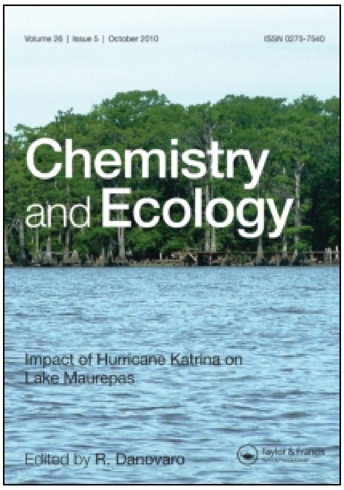

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Tao Zuyi[a]; Liu Shifang[a]; Zhai Jianjun[a]; Sheng Fenling[a]
[a] Department of Modern Physics, Analysis and Testing Centre, Lanzhou University, Lanzhou, P.R. China

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STUDIES OF THERMAL TRANSFORMATIONS OF HUMIC AND FULVIC ACIDS IN SOILS I. INFRARED SPECTROSCOPY AND TEMPERATURE–PROGRAMMED PYROLYSIS MASS SPECTROMETRY

TAO ZUYI*, LIU SHIFANG,
ZHAI JIANJUN and SHENG FENLING

*(Department of Modern Physics, Analysis and Testing Centre,
Lanzhou University, Lanzhou, P.R. China, 730 000)*

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Temperature–programmed pyrolysis mass spectrometry and Fourier–transform infrared spectroscopy have been used to monitor structural changes of humic and fulvic acids isolated from soils in China, in the temperature range of 25–550°C. In this work, we found that decarboxylation is obvious as the main reaction with dehydration reaction from 150°C to 400°C, the anhydride can be identified from FT–IR spectra at temperature range from 200°C to 400°C; there are evident changes of the aromatic nucleus of humic and fulvic acids above 400°C, even remaining up to 550°C. Besides, some changes of adsorption water can be distinguished before 200°C, and the mass signal of sulphur dioxide was detected.

Keywords: Thermal transformation; humic acid (HA); fulvic acid (FA); infra-red; pyrolysis mass spectrometry

INTRODUCTION

Humic substances are the most distributed organic materials in soils, but chemical degradations are laborious and time consuming and the use of a thermal method in structural investigations appears attractive.

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*Corresponding author.

Studies of the humic and fulvic acids have been carried out using a number of techniques such as Infra-red Spectroscopy (IR), Pyrolysis Mass Spectrometry (Py/Ms), Pyrolysis–Gas Chromatography/Mass Spectrometry (Py–Gc/Ms) and Thermogravimetric analysis (TG). However, these analyses are probably not thought to be sufficiently conclusive to make further research unnecessary, because humic and fulvic acids are very complex organic materials and the identification of signals from these materials is almost impossible without additional information. Thermogravimetric analysis combined with IR and mass spectrometric analyses are powerful tools for studying thermal transformation pathways of humic and fulvic acids. Coupling TG with IR spectroscopy and Pyrolysis/Mass Spectrography may yield additional information on the volatile products and the residues of thermal transformation.

This paper and a following paper present a detailed examination of thermal transformations of humic and fulvic acids isolated from the soils in China by combining the results from IR spectra, Py/Ms and thermogravimetric analysis. In this paper, the IR spectra and mass spectra of humic and fulvic acids isolated from the soils are obtained during pyrolysis at the temperature ranges 25–550°C and 25–400°C, and the results are discussed in order to determine the chemical changes of humic and fulvic acids, and to infer the processes that may be involved in the transformations of organic materials in soils.

EXPERIMENT SECTION

Material

All soil humic and fulvic acids were the generous gifts from Institute of Soil Science (Chinese Academy of Sciences). The five soil FAs and five HAs were extracted from the soils in different areas of China according to procedures recommended by International Humic Substances Society (Machesky *et al.*, 1992). Table I shows the origins, the elemental compositions, the moisture and ash contents of these samples. All data are expressed on a dry-ash free basis. Carbon, hydrogen and nitrogen were determined with a 1106 Model Element Analyzer (Italy), sulphur content was measured by an oxygen flask combustion

TABLE I The name, elemental composition, moisture and ash contents of HAs and FAs

No	*Name*	*Elemental composition* C(%)	H(%)	O(%)	N(%)	S(%)	H_2O(%)	Ash(%)
A	Red earth HA (Guangdong, Da-Ya-bay)	55.51	5.21	33.05	5.29	0.94	5.02	3.21
B	Red earth FA (Guangdong, Da-Ya-bay)	54.68	4.73	35.90	3.72	0.97	5.50	8.80
C	Dark loessial soil HA (Gansu)	60.44	3.53	31.31	4.22	0.50	7.61	4.02
D	Dark loessial soil FA (Gansu)	50.15	4.42	39.56	5.38	0.49	6.50	3.58
E	Black soil HA (Heilongjiang)	62.61	3.65	29.21	3.92	0.61	8.90	6.04
F	Black soil FA (Heilongjiang)	52.53	3.94	38.74	3.90	0.89	8.51	5.98
G	Cumulative loessial soil HA (Gansu)	57.63	4.55	31.59	5.10	1.13	8.96	0.65
H	Cumulative loessial soil FA (Gansu)	53.72	5.18	33.61	6.29	1.20	9.72	6.11
I	Lime concretion fluvioaquic soil HA (northern part of Anhui province)	62.04	2.68	30.81	4.05	0.42	6.81	2.38
J	Lime concretion fluvioaquic soil FA (northern part of Anhui province)	56.34	3.49	34.32	5.10	0.75	9.36	7.72

method. Oxygen was calculated by difference. Moisture and ash content were determined by using thermogravimetry.

Apparatus and Experimental Conditions

The ZAB–HA type mass spectrometer was used in Py/Ms studies. The instrument was operated in following conditions: sample size about 0.5 mg; heating rate 0.5°C s^{-1}; maintaining at 30°C for 30 min, and linear-heating to 400°C, then still maintaining at 400°C for 30 min, finally cooling to room temperature; mass resolution 1000. The data of mass spectra are obtained by the VG PDP 17/250 data processing system.

FT–IR spectra (4000–333cm^{-1}) of these samples were recorded at a nominal resolution of 4 cm^{-1} with KBr discs using a Nicolet 170SX Fourier transform infra-red spectrometer. The samples were heated in an electric muffle furnace at a certain temperature for 30 min and then stored in a vacuum desiccator for eliminating the moisture. To ensure sufficiently high S/N ratio, 1000 scans were also added.

RESULTS

1. Infra-red Spectroscopy

The IR spectra of samples A and B and of residues heated to different temperatures are shown in Figures 1 and 2. Comparing the spectra of samples A and B at 20°C, we observe a similar series of bands, indicating that the same types of chemical groups are present in HA and FA. In the spectra of samples A and B at 20°C, there are only a few of poorly resolved broad bands which were assigned by many authors (Vassallo and Attalla, 1992; Vassallo and Finnie, 1992; Bowell R. J. *et al.*, 1993) (see Table II). The main features include strong absorption at about 3400–3300 cm^{-1} due to hydroxyl groups in phenols, alcohols and acids, and at about 1720 cm^{-1} due to C=O in carboxylic acids and esters.

As shown in Figures 1 and 2, the intensities of the hydroxyl absorption at about 3310 cm^{-1} in the residues heated to 90°C and 125°C and in the unheated samples are almost identical, and no shift in the

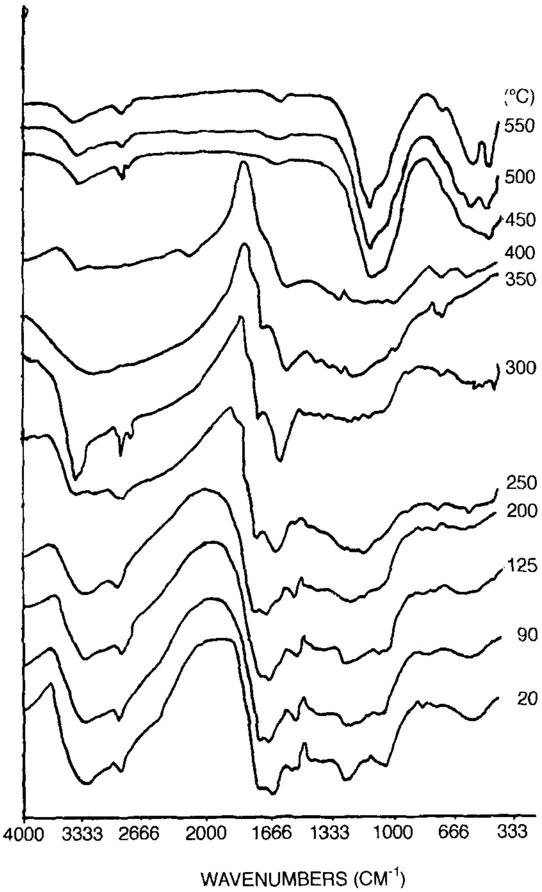

FIGURE 1 The IR spectra of sample A and of residues heated to different temperatures.

position of this band occurs. However, the intensities of the hydroxyl absorption decrease rapidly in the residues heated above 200°C, and fall to a very low value at 400°C and higher temperatures, and the position of this band shifts toward a higher wave number (3400 cm^{-1}). The shift of position of this band demonstrates that the hydrogen/bonding interaction among molecules becomes strong.

The most obvious changes occur in the 1720 cm^{-1} to 1600 cm^{-1} region. In the case of sample A, the intensities and the position of both

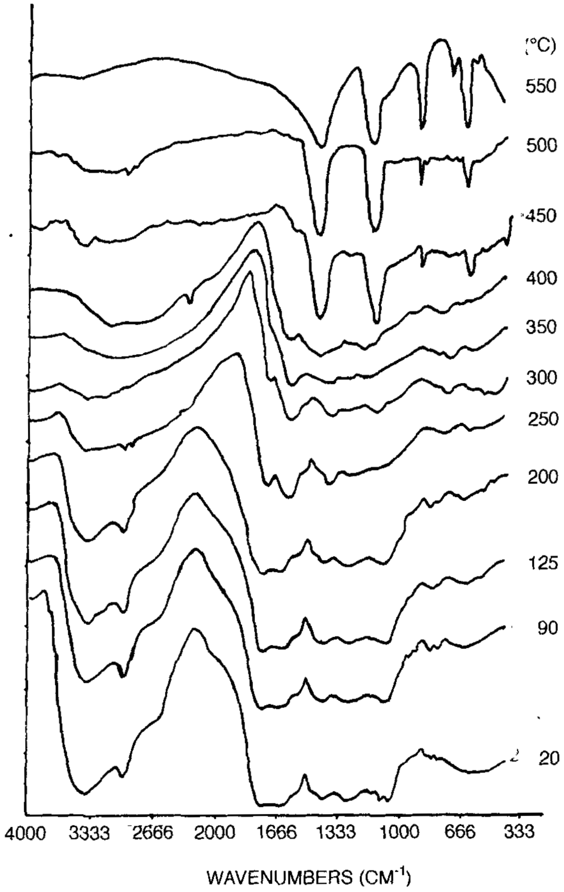

FIGURE 2 The IR spectra of sample B and of residues heated to different temperatures.

bands for the original sample and the residues heated to 90°C and 125°C are almost identical. Similarly, in the case of sample B, the intensities and positions/of both bands for the original sample and the residues heated to 90 and 125°C are also almost identical. In the case of sample A, in the residue heated to 250°C, the band originally at 1722 cm^{-1} has shifted to 1715 cm^{-1}, and in the residue heated to 300°C and 400°C the same band has been lowered to 1715 and 1707 cm^{-1}. On the contrary, in the case of sample B, in the residues heated

TABLE II Observed infra-red bands of sample A and B

Band (cm^{-1})	*Proposed assignment*	*Relative intensity*	
		Sample A	*Sample B*
3340–3327	OH stretch of phenolic OH (contribution from aliphatic OH and possible—NH) or some water	vs	vs
3080	—CH stretch (aromatic)	no	vw
2931 2936	—CH$_3$, —CH$_2$ asym-or sym-stretch bonded —OH stretch of —COOH	ms	ms
1820	—C=O sym-stretch of anhydrides of esters	w	w
1715 1716	—C=O stretch of —COOH	vw	vw
1673–1662	—C=O stretch of —COOH	ms	s
1636–1616	—C=C stretch (C=C)	vw	v
1516–1509	aromatic ring stretch (para- and ortho-disubstituted)	mw	w
1450–1417	—CH$_3$ asym-bend; —CH$_3$ sym-bend (methoxy) aromatic ring stretch or C—O stretch of carbon	vw	mw
1385	—CH$_3$ sym-stretch at 2 or 3 degrees carbon, or COO$^-$ symmetric stretch and CH deformation, C—O stretching of phenolic	ms	ms
1259–1228	—C—O stretch (aromatic ether ArOR, acid dimer with electron-withdrawing group); amide (C—N stretch)—COH deformation of COOH and phenolic group	s	s
1127–1123	aromatic ring bending (para- and ortho-disubstituted); C—O—C stretch (alkyl ester) or S—O stretch of sulphovinate	mw	mw
1073–1036	—C—O stretch (hydrated polys and carbon hydrates); —C—O stretch (aromatic ether, ArOR)	ms	ms

* Relative peak intensity:
vs, very strong; s, strong; ms, medium strong; m, medium; mw, medium weak; vw, very weak; no, not observed.

to 250°C, no shift of the band originally at 1715 cm^{-1} occurs, but in the residue heated to a higher temperature, the same band has lowered.

It can be seen in the Figures 1 and 2, the most rapid loss of signals in the 1720 cm^{-1} and the 1715 cm^{-1} regions occurs in the range 300–400°C, and complete loss of signal is seen at 400, 450 and 550°C. In parallel with decreasing the intensities of bands at 1720 cm^{-1} and 1715 cm^{-1} in the range 200–300°C, anhydride formation is evident because the bands at 1836 and 1775 cm^{-1} also become apparent across this temperature range, but at a higher temperature, both bands disappear.

With increasing temperature, the shoulders at about 1600 cm^{-1} and 1610 cm^{-1} become more intense, so that by 250°C both bands are clearly defined. Both bands can be assigned to the carbon–carbon ring stretching mode in aromatic rings. Beyond 250°C the positions of both bands are lowered and intensities of both increase at first and then decrease at 400 and 450°C, and at 500 and 550°C both bands disappear. However, at 550°C, the shoulders at about 1618 cm^{-1} can be detected. Beyond 450°C, the residues of sample A exhibit strong absorption at about 1109, 1105, 550 and 463 cm^{-1}, and the residues of sample B exhibit strong absorption at 1430, 1135, 878 and 623 cm^{-1}, and these peaks can be assigned to silicate, silica, inorganic carbonate and sulphate.

The IR spectra of samples E and F and of residues at 125°C, 300°C, 400°C and 500°C are shown in Figures 3 and 4, and the similar changes in the spectra with increasing temperature can be seen.

2. Temperature-Programmed Pyrolysis Mass Spectrometry

The pyrolysis total ion current chromatography spectra, the mass chromatography spectra and the pyrolysis spectra of the mass signals m/z 18, 28, 44 for samples A, B, C, D, E and F are shown in Figures 5, 6 and 7. Using linearly programmed heating rate, the mass chromatography spectra enable the description of the temperatures

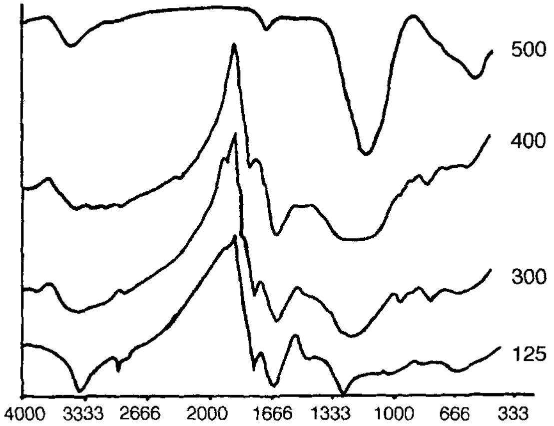

FIGURE 3 The IR spectra of sample C and of residues heated to different temperatures.

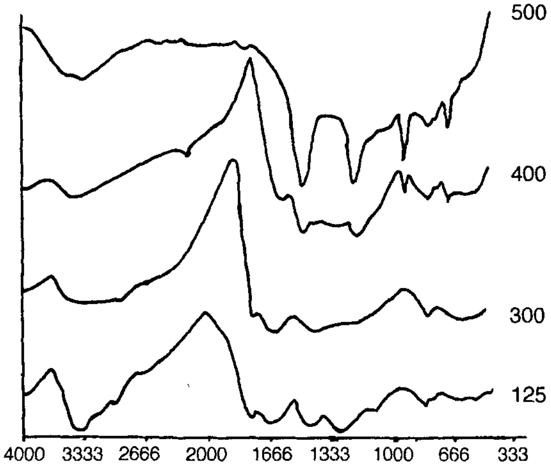

FIGURE 4 The IR spectra of sample D and of residues heated to different temperatures.

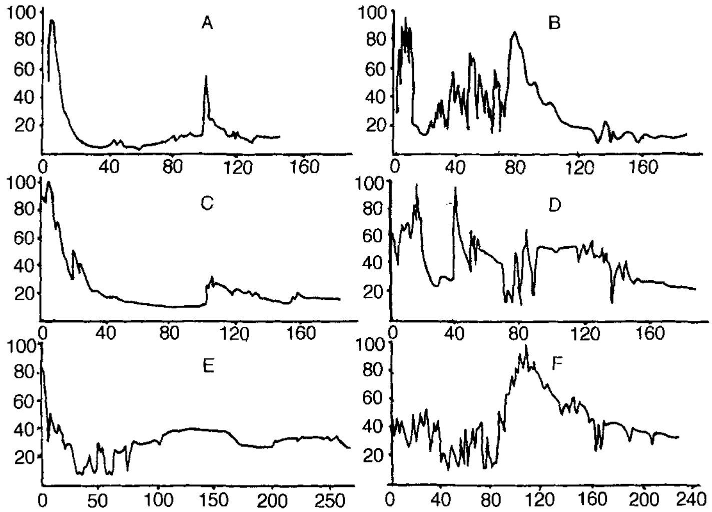

FIGURE 5 The pyrolysis total ions current chromatography spectra of samples A, B, C, D, E and F.

where H_2O, CO and CO_2 are volatilized (Leinweber, P. *et al*, 1992; Schulten H.-R., 1994). As can be seen from Figures 5–7, for all samples, the mass signals m/z 18 occur in the all temperatures, but

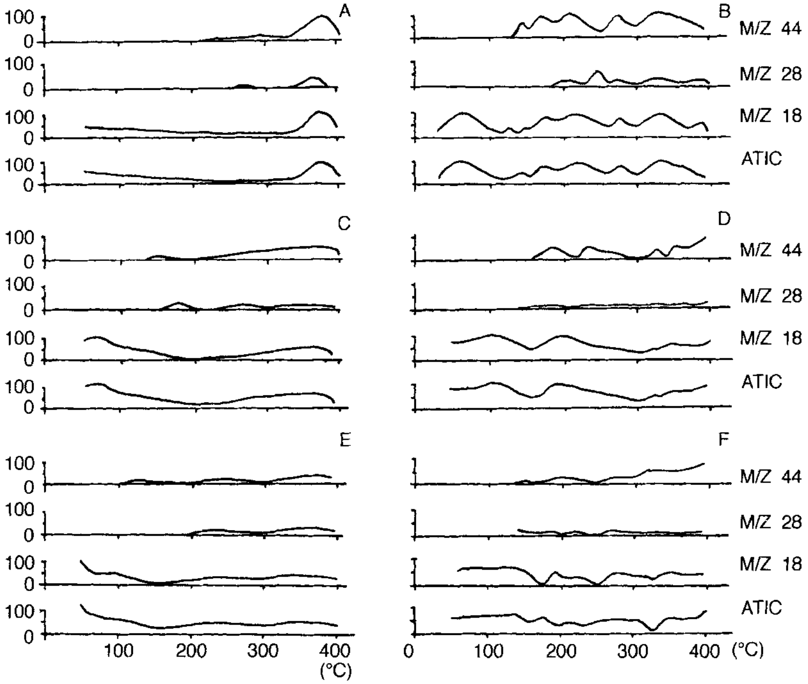

FIGURE 6 The mass chromatography spectra of the mass signals m/z 18, 28, 44 for samples A, B, C, D, E and F.

they are less resolved into distinct reaction steps, although they reach first their maximum values at near 100°C and the mass signals m/z 28 and m/z 44 have not appeared below about 150°C. Combining the results of IR spectra below 125°C, it may be concluded that the chemical structural changes have not occurred and the reaction step is solely the elimination of moisture below 150°C.

As compared with the mass chromatography spectra of samples A, C and E in Figure 6, the mass signals m/z 18 of samples B, D and F are more complex, and over 150°C there are two or more maximum values. Parallel with appearance of the complex mass signals m/z 18, and beyond 150°C, the mass signals m/z 28 and m/z 44 of samples B, D and F are more complex than those of samples A, C and E which reach only one or two maxima. Below 150°C, no mass signals m/z 28 and m/z 44 occur for any samples. Coupling Py/Ms with IR spectra, it

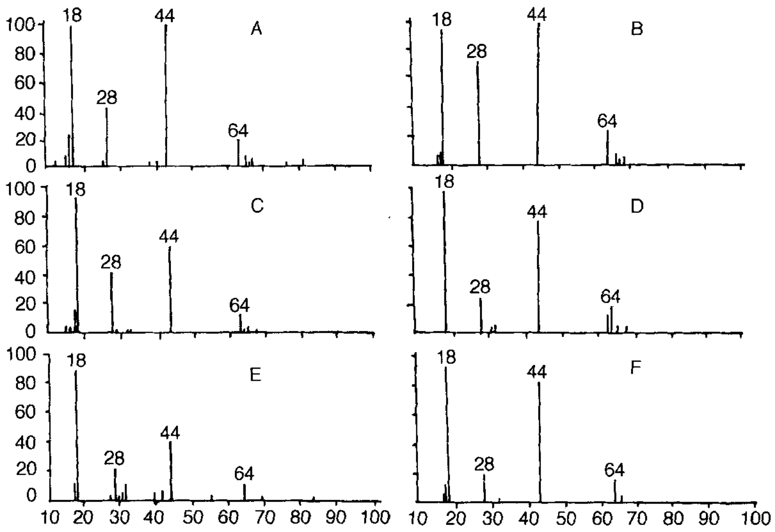

FIGURE 7 The pyrolysis mass spectra of samples A, B, C, D, E and F.

may be concluded that beyond 150°C, a combination of dehydration and decarboxylation occurs for all samples. Furthermore, for FA samples, carboxylic acid groups may be divided into two or more groups with different thermal instabilities. It would appear, therefore, that below 400°C, the reaction steps involve mainly the expulsion of function groups, and beyond 400°C the reaction steps involve the decomposition of the aromatic rings remaining after removal of peripheral functional groups.

The pyrolysis mass spectra of samples A, B, C, D, E and F are shown in Figure 7. Comparing these spectra for all samples we have also observed a similar series of bands except in sample E, where it is demonstrated that the similar individual constituents and binding blocks are present in all FAs and HAs samples.

As shown in Table I, though the contents of sulphur are as low as 1%, the mass signal m/z 64 representing sulphur dioxide are evident. For the sample E, the mass signals m/z 32, 39, 55 and 83 represent the aliphatic chains of humic substances.

Based on the FT–IR and pyrolysis mass spectra, it may be concluded that the main reactions governing the pyrolysis of humic and fulvic acids isolated from some soils in China were found to be: (a) elimination of moisture (up to 150°C); (b) a combination of dehydration and decarboxylation (between 150 to 400°C); (c) decomposition of the aromatic ring (beyond 400°C).

CONCLUSIONS

Combining Py/Ms with IR spectroscopy at high temperature is a feasible method for studying the thermal transformations of humic and fulvic acids in soil, and the mechanism of the pyrolysis of these humic substances in soil was explored.

It was found that these samples from different areas from a subtropical zone to a boreal zone show similar pyrolytic properties. When the temperature reached 150–400°C, fission took place mainly in aliphatic side chain and hydrogen bounded–OH group; when the temperature reached 400–500°C, the fission took place chiefly in the aromatic nucleus. Below 150°C, the chemical structural changes have not occurred and the reaction step was solely the elimination of moisture.

Acknowledgement

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References

Bowell, R. J., Gize, A. P. and Faster, R. P. (1993) The role of fulvic acid in the supergene migration of gold in tropical rain forest soils, *Geochimica Cosmochimica Acta*, **57**, 4179–4190.

Leinweber, P. and Schulten, H. -R. (1992) Differential thermal analysis, thermogravimetry and in-source pyrolysis-mass spectrometry studies on the formation of soil organic matter, *Thermo Chimica Acta*, **200**, 151–167.

Machesky, M. L., Andrade, W. O. and Rose, A. W. (1992) Interaction of gold (III), chloride and elemental gold with peat-derived humic substances, *Chemistry and Geology*, **102**, 53–71.

Schulten, H. -R. (1994) Humic Substance in the Global Environment and Implications in Human Health, N. Senesi, T. M. Miano (Eds.), Elsevier, Amsterdam, 43–56.

Vassallo, A. M. and Attalla, M. I. (1992) Studies of thermal transformations of fulvic acids using Fourier transform-infra-red emission spectroscopy, *Journal of Analytical and Applied Pyrolysis*, **23**, 73–85.

Vassallo, A. M. and Finnie, K. S. (1992) Infra-red emission spectroscopy of some sulfate minerals, *Applied Spectroscopy*, **46**, 1477–1482.