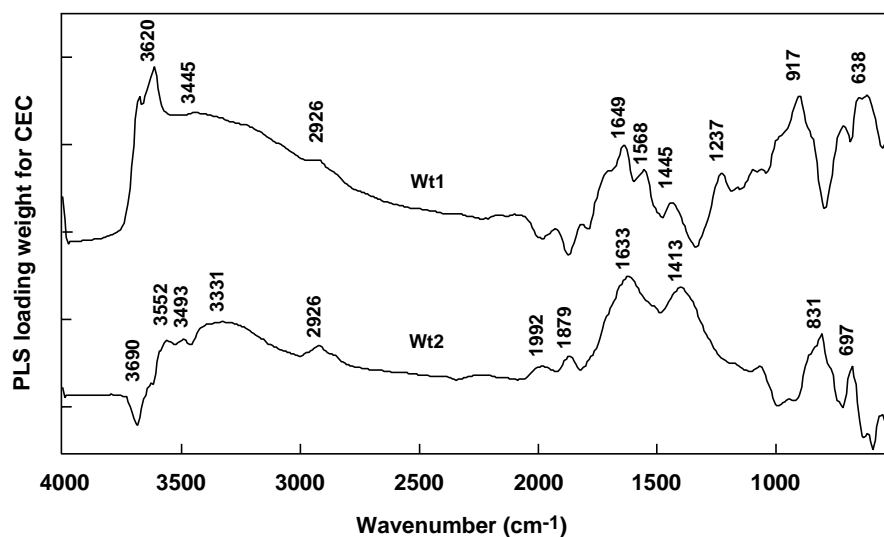
$$Y = 0.826X + 12.73 \quad (R^2 = 0.883, n = 183).$$

enhancing the spectra of the underlying organic matter (Nguyen *et al.* 1991).

In spite of its complexity, soil organic matter is usually determined only as total organic carbon by oxidation with acidified dichromate (Walkley 1947; Heanes 1984) or by dry combustion (Merry and Spouncer 1988). MIR-PLS has been shown to be an

effective surrogate to traditional chemical determinations of total carbon. Surprisingly, in spite of its power and simplicity, the combination of MIR and PLS has received very little attention except for a few predictive studies (Janik and Skjemstad 1995; Hazel *et al.* 1997; Merry *et al.* 1997). In a comprehensive study of 300 soils throughout Australia, Janik and Skjemstad (1995) have shown an excellent correlation ( $R^2 = 0.92$ ) between total organic carbon determined by Leco and MIR. In an extension of their PLS analysis for soils from southern South Australia, Merry *et al.* (1997) achieved a similar precision for organic carbon and total nitrogen, with  $R^2 = 0.93$  and  $0.86$  respectively as shown in Figure 5 for organic carbon. The result for the MIR-PLS prediction for whole soil organic carbon, shown in Table 1, compares favourably with NIR-PLS predictions for organic carbon in the silt and clay fractions of surface soils by Morra *et al.* (1991), who achieve a PLS prediction for organic carbon with an  $R^2 = 0.93$ ; considerably higher than that reported by others (Sudduth and Hummel 1991, 1993; Ben-Dor and Banin 1995a, 1995b).

In the MIR-PLS analysis by Janik and Skjemstad (1995), there was a significant curvature in the regression, with very high values of organic carbon being underestimated. These authors suggested that there may be a variation in type of carbon for this very large range of concentrations (0–23% organic carbon). For these soils, values higher than 10% organic carbon were relatively rare (only 13 of the 300 soils analysed). When the selected range was restricted to 0–2.5% organic



**Figure 8.** FT-MIR PLS loading weights 1 (Wt1) and 2 (Wt2) for the PLS prediction of cation exchange capacity (CEC). Weight values range from 0.10 to  $-0.10$ , but are offset for Wt1 and Wt2 for clarity.

carbon, the  $R^2$  increased to 0.99 (i.e. the model was better able to predict the lower values than the higher values for which there were fewer calibration samples). The overall distribution of chemical species in the organic matter can be inferred from the first few loading weights. Peaks in the first factor loading weights for PLS analysis of soil organic carbon corresponded with those for clay content, lime requirement and exchange capacity, confirming the high correlation of soil organic carbon with these other properties. For example, the loading weights for organic carbon, depicted in Figure 6, clearly show the similarities in soil constituents described by the first 2 loading weights and those for lime requirement in Figure 2.

Chemical extraction of soil organic matter into various humic components is one technique used to characterise the variation in chemistry of soil organic matter (Swift 1986). Such extracted humic materials, through the use of concentrated NaOH, have been thought to 'characterise' the variation in soil organic matter (Schnitzer 1965, 1978; Stevenson 1982; Huffman and Stuber 1986) and are assumed to represent the reservoir of global organic carbon. In a review of soil organic matter (Aiken *et al.* 1986), the chemistry of humic and fulvic acids, extracted by dissolution-fractionation procedures (Hayes 1986) using NaOH, or acidic solutions of dipolar aprotic solvents (Piccolo *et al.* 1989), were then analysed with MIR (Schnitzer 1965, 1978; Stevenson 1982; Piccolo 1988; Bloom and Leenheer 1989), by  $^{13}\text{C}$ -NMR (Skjemstad and Dalal 1987), or by mass spectroscopy (Bracewell *et al.* 1989).

It is by no means certain that approaches using dissolution procedures are complete and do not alter the organic matter (Theng and Tate 1989), and an alternative way of studying soil organic matter would be to look at it *in situ* (i.e. while it is still in the soil in its natural forms, albeit often with some form of physical separation) (Tisdall and Oades 1982; Tiessen and Stewart 1983; Skjemstad *et al.* 1996a; Parfitt *et al.* 1997). Humic and fulvic acids may be considerably altered during separation from the soil, and in fact may not exist in their extracted forms in soils, and the ability to characterise a soil in terms of its extracted fractions therefore does not ensure a true knowledge of its behaviour in the field. Partial least squares analysis with MIR can be readily applied to the study of whole soils, and it also offers an advantage in terms of speed and low cost, enabling mechanistic and qualitative information to be derived, particularly for use in carbon models.

#### *Exchangeable cation related soil properties*

The MIR-PLS technique has also been used to successfully predict exchangeable cation-related properties; for example, cation exchange capacity (CEC)

with  $R^2 = 0.88$ , sum of exchange cations ( $\Sigma\text{cats}$ ) with  $R^2 = 0.84$ , exchangeable calcium, magnesium, aluminium and manganese with  $R^2 = 0.89, 0.76, 0.64$  and  $0.66$  respectively (Janik *et al.* 1995; Merry *et al.* 1997). Exchangeable sodium and potassium could only be predicted with an  $R^2 = 0.33$ . Some examples from their predictions are included in Tables 1 and 2.

The excellent regression between predicted versus known CEC values, plotted in Figure 7, result from the high sensitivity of the MIR for clay type, clay content and organic matter, which are all implicated in cation exchange phenomena. Partial least squares analysis loading weights for CEC, depicted in Figure 8, support the strong correlation with smectitic clay, with a strong peak near  $3620\text{ cm}^{-1}$  and a broad band at about  $3445\text{ cm}^{-1}$  for smectite in loading weight 1, and organic matter peaks near  $2926\text{--}2850\text{ cm}^{-1}$ ,  $1633$  and  $1413\text{ cm}^{-1}$  typical of organic matter carboxylate species. The second loading weight for CEC prediction was different to that of the organic carbon in that it was dominated by carboxylate rather than proteinaceous material. This data supports the view that the type of organic matter is important, not just the amount of organic carbon and that MIR is much more suited to discrimination of these organic components than many traditional laboratory extraction procedures.

Partial least squares analysis results for other exchangeable cation-related properties, included in Table 1, demonstrate the potential for MIR to obtain a quick and cheap prediction of some properties relating to soil acidity in place of the more commonly used extraction procedures. However, the possibility of strong cross correlations among some of these characteristics must be considered.

#### *Phosphorus adsorption and availability parameters*

Methods for determination of adsorption and nutrient availability properties of soils usually involve lengthy incubations, or equilibrations of solutions of known initial concentrations, with soil suspensions (Rayment and Higginson 1992). Isotherms are generated allowing relevant parameters to be determined. Where these parameters are related to soil properties, the infrared PLS method offers a rapid surrogate method. As pointed out above, however, if the soil solution is most important, or the adsorption or availability parameters are dependent on more transient criteria, the infrared method may fail.

Apart from lime requirement, there is great interest in developing more rapid (and precise) techniques for phosphorus adsorption and availability determinations. Total phosphorus adsorption is dependent on the chemistry of the soil matrix (i.e. certain minerals such as iron-oxyhydroxides and carbonates), and organic matter/aluminium complexes which are known to strongly sorb phosphate anions. The MIR-PLS method

would be expected to effectively predict the phosphorus adsorption capacity with a high correlation (see Table 1). On the other hand, phosphorus adsorption and bicarbonate-available phosphorus would show very poor correlations with the MIR technique (see Table 2) since they are related as much to the level of phosphorus in solution rather than to the chemistry of the soil matrix.

#### *Soil physical measurements*

Soil physical measurements frequently relate to the size, composition and surface properties of soil constituents, and to the water content. In addition to 'recognising' clay size soil particles (Table 1), MIR-PLS is also able to characterise the specific kind of clay. Associated with the clay are physical properties such as particle size and moisture content, and consequently strong prediction for these determinations was obtained by Janik and Skjemstad (1995) and Merry *et al.* (1997) with  $R^2 = 0.84$ , 0.94 and 0.70 for clay, sand and ADM respectively. Future work in developing an infrared method for predicting soil texture would be a major advantage in soil characterisation and preliminary work suggests that such a surrogate would be entirely feasible.

#### *Biological indicators*

The spectral contribution of *in situ* soil microorganisms in the soil is expected to be only minor, in consideration of the relatively small fraction of total biomass (about 5%) in the total organic carbon. Spectral signatures of microorganisms are therefore usually difficult to detect *in situ* in most soils due to masking by soil mineral and other organic peaks. For example, Filip (1977) isolated bacteria from 2 soils, producing spectra characterised by acidic, proteinaceous and lipid species, but dismissed the whole-soil spectra as 'rather simple and monotonous', being largely dominated by quartz, montmorillonite and kaolinite.

An alternative approach is to use GC-FAME (gas chromatograph + fatty acid methyl ester) chromatograms to represent the effective carbon length profiles of fatty acids, the distributions of which may be characteristic of particular soil microorganisms. The methylated fatty acid constituents of soil microorganisms are derived from the lipid fraction of the soil organic matter using NaOH/methanol and extracted into hexane/methyl tert butyl ether. For most soil organisms, these chromatograms represent hundreds of constituent peaks. This procedure is being considered as the basis for a rapid, multi-factored and inexpensive measure of soil health.

In a recent study (Pankhurst *et al.* 1997), the GC-FAME spectra were correlated with the MIR spectra of the same soils using covariance and PLS regression analysis. Twenty-three FAME peaks, 14 of which are found in bacteria and 7 in fungi and other eukaryotes were found to correlate with the MIR spectra with  $R^2$  values  $>0.5$  (with some  $R^2$  values  $>0.75$ ) suggesting

that the infrared spectra could explain 75% of the variability in the FAME data. In the above study, Pankhurst *et al.* (1997) suggested that it would not only be possible to predict the bacterial and fungal biomass in the soil using MIR spectral data, but also allow conclusions to be made regarding the soil chemistry favourable for particular soil microorganisms from the appearance of the PLS loading weights. Since MIR spectra can be obtained much more rapidly compared with current conventional methods for measuring bacterial and fungal biomass which rely on laborious microscopy or lengthy and expensive bioassays, there is an opportunity to use the predictive capacity of such PLS models as a simple biomonitor of soil health with opportunities for soil biological mapping.

#### **Near infrared capabilities**

In spite of the lower precision of the NIR analysis demonstrated for lime requirement and other analyses, the opportunity to carry out field studies using high density sampling with the less precise but practical FPD spectrometer may offer considerable advantages. The precision of NIR data may be entirely adequate for example geographic information (GIS) and other farm-scale, spatial variability applications, serving to enhance the number of analysed points very rapidly and at relatively low cost.

Partial least squares prediction of physicochemical soil properties, including organic carbon and biomass, from NIR spectra of soils and soil humus has been reported (Fritze *et al.* 1994) in spite of the relatively weak organic peaks in the NIR compared with the mineral components. Near infrared has a potential advantage over MIR in that the spectrometers can be much smaller, cheaper and field portable. Although portable MIR instruments have recently become available, they require gas purging that somewhat negates portability. Further reduction in costs in NIR can be achieved through the use of filters instead of a dispersing grating or interferometer.

Near infrared satellites and aerial photographic images are now common-place and the ability to predict soil properties and classify soils from their NIR spectra is routine (Ben-Dor and Banin 1995b; Palacios-Orueta and Ustin 1996) although for soil applications, spectra are often affected by surface cover such as vegetation. The recent use of field-portable NIR spectrometers for organic carbon predictions (Sudduth and Hummel 1993) further highlights the successful advances made in infrared technology suitable for soil studies.

In spite of their wide-spread use, NIR suffers from a number of limitations regarding its reduced sensitivity to some common soil minerals and organic species. In most Australian soils, quartz is a major component, yet it is transparent to the electromagnetic radiation at



frequencies from about 5000 nm through to the ultraviolet. In contrast, quartz gives a very intense signal in the MIR, even though it often interferes with or masks weaker organic peaks. Further difficulties with NIR analysis of soils are due to the relatively weak intensities of the organic peaks in soil spectra compared with those for the MIR spectra.

### Field-scale mid infrared applications

Although there is a need for further laboratory studies of the relationships between soil properties and soil chemistry, there is an urgent and increasing need for the availability of spatially dense soil analytical data in broad-scale and in field applications. There is little documented information on infrared applications of high throughput soil analysis. Acquisition of such data must be able to be justified in terms of its cost and utility, a factor often not considered as important in more detailed research applications. Recent developments that enhance the potential usefulness of infrared are: (i) faster, smaller, more robust and cheaper equipment; (ii) the promise of field portability for both NIR and MIR; (iii) availability of commercial statistical and data handling software, able to quickly process the spectral information; (iv) the need for fast acquisition of spatially dense data in precision and prescription farming; and (v) the possibility of linking the surface chemistry and other surface properties of soils to agronomically important soil properties.

### Infrared analysis costs and utility

A laboratory-based FT-infrared spectrometer, computer and basic spectroscopy software for soil studies should be within the cost limits of most soil laboratories. Field-portable MIR equipment has recently become commercially available but is expensive compared with field-portable NIR equipment. Software for PLS analysis may be a significant additional cost, as would be hardware add-ons to the spectrometer such as DRIFT accessories, fibre-optic probes and NIR extension. Laboratories intending to use infrared analysis would need to have access to suitable calibration soil samples, either purchased, exchanged or from their own sources, and laboratory staff may need to develop sufficient expertise to handle PLS analysis if intending to attain full, in-house capability. It is expected that spectral interpretation through expert systems, and commercial software linking the PLS output and land management decision support systems will become increasingly available.

Sample preparation for research infrared analysis is usually not regarded as a limitation, but for high sample throughput, in situations where spatially dense analysis is required, minimisation of sample preparation becomes a priority. For example, sample grinding time can take

5–6 min per sample to complete. Since usually only a very small spot size (a few millimetres) is actually analysed during DRIFT analysis, some effort is required to obtain a suitably representative subsample. Air-dry samples may need to be finely ground to a size much smaller than the analysed spot size (e.g. in the order of 0.2 mm), but this requirement should be further investigated.

Acquisition of spectra by FT-infrared is fast, typically 1 scan per second, depending on the resolution and instrument parameters, although rates as high as 20–40 scans per second at reduced resolution and increased spectral noise can be achieved. This enables fast routine throughput and computer storage of the digital spectral data set, ready for further processing for use by a PLS prediction module. Prediction is also very rapid, in the order of fractions of a second per sample. Many soil properties for a particular unknown sample can be predicted simultaneously from the same spectrum which, at a later date, can be re-used for the prediction of new properties when calibrations for these become available. This is in contrast to many routine analyses which can often only determine one single property at a time.

### Conclusions

Infrared spectroscopy, particularly when used with multivariate analytical methods, has been shown to be able to predict many soil properties with a high degree of accuracy and precision. It can achieve this rapidly and with a minimum of sample preparation for a number of soil properties from a single spectrum, an important advantage for large soil sets.

Where traditional analytical methods are slow, complicated or inaccurate, the links between the analytical data and relevant soil processes can be poorly understood, thus limiting the scope and utility of the analytic data and leading to serious questions of acceptability by the soil science and agriculture industry. In particular, the speed, low cost and accuracy of the infrared method opens up its possible use in broad-scale precision farming and land assessment and for spatially dense data in soil mapping applications. In contrast, extractive analytical procedures are usually poorly suited and difficult to incorporate into these applications.

So, can MIR analysis replace soil extractions? In some cases yes, but in general it should be thought of mostly as adding value to, or expanding, existing extraction methods and adding to the understanding of the underlying relationships between soil properties and soil chemistry. A single property, such as lime requirement or organic carbon, is often related to complex and inter-related underlying soil chemistry which the MIR-PLS method may help to resolve. For a number of soil analyses, the traditional analytical methods have been found to be slow, complicated or



inaccurate, or inappropriate extraction procedures used, resulting in links between the analytical data and relevant soil processes which may be poorly understood or defined. This deficiency has often limited the scope and utility of the analytical data, leading to serious questions of acceptability by the farming industry. While it is not expected that MIR-PLS will replace the extractable nutrient analyses used in conventional soil fertility assessment, infrared methods have the potential to add considerable value to soil analysis. The nature of infrared analysis suggests that it may be well suited for use in decision support systems.

The inherent speed, low cost and accuracy of the DRIFT-MIR method therefore opens up its possible use in broadscale precision farming and land assessment applications, particularly utilising spatially dense data. There are a wide range of infrared-based approaches, from remote NIR to research laboratory MIR, that have the potential to transform the way in which soil analyses are carried out, interpreted and applied. Even though new probes are continually becoming available for the NIR, the MIR range is inherently more sensitive to molecular information, and technical advances in sampling and portability are expected to continue to improve the technique for greater utility in soil analysis.

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