Journal of Thermal Analysis and Calorimetry, Vol. 57 (1999) 517-526

THERMAL PROPERTIES OF STANDARD AND REFERENCE HUMIC SUBSTANCES BY DIFFERENTIAL SCANNING CALORIMETRY

M. R. Provenzano and N. Senesi

Istituto di Chimica Agraria, Università di Bari, Via Amendola 165/a, 70126 Bari, Italy

(Received May 14, 1998; in revised form September 5, 1998)

Abstract

Differential Scanning Calorimetry combined with Fourier transform infrared spectroscopy, was applied to the study of a number of fulvic and humic acids extracted from soils, peat, river and seawater. The thermal patterns obtained were related to the nature and origin of samples. The low-temperature endotherms were attributed to dehydration and loss of peripheral polysaccharide chains. The endotherm at 250°C observed for soil FA was ascribed to partial decarboxylation of more labile surface COOH groups, whereas the high-temperature exotherms at about 500°C were related to the degree of polycondensation of the aromatic network of the humic molecules.

Keywords: DSC, humic substances, thermal properties

Introduction

The organic matter in soils consist of a mixture of plant and animal residues in various stages of decomposition, of chemically and biologically synthetized substances from the breakdown products, and of microorganism and small animals and their decomposing remains. Soil organic matter is usually partitioned into non humic and humic substances. Non humic substances include those with still recognizable physical and chemical characteristics such as carbohydrates, proteins, peptides, amino acids, fats, waxes, alkanes and low molecular mass organic acids. Most of these compounds are attacked relatively readily by microorganisms in the soil and have a short survival span. The major matter in most soils and water, however, consists of humic substances. These are amorphous, dark-colored, hydrophilic, acidic, polyaromatic, chemically complex organic substances that range in molecular mass from a few hundred to several thousand. Based on their solubility in alkali and acid, humic substances are partitioned into three main fractions: humic acid (HA), which is soluble in dilute alkali but is precipitated by acidification of the alkaline extract; fulvic acid (FA), which is soluble in both dilute alkali and dilute acid, and humin, which is the humic fraction that cannot be extracted from the soil or sediment by dilute base and acid.

Differential thermal analysis (DTA) has been widely used to obtain information on the thermal behaviour of soil organic matter fractions including humic sub-

1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

stances, organo-mineral fractions [1, 2], and even bulk soil samples [3]. Several data are available in literature on DTA applied to the study of many HAs and FAs from widely distributed soil types in former USSR, Mediterranean area, acidic or near neutral to alkaline Vertisols, etc. Due to the intrinsic molecular complexity of these materials, the interpretation of the thermal curves and related processes is not immediate and not yet completely clear. However, all the experimental results provide similar evidences, that are: a) an endothermic peak in the range 433–473 K, b) an exotherm between 673 and 733 K and c) a prominent exotherm in the range 813–873 K. The low-temperature endotherms are attributed to dehydration processes and the exotherms respectively to decarboxylation reactions and decomposition of the aromatic core of the molecule [4–12].

Despite the large number of DTA studies of humic materials, limited research is available on differential scanning calorimetry (DSC) of these substances [13–17]. The basic difference between DTA and DSC systems is that, in latter, sample and reference are both provided with individual heaters and this makes it possible to use a ‘null-balance’ principle. Thus, the temperature of the sample holder is always kept the same as that of the reference holder by continuous and automatic adjustment of the heater power. A signal, proportional to the difference between the heat input to the sample and that to the reference, dH/dt, is fed into a recorder. So, with DSC is possible to make a conversion of the peak area into energy unit. The technique is, therefore, promising for further application to study chemical aspects of thermal reactions occurring in humic substances, especially when they interact with pesticides and metal ions.

The objective of this paper is to present results of a combined DSC-FTIR investigation of FAs and HAs of various origin and nature.

Materials and methods

Five HA and four FA samples were used in this work, which were obtained from the standard and reference collection established by the International Humic Substances Society (IHSS), with the purpose of mantaining a collection of humic substances of different origin and nature available to studies and researches by scientists worldwide [18]. HA and FA were extracted from the bulk-solid earth materials by a 20-step procedure based upon NaOH extraction that was formulated by an international group of humic substances researchers in 1981, on the basis of information then available, as the most suitable for these materials. The fundamental characterization of these samples is currently in progress. Several methods, including elemental and functional group analyses, chemical component analysis, molecular mass and size determination, ash analysis, and numerous spectroscopic techniques, such as FTIR, ESR, NMR, fluorescence and UV-visible spectroscopy are being applied. The HA and FA samples used in the present work are: (a) the Summit Hill soil HA (IHSS code, 1R106H); (b) the Eliot soil HA (IHSS code, 1R102H) and FA (IHSS code, 1R102F); (c) the Pahokee peat HA (IHSS code, 1R103H) and FA (IHSS code, 1R103F); (d) the Suwannee river HA (IHSS code, 1S101H) and FA (IHSS code, 1S101F); and (e) the Nordic aquatic HA (IHSS code, 1R105H) and FA (IHSS code, 1R105F). Details on isolation, fractionation and purification methods and information on chemical and spectroscopic properties of the samples examined have been published previously [19–22]. Major elemental composition, atomic ratios, ash contents and E_4/E_6 ratios of samples utilized are reported in Table 1. E_4/E_6 ratios were determined by dissolving 1.0 mg of each sample in 5 ml of $NaHCO_3$ and the pH was adjusted to 8.3 with NaOH. The absorbances at 465 nm and 665 nm were measured on a spectrophotometer series λ 15 Perkin Elmer. The ratio of these absorbances gives the E_4/E_6 ratio. Ratios considered in the table are related to the degree of condensation of aromatic groups, i.e. to the humification degree.

DSC curves were obtained by a Perkin Elmer DSC 7, equipped with a thermal analysis (TA) automatic program. Aliquots of 5 mg of each sample were placed in an aluminum pan of 50 μ l capacity and 0.1 mm thickness, press-sealed with a not perforated aluminum cover of 0.1 mm thickness. An empty pan sealed in the same way was used as reference. DSC thermograms were measured by heating the sample from 323 to 923 K at a rate of 293 K min^{-1}, under an air-flow of 20 cm^3 min^{-1}. Indium was used as standard for calibrating the temperature. Reproducibility was checked running the sample in triplicate. The baseline was subtracted by all DSC curves.

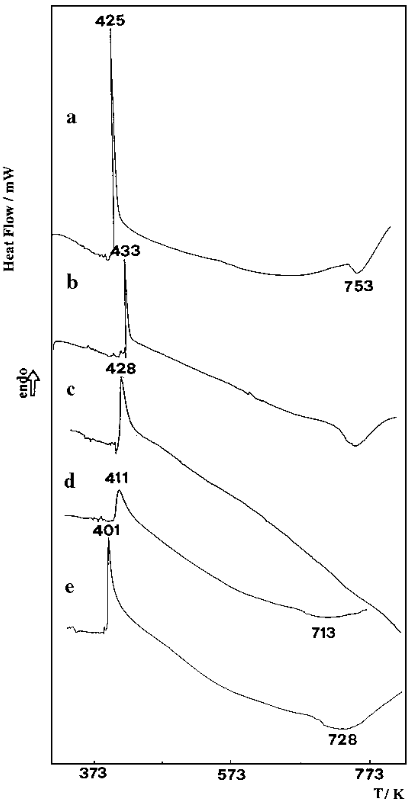

Fig. 1 DSC curves of HA from Summit Hill soil (a), Eliot soil (b), Pahokee peat (c), Suwannee river (d) and Nordic Sea (e)

Table 1 Major elemental composition, atomic ratios, ash contents, E_4/E_6 ratios of FA and HA

Sample	Elemental composition/%					Atomic ratios			Ash/ %	E_4/E_6
	C	H	N	S	O	C/N	C/H	O/C		
Summit Hill HA	57.99	3.78	4.18	0.41	33.69	16.2	1.28	0.44	0.90	5.6
Eliot HA	49.92	4.84	4.98	1.22	39.04	11.7	0.86	0.56	0.83	5.7
Eliot FA	46.35	3.82	2.86	1.07	45.90	19.4	1.01	0.72	0.79	14
Peat HA	51.51	3.61	3.75	0.98	40.15	16.1	1.19	0.56	0.90	5.4
Peat FA	47.63	3.35	2.65	0.94	45.43	21.0	1.19	0.74	3.51	18.2
Suwannee river HA	50.71	3.46	1.11	0.61	44.46	53.3	1.22	0.66	3.19	10.8
Suwannee river FA	49.22	4.13	0.76	0.48	45.41	75.8	1.00	0.69	0.83	21.8
Nordic aquatic HA	50.72	3.50	1.59	0.91	43.28	37.3	1.21	0.64	1.06	12.8
Nordic aquatic FA	48.71	3.41	0.90	1.12	45.86	63.3	1.19	0.71	0.39	18.8

In order to elucidate the molecular tranformations occurring during thermal processes, FTIR spectra were measured in the 400 to 4000 cm^{-1} wavenumber range on samples withdrawn from DSC experiments after heating to 373, 473, 573, 673, 773 K, using a Nicolet 5PC FTIR spectrophotometer. KBr pellets were obtained by pressing, under reduced pressure, uniformly prepared mixtures of 1 mg sample and 400 mg KBr, spectrometry grade.

Results and discussion

In general, DSC curves of HA and FA samples examined show similar pattern with thermal peaks occurring at similar temperatures, but with different intensities, which depend on the origin and nature of the sample.

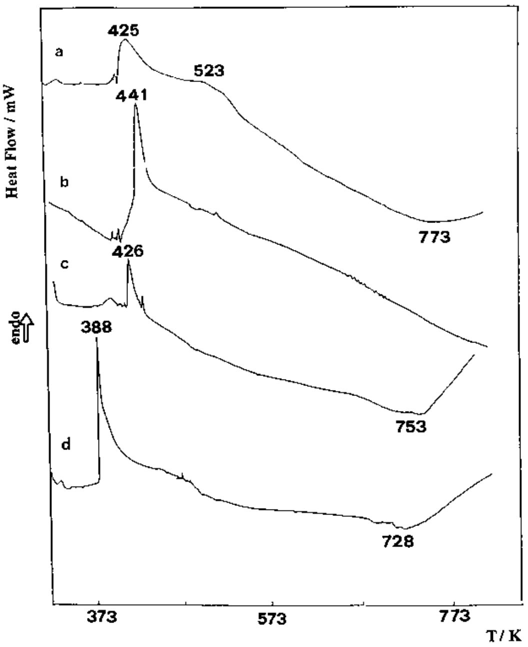

Fig. 2 DSC curves of FA from Eliot soil (a), Pahokee peat (b), Suwannee river (c) and Nordic Sea (d)

In particular, DSC curves of HAs from Summit Hill and Eliot soils (Fig. la, and Fig. 1b), show a strong endotherm respectively at 425 and 433 K and an exotherm at 753 K. FA from Eliot soil (Fig. 2a) displays the endotherm at 525 K and the exotherm at 773 K and in addition it shows an endothermic shoulder at about 523 K.

FTIR spectra provide a useful tool for the interpretation of thermal reactions indicated by the peaks observed in DSC curves. Main IR adsorption bands for HAs and FAs are listed in Table 2. FTIR spectra of Summit Hill and Eliot soils (Fig. 3a) HAs after heating to 373 and 473 K are similar to those of original samples, which suggests that no relevant structural and functional modifications have occurred. A

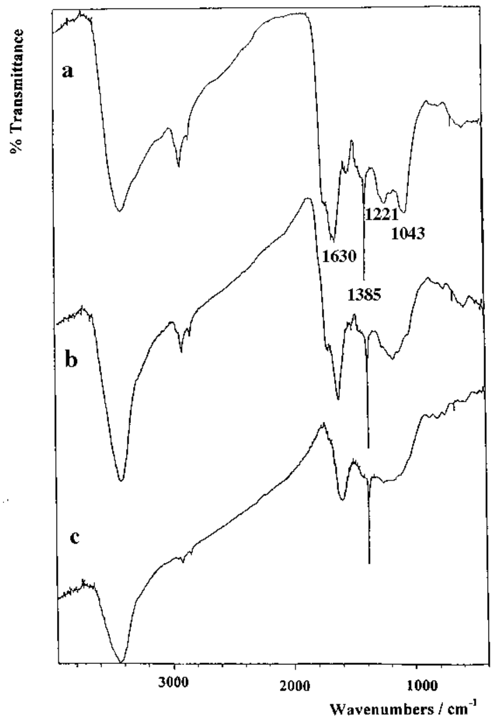

Fig. 3 FTIR spectra of soil HA (a), soil HA heated to 573 K (b) and soil HA heated to 773 K (c)

Table 2 Main IR adsorption bands of humic substances

Frequency/cm^{-1}	Assignment
3400–3300	O–H stretching, N–H stretching (trace)
2940–2900	Aliphatic C–H stretching
1725–1720	C=O stretching of COOH and ketones (trace)
1660–1630	C=O stretching of amide groups (amide I band), quinone C=O and/or C=O of H-bonded conjugated ketones
1620–1600	Aromatic C=C, strongly H-bonded C=O of conjugated ketones
1590–1517	COO^- symmetric stretching, N–H deformation, C=N stretching (amide II band)
1460–1450	Aliphatic C–H
1400–1390	OH deformation and C–O stretching of phenolic OH, C–H deformation of CH_2 and CH_3 groups, COO^- antisymmetric stretching
1280–1200	C–O stretching and OH deformation COOH
1170–950	C–O stretching of polysaccharide or polysaccharide-like substances, Si–O of silicate impurities

marked reduction of the IR band at 1043 cm^{-1} is apparent after heating to 573 K (Fig. 3b). This result shows that between 473 and 573 K a loss of peripheral polysaccharide chains occurs, but this evidence is not confirmed on DSC curves of both soils HAs. FTIR spectrum of Eliot soil FA (Fig. 4a), heated to 573 K (Fig. 4b) exhibits a marked reduction of the relative intensity of adsorptions at 1718 cm^{-1} (COOH) compared with that at 1630 cm^{-1} (COO^{-}). This result may be ascribed to partial decarboxylation as showed by the thermal effect occurring at 523 K. The FTIR spectra of soil HAs and FA heated to 673 K do not show any relevant variation compared to the previous spectra. The FTIR spectra of all soil samples heated to 773 K feature only strong peaks at 3420, 1385 cm^{-1} (possibly phenolic OH) and a broad band at about 1700 cm^{-1} (possibly attributed to carbonyl groups) (Fig. 3c and Fig. 4c). The possible oxydation of the aromatic nuclei of the molecules may have occurred as suggested by the exotherm observed at about 773 K.

DSC curves of peat HA (Fig. lc) and FA (Fig. 2b) are very similar to each other, featuring only a strong endotherm at 428 K for HA and at 441 K for FA. FTIR spectra are similar for peat HA and FA (Fig. 5).Spectra obtained on samples heated to

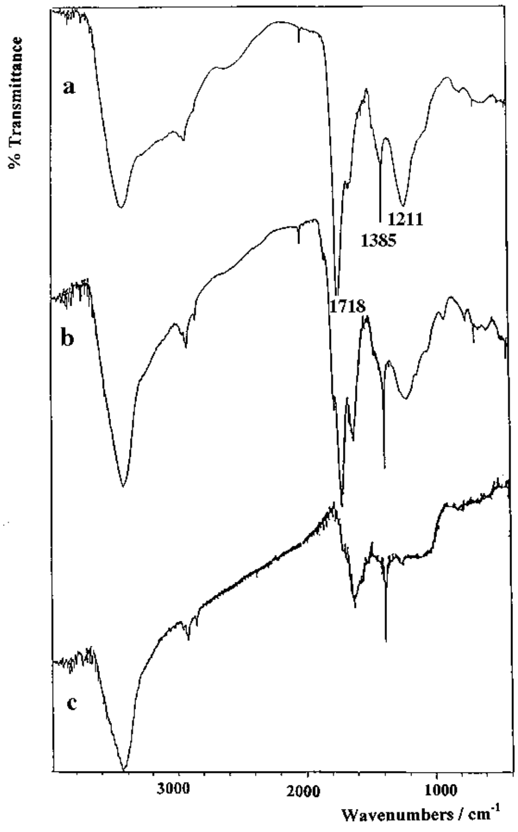

Fig. 4 FTIR spectra of soil (FA) (a), soil FA heated to 573 K (b) and soil FA heated to 773 K (c)

373, 473 and 573 K are similar to those of the original ones. After heating to 673 K (Fig. 5b), a reduction in intensity of the IR bands at 1385 cm^{-1} (phenolic OH) and 1716 cm^{-1} (COOH) and an increase in the relative intensity of the broad band at 1624 cm^{-1} (COO^{-}) are observed. After heating to 773 K (Fig. 5c) peaks at 1717 cm^{-1} (COOH/CO) and 1385 cm^{-1} (phenolic OH) disappear and the intensity of the bands at 1624 cm^{-1} (COO^{-}) and 1211 cm^{-1} (aromatics) decreases. These results suggest a lower thermal stability of phenolic OH in peat HA and FA, compared with soil FA and HA.

DSC curves of the Suwannee river HA (Fig. ld) features an endotherm at 411 K and a broad exotherm with a minimum at about 713 K, whereas the corresponding FA (Fig. 2c) shows the same endotherm at 426 K and an exotherm at 753 K. Nordic aquatic HA (Fig. 1e) and FA (Fig. 2d) samples are characterized by an endothermic peak occurring at 403 K for HA and 388 K for FA, and by a broad exotherm centered at about 728 K for both samples. Nordic aquatic and Suwannee river HAs and FAs show a similar trend in their FTIR spectra (Fig. 6a). Samples heated to 373, 473, 573 K are similar to those of corresponding original samples. When heated to 673 K

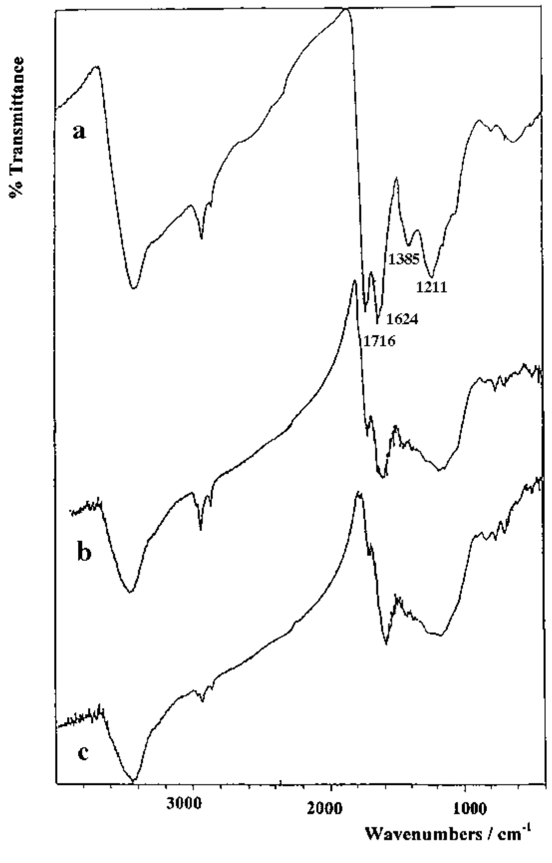

Fig. 5 FTIR spectra of peat (HA) (a), peat HA heated to 673 K (b) and peat HA heated to 773 K (c)

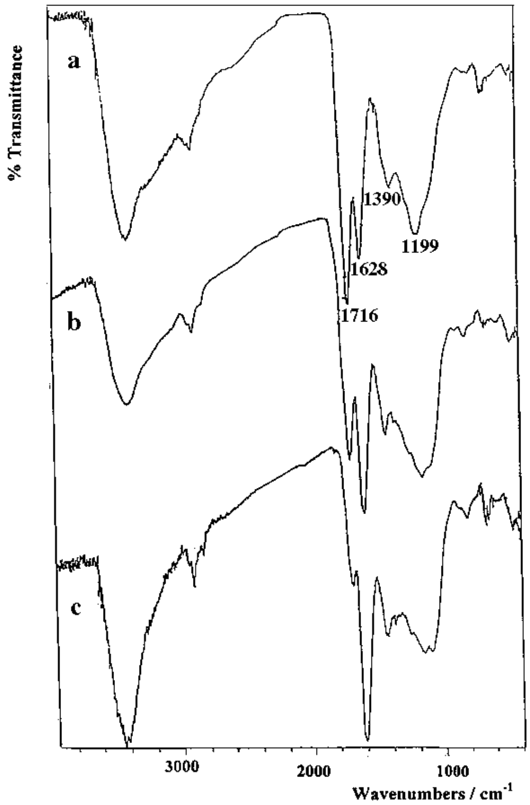

Fig. 6 FTIR spectra of aquatic HA (a), aquatic HA heated to 673 K (b) and aquatic HA heated to 773 K (c)

(Fig. 6b), they exhibit the previously described decrease in the relative intensity of the IR peak at 1716 cm^{-1} (COOH), compared to that at 1628 cm^{-1} (COO^{-}). After heating to 773 K (Fig. 6c) a further reduction occurs in the relative intensity of the peak at 1716 cm^{-1} and infrared spectra are strongly modified showing residual adsorptions due to aromatic structures.

These results support the data reported in literature according to that the high-temperature exotherm may be ascribed to the possible rearrangement and polycondensation of aromatic nuclei of the humic molecule.

Conclusions

The combined DSC and FTIR analyses of HAs and FAs of various nature and origin provide useful information on the thermal behaviour and thermal stability/lability of structural and functional components of humic macromolecules. In particular, the strong endothermic peak appearing in the low-temperature region for all samples indicates loss of hydration water and /or structural water, and of labile peripheral polysaccharide chains. The endotherm at about 623 K for soil FA may be ascribed to partial decarboxylation of more labile, not H-bonded, surface COOH groups. The broad exotherm around 773 K may be assigned to thermal reactions involving rearrangements of aromatic nuclei of the humic molecules. This evidence is suggested by FTIR spectra after heating to 773 K, in which residual adsorptions ascribed to aromatic structures are still present. The presence or absence, and the relative intensity of the various thermal peaks observed appear to be related to the nature and origin of HA and FA samples studied. For instance, the high-temperature exotherm is absent in peat HA, whereas it shows lower intensity in Nordic aquatic and Suwannee river FAs and HAs than in soil FAs and HAs.

These results are related to the low degree of humification of the aromatic network in aquatic HAs and FAs, compared to soil and peat FAs and HAs that are well known to be structurally complex and polycondensed organic macromolecules.

References

1 M. Schnitzer and I. Hoffman, Geochim. Cosmochim. Acta, 29 (1965) 859.
2 T. Satoh, Sci. Plant Nutr., 30 (1984) 95.
3 T. Satoh, Sci. Plant Nutr., 30 (1984) 1.
4 R. C. Turner and M. Schnitzer, Soil Sci., 93 (1962) 225.
5 M. Schnitzer and I. Hoffman, Proc. Soil Sci. Soc. Am., 28 (1964) 520.
6 M. Schnitzer, R. C. Turner and I. Hoffman, Can. J. Soil Sci., 44 (1964) 7.
7 D. S. Orlov, V. N. Dublin and D. M. Elkina, Agrochemistry, 1 (1968) 68.
8 E. A. Shurigina, N. K. Larina, Ma. A. Chubarova and M. M. Kononova, Geoderma, 6 (1971) 169.
9 Y. Chen, N. Senesi and M. Schnitzer, Geoderma, 20 (1978) 87.
10 H. Kodama and M. Schnitzer, Soil Sci., 5 (1970) 265.
11 M. B. Holder and S. M. Griffith, Can. J. Soil Sci., 63 (1983) 151.
12 U. Reh, W. Kratz, G. Kraepelin and C. Angehrn-Bettinazzi, Biol. Fertil. Soils, 9 (1990) 188.
13 M. R. Provenzano and N. Senesi, Abs. ‘Journeé Mediterranées de Calorimetrie et d’Analyse Thermique’, Corte 1993, p. 37.
14 M. R. Provenzano and N. Senesi, Abs. ‘6th European Symposium on Thermal Analysis and Calorimetry’, Grado 1994, p. 243.
15 M. R. Provenzano and N. Senesi, Abs. ‘Giornate Mediterranee di Calorimetria e Analisi Termica’, Cagliari 1995, p. 264.
16 M. R. Provenzano and N. Senesi, Abs. ‘XVIII Convegno Nazionale della Società Italiana di Calorimetria e Analisi Termica’ Pavia, 1996, p. 12.
17 M. R. Provenzano, N. Senesi and G. Piccone, Compost Sci. and Utiliz., (1998) in press.
18 M. R. Provenzano, N. Senesi and V. Miikki, J. Therm. Anal. Cal., 52 (1998) 1037.
19 International Humic Substances Society, Bylaws, Art. II, Section 3, 1982.
20 International Humic Substances Society, List of characterization, Comm. to Purchasers of Standard and Reference Humic and Fulvic Acids, 1985.
21 International Humic Substances Society, Sample of analytical data for IHSS standard and reference humic and fulvic acids, Comm. to Members, 1987.
22 N. Senesi, T. M. Miano, M. R. Provenzano and G. Brunetti, The Sci. of the Total Environ., 81/82 (1989) 143.
23 P. MacCarthy, R. L. Malcolm, M. H. B. Hayes, R. S. Swift, M. Schnitzer and W. L. Campbell, IHSS Comm. to Members, 1985.