



Revista Brasileira de Ciência do Solo

ISSN: 0100-0683

revista@sbcs.org.br

Sociedade Brasileira de Ciência do Solo
Brasil

DICK, D. P.; SANTOS, J. H. Z.; FERRANTI, E. M.
CHEMICAL CHARACTERIZATION AND INFRARED SPECTROSCOPY OF SOIL ORGANIC
MATTER FROM TWO SOUTHERN BRAZILIAN SOILS
Revista Brasileira de Ciência do Solo, vol. 27, núm. 1, 2003, pp. 29-39
Sociedade Brasileira de Ciência do Solo
Viçosa, Brasil

Available in: <http://www.redalyc.org/articulo.oa?id=180217698004>

- How to cite
- Complete issue
- More information about this article
- Journal's homepage in redalyc.org

redalyc.org

Scientific Information System
Network of Scientific Journals from Latin America, the Caribbean, Spain and Portugal
Non-profit academic project, developed under the open access initiative

SEÇÃO II - QUÍMICA E MINERALOGIA DO SOLO

CHEMICAL CHARACTERIZATION AND INFRARED SPECTROSCOPY OF SOIL ORGANIC MATTER FROM TWO SOUTHERN BRAZILIAN SOILS⁽¹⁾

D. P. DICK^(2, 3), J. H. Z. SANTOS⁽²⁾ & E. M. FERRANTI⁽⁴⁾

SUMMARY

Soil organic matter from the surface horizon of two Brazilian soils (a Latosol and a Chernosol), in bulk samples (*in situ* SOM) and in HF-treated samples (SOM), was characterized by elemental analyses, diffuse reflectance (DRIFT) and transmission Fourier transform infrared spectroscopy (T-FTIR). Humic acids (HA), fulvic acids (FA) and humin (HU) isolated from the SOM were characterized additionally by ultraviolet-visible spectroscopy (UV-VIS). After sample oxidation and alkaline treatment, the DRIFT technique proved to be more informative for the detection of "*in situ* SOM" and of residual organic matter than T-FTIR. The higher hydrophobicity index (HI) and H/C ratio obtained in the Chernosol samples indicate a stronger aliphatic character of the organic matter in this soil than the Latosol. In the latter, a pronounced HI decrease was observed after the removal of humic substances (HS). The weaker aliphatic character, the higher O/C ratio, and the T-FTIR spectrum obtained for the HU fraction in the Latosol suggest the occurrence of surface coordination of carboxylate ions. The Chernosol HU fraction was also oxygenated to a relatively high extent, but presented a stronger hydrophobic character in comparison with the Latosol HU. These differences in the chemical and functional group composition suggest a higher organic matter protection in the Latosol. After the HF treatment, decreases in the FA proportion and the A_{350}/A_{550} ratio were observed. A possible loss of FA and condensation of organic molecules due to the highly acid medium should not be neglected.

Index terms: hydrophobicity, organo-mineral interactions, HF-treatment, humic substances.

⁽¹⁾ Trabalho apresentado no 9th IHSS, Adelaide, Austrália, de 20 a 25 de setembro de 1998. Recebido para publicação em janeiro de 2001 e aprovado em julho de 2002.

⁽²⁾ Professor Adjunto do Instituto de Química, Universidade Federal do Rio Grande do Sul - UFRGS. Av. Bento Gonçalves, 9500. CEP 91501-970 Porto Alegre (RS). E-mail: jhzds@iq.ufrgs.br

⁽³⁾ Docente do PPG Ciência do Solo, UFRGS. Bolsista do CNPq. E-mail: dpdick@iq.ufrgs.br

⁽⁴⁾ Estudante do Curso de Engenharia Química, UFRGS. Bolsista de Iniciação Científica do CNPq.

RESUMO: *CARACTERIZAÇÃO QUÍMICA E ESPECTROSCOPIA DE INFRAVERMELHO DA MATÉRIA ORGÂNICA DE DOIS SOLOS DO SUL DO BRASIL*

A matéria orgânica de horizontes superficiais de dois solos (um Latossolo e um Chernossolo) foi caracterizada em amostras não tratadas (*in situ* SOM) e em amostras tratadas com HF (SOM) por análise elementar, espectroscopia infravermelho com transformada de Fourier por reflectância difusa (DRIFT) e por transmissão (T-FTIR). Ácidos húmicos (HA), ácidos fúlvicos (FA) e humina (HU), isolados da SOM, foram caracterizados também por espectroscopia UV-VIS. A técnica de DRIFT mostrou-se mais informativa do que a de T-FTIR na detecção da *in situ* SOM, bem como da matéria orgânica residual após a oxidação da amostra e após o tratamento alcalino. Os maiores valores de índice de hidrofobicidade (HI) e da razão H/C obtidos para o Chernossolo indicam que a matéria orgânica neste solo apresentou um caráter alifático superior ao observado no Latossolo. Neste último, observou-se acentuado decréscimo do HI após a remoção das substâncias húmicas (HS). O menor caráter alifático, o maior valor para a razão O/C e o espectro de T-FTIR, obtidos para a fração HU nestes solos, evidenciam a ocorrência de coordenação de superfície de íons carboxilatos. A fração HU do Chernossolo também apresentou elevado grau de oxigenação, mas, em oposição à HU do Latossolo, o caráter hidrofóbico foi mais elevado. As diferenças químicas e na composição de grupos funcionais indicam maior proteção da matéria orgânica no Latossolo. Após o tratamento com HF, foram observados decréscimos na proporção de FA e da razão A_{350}/A_{550} e a possível perda de FA e condensação de moléculas orgânicas em decorrência do meio fortemente ácido, deve ser considerada.

Termos de indexação: hidrofobicidade, interação organo-mineral, tratamento com HF, substâncias húmicas.

INTRODUCTION

Most of the research with humic substances has been performed either with humic acids (HA) or with soil organic matter (SOM), employing chemical and spectroscopic methods. Modifications in composition and structure of humic substances (HS) as a consequence of the extraction procedure is still an issue of controversy (Tan et al., 1991; Senesi et al., 1994; Dick & Burba, 1999). On the other hand, the investigation of *in situ* SOM may be limited by the low C content and by the presence of paramagnetic ions, which can interfere with the resolution of some magnetic resonance techniques (Rivero et al., 1998). In order to diminish such interference, the treatment of soil with HF solution has lately been used (Skjemstad et al., 1994; Schmidt et al., 1997; Dai & Johnson, 1999). Nevertheless, Piccolo (1988) had observed that treating HS with strong acid mixtures could cause HS condensation in higher molecular weight structures.

IR spectroscopy using Fourier transform IR spectrometers (FTIR) has found widespread use for the characterization of HS (Piccolo, 1988; Baes & Bloom, 1989; Stevenson, 1994; Celli et al., 1997; Rivero et al., 1998; Baranciková et al., 1999). In transmission FTIR spectroscopy (T-FTIR), however, problems associated to the KBr pressed pellet method and the interference of water can become considerable. There are no such difficulties with diffuse reflectance FTIR (DRIFT) spectroscopy, which

can be conducted with bulk samples, and represents a much more rapid and practical IR technique (Baes & Bloom, 1989; Niemeyer et al., 1992). This technique finds its principal application in studies on HS surface reactions and simple organic compounds with soil minerals (Hinedi et al., 1993; Capriel, 1997; Kaiser et al., 1997). Capriel et al. (1995) proposed an index obtained by DRIFT spectroscopy to evaluate the SOM hydrophobicity. A close relationship between the *hydrophobicity index* (HI) of SOM and the texture of a group of 92 arable soils was found in that study, where higher HI values indicated a stronger hydrophobic character. According to the authors, the SOM hydrophobicity is mainly determined by the C-H group proportion. The intensity of the C-H absorption bands around 3.000 to 2.800 cm^{-1} in the IR spectra could therefore express the hydrophobic character of the investigated SOM.

The UV-VIS spectroscopy of humic substances provides the ratio E_4/E_6 (Chen et al., 1977); a useful tool to estimate the humification degree and molecular size of the investigated sample (Martin-Neto et al., 1998). Nevertheless, other ratios like A_{350}/A_{550} can be used for the same purpose (Dick & Burba, 1999).

While there is a considerable amount of information about organic matter from temperate climate soils, organic matter from Brazilian soils has only recently become a subject of systematical studies with chemical and advanced spectroscopy

techniques (Martin-Neto et al., 1991; Nascimento et al., 1992; Dick & Burba, 1999; Novotny et al., 1999).

Main objectives of this study were (I) to compare the chemical characteristics of SOM and its humic fractions from two soils of different mineralogy by elemental analysis and UV-VIS and FTIR spectroscopy; and (II) to evaluate the potential capacity of DRIFT spectroscopy for research on the *in situ* SOM.

MATERIALS AND METHODS

Soil samples

Samples from the A horizons of a Chernosol and a Latosol from Rio Grande do Sul State were collected and the < 2 mm fraction was obtained by sieving the crushed soil after previous mechanical removal of plants and root debris. According to soil taxonomy, they are classified as Mollisol and Oxisol, respectively (Soil Survey Staff, 1998).

The Chernosol (Rio Pardo), collected under native vegetation, contained 261 g kg⁻¹ of clay, which consisted mainly of 2:1 clay minerals and kaolinite. The Latosol (Santo Ângelo), collected from a two-year-old field experiment under oat/soybean crop rotation, contained 650 g kg⁻¹ of clay, dominated by Fe-oxides and kaolinite. In order to explore the DRIFT technique further, an additional sample from the same Latosol was collected from a neighboring 19-year-old field experiment of oat/soybean crop rotation.

HF solution treatment

The procedure of concentrating organic matter with a 10 % HF solution was adapted from Schmidt et al. (1997). In a polyethylene tube, 50 mL of 10 % (v/v) HF were added to 10 g of soil. After 2 h of mechanical agitation, the suspension was left to stand for about 24 h, and the supernatant removed by decantation. This procedure was repeated 13 times. The concentrated organic matter (SOM) was rinsed five times with distilled water and dried at 60 °C in a vacuum oven. Part of it was separated for further analysis and the remaining material was submitted to chemical fractionation of HS.

Chemical fractionation of HS

Five grams of SOM were shaken with 20 mL of 0.5 mol L⁻¹ NaOH for 3 h. The extract containing the extractable HS was separated by centrifugation and stored in a collector flask. This procedure was repeated until the supernatant became colorless. The volume of the alkaline extract was measured and an aliquot of 5 mL collected and stored for the UV/VIS analysis. The pH was lowered to 2 with 4.0 mol L⁻¹ of HCl and the suspension was allowed

to settle for 24 h. The precipitated HA was separated from the FA by centrifugation and rinsed three times with distilled water. The rinsing supernatant was added to the FA extract. After measuring the FA extract volume, an aliquot of 2 mL was collected and stored for the UV/VIS analysis. The extraction residue containing the HU was washed with distilled water and dried at 60 °C in a vacuum oven.

For the chemical HS fractionation of the natural soil, a previous treatment with 20 mL of 0.1 mol L⁻¹ HCl was carried out (2 h of mechanical agitation) and the supernatant disposed of. This procedure was repeated three times.

Purification of HA and FA extracted from SOM

The HA was treated with 20 mL of 5 % (v/v) HF-HCl (1 h of mechanical agitation, repeated three times). The purified HA was washed with distilled water until the chloride test was negative and dried at 60 °C in a vacuum oven.

The acid FA extract was run over an acidified XAD-8 resin and eluted with 0.1 mol L⁻¹ NaOH. The pH of the eluted FA was neutralized with 0.1 mol L⁻¹ HCl and the suspension was shaken during 1 h with the cationic resin Amberlite IR-120 at pH 4. The resin was separated by decantation and the FA dried at 60 °C in a vacuum oven.

Oxidation with 30 % (v/v) H₂O₂

Approximately 2.5 g of soil sample were treated with 10 mL of 30 % (v/v) H₂O₂ in a beaker on a heating plate under magnetic stirring, until bubbles ceased to emerge. The supernatant was removed by decantation and the treatment repeated nine times. The oxidized soil residue was dried at 60 °C in a vacuum oven.

Elemental analysis

The C, H, and N contents were determined in replicates using a Perkin Elmer 2400 elemental analyzer. After correcting the results to an ash-free basis, the O content was calculated by difference. The ash content was determined by calcination of the SOM samples and their fractions HA, FA and HU at 750 °C for 4 h.

DRIFT and T-FTIR spectroscopy

The T-FTIR and DRIFT spectra were recorded on a Bomem MB-102 Spectrometer, coding 32 (T-FTIR) and 600 (DRIFT) scans at a resolution of 4 cm⁻¹ and within a spectral range of 4000-400 cm⁻¹. Prior to analysis, the samples were vacuum-dried for 48 h. The T-FTIR spectra were obtained from the samples pressed into KBr pellets, under 12 MPa. The DRIFT analyses were performed with sample powders, without the addition of KBr, due to reproducibility problems, as reported by Urban (1993). These spectra were collected as reflectance units and

transformed to Kubelka-Munk units. The spectra interpretation and the absorption band assignments were based on Farmer (1974), Tan (1996), Celli et al. (1997) and Kaiser et al. (1997). The hydrophobicity index (HI) was calculated according to Capriel et al. (1995) by dividing the integrated area of the aliphatic absorption band (3.000 to 2.800 cm^{-1}) by the sample's C content.

UV-VIS spectroscopy

The UV-VIS spectra of the alkaline HS and FA extracts were performed on a Shimadzu 160-UV spectrometer from 200 to 800 nm. The pH of the FA aliquot (taken before the purification procedure) was elevated to pH 13 by adding 3 mL of 0,1 mol L⁻¹ NaOH to 1 mL of FA sample. The FA/HS index ratio was estimated according to Dick & Burba (1999): $\text{FA/HS} = (A_{400} - A_{750})_{\text{FA}} \times V(\text{mL})_{\text{FA}} / (A_{400} - A_{750})_{\text{HS}} \times V(\text{mL})_{\text{HS}}$, where A_{400} and A_{750} are the absorbances at 400 and 750 nm, respectively, and $V(\text{mL})$ the volume extract. The A_{350}/A_{550} ratio was also calculated where A_{350} and A_{550} are the absorbances at 350 and 550 nm, respectively (Dick & Burba, 1999).

RESULTS AND DISCUSSION

DRIFT spectroscopy

The DRIFT spectrum of the *in situ* SOM of the Chernosol (Figure 1, spectrum a) presented the

following main absorption bands associated to organic matter: (a) a broad band centered at 3.400 cm^{-1} due to H bonded to OH groups (also from the minerals); (b) bands between 2.950 and 2.850 cm^{-1} attributed to aliphatic C-H stretches; (c) a peak at 1.628 cm^{-1} associated to a structural vibration in the aromatic C = C and antisymmetric C = O stretch of COO⁻; (d) a peak at 1.531 cm^{-1} (amide II), (e) a peak at 1.370 cm^{-1} assigned to a symmetric C = O stretch of COO⁻ and -CH bending of aliphatics.

Main features associated to the inorganic counterparts were: (a) sharp bands around 3.700 and 3.600 cm^{-1} , assigned to OH groups from the Al-OH and Si-OH surface, (b) bands between 1.900 and 1.750 cm^{-1} , assigned to Al-O groups from the clay mineral surface, and a shoulder at 1.680 cm^{-1} due to mineral structure groups; (c) a broad band around 913 cm^{-1} associated to mineral structure surface groups.

The presence of carboxylic group absorption bands at a lower wave number (1.628 cm^{-1}) is an indicative of coordination between SOM and minerals (surface complex) and, or ions (Celli et al., 1997). The shift from 1.725 to 1.625 cm^{-1} of carboxylic group absorption bands due to SOM adsorption on goethite and amorphous Al(OH)₃ has been reported by Kaiser et al. (1997). In the Chernosol of the present study, adsorption probably occurred at the edges of the kaolinite particle, where aluminol groups, the most reactive sites, are located (Sposito, 1989).

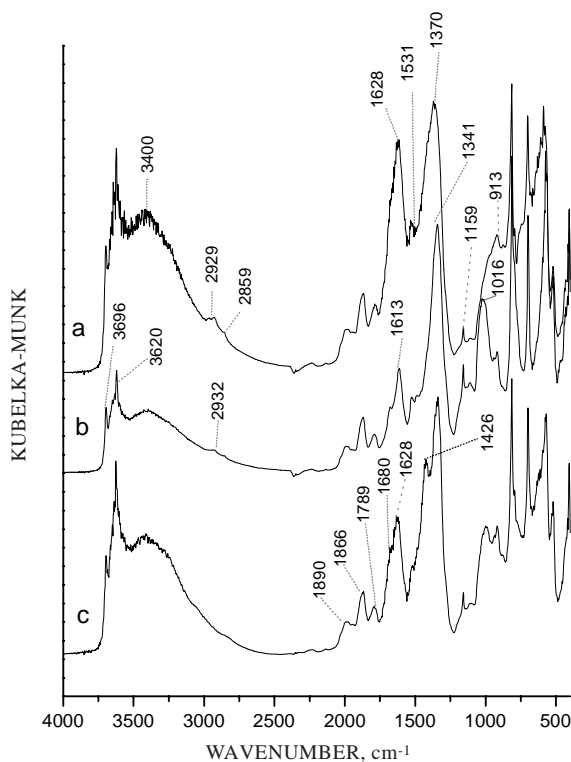


Figure 1. DRIFT spectra of the whole soil (a), of the HS-extracted soil (b) and of the oxidized soil (c) of the Chernosol.

After the removal of HS, a strong decrease in absorption intensity of the region 2950 to 2850 cm^{-1} was observed in the DRIFT spectrum (Figure 1, spectrum b) while the bands at 1.628 cm^{-1} and at 1.370 cm^{-1} disappeared. The C content dropped from 20.2 to 7.1 g kg^{-1} (Table 1) after the alkaline treatment. Similarly, soil oxidation also caused a pronounced reduction of the aliphatic stretching intensity (Figure 1, spectrum c) and the carbon content (3.4 g kg^{-1}). The occurrence of absorption peaks at 1.628 and 1.426 cm^{-1} in this spectrum could indicate that SOM, which was strongly coordinated to the mineral surface, resisted oxidation.

The DRIFT spectra of the *in situ* SOM, of the residue after HS removal and of the oxidized sample of the Latosol (Figure 2) showed less prominent bands of the SOM than the corresponding samples of the Chernosol (Figure 1). The C content dropped from 22.4 (untreated sample) to 8.9 g kg^{-1} after the HS extraction and to 3.8 g kg^{-1} after oxidation. These values lie in the same range as those obtained for the Chernosol (Table 1).

Due to the higher clay amount (650 g kg^{-1}) in the Latosol, the occurrence of SOM within clay-sized aggregates is more common than in the Chernosol (260 g clay kg^{-1}). Therefore, the organic matter is less accessible to IR radiation, producing a spectrum with less prominent absorption bands. Physical protection of SOM within microaggregates has been reported by Skjemstad et al. (1993), among others.

Transmission FTIR spectroscopy

In both samples, the transmission spectra of the whole soil provided much less information about SOM than the DRIFT spectra (Figures 3 and 4), since the absorption bands associated to organic matter were comparatively weaker. A similar observation was reported by Niemeyer et al. (1992). The same effects caused in the DRIFT spectra by HS removal and by sample oxidation were also observed in the transmission technique.

Table 1. Hydrophobicity Index (HI) and C content of the *in situ* SOM, of the HS-residue (residue after HS alkaline extraction), of the SOM (HF-treated sample) and its extracted HA. Latosol 19: Latosol sample under crop during 19 years

Sample	HI	C	Sample	HI	C
		g kg^{-1}			g kg^{-1}
Chernosol:			Latosol:		
<i>In situ</i> SOM	23	20.2	<i>In situ</i> SOM	18	22.4
HS-residue	20	7.1	HS-residue	10	8.9
SOM	4.9	278	SOM	5.1	310
HA	0.20	492	HA	0.22	478
			Latosol 19:		
			<i>In situ</i> SOM	9.9	26.2
			SOM	6.0	304

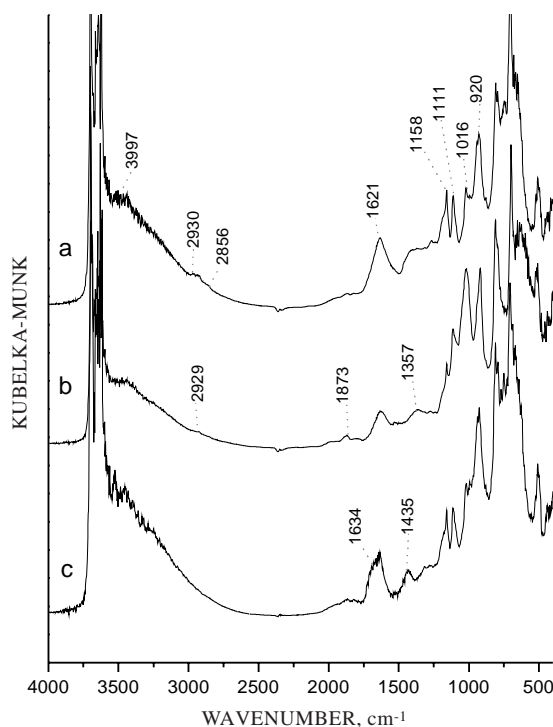


Figure 2. DRIFT spectra of the whole soil (a), of the HS-extracted soil (b) and of the oxidized soil (c) of the Latosol.

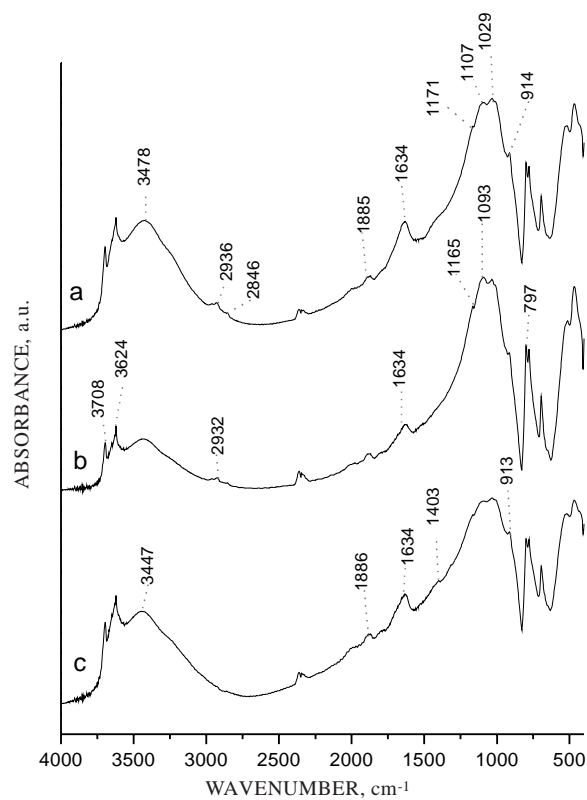


Figure 3. Transmission FTIR spectra of the whole soil (a), of the HS-extracted soil (b) and of the oxidized soil (c) of the Chernosol.

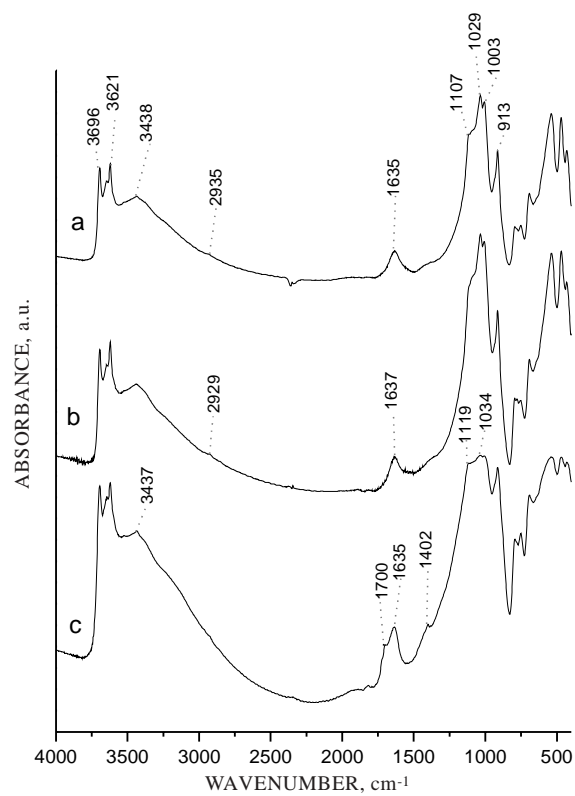


Figure 4. Transmission FTIR spectra of the whole soil (a), of the HS-extracted soil (b) and of the oxidized soil (c) of the Latosol.

The transmission FTIR spectrum of the Chernosol SOM (Figure 5, spectrum a) revealed a typical pattern of humified organic matter. In addition to the absorption regions already observed in the DRIFT spectrum of the *in situ* SOM, the T-FTIR spectrum showed (a) a peak at 1.724 cm^{-1} due to -C=O stretching of -COOH , (b) shoulders at $1.450\text{-}1.420\text{ cm}^{-1}$, assigned to -CH_3 and -CH_2 bending; (c) a peak at 1.243 cm^{-1} due to antisymmetric -C-O stretching and OH deformation of -COOH , -C-OH bending of phenols and of tertiary alcohol; (d) a shoulder at 1.158 cm^{-1} ascribed to symmetric -C-OH stretching of aliphatics; (e) a broad peak at 1.061 cm^{-1} , assigned to -C-O stretching of phenols, polysaccharides and, or, aliphatic groups.

In a comparison with the whole soil spectrum, the occurrence of antisymmetric -COO^- stretching at a higher wave number (1.645 cm^{-1}) in the Chernosol's SOM spectrum confirms (Figure 1, spectrum a, 1.626 cm^{-1}) that the *in situ* SOM was strongly coordinated to the mineral surface.

Compared to the HA, the carboxylic content is higher in the FA, indicated by more intense bands at 1.718 cm^{-1} and at 1.225 cm^{-1} (Figure 5, spectra b and c). Moreover, the peak at 1.031 cm^{-1} ($\nu_{\text{Si-O-Si}}$) in the HA shows that the purification was not very effective.

In the HU fraction (Spectrum d, Figure 5), the stronger absorption bands at 1.593 and 1.397 cm^{-1} indicate the presence of carboxylate anions strongly bonded to metals and, or, minerals. The contribution of aromatic and aliphatic moieties in this region, though, should not be neglected. The pronounced band at 1.068 cm^{-1} suggests the presence of ether groups.

The SOM ash content was 150 and 260 g kg^{-1} , respectively, in the Chernosol and in the Latosol (Table 3). In the HU fraction, the ash content reached 470 and 610 g kg^{-1} , respectively, indicating a relative enrichment of the inorganic components in this alkali-insoluble fraction. It appears that, in the present study, humin does not only consist of hydrophobic moieties, but also of carboxylated structures strongly coordinated to inorganic components, composing a very stable organomineral association. This association seems to be more relevant in the Latosol, since the HU fraction in this soil presented a much higher ash content. Fründ & Lündemann (1991) had already pointed out the insolubility of organic matter in alkaline solution due to binding or complexation with minerals in the soil. The occurrence of carboxylic groups and of humic acid-like structure in humin has also been reported earlier by other authors (Preston & Ripmeester, 1982; Rice & McCarthy, 1989; Stevenson, 1994; Malekani et al., 1997). Nevertheless, one should

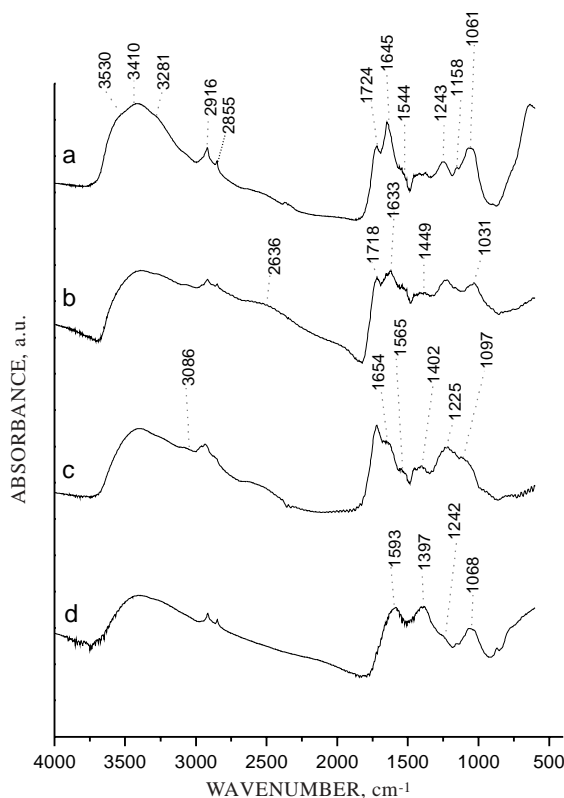


Figure 5. Transmission FTIR spectra of SOM (a) and its fractions: HA (b), FA (c) and HU (d) of the Chernosol.

not discard the possibility that this organomineral complex could be an artifact from the previous HF treatment.

The T-FTIR spectra obtained for the Latosol fractions (Figure 6) showed similar features to those of the Chernosol and the same considerations expressed above are valid in this case. Humic and fulvic acids extracted from the natural soil showed T-FTIR spectra similar to those obtained for the HA and FA fractionated from the SOM and are therefore not shown here.

UV-VIS spectroscopy, hydrophobicity index (HI) and elemental composition

The values calculated for the FA/HS ratio (Table 2) show that the SOM concentration treatment reduced the fulvic acid yield, indicating that part of the FA was lost during the HF treatment.

For the Latosol, the A_{350}/A_{550} values were lower in all humic fractions extracted from SOM when compared with those extracted from untreated soil (Table 2), suggesting that the former had a higher molecular size/condensation ratio (Chen et al., 1977; Dick & Burba, 1999). The occurrence of molecular condensation due to the strong acid treatment, as already observed by Piccolo (1988), can be considered the cause for the decrease in the A_{350}/A_{550} ratio. Additionally, the loss of organic moieties with lower molecular weight should also be considered. In the

Chernosol, this behavior was only observed for the FA (Table 1), while the A_{350}/A_{550} ratio for the HA fraction was less affected by the HF treatment.

The hydrophobicity indices (HI) obtained for the *in situ* SOM and HS-residue (Table 1) are in the range of those observed in arable soils by Capriel et al. (1995) and Capriel (1997).

The HI for the *in situ* SOM was higher in the Chernosol than in the Latosol, indicating a higher hydrophobicity character for the organic matter in the former. Considering that the aliphatic groups

Table 2. FA/HS and A_{350}/A_{550} ratios of humic fractions extracted from the natural soil sample and from SOM (HF-treated soil) (*)

Soil	FA/HS		A_{350}/A_{550}	
	Soil	SOM	Soil	SOM
Chernosol	0.20	0.12	-	-
HS	-	-	2.60	3.40
HA	-	-	2.50	3.20
FA	-	-	7.60	4.70
Latosol	0.36	0.14	-	-
HS	-	-	6.40	3.90
HA	-	-	6.10	3.70
FA	-	-	9.30	7.30

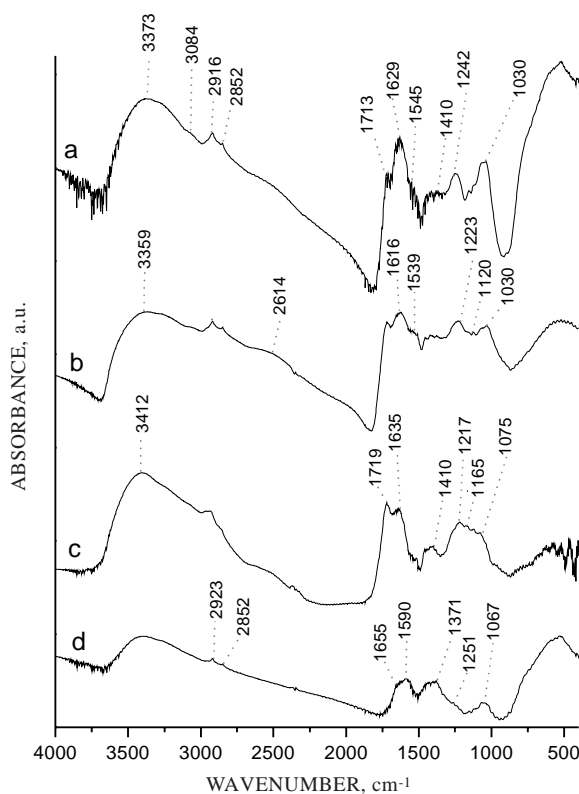


Figure 6. Transmission FTIR spectra of SOM (a) and its fractions: HA (b), FA (c) and HU (d) of the Latosol.

are the most recalcitrant structures in the SOM (Baldock et al., 1997) it follows that the humification degree is higher in the soil with 2:1 mineralogy than in the Latosol.

After the alkaline removal of soluble HS, the HI dropped considerably in the Latosol, showing that the remaining HU fraction has a less hydrophobic character. This result agrees with the findings of the T-FTIR analysis, where the HU fraction spectrum revealed a strong coordination of the organic matter to the mineral or metal surfaces by its carboxylate groups. In the Chernosol, where the organomineral interaction was less strong, the HI value changed little with the removal of HS substances and no preferential extraction occurred. The values obtained for the *in situ* SOM in the OX-19 sample show that the long term cultivation caused a decrease in the hydrophobicity index as already pointed out by Capriel (1997).

For both soils, the HI values for the SOM were much lower than those obtained for the *in situ* SOM (Table 1). An extreme situation was verified with the HA, where the HI values were lower than one. The occurrence of a major chemical alteration due to the HF treatment, as well as a preferential dissolution of hydrophobic structures by the acidic hydrophilic medium are most unlikely (Piccolo, 1988; Schmidt et al., 1997). For the relationship between HI and hydrophobicity established by Capriel et al. (1995), the C content varied between 6.4 and 64.9 g kg⁻¹. It seems that for higher C contents, as observed for the SOM and HA in the present study, this relationship is not suitable.

In both soils, the elemental composition of the SOM, HU and HA differed among each other, indicating that neither the HU nor the HA could solely be used to estimate the composition of the whole SOM (Table 3). In the Chernosol, the H/C ratio was higher in the SOM, compared to that of the HU and the HA. This higher aliphaticity might be related to the contribution of the FA for the whole organic matter.

Between the two soils, the SOM of the Chernosol presented a higher H/C ratio which can be associated to the higher HI calculated for the *in situ* SOM (natural sample) in this soil, when compared to the SOM of the Latosol. The use of HI as an aliphaticity index should, though, be checked by further studies with a larger number of samples. The O/C ratio was also higher for the Chernosol SOM, indicating a lower oxygenation degree in the Latosol SOM. Similar behavior has been observed earlier with the humic substances of these two soils by means of ¹³C-NMR spectroscopy (Dick et al., 1999).

The higher O/C ratios obtained for the HU fraction in both soils points to a higher Oxygen content in the humin fraction, and this fact tallies well with the presence of carboxylate groups, identified previously by T-FTIR spectroscopy (Figures 5 and 6, spectrum d). In the specific case of the Latosol, the humin also showed a lower H/C ratio than the other two analyzed fractions in agreement with the lower HI value obtained for the HS-residue (Table 1). Almendros et al. (1996) obtained H/C values around 1.5 for humins from Spanish soils isolated with methyl isobutyl ketone (MIBK method). The lower H/C values obtained in the present work might be due to the employed alternative procedure: SOM concentration with HF solution, followed by the alkaline extraction of HS.

Both HA presented a lower O/C ratio than the other two organic fractions, in agreement with their lower content of carboxylic groups, identified by T-FTIR spectroscopy (Figures 5 and 6). Furthermore, the lower H/C ratio observed for HA in comparison with the respective SOM (Table 3) suggests that the contribution of aromatic groups to the absorption band at 1.633-1.619 cm⁻¹ (Figures 5 and 6, spectrum b,) is greater than that of the COO⁻ groups.

The SOM of the two soils presented similar values for the C/N, while the HA and HU fractions showed distinct variation regarding this ratio (Table 3). In the Latosol, the HU and HA were poorer in nitrogen, in comparison to the whole SOM. Either the Latosol

Table 3. Elemental composition, C/N, H/C, and O/C ratios of the SOM and its fractionated HU and HA

Sample	Ash	C ⁽¹⁾	H ⁽¹⁾	N ⁽¹⁾	O ⁽²⁾	C/N	H/C ⁽³⁾	O/C ⁽³⁾	
<hr/>									
Chernosol:	g kg ⁻¹								
	SOM	150	439	45	58	458	7.6	1.23	0.78
	HU	470	434	40	64	462	6.8	1.11	0.80
	HA	60	524	46	72	358	7.3	1.05	0.51
Latosol:									
	SOM	260	500	46	69	385	7.2	1.10	0.58
	HU	610	454	37	46	463	9.9	0.98	0.76
	HA	90	529	51	58	362	9.1	1.16	0.51

⁽¹⁾ Ash-free basis. ⁽²⁾ Calculated by difference of 1.000 g kg⁻¹. ⁽³⁾ Atomic ratio.

FA was relatively enriched with nitrogen or some nitrogenated compounds of low molecular weight had been extracted by the previous chemical treatments. The T-FTIR spectra (Figure 6) support the second hypothesis, since the amide absorption band (around 1.540 cm^{-1}) was less intense in the FA spectrum (spectrum c), in comparison to the other spectra. In the Chernosol, the C/N ratio was relatively similar in the three analyzed organic fractions, indicating a uniform nitrogen distribution (Table 3).

CONCLUSIONS

1. The DRIFT technique has shown to be a much more informative method to detect *in situ* SOM than the T-FTIR. It also made the identification of the remaining organic matter after the oxidation treatment possible, and of the humin fraction in the soil residue after the alkaline HS extraction. The applicability of the HI as an inference of the hydrophobic character appears to be limited by the sample's C contents and can not be employed in concentrated SOM samples.

2. The *in situ* SOM of the Chernosol was more hydrophobic and more aliphatic than that of the Latosol, as indicated by the HI index and H/C ratio. The variations of both indexes might be correlated. Nevertheless, further studies must be developed to check this assumption.

3. The organomineral association, more pronounced in the Latosol, probably promoted physical protection of the organic matter, leading to a less humified SOM in this soil.

4. The treatment with the HF solution allowed the acquisition of a more informative T-FTIR spectrum of the SOM as well as the determination of its elemental composition. Furthermore, the humin fraction could be isolated and also investigated by means of infrared spectroscopy and chemical analysis. However, there is some evidence that part of the fulvic acid was lost during the acid treatment and that some condensation might have occurred. The formation of inorganic artifacts in the humin fractions should be considered as well.

ACKNOWLEDGEMENTS

FAPERGS and CNPq (Brazil) financially supported this work; E.M. Ferranti thanks FAPERGS for a scholarship.

LITERATURE CITED

- ALMENDROS, G.; GUADALIX, M.E.; GONZÁLEZ-VILA, F.J. & MARTIN, F. Preservation of aliphatic macromolecules in soil humins. *Org. Geochem.*, 24:651-659, 1996.
- BAES, A. & BLOOM, P.R. Diffuse reflectance and transmission Fourier Transform infrared (DRIFT) spectroscopy of humic and fulvic acids. *Soil Sci. Soc. Am. J.*, 53:695-700, 1989.
- BALDOCK, J.A.; OADES, J.M.; NELSON, P.N.; SKENE, T.M.; GOLCHIN, A. & CLARKE, P. Assessing the extent of decomposition of natural organic materials using solid-state ^{13}C NMR spectroscopy. *Aust. J. Soil Res.*, 35:1061-1083, 1997.
- BARANCIKOVÁ, G.; SENESI, N. & BRUNETTI, G. Chemical and spectroscopic characterization of humic acids isolated from different Slovak soil types. *Geoderma*, 78:251-266, 1997.
- CAPRIEL, P.; BECK, T.; BORCHERT H.; GRONHOLZ, J. & ZACHMANN, G. Hydrophobicity of the organic matter in arable soil. *Soil Biol. Biochem.*, 27:1453-1458, 1995.
- CAPRIEL, P. Hydrophobicity of organic matter in arable soils : influence of management. *Eur. J. Soil Sci.*, 48:457-462, 1997.
- CELLI, L.; SCHNITZER, M. & NÈGRE, M. Analysis of carboxyl groups in soil humic acids by wet chemical method, Fourier-Transform infrared spectrophotometry, and solution-state carbon-13 nuclear magnetic resonance. A comparative study. *Soil Sci.*, 162:189-197, 1997.
- CHEN, Y.; SENESI, N. & SCHNITZER, M. Information provided on humic substances by E4/E6 ratio. *Soil Sci. Soc. Am. J.*, 41:352-358, 1977.
- DAÍ, K.H. & JOHNSON, C.E. Applicability of solid-state ^{13}C CP/MAS NMR analysis in Spodosols: chemical removal of magnetic materials. *Geoderma*, 93:289-310, 1999.
- DICK, D. P. & BURBA, P. Extraction kinetics and molecular size fractionation of humic substances from two Brazilian soils. *J. Braz. Chem. Soc.*, 10:146-152, 1999.
- DICK, D.P.; BURBA, P. & HERZOG, H. Influence of extractant and soil type on molecular characteristics of humic substances from two Brazilian soils. *J. Braz. Chem. Soc.*, 10:140-145, 1999.
- FARMER, V.C. The infrared spectra of minerals. Surrey, Mineralogical Society, Adlard & Sons, Bartholmew Press, 1974. 573p. (Monograph, 4)
- FRÜND, R. & LÜDEMANN, H.-D. Quantitative characterization of soil organic matter and its fractionation products by solid state high resolution C-13 (CPMAS) spectroscopy. *Z. Naturforsch.*, 46c:982-988, 1991.
- HINEDI, Z.R.; JOHNSTON, C.T. & ERICKSON, C. Chemisorption of benzene on Cu-Montmorillonite characterized by T-FT-IR and ^{13}C MAS NMR. *Clays Clay Min.*, 41:87-93, 1993.
- KAISER, K.; GUGGENBERGER, G.; HAUMEIER, L. & ZECH, W. Dissolved organic matter sorption on subsoils and minerals studied by ^{13}C NMR and DRIFT spectroscopy. *Eur. J. Soil Sci.*, 48:301-310, 1997.
- MALEKANI, K.; RICE, J.A. & LIN, J.S. The effect of sequential removal of organic matter on the surface morphology of humin. *Soil Sci.*, 162:333-342, 1997.
- MARTIN-NETO, L.; NASCIMENTO, O.R.; TALAMONI, J. & POPPI, N.R. EPR of micronutrient-humic substance complexes extracted from a Brazilian soil. *Soil Sci.*, 151:369-376, 1991.

- MARTIN-NETO, L.; ROSELL, R.; SPOSITO, G. Correlation of spectroscopic indicators of humification with mean annual rainfall along a temperate grassland climosequence. *Geoderma*, 81:305-311, 1998.
- NASCIMENTO, V.M.; ALMENDROS, G. & FERNANDES, F.M. Soil humus characteristics in virgin and cleared areas of the Paraná river basin in Brazil. *Geoderma*, 54:137-150, 1992.
- NIEMEYER, J.; CHEN, Y. & BOLLAG, J.-M. Characterization of humic acids, composts, and peat by diffuse reflectance Fourier transform infrared spectroscopy. *Soil Sci. Soc. Am. J.*, 56:135-140, 1992.
- NOVOTNY, E.H.; BLUM, W.E.H.; GERBAZEK, M.H. & MANGRICH, A.S. Soil management system effects on size fractionated humic substances. *Geoderma*, 92:87-109, 1999.
- PICCOLO, A. Characteristics of soil humic extracts obtained by some organic and inorganic solvents and purified by HCl-HF treatment. *Soil Sci.*, 146:418-426, 1988.
- PRESTON, C.M. & RIPMEESTER, J.A. Application of solution and solid-state ^{13}C NMR to four organic soils, their humic acids, fulvic acids, humins and hydrolysis residues. *Can. J. Spec.*, 27:99-105, 1982.
- RICE, J. & MCCARTHY, P. Isolation of humin by liquid-liquid partitioning. *Sci. Total Environ.*, 81/82:61-69, 1989.
- RIVERO, C.; SENESI, N.; PAOLINI, J. & D'ORAZIO, V.D. Characteristics of humic acids of some Venezuelan soils. *Geoderma*, 81:227-239, 1998.
- SCHMIDT, M.W.I.; KNICKER, H.; HATCHER, P.G. & KÖGEL-KNABER, I. Improvement of ^{13}C and ^{15}N CPMAS NMR spectra of bulk soils, particle size fractions and organic material by treatment with 10 % hydrofluoric acid. *Eur. J. Soil Sci.*, 48:457-462, 1997.
- SENESE, N.; MIANO, T.M. & BRUNETTI, G. Methods and related problems for sampling soil and sediment organic matter. Extraction, fractionation and purification of humic substances. *Quím. Anal.*, 13:26-33, 1994.
- SKJEMSTAD, J.O.; JANIK, L.J.; HEAD, M.J. & MCCLURE, S.G. High energy ultraviolet photo-oxidation: a novel technique for studying physically protected organic matter in clay- and silt-sized aggregates. *J. Soil Sci.*, 44:485-499, 1993.
- SKJEMSTAD, J.O.; CLARKE, P.; TAYLOR, J.A.; OADES, J.M. & NEWMAN, R.H. The removal of magnetic materials from surface soils. A solid-state ^{13}C CP/MAS NMR study. *Aust. J. Soil Res.*, 32:1215-1229, 1994.
- SPOSITO, G. The chemistry of soils. New York, Oxford University Press, 1989. p.127-146.
- SOIL SURVEY STAFF. Keys to soil taxonomy. 8.ed. Washington, USDA-NRCS, 1998, 327p.
- STEVENSON, F.J. Humus chemistry. Genesis, composition, reactions. 2ed. New York, John Wiley & Sons, 1994, p.303-324.
- TAN, K.H.; LOBARTINI, J.C.; HIMMELSBACH, D.S. & ASMUNSEN, L.E. Composition of humic acids extracted under air and nitrogen atmosphere. *Comm. Soil Sci. Plant Anal.*, 22:861-877, 1991.
- TAN, H.K. Infrared spectroscopy. In: TAN, H.K. Soil sampling, preparation and analysis. New York, Marcel Dekker, 1996. p.278-298.
- URBAN, M.N. Vibrational spectroscopy of molecules and macromolecules on surfaces. New York, Wiley & Sons, 1993. 215p.

