

## Use of Fe<sup>3+</sup> Ion Probe to Study Intensively Weathered Soils utilizing Electron Paramagnetic Resonance and Optical Spectroscopy

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Análises por espectroscopias de ressonância paramagnética eletrônica (EPR) e de ultravioleta-visível por refletância difusa (DRUV-VIS) de solos intensamente intemperizados contendo altos níveis de óxidos-hidróxidos de ferro, a partir de um projeto-piloto de agricultura de precisão, incluindo 13 fazendas no sudoeste do estado do Paraná, Brasil, foram realizadas, visando definir parâmetros de fertilidade dos solos. Os resultados dos estudos espectroscópicos no laboratório foram comparados com aqueles obtidos através da utilização de um espectrorradiômetro portátil, em condições de campo. Os solos estudados apresentaram como constituintes inorgânicos, principalmente minerais de argila 1:1, óxidos e hidróxidos de ferro (principalmente goetita e hematita) e de alumínio (principalmente gibbsita), características de solos altamente intemperizados, como por exemplo, Latossolos. Os espectros de EPR, típicos de agregados de íons Fe<sup>3+</sup> com interação magnética, apresentaram aumento na largura da linha do sinal em *g ca. 2* quando obtidos em temperatura de nitrogênio líquido, em comparação com os obtidos a temperatura ambiente. Este fenômeno pode ter sido causado por mudanças no ambiente do campo cristalino dos íons Fe<sup>3+</sup> ou pelo mecanismo de relaxação spin-spin, o que provoca aumento da largura de linha quando a temperatura diminui. As curvas espectrais eletrônicas obtidas com o espectrorradiômetro portátil apresentaram-se menos detalhadas, porém mais específicas de cada amostra de solo analisada. Os resultados indicam que o uso do espectrorradiômetro portátil juntamente com ferramentas matemáticas, como a segunda derivada da função Kubelka-Munk, é uma boa alternativa para analisar solos argilosos ricos em óxidos-hidróxidos metálicos. Foram feitas atribuições das absorções espectrais, principalmente para as transições eletrônicas d-d entre níveis de energia de pares de íons Fe<sup>3+</sup>-Fe<sup>3+</sup>.

Electron paramagnetic resonance (EPR) spectroscopy and optical analyses of intensively weathered soils containing high levels of oxide-hydroxide of iron from a pilot project on precision agriculture, including 13 farms in the southwest of Paraná state, Brazil, were carried out, aiming at defining parameters of soil fertility. The results of the optical studies in the laboratory were compared with those obtained by the use of a portable spectroradiometer in field conditions. The studied soils were mainly composed of 1:1 clay minerals, oxides and oxide hydroxides of iron (mainly goethite and hematite) and aluminum (mainly gibbsite), characteristics of highly weathered soils, as for example Ferralsols. The EPR spectra, typical of mutual magnetic interaction of aggregated Fe<sup>3+</sup> ions, showed a signal linewidth increase at *g ca. 2* upon cooling. This phenomenon can be caused by changing the crystal field environment of Fe<sup>3+</sup> ions or by the spin-spin relaxation mechanism, which causes an increase of linewidth when the temperature decreases. The optical spectral curves obtained from the portable spectroradiometer presented less detailed but more specific features for each soil sample analyzed. The results indicate that use of the portable spectroradiometer along with mathematical tools such as the second derivative mode of the Kubelka-Munk function is a good alternative to analyze clay soils rich in metallic oxide and oxide hydroxides. A full attribution of the spectra features was made, mainly for the electronic transitions between energy levels into Fe<sup>3+</sup>-Fe<sup>3+</sup> couples.

**Keywords:** spectroradiometer, EPR spectroscopy of soils, optical spectra of iron oxides, remote sensing, spectra of intensively weathered soils

## Introduction

“Human welfare is intimately linked to soil quality and its management. Principal global issues of the 21st century, whose solution to a great extent depends on sustainable management of world soils, include food insecurity and hidden hunger, global warming and carbon sequestration, water scarcity and eutrophication, soil degradation and desertification, energy scarcity and biofuels, excessive urban and industrial wastes, and environmental pollution. There exists a direct link between these global issues and sustainable use of world’s finite and fragile soil resources, which must never be taken for granted”.<sup>1</sup> Brazil has a huge landmass, covering approximately the half of South America. It is largely located in the tropical zone, with strong sunlight incidence. This, along with ample rainfall in much of the country, makes it one of the world’s major food and biofuel producers. However, most farmed Brazilian soils are ferrous and highly weathered.<sup>2</sup> This is particularly true of the State of Paraná, in the south of the country. Although agriculture is the State’s main economic activity, its soils are generally poor (highly weathered with low fertility), particularly in the southwestern part of the state. The lack of information about the capabilities and needs of soils with these attributes and the pursuit of higher productivity have led the farmers to apply excessive amounts of fertilizers and soil conditioners such as lime. This increases production costs, besides contaminating both soil and water with accumulated chemical residues, especially of soluble fertilizers and their byproducts from hydrolysis. Thus, a better understanding of the soil conditions and the implementation of modern sustainable technology are important for the region’s continued agricultural development and health. Conventional soil sampling and laboratory analyses cannot efficiently provide this information because they are slow and expensive.<sup>3</sup> On the other hand, *in situ* spectroradiometric analyses are fast and provide knowledge of soil spectral behavior considering the spatial and timing variability of edaphoclimatic factors (climate, relief, temperature and humidity).<sup>4</sup> Typically the spectroradiometric data are collected by sensors that capture the sunlight reflected from the earth’s surface, by equipment carried by airplanes or satellites. However, more detailed soil data can be obtained from portable spectroradiometers, with accuracy to the nearest meter.<sup>5</sup> Independent of the data acquisition level, the non-lambertian (anisotropic) characteristics of the soil reflectance obtained in this kind of analysis must be taken into account.<sup>6</sup> The spectral characterization of soils is performed by observing the bidirectional reflectance factors (BRF).<sup>7</sup> The BRF depend on sample properties, illumination and geometries of the

spectral range considered. The bidirectional term refers to the two geometric conditions involved: one for the source and the other for the sensor position.<sup>6</sup> These have to be the same for comparative analysis.

Despite the great potential of spectroradiometric analysis, there are few spectral studies about highly weathered soils, *e.g.* Ferralsols<sup>8</sup> in Brazil. Thus, the objective of this work is to evaluate the EPR and optical spectral features of intensively weathered clay soils from the southwestern region of Paraná State, comparing optical spectral data provided by a portable spectroradiometer with those obtained by laboratory spectrometric techniques, to support precision agriculture. Using the Fe<sup>3+</sup> ions of the oxide-hydroxides structures as a paramagnetic probe, EPR spectroscopy was used in combination with diffuse reflectance ultraviolet-visible-spectroscopy (DRUV-VIS), aiming to develop more suitable methods to shed light on the Ferralsols, attributing, in terms of chemical structures, most of the spectral features of the soil spectra.<sup>9,10</sup>

## Experimental

### *Chemical reagents and soil samples*

All chemical reagents and solvents were highly pure so were used without prior purification. Distilled and deionized water was used to prepare all aqueous solutions. The research was performed on ferralsol samples of 13 farms in the southwest of Paraná State. That region is characterized by a humid mesothermal climate with geological formations composed of basaltic rocks of the Serra Geral formation, São Bento group. The analyses were carried out using 10 samples, randomly collected at 0 to 20 cm depth from each property. The soils from each farm were mixed to produce a representative sample, which were identified as S1, S4, S5, S6, S7, S8, S9, S11, S12, S13, S14, S15 and S16. The *in situ* radiometric measurements were performed in the vertical position about 1.2 m above the soil surface. On each farm, ten points of bare soil were measured and the median of the data was used to represent the sample.

### *X-ray fluorescence spectroscopy (XRF) analyses*

To determine the percentage, in terms of oxides, of the chemical elements Si, Al, Fe, and Ti, normally the markers of the weathering process,<sup>7</sup> the soil samples were analyzed by XRF spectroscopy. This entailed weighing 7 g of each sample mixed with 1.4 g of an organic wax glue (*N,N'*-bis-estearoil ethylenodiamine). The samples were homogenized, pressed and then analyzed in a Philips PW 2400 spectrometer.

### Diffuse reflectance ultraviolet-visible spectroscopy (DRUV-VIS) analysis in the laboratory

The soil samples were analyzed by the DRUV-VIS technique using a Shimadzu UV-2401PC spectrophotometer, equipped with a 240-52454-01 integration sphere accessory. The solid material was ground in a pan grinder to 200 mesh size, and then analyzed after being compressed carefully in the spectrometer cell.

### Portable spectroradiometer analyses in the field

For the bidirectional reflectance factor (BRF) measurements in the field, a FieldSpecPro portable spectroradiometer was used, which has a detection range from visible to short wave infrared (400-2,500 nm).

### Electron paramagnetic resonance spectroscopy (EPR)

EPR spectroscopy analyses were performed on soil samples at room temperature (*ca.* 300 K) and at liquid nitrogen temperature (77 K), with the samples firmly accommodated in quartz tubes. A Bruker EMX spectrophotometer was operated at a frequency around 9.5 GHz (X-band), precisely determined, with a modulation frequency of 100 kHz, amplitude modulated from 2.024 G and microwave power of approximately 20 mW.

### Theory

In recent years we have used EPR and DRUV-VIS spectroscopy to assess the presence of inorganic structures in soils, especially using the Fe<sup>3+</sup> ion as a probe, due to the sensitivity of these techniques and ubiquity of this ion in the environment.<sup>10-12</sup> The EPR spectra for all samples with high iron content present two kinds of Fe<sup>3+</sup> ion domains. The first is a diluted domain, attributed to isolated Fe<sup>3+</sup> ions, which exhibits sharp EPR lines at a magnetic field, lower than 150 mT. The other domain, characterized by having no homogeneously broadened lines by magnetic dipole-dipole interactions among Fe<sup>3+</sup> ion centers ( $\Delta H_{pp} > 50$  mT and *g ca.* 2), is referred to as a concentrated or clustered

domain. The concentrated domain can be attributed to spin-spin interactions among irons in the oxide-hydroxide structures.<sup>11</sup>

By DRUV-VIS spectroscopy, the Fe<sup>3+</sup> ions in solid chemical structures present spectra with features corresponding to two types of electronic transitions. According to electronic spectroscopy rules, only the ligand to metal charge transfer transitions (LMCT), O<sup>2-</sup> → Fe<sup>3+</sup>, would be allowed. The d-d transitions would be forbidden as a consequence of parity (Laporte) and multiplicity rules. However, the existence of magnetically coupled adjacent Fe<sup>3+</sup>-Fe<sup>3+</sup> ion pairs in structures like that of iron oxide-hydroxides with magnetic interaction makes the d-d transitions permitted.<sup>10,12,13</sup> The name of hematite,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, is related to the red color commonly observed in many intensively weathered soils and sedimentary rocks.<sup>14</sup> The intense red color observed is because the oxide ion octahedres with the Fe<sup>3+</sup> ions in the symmetry centers in the hematite structures are face-linked, causing the Fe<sup>3+</sup>-Fe<sup>3+</sup> ions from the neighboring pairs to be closer together. The closer they are, the higher the magnetic interaction between them and the more allowed the d-d transitions are.<sup>15</sup> The DRUV-VIS spectra were converted to the Kubelka-Munk remission function, defined by,  $f(KM) = (1 - R)^2/2R = k/s$ , where R is the reflectance, k is the absorption coefficient, and s is the scattering coefficient.<sup>12,14,15</sup> In order to increase the resolution of the spectral curves, we applied the second derivative mode of the Kubelka-Munk function,  $f(K-M)$ .<sup>12</sup>

## Results and Discussion

### Chemical analyses

The soil layer from 0 to 20 cm is the most intensely modified, through tilling and application of correctives, fertilizers and crop residues. Table 1 shows a high concentration of organic matter (OM), above 4%, in all the soil samples tested. Although this is a positive indicator for soil fertility, OM makes the soils darker, which is a negative factor for spectroscopic analyses since it reduces the reflectance.<sup>3,16</sup> The highest OM concentrations were found in the soils S8, S12 and S16.

**Table 1.** Physical-chemical analysis of the soil samples (SN) studied

Analyses	S1	S4	S5	S6	S7	S8	S9	S11	S12	S13	S14	S15	S16	
Physical	Clay / (%)	71.8	70.8	66.3	63.9	61.5	60.2	62.0	54.0	59.3	65.1	63.6	55.9	60.9
	Silt / (%)	24.1	23.4	31.2	29.4	29.9	33.0	28.6	37.2	35.1	25.9	30.3	38.0	30.7
	Sand / (%)	4.10	5.80	2.50	6.72	8.59	6.82	9.40	8.85	5.61	8.99	6.12	6.07	8.41
Chemical	OM / (%)	5.10	4.02	4.02	4.83	5.90	6.03	4.83	5.10	6.03	5.36	4.42	4.42	6.43
	pH(CaCl <sub>2</sub> )	5.00	4.70	5.00	4.80	5.00	4.70	4.80	5.00	5.60	4.40	4.80	5.00	4.90

In general, all soil samples were found to be acidic, as is typical for intensively weathered Ferralsols of Brazil. Soil S13 (pH 4.40) is the more acidic and S12 (pH 5.60) the less so. Concerning composition, the soils studied in general contained high levels of clay. Soil samples S1 and S4 had the highest clay content while S11 and S15 had the lowest. Such soils with high clay content retain more water than sandy ones. A soil's moisture content affects its reflectance at all wavelengths.<sup>16</sup> As expected, the studied soils presented low values of reflectance.

Table 2 presents the main metal concentrations, in terms of oxides, in the top soils and the rock parent material. The values were obtained by X-ray fluorescence. The chemical components, which can be in the form of aqueous soluble substances like Si, in the form of  $\text{Si}(\text{OH})_4$ , have lower concentrations than in the mother rock, while the chemical elements, which normally appear in the form of insoluble structures, such as  $\text{Al}(\text{OH})_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{FeOOH}$ , are present in higher concentrations in the intensively weathered soils than in the rock parent material.

Soils S1, S8, S9, S11, S14, S15 and S16 had the highest concentrations of  $\text{Fe}_2\text{O}_3$ .

In decreasing order, soils S5, S13, S9 and S7 had the highest concentrations of  $\text{Al}_2\text{O}_3$ . Soil S11 presented the highest concentration of silicon and S16 had the highest concentration of titanium. The main feature of titanium existing in all the soils was the intense absorption in the direction of the red band, because impurity of  $\text{Ti}^{3+}$  in complex octahedral structure presents blue color.<sup>17</sup>

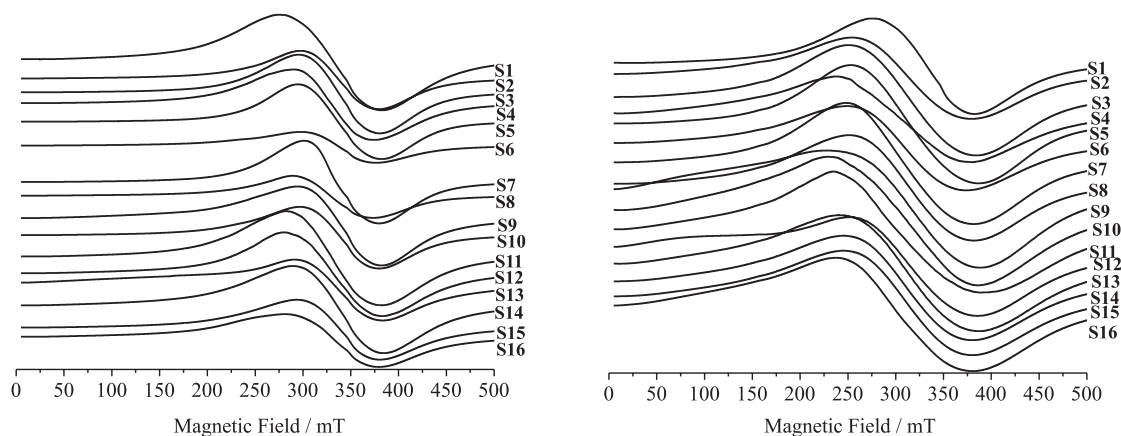
### EPR studies

All EPR spectra of the soil samples (Figure 1) present broad lines at  $g \text{ ca. } 2$ , referring to concentrated domains of  $\text{Fe}^{3+}$  ions. These can be attributed to oxides and oxy-hydroxides of trivalent iron alone or combined on the inner surface of clays.<sup>11</sup> This can be seen in the spectra and in Table 3 below, which show line widths of the absorptions due to  $\text{Fe}^{3+}$  in concentrated dominium of the spectra obtained at room temperature and at 77 K. The spectra obtained at 77 K have broader lines than those obtained at room temperature (*ca.* 300 K).

This broadening of the EPR line at  $g \text{ ca. } 2$  is caused by variation in the dipolar interaction between the  $\text{Fe}^{3+}$

**Table 2.** X-ray fluorescence analysis results for Si, Al, Fe and Ti, in terms of oxides %

Oxide	Rock	S1	S4	S5	S6	S7	S8	S9	S11	S12	S13	S14	S15	S16
$\text{SiO}_2$	50.4	31.5	33.4	32.3	36.2	30.4	30.4	29.5	35.9	30.3	31.0	34.2	29.9	34.1
$\text{Al}_2\text{O}_3$	12.6	22.3	23.4	26.1	21.3	25.0	24.9	25.1	19.0	24.5	25.4	21.5	24.6	21.3
$\text{Fe}_2\text{O}_3$	15.3	21.8	19.9	19.2	20.1	20.6	21.9	19.2	21.3	20.9	19.9	21.1	21.5	21.1
$\text{TiO}_2$	3.5	5.9	5.4	4.4	6.4	1.1	4.1	5.7	6.8	5.3	5.6	6.7	5.6	7.1



**Figure 1.** EPR spectra obtained at room temperature (*ca.* 300 K) (left) and 77 K (right).

**Table 3.** Line width (mT) of the EPR line around  $g \text{ ca. } 2$  at room temperature (*ca.* 300 K) and liquid nitrogen temperature (77 K)

*T / K	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14	S15	S16
<i>ca.</i> 300 K	103	50	83	72	87	74	79	82	86	76	101	102	92	91	83	90
77 K	104	121	133	137	133	118	130	128	153	149	152	128	141	137	131	140

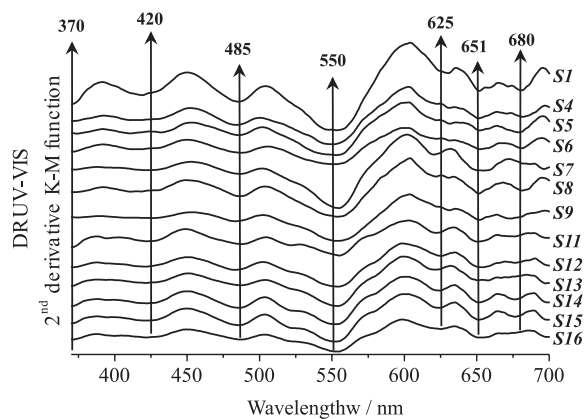
\*sample temperature.

ions with decreasing temperature. Furthermore, the spin-spin relaxation causes an increase in line width when the temperature decreases. This phenomenon can also be caused by other mechanisms, such as a change in the crystal field environment around the Fe<sup>3+</sup> ions.<sup>18</sup> An increase in line width with declining temperature can also be caused by other mechanism. The high clay content of the studied soils (Table 1) and the results of the X-ray diffraction analysis (not shown) of the soils indicate the presence of a reasonable concentration of kaolinite. Ionizing energetic particles resulting from nuclear decay in soils can drag out electrons from Si-O bonds, giving rise to the so-called A and A' paramagnetic defect centers, while the removal of one electron from the Al-O bond produces B paramagnetic defect centers. These paramagnetic center defects can interact with the Fe<sup>3+</sup> ions provoked by the decrease in temperature, inducing modification of the crystal field in the environment of Fe<sup>3+</sup> ions, resulting in line broadening.<sup>19</sup>

#### Diffuse reflectance ultraviolet-visible spectra (DRUV-VIS)

Figure 2 shows the second derivative mode (peaks downward) of the K-M function for the spectral responses by DRUV-VIS spectroscopy, obtained with the spectrometer in the laboratory at wavelengths from 370 to 700 nm. The spectral curves showed similar characteristics, with slight nuances in each soil sample studied. Absorption bands in 360-380 nm range correspond to the  ${}^6A_{1g} \rightarrow {}^4E_g$  ( ${}^4D$ ) ligand field d-d transition for the Fe<sup>3+</sup>-Fe<sup>3+</sup> ion couple in goethite, lepidocrocite and maghemite, the ferromagnetic minerals most commonly found in less weathered soils.<sup>14,15</sup> So, in our case the band at 370 nm could be attributed to the electronic transition,  ${}^6A_{1g} \rightarrow {}^4E_g$  ( ${}^4D$ ), in goethite and lepidocrocite.

Sherman and Waite,<sup>15</sup> reported a very strong and well-defined d-d transition band in the 430 nm region



**Figure 2.** DRUV-VIS 2<sup>nd</sup> derivative Kubelka-Munk function, wavelength (240-700 nm) of the studied soil samples.

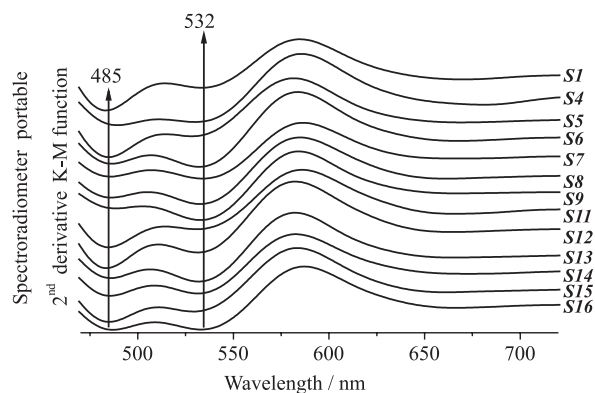
of the spectrum for the transition  ${}^6A_{1g} \rightarrow {}^4E_g$   ${}^4A_{1g}$  ( ${}^4G$ ) of the hematite structure, but for other minerals they only observed an almost imperceptible shoulder in the spectra. In contrast, the soils in this study presented a wide band with slight inflexion located between 420 and 434 nm, suggesting that hematite is associated with other minerals. Stronger evidence of goethite in the soils studied here is provided by the deep absorption band at 485 nm, credited to the double transition,  $2({}^6A_{1g}) \rightarrow 2({}^4T_{1g})$  ( ${}^4G$ ), attributed to this mineral.<sup>14</sup>

Centered at 550 nm in the DRUV-VIS spectra, the double transition band,  $2({}^6A_{1g}) \rightarrow 2({}^4T_{1g})$  ( ${}^4G$ ), is the most intense absorption of hematite. The steep absorption edge at 550 nm gives these minerals their red color. The presence of bernalite, Fe(OH)<sub>3</sub>, was detected in soil samples S12, S13, S14, S15 and S16 from the transition band,  ${}^6A_{1g} \rightarrow {}^4T_{2g}$  ( ${}^4G$ ), centered near 625 nm.<sup>14</sup> In soils S7 and S11, the inflexion was more intense, located at 620 nm, and in S1 it appeared at 630 nm. These small displacements could be associated with the particles' size variation.<sup>14</sup> The band observed in all soils near 651 nm is characteristic of the transition,  ${}^6A_{1g} \rightarrow {}^4T_{2g}$  ( ${}^4G$ ), of goethite, lepidocrocite and hematite structures.<sup>20</sup> The band around 680 nm could be attributed to the four quantum overtone transitions of water ( $\nu_1 + 3\nu_3$ ), where  $\nu_1$  is responsible for the symmetric and  $\nu_3$  for the antisymmetric stretching vibration of water.<sup>21</sup>

#### Field studies

Figure 3 shows the second derivative mode of the K-M function for the spectral curves obtained with the portable spectroradiometer *in situ* in the wavelength range from 470-720 nm. There was only partial similarity between the spectra obtained in the laboratory (Figure 2) and the spectral curves obtained from the portable spectroradiometer.

The analyses with the portable spectroradiometer, besides showing the chemical characteristics of soil, can

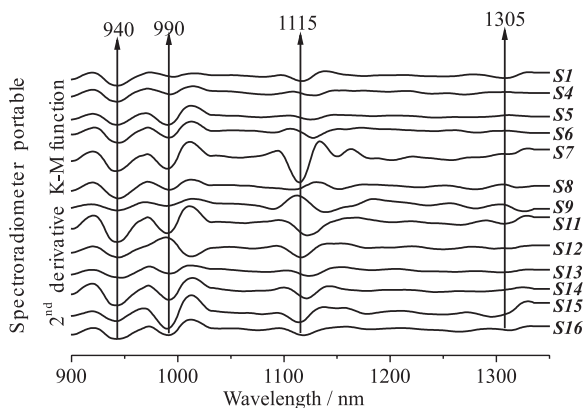


**Figure 3.** Portable spectroradiometer 2<sup>nd</sup> derivative Kubelka-Munk function, wavelength (450-730 nm).

provide information about the actual conditions of the site at the moment of analysis. Such information is more related to the climatic conditions, soil handling and use of correctives and fertilizers.

Only two absorption bands were clearly discernable. The inflections relative to the iron oxides goethite and hematite for the double transition  $2(^6A_{1g}) \rightarrow 2(^4T_{1g})$  ( $^4G$ ) appeared in all soils, centered around 485 and 532 nm, respectively. These spectra enable clearly seeing the different relative absorption intensities of the two types of iron oxide structures. We classified the soils into three groups, based on spectral curves with different relative intensities in the 485 and 534 nm absorption bands. These groups are: type I (S1, S5, S11, S12 and S15), presenting a more distinct 485 nm band of goethite than the 534 nm band of hematite; type II (S4, S6, S7, S14 and S16), with similar intensities for both bands; and type III (S8, S9 and S13), with stronger intensity in the 534 nm band than the 485 nm band. This was the first time in analyses with this portable spectroradiometer that we managed to obtain effective differentiation among the studied soils.

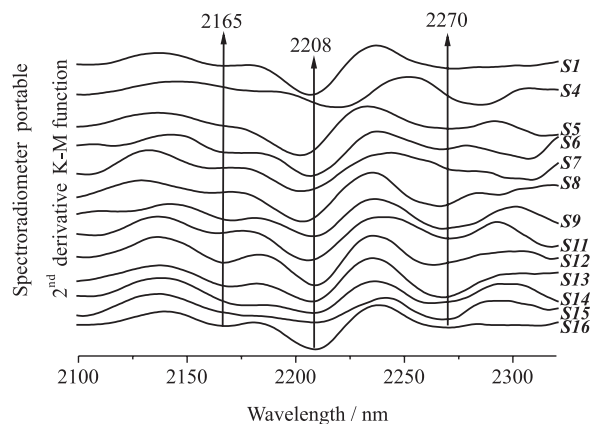
Figure 4 shows the spectra obtained with the portable spectroradiometer as the second derivative K-M function in the wavelength range from 900 nm to 1350 nm, also with marked differences among the spectra. The wide bands at 940 and 990 nm are attributed to the,  $^6A_{1g} \rightarrow ^4T_{1g}$  ( $^4G$ ), transition band, characteristic of  $Fe^{3+}$  in octahedral coordination.<sup>22</sup> In soil S12, the less energetic absorption band appeared at 1012 nm, possibly due to the presence of the trivalent iron ion replacing  $Mg^{2+}$  in the dolomite structure, indicating the presence of dolomitic limestone in sample S12.<sup>22</sup> All soil samples presented an absorption band around 1115 nm, which indicates the presence of hornblende (silicate containing calcium, sodium, magnesium, iron, aluminum and hydroxyl).<sup>21</sup> The band at 1305 nm could result from the addition or subtraction of the OH deformation mode from



**Figure 4.** Portable spectroradiometer 2<sup>nd</sup> derivative Kubelka-Munk function, wavelength (900-1350 nm).

the doubling of the first fundamental overtone of the OH stretching vibration ( $2\nu_1 \pm \delta\nu$ ).<sup>23</sup>

Figure 5 shows the portable spectroradiometer soil sample spectra's second derivative K-M function, in the wavelength range from 2100 to 2320 nm. The absorption band at 2165 nm is attributed to the presence of the  $CO_3^{2-}$  anion, as a consequence of the intensive use of limestone to increase the soil pH. The absorption at 2208 nm is attributed to the coupled stretching and bending bands of the internal Al-O-H group of kaolinite. For the S4 soil sample the band was shifted to a less energetic region of the spectrum (2222 nm). Gibbsite, the last product of soil weathering, is characterized by the same Al-O-H vibrations coupled bands in the region of 2260-2275 nm.<sup>23</sup> All the samples presented an absorption band at 2270 nm, or around it, as a consequence of the weathering intensity of these soils.



**Figure 5.** Portable spectroradiometer 2<sup>nd</sup> derivative Kubelka-Munk function, wavelength (2100-2320 nm).

## Conclusions

The layers from 0 to 20 cm in all soils had high concentrations of organic matter, above 4%. This is not common for weathered soils. Organic matter makes soils darker, which impairs spectroscopic analyses since it reduces reflectance. In general, we found the soils to be acidic and with high levels of clay, making them prone to retain water and with low reflectance, as is typical of the highly weathered soils of Brazil. All soil samples presented EPR spectra with broad lines in the *g ca. 2* regions, attributed to oxides and oxyhydroxides of trivalent iron, alone or combined on the inner surface of clays. The linewidths increased as the temperature of the soil samples decreased. This phenomenon can be attributed to the increase in the dipolar interaction between the  $Fe^{3+}$  ions, or between others paramagnetic centers of kaolinite structures and  $Fe^{3+}$  ions, due to the decrease of the distance between them.

The second derivative mode of the Kubelka-Munk function was a good alternative in the optical analysis in the laboratory, and especially in the spectroradiometer results from the field. The best evidence of goethite in the soils studied was from the deep absorption band at 485 nm, which can be attributed to the double transition,  $2(^6A_{1g}) \rightarrow 2(^4T_{1g})$  ( $^4G$ ). The best indication of hematite was from the band at 550 nm, due the same double transition band in this iron oxide structure.

From the field analyses, only two absorption bands were clearly discernable, relative to the iron oxides goethite and hematite, centered on 485 and 532 nm, respectively. The portable spectroradiometer soil sample spectra showed an absorption band at 2165 nm, which can be attributed to the presence of the CO<sub>3</sub><sup>2-</sup> anion as a consequence of the intensive use of limestone to increase the soil pH. The absorption at 2208 nm can be attributed to coupled absorption bands of the internal Al-O-H group of kaolinite. The results show that the portable spectroradiometer gives similar data to those obtained from laboratory spectroscopy, and has the advantage of providing data on the soil condition at the moment of analysis. However, in the *in situ* analyses some relevant data were not observed because of the limitations in the spectra at wavelengths from 1350 to 1450 nm and 1800 to 2000 nm. Therefore, portable spectroradiometers can be a cost-effective alternative to analyze and to map Ferralsols rich in 1:1 clay, like kaolinite and metallic oxide and oxide hydroxides.

## Acknowledgments

We thank the LAMIR (Laboratório de Análises de Minerais e Rochas) of the Universidade Federal do Paraná (UFPR), INPE (Instituto Nacional de Pesquisas Espaciais), UTFPR (Universidade Tecnológica Federal do Paraná-Pato Branco Campus), INCT de Energia e Ambiente (INCT E&A) and the UFPR Departamento de Química for providing the devices and technical support in performing these analyses.

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Submitted: March 26, 2011

Published online: July 5, 2011

FAPESP has sponsored the publication of this article.