*Geoderma*, 57 (1993) 263-274
Elsevier Science Publishers B.V., Amsterdam

# Structural investigations of humic acid from leonardite by spectroscopic methods and thermal analysis

Giuliana Ricca[a], Linda Federico[b], Carla Astori[b] and Raffaele Gallo[c]
[a]*Centro di Studio per le Sostanze Naturali del CNR, Dipartimento di Chimica Organica e Industriale. Università di Milano, Via Venezian 21, 20133 Milano, Italy*
[b]*Dipartimento di Fisiologia delle Piante coltivate e Chimica Agraria dell'Università di Milano, Via Celoria 2, 20133 Milano, Italy*
[c]*Dipartimento di Chimica Industriale dell'Università di Messina, 98100 Messina, Italy*

(Received February 24, 1992; accepted after revision June 24, 1992)

## ABSTRACT

Ricca, G., Federico, L., Astori, C. and Gallo, R., 1992. Structural investigations of humic acid from leonardite by spectroscopic methods and thermal analysis. Geoderma, 57: 263–274.

Humic acid from leonardite, an immature coal, has been examined by spectroscopic methods (UV-VIS, IR-FT, $^{1}$H, $^{31}$P, $^{13}$C-NMR), mass spectrometry (FAB-MS) and thermal analysis. These techniques provided complementary informations. A quantitative $^{13}$C-NMR technique was applied to this humic acid: the aromaticity calculated from the NMR data is high, about 76%, in agreement with mass spectrometric and thermal analysis data.

## INTRODUCTION

Materials classed as very immature coals are heteropolycondensed substances almost completely soluble in aqueous alkali and can thus be considered an abundant source of natural humic acids.

Among these materials is Leonardite, a coal-like substance extracted from superficial layers of North Dakotan lignite mines and similar in structure to lignite (Young and Frost, 1963; Lynn, 1967; Saeed, 1978). The major difference between Leonardite and lignite is the higher oxygen content of the former, which is entirely due to a larger number of carboxyl and phenolic groups. Till now Leonardite has been studied as soil conditioner or organic fertilizer (Schwartz et al., 1965; Gaur, 1969; O'Donnell, 1973; Harrel and Saeed, 1977; Ciavatta et al., 1988); beside, it was utilized as humified material in many

---

*Correspondence to:* G. Ricca, Centro di Studio per le Sostanze Naturali del CNR, Dipartimento di Chimica Organica e Industriale. Università di Milano, Via Venezian 21, 20133 Milano, Italy.

laboratory investigations (Piccolo and Camici, 1990; Contin and De Nobili, 1990). At present it seems that no significant study has been concerned to the structure of this material.

The object of this paper is a structural investigation of the humic acid (HA) from Leonardite by means of: UV-VIS, IR, magnetic nuclear resonance ($^1$H-NMR, $^{13}$C-NMR, $^{31}$P-NMR) spectroscopy; thermogravimetric analysis and differential scanning calorimetry (DSC); mass spectroscopy.

## MATERIALS AND METHODS

### *Materials*

Organic matter was extracted twice from Leonardite according to a modified method described by Schnitzer and Skinner (1982) by 0.5N NaOH, using a solvent:leonardite ratio of 10:1 and once with distilled water. All extractions and subsequent treatments of the extracts, while in alkaline state, were done under nitrogen. The humic acid was separated from the fulvic acid by acidification at pH 1. Afterwards the raw materials were dialysed against distilled water and passed twice through a column of Amberlite IR-120 exchange resin in the H-form. Successively the solution was concentrated under vacuum at room temperature and the residue was lyophilized.

### *Chemical methods*

The organic carbon was determined according to Springer and Klee (1954); total P by colorimetry after mineralization of the sample. The proton exchange capacity of the humic acid was determined by potentiometric titration. The total acidity (carboxylic and phenolic groups) was determined with $Ba(OH)_2$ and calcium acetate (Schnitzer and Gupta, 1965).

### *Spectroscopic methods and thermal analysis*

For UV-VIS spectra, HA was dissolved in a $NaHCO_3$ 0.05N or in a NaOH 0.05N solution (about 200 mg/l of HA).

UV and VIS spectra were obtained with a Perkin Elmer 554 UV/VIS spectrophotometer.

IR spectra were recorded on KBr pellets (1 mg of sample + 200 mg of dry KBr) from 4000 to 600 cm$^{-1}$ in a FTIR Perkin Elmer mod. 710 spectrophotometer.

A $^{31}$P-NMR proton decoupled spectrum of HA solution was obtained at 80.96 MHz on a Varian XL 200 spectrometer. The NMR sample was prepared by dissolving 60 mg of HA in 0.5 ml of NaOD 3M solution. For $^{31}$P-NMR the following conditions were used: spectral width SW = 4000 Hz; acquisition time AT=0.5 s; number of transients NT=121,131, pulse width PW=45°; external standard 85% $H_3PO_4$.

Proton decoupled $^{13}C$-NMR spectra of humic acid solutions were obtained at 75.432 MHz on a Bruker AC 300 spectrometer. The NMR sample was prepared by dissolving 60 mg of HA in 0.5 ml NaOD 3M solution. Conditions were chosen to obtain reasonably quantitative intensity distributions while maintaining usable signal-to-noise ratios (Preston and Blackwell, 1985). The spectrum was obtained using inverse-gated-decoupling [acquisition time 0.2 s, and 45° pulse; relaxation delay (decoupler off $D_2$= 1.8 s); total acquisition times were 48 h]. The free induction decays were processed by applying 20 Hz linebroadening and baseline correction both using Bruker software as supplied (Preston and Blackwell, 1985). The uncertainty in the area measurements was approximately ±10% and depended both on signal to noise ratio (S/N) and extent of overlap of spectral regions.

Chemical shifts were determined from internal dioxane and are quoted relative to external TMS. The spectra obtained by DEPT (distortionless enhancement by polarization transfer), provide informations on carbon multiplicities, producing characteristic changes in the time intensities at $CH_3$, $CH_2$, CH and C groups.

$^1H$-NMR spectra of HA solution were obtained at 300 MHz under homogated decoupling condition in which the HOD peak produced by water impurities and proton exchange was irradiated. The radiofrequency (RF) level of HOD irradiation was optimized for this sample. Chemical shifts are quoted with respect to internal DSS [4,4 dimethyl-4-silapentanesulphonic acid (Na-salt)]. NMR samples were prepared by dissolving 10 mg of HA in 0.5 ml NaOD 0.5M.

The mass apparatus used is a 7070 EQVG Analytical Organic Mass Spectrometer by FAB technical (Fast Atom Bombardment).

DSC curves were obtained on a Perkin-Elmer DSC-2 instrument equipped with a Perkin-Elmer Thermal Analysis Data Station 3600. Samples of 0.3–3.5 mg were weighed in aluminium pans. The instrument was preset at 323 K and the sample was heated at 20 K $min^{-1}$ (dynamic test). Indium was used as the standard for calibrating the temperature axis and enthalpy output. Thermogravimetric curves were obtained on a Perkin-Elmer TGS-2 instrument under air or nitrogen at 20 K $min^{-1}$.

## RESULTS AND DISCUSSIONS

### *Chemical analysis*

The water content of leonardite used in our experiments is 15.4%. In the dried material the ash content is 20.9% and the total carbon is 63.9% of the dry matter ash free.

TABLE 1

| | |
|---|---|
| Total acidity [$Ba(OH)_2$], meq/g | 12.9 |
| COOH Groups [$Ca(OAc)_2$], meq/g | 3.96 |
| Phenolic groups –OH, meq/g | 8.94 |
| COOH Groups[1], meq/g in $H_2O$ | 5.94 |
| COOH Groups[1], meq/g in DMSO | 6.79 |
| C (%) | 51.31 |
| H (%) | 6.93 |
| N (%) | 1.27 |
| O (%) | 40.63 |
| Residue[2] (%) | 3.92 |

[1] Measured by potentiometric titration. These data are also referred as proton exchange capacity.
[2] On dry basis.

HA from leonardite is fairly soluble in NaOH, dimethyl sulphoxide, dimethylformamide; moderately soluble in methanol, ethanol, tetrahydrofuran; insoluble in water, benzene, toluene.

In Table 1 data of elemental analysis, total acidity, carboxyl and phenolic groups' contents are reported. The elemental composition values are normalized to 100%; the oxygen was calculated by difference. According to the results obtained by Schnitzer and Gupta (1965), the carboxyl and phenolic groups represent 30.7 and 69.3% of the total acidity, respectively. The number of COOH groups present in 100 carbon atoms, as calculated from potentiometric titrations, is 7.14 and 8.15 in $H_2O$ and DMSO respectively, while it is 4.75 on the basis of the calcium acetate method.

## *Spectroscopic data*

The ultraviolet–visible spectroscopy of humic substances gives featureless UV–visible spectra (Ureta Baes, 1988).

The shoulder observed about 260 nm in the spectrum of humic acid from leonardite indicates the presence of aromatic structures in humic acid.

The E4/E6 ratio using the 0.05M $NaHCO_3$ solutions at 465 nm and 665 nm is 5.63 for humic acid from leonardite and is comparable with typical values from humic acids (Chen et al., 1977).

Major absorption bands in IR spectrum of HA are in agreement with the attributions reported by Ureta Baes (1988).

The broad band at 3400 $cm^{-1}$ may be due to hydrogen bonded hydroxyls and, probably, to hydrogen bonded NH.

Peaks characteristic of CH stretching bands of methyl and methylene groups are observed in the 2970–2860 $cm^{-1}$ region, while the shoulders at 1450 $cm^{-1}$ and 1380 $cm^{-1}$ are assigned to the asymmetric and symmetric deformation of $CH_2$ and $CH_3$ groups.

The broad band at about 2600–2500 $cm^{-1}$ is due to the OH stretching vibrations of the H-bonded COOH. The sharp, strong band at 1715 $cm^{-1}$ is due to the C=O stretching vibration of COOH groups in aliphatic acids and also to a contribution of meta dicarboxylic benzoic acid (Avran and Mateescu, 1966). The very large band at 1630 $cm^{-1}$ could result by overlaying of the asymmetric vibration of carboxylate anion and of the C=O stretching band of COOH groups having H-bonded OH groups in ortho, as in salicylic acid and 2,4 dihydroxybenzoic acid, and probably of the -CO stretching of amide. The band at 1400 $cm^{-1}$ is assigned to the symmetrical stretching vibration of carboxylate anion.

The broad band centered at 1250 $cm^{-1}$ confirms the presence of COOH groups, this band could be due to the OH deformation mode coupled with the -C-O- stretching mode in carboxylic groups as suggested by Schnitzer (1971) and Stevenson and Goh (1971). Besides, the C–OH stretching vibrations of phenolic groups may also contribute to this absorbance in the same region.

The broad and weak bands between 1150 and 1000 $cm^{-1}$ can be attributed to C–O stretching vibrations in aliphatic alcohols, while the bands between 900 and 730 $cm^{-1}$ are due to CH out of plane bending vibrations of aromatic rings.

The $^{31}P$-NMR spectrum shows one signal at 5.83 ppm, indicative of inor-

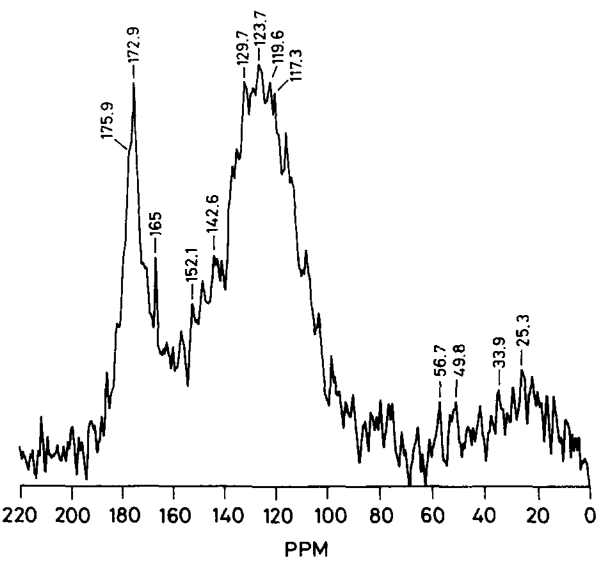
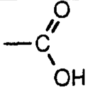
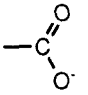
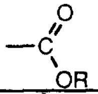
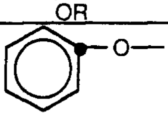
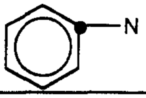
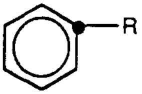
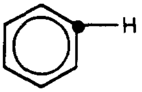


Fig. 1. $^{13}C$-NMR spectrum of humic acid from leonardite in NaOD solution.

TABLE 2

$^{13}$C-chemical shifts, assignments and C% from $^{13}$C

| REGION[a] (ppm) | CHEMICAL SHIFT $\delta_C$ (ppm) | ASSIGNMENT | C % |
|---|---|---|---|
| A<br>200-170 | 181.1 (m)[b]<br>178.1 (w)[b]<br>176.0 (s)[b]<br>172.9 (s)[b]<br>170.4 (m)[b] |  $-C(=O)OH$ carboxylic acids<br> $-C(=O)O^-$ carboxylic ions<br> $-C(=O)OR$ esters | 16.3 |
| B<br>170-150 | 169.0 (m) [b]<br>165.0 (m) [b]<br>152.1 (w) [b] |  phenols<br> substituted aromatic rings | 12.2 |
| C<br>150-130 | 147.2 142.6 (w)[b]<br>139.6 138.0 137.1 (w)[b]<br>135.1 132.9 (m)[b] |  substituted aromatic rings<br>R= COOH; R= CH$_2$-CH$_3$ | 21.3 |
| D<br>130-70 | 130.5 (s)[d]<br>129.7 127.7 (s)[d]<br>126.7 136.1 125.7 (s)[d]<br>124.5 123.7 119.6 (s)[d]<br>113.4 111.3 106.5 (s)[d] |  aromatic rings<br>=CH- olefins | 42.6 |
| E<br>70-0 | 56.7 (w)[d]<br>49.8 37.8 (w)[c]<br>33.9 28.5 (w)[c]<br>25.3 21.2 (w)[d]<br>19.3 (w)[c]<br>13.3 9.42 (w)[d] | CH$_3$-O-<br>-CH$_2$-COOH<br>-CH$_2$-CH$_2$-COOH<br>-C-H<br>-(CH$_2$-CH$_2$)$_n$- polymethylene<br>CH$_3$- terminal methyls | 7.5 |

(s) = strong; (w) = weak; (m) = medium.

[a] A, B, C D and E are defined in the text.

[b] cancelled in DEPT spectrum.

[c] inverted signal negative (-CH$_2$).

[d] positive signal (C-H).

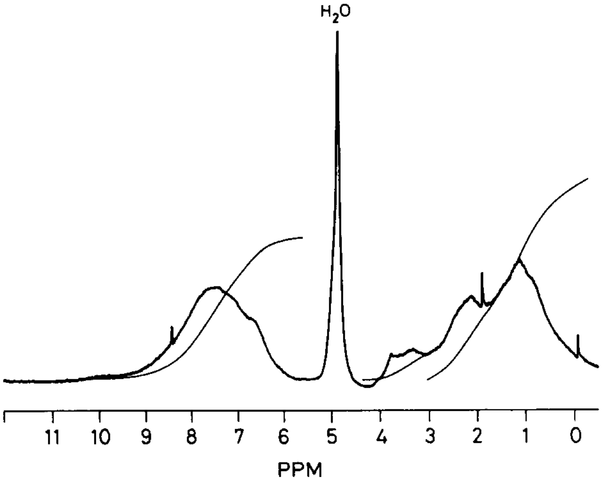


Fig. 2. $^1$H-NMR spectrum of humic acid from leonardite.

TABLE 3

Approximate estimates of carbon and hydrogen types in humic acid

| % Carbon types | | | | % Hydrogen types | | | Ratios | |
|---|---|---|---|---|---|---|---|---|
| Carboxyl[a] | Aryl[b] | O-alkyl | Alkyl | Aryl $H_{ar}$ | O-alkyl $H_{C-O}$ | $H_\alpha + H_0$ | Aryl H/C | Aliphatic H/C[c] |
| 16.3 | 76.1 | — | 7.5 | 41.3 | 4.1 | 54.6 | 0.54 | 2.29 |

[a] Includes salt, ester and amide carbon.
[b] Includes olefinic carbon.
[c] Includes % carboxyl carbon.

ganic ortophosphate (Condron et al., 1985). The small amount found (about $1.7 \times 10^{-3}$ g in 100 g of the acid) is probably an impurity.

The $^{13}$C-NMR spectrum of HA in NaOD solution is shown in Fig. 1.

The assignments reported in Table 2 agree with the published data concerning coal humic acid (Verheyen et al., 1982).

All the spectra show strong signals in the range 200–170 ppm. These signals may arise mainly from carboxyl carbons and carboxylate anions, but may be due also to esters and amino acids, which probably are present.

The small but distinct signals between 165 and 150 ppm, appear to arise mainly from phenolic carbons. These attributions are in agreement with the work by Schnitzer and Preston (1986).

The aromatic carbons show signals between 150 and 130 ppm; the weak signals at 147.2 and 146.6 ppm and the medium intense signals at 135.1 and 132 ppm suggest substitution of the aromatic ring by COOH groups or $CH_2$–

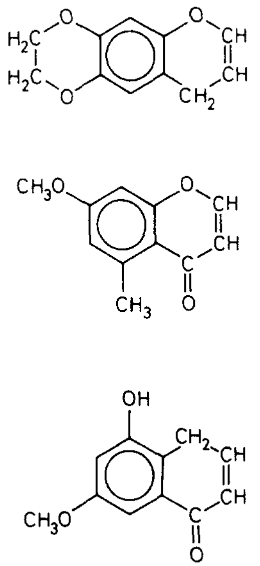


Fig. 3. Hypothetical structures of the fragment at 190 m/e having formula $C_{11}H_{10}O_3$ from FAB-MS.

$CH_3$ groups. Spin-echo measurements (sequence DEPT) reveal the cancellation of the signals, and this fact indicates that quaternary aromatic carbons are present.

The wide range of aromatic resonances (130–106 ppm) indicates highly protonated aromatic rings.

Weak signals appear between 70 and 10 ppm in the range corresponding approximately to the resonance of aliphatic carbons.

The spin-echo measurements in the region show a partial inversion of these signals. It indicates mixed carbon atoms' multiplicity and tentatively may be attributed to methoxyl groups, methylene groups neighbouring carboxyl groups, and methyl and methylene groups in chains.

No signals appear between 102 and 63 ppm, typical for carbohydrate.

According to Verheyen et al. (1982) it is convenient to divide the $^{13}$C-NMR spectra of coal humic acids into five regions: region A (200–170 ppm), region B (170–150 ppm), region C (150–130 ppm), region D (130–70 ppm) and region E (70–0 ppm), corresponding approxymately to carboxyl carbon (A), phenolic type aromatic carbons (B), aromatic ring carbons (C, D) and aliphatic carbons (E) present in the humic acid structure. Table 2 reports the relative intensities obtained using inverse-gated decoupling for the five regions of the $^{13}$C-NMR spectrum of the humic acid from leonardite.

The spectrum with quantitative intensity distributions indicates that there are 16.3% of carboxyl carbons, 7% of aliphatic carbons and 76% of aromatic carbons.

The contribution of ethers and alcohols to the structure of HA was obviously minor, due to no distinguishable resonances attributable to these oxygen linkages.

An insight into the significance of the oxygen bonded carbon resonances in the aliphatic region can be made by comparison of O/C ratios.

If all the oxygen in the humic acid structure was present as carboxylic and phenolic functions represented by regions A and B respectively in Table 2, the O/C ratio calculated as a result of this assumption should be comparable to that from elemental analysis previously reported in Table 1. The difference $\Delta = -0.22$ obtained by O/C* 13C-NMR=0.57 and O/C=0.79 ratios confirms that ether oxygen and alcohols are minor components compared with carboxyl and phenolic functional groups. Moreover the 4% content of hydrogen atoms in alcohol and ethers obtained by $^1$H-NMR confirms these data.

The $^1$H-NMR spectrum reported in Fig. 2 can be broadly divided into four regions: 0.5–1.8 ppm (alkyl protons attached to carbons removed from aromatic rings or carboxylic groups, $H_O$); 1.8 –3 ppm (protons attached to carbons in a to aromatic rings and carboxylic groups, $H_\alpha$); 3.0–4.75 ppm (alcohol and ether protons attached to carbons in $\alpha$ to oxygen, $H_{C-O}$) and 6.4–9 ppm (aromatic and olefinic protons, $H_{ar}$).

The approximate proportions of these hydrogen atoms (excluding exchangeable hydrogens) are shown in Table 3. The data in this table give approximate indications concerning H/C ratios for aromatic and aliphatic components present in the structure of HA. The H/C ratio between aromatic protons and carbon results 0.54: it indicates the aromatic substitution, while the H/C ratio between the aliphatic hydrogens and carbon indicates the presence of aliphatic chains having about six carbon atoms.

The FAB-MS spectrum of the sample dissolved in glycerol shows a large production of ion fragments, and no high molecular weight ion (above m/e 300) was detected. This spectrum is rich of small fragments, and only a prominent peak at 190 m/e is observed; it may correspond to a ionization product of formula $C_{11}H_{10}O_3$ having, probably, one of the structures in Fig. 3.

## *Thermal properties*

The DSC curve obtained with HA from leonardite shows a very large endothermic peak in the range from 321.2 to 428.4 K (maximum at 366.9 K) having a $\Delta H$ value of 233.9 J/g. After cooling the sample, subject to a second dynamic test, yields still a very large endothermic peak between 326.6 and 437.1 K (maximum at 365.1 K) having a $\Delta H$ value of 81.6 J/g; this peak probably overlays to a phase transition of the humic acid at about 442 K.

---

*$O/C = 2(A+B/100$; $\Delta = O/C$ ($^{13}$C-NMR) $-$ O/C (elemental analysis).

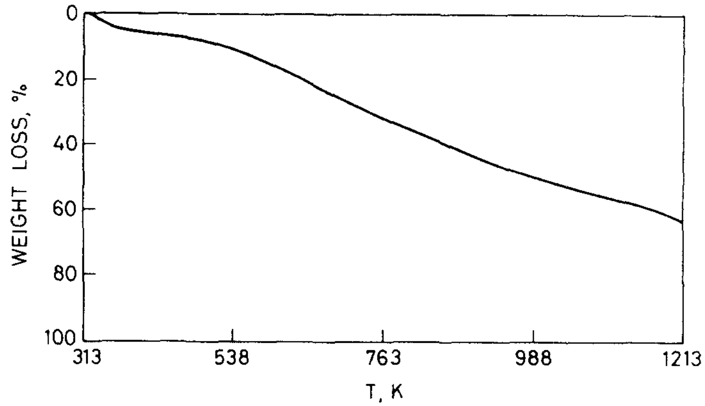


Fig. 4. Thermogravimetric curve under nitrogen of humic acid from leonardite; scanning rate: 20 K$^{-1}$.

The thermal stability of HA has been studied by means of thermogravimetric measurements both under air and nitrogen.

The thermogravimetric curves (Fig. 4) show that the weight loss is 20% below 653 K both under nitrogen or air. This is indicative of a small proportion of carbohydrates and hydroxylated aliphatic structures in humic acid from coals (Jüntgen, 1984), as shown also by the $^{13}$C and $^{1}$H NMR spectra. While the formation of a 36% residue at 1223 K under nitrogen indicates the formation of condensed polynuclear aromatic compounds (Sheppard and Forgeron, 1987) coming from aromatic structures present in Leonardite humic acid.

## CONCLUSIONS

Spectroscopic and thermogravimetric data show that aromatic structures clearly prevail in Leonardite humic acid.

$^{13}$C-NMR spectroscopy gives a content of carboxyl groups higher than the value obtained by chemical methods.

The little amount of P contained in leonardite humic acid is an impurity being constituted by inorganic orthophosphate.

The leonardite humic acid is very similar to that extracted from brown coal (Verheyen et al., 1982), while it is very different from soil humic acids.

The leonardite humic acid is useful as soil conditioner. It is not explained yet how a so complex structure participates to the general turnover of the organic soil matter.

## ACKNOWLEDGEMENT

We thank Mr. S. Crippa who executed the NMR spectra.

## REFERENCES

Avran, M. and Mateescu, G.H., 1966. Infrared Spectroscopy: Applications in Organic Chemistry. Wiley, New York.

Chen, Y., Senesi, N. and Schnitzer, M., 1977. Information provided on humic substances by $E_4/E_6$ ratios. Soil Sci. Am. J., 41: 352–358.

Ciavatta, C., Vittori Antisari, L. and Sequi, P., 1988. A first approach to the characterization of the presence of humified materials in organic fertilizers. Agrochimica, 32: 510–517.

Condron, L.M., Goh, K.H. and Newman, R.H., 1985. Nature and distribution of soil phosphorus as revealed by a sequential extraction method followed $^{31}P$ nuclear magnetic resonance analysis. J. Soil Sci., 36: 199–207.

Contin, M. and De Nobili, M., 1990. Effetto dei alcuni parametri sperimentali sulla determinazione di gruppicar bossilici in sostanze umiche mediante cetiltrimetilammonio. 8th Naz. Congr. SICA, Bari, 25–27 September, pp. 79–80.

Gaur, A.C., 1969. Studies on the availability of phosphate in soil as influenced by humic acid. Agrochimica, 14: 62–64.

Harrel, J.W. and Saeed, M., 1977. Effect of leonardite on diffusion of phosphorus in coal mine spoils. Soil Sci., 124: 285–290.

Jüntgen, H., 1984. Review of kinetics of pyrolysis and hydropyrolysis in relation to the chemical constitution of coal. Fuel, 63: 731–737.

Lynn, K. Porter, 1967. Factors affecting the solubility and possible fractionation of organic colloids extracted from soil and Leonardite with an acetone–$H_20$–HCl solvent. J. Agric. Food Chem., 15: 807–811.

O'Donnel, R.W., 1973. The auxin-like effects of humic preparations from leonardite. Soil Sci., 116: 106–112.

Piccolo, A. and Camici, L., 1990. Adsorbimento di atrazina su sostanze umiche di diversa origine. 8th. Naz. Congr. SICA, Bari, 25–27 September, pp. 183–186.

Preston, C.M. and Blackwell, B.A., 1985. Carbon-13 nuclear magnetic resonance for a humic and fulvic acid: signal-to-noise optimization, quantitation, and spin-echo techniques. Soil Sci., 139: 88–96.

Saeed, M., 1978. Use of sorption isotherms for evaluating the effect of Leonardite on phosphorus availability in a coal mine spoil. Soil Sci., 126: 157–164.

Schnitzer, M., 1971. Characterization of humic constituents by spectroscopy. In: A.D. McLaren and J. Skujins (Editors), Soil Biochemistry, 2. Marcel Dekker, New York.

Schnitzer, M. and Gupta, U.C., 1965. Determination of acidity in soil organic matter. Soil Sci. Soc. Proc., 29: 274–277.

Schnitzer, M. and Preston, C.M., 1986. Analysis of humic acids by solution and solid-state Carbon-13 nuclear magnetic resonance. Soil Sci. Soc. Am. J., 50: 326–331.

Schnitzer, M. and Skinner, R., 1982. Organic matter characterization. In: Method of Soil Analysis, Part 2. Chemical and Microbiological Properties. Agronomy Monograph 9. ASA-SSSa, 677 S. Segoe Rd. Madison, WI 53711, USA, pp. 581–594.

Schwartz, D., Asfeld, L. and Green, R., 1965. The chemical nature of carboxyl groups of humic acids and conversion of humic acids to ammonium nitrohumates. Fuel, 44: 417–424.

Sheppard, J.D. and Forgeron, D.W., 1987. Differential thermogravimetry of peat fractions. Fuel, 66: 232–236.

Springer, U. and Klee, Y., 1954. Z. Pflanzenernahr. Dung. Bodenkd., 64: 1–26.

Stevenson, F.J. and Goh, K.M., 1971. Infrared spectra of humic acids and related substances. Geochim. Cosmochim. Acta, 35: 471–483.

Ureta Baes, A., 1988. Infrared and ultraviolet–visible absorption spectroscopy of humic and fulvic acids and their copper(II) complexes. U.M.I. Dissertation, Information Service, 300 N., Zeeb Road, Ann Arbor, MI 48106, USA.

Verheyen, T.V., Johns, R.B. and Blackburn, D.T., 1982. Structural investigations of Australian coals II: A $^{13}$C-NMR study of humic acids from Victorian Brown coal lithotypes. Geochim. Cosmochim. Acta, 46: 269–277.

Young, R.W. and Frost, C.M., 1963. Humic acid from leonardite—A soil conditioner and organic fertilizer. Symposium on Non-fuel Uses of Coal. American Chem. Society, Division of Fuel Chemistry, Washington, DC.