

Comparison of humic and fulvic acids from different soils by pyrolysis mass spectrometry

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In the last years the knowledge about the structure of soil humic substances has been considerably improved by employment of chemical degradative methods in combination with powerful analytical tools, which permit the identification of the reaction products. Comparatively, thermal degradations have received little attention. The most interesting techniques are pyrolysis-gas chromatography, pyrolysis-gas chromatography-mass spectrometry, and pyrolysis-mass spectrometry.

Pyrolysis-gas chromatography have been used by MARTIN (1975, 1977) and BRACEWELL and ROBERTSON (1977) to study humic and fulvic acids from different soil types, and total soil samples, respectively. Pyrolysis-gas chromatography-mass spectrometry permit the safe identification of compounds originated by the thermal breakdown of humic fractions. In the low boiling point fraction, MARTIN et al. (1977) have identified 35 compounds, which are mainly alkanes, olefins, nitriles, furanes, aromatics and others, arising from polysaccharides, proteins, and aliphatic components of the humic fractions. Furthermore, the same authors have identified 46 high boiling point compounds, namely heterocyclic nitrogen compounds, lignin-derived phenols, aliphatic and aromatic compounds (MARTIN et al., 1978).

In previous papers it was pointed out that pyrolysis-mass spectrometry allows the characterization of soil organic matter and its fractions (SAIZ-JIMENEZ et al., 1978) in a relatively short time. It is a survey technique giving preliminary informations about the composition of humic acids from soils, peats, composted straw, fungal melanins (NAGAR et al., 1975; MEUZELAAR et al., 1977) and many other polymers (MEUZELAAR et al., 1974). As compared to the pyrolysis-gas chromatography, this technique gives an immediate information about any of the thermal degradation compounds of the pyrolysa-

te. However, the quadrupole mass spectrometer used allows only to detect splitting products of a molecular weight up to 180.

The method has been largely described in previous papers (e.g. MEUZELAAR et al., 1974, 1977; HAIDER et al., 1977). Briefly, it consists of a Curie-point pyrolyser coupled to a fast scanning quadrupole mass filter and a multichannel signal averager. Samples of about 50 μ g were pyrolysed at a Curie temperature of 510°C.

Figure 1 provides spectra of an untreated soil sample from the A₁ horizon of a brown soil and its main fractions: humic and fulvic acids, humin, and polysaccharide. The most prominent peaks in the spectrum of the untreated soil sample agree with those obtained from the polysaccharide fraction from this soil. These were related to acetic acid (m/e 60), furan (m/e 68), methylfuran (m/e 82), hydroxyfuran (m/e 84), furfural (m/e 96) and their partly methylated derivatives (m/e 112 and 126). Peaks at m/e 114 and 128 were shown to be related to pentose and deoxyhexose units, respectively, and were not present in simple polysaccharides as cellulose. Smaller peaks at m/e 67, 81, 95 and 117 are typical for proteinaceous materials and likely represent (alkyl) pyrroles and indole. A prominent peak at m/e 17 shows the presence of ammonia. Possible fragments of amino sugar origin appear to be present as evidenced signals at m/e 95, 109, 125, 137 and 151 in the polysaccharide fraction and in the untreated soil sample. Peaks at m/e 124, 138, 150, 152 and 164 strongly suggest the presence of guaiacyl units derived from lignin residues in the soil sample (HAIDER et al., 1977). In comparison with the very prominent polysaccharide related peaks, these peaks indicate relatively small amount of lignin residues in the soil sample.

The spectrum of the fulvic acid fraction (fraction D of Forsyth's method) shows dominant signals similar to those observed in the spectrum from the polysaccharide fraction (m/e 68, 82, 84, 96, 98, 110, 112, 114, 126, and 128). Nitrogen containing fragments are low, except for pyridine (m/e 79). Also low are the peaks related to phenols.

The spectrum of humin resembles that of humic acid. The ion intensity of the peaks from protein-like and aromatic compounds are similar, however, signals from polysaccharide are more evident. Peaks at m/e 124, 138 are comparable to humic acid, but those at m/e 150, 162, and 164 are slightly higher.

From the spectra shown in the figure 1 it appears that each of the humic fractions has its typical feature. Humic acid presents signals from protein, phenol and carbohydrate related materials. Humin is similar with humic acid, but richer in polysaccharides. Fulvic acid has an obvious relationship to polysaccharide-like materials. In order to confirm this for a greater number of soil types and of different geographical origins, spectra of their humic and fulvic acids were studied.

Figure 2 shows the spectra from 5 humic acids, from a podzol of N.W. Spain, and andosol of Tenerife Island, a red soil and a vertisol of S.W. Spain, and a Canadian forest soil, respectively. All the samples have similar characteristics to the humic acid from the brown soil previously shown. Series of homologous ions of polysaccharide and protein related materials show little variability. However, alkanes and lignin related peaks present different intensities. Podzol humic acid shows a weak ion series of lignin phenols, which agree with previous data reported for humic acids from the same soil type by MEUZELAAR et al. (1977). Only the humic acid isolated

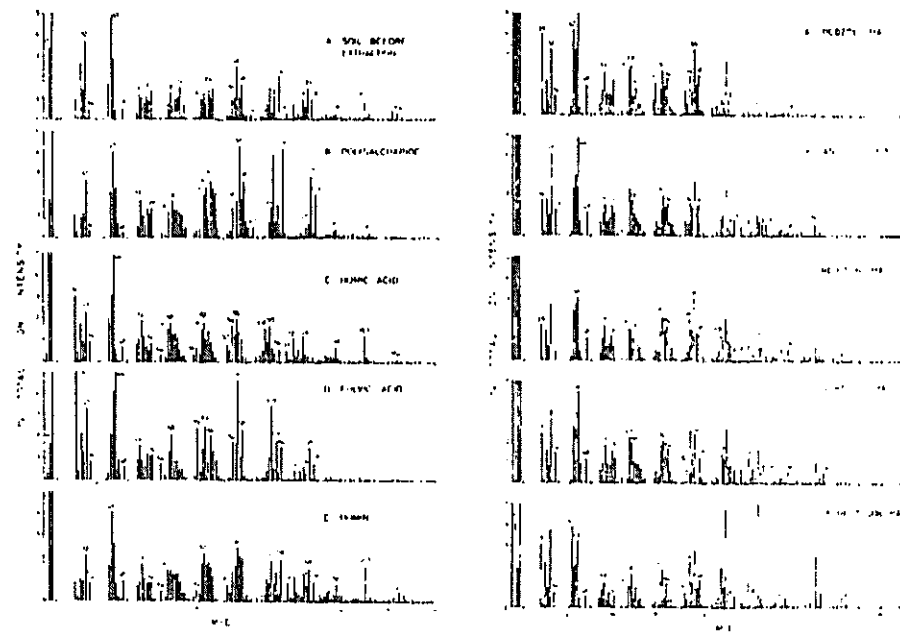


FIG. 1. — Pyrolysis mass spectra of a total soil before extraction and some of its organic fractions.

FIG. 2. — Pyrolysis mass spectra of humic acids from different soil types.

from the Canadian forest humus layer shown a very high contribution of lignin-type phenols. Forest humus layers, which contain a great deal of woody residues in all stages of decomposition, seem to contain constituents derived directly from plant tissues of intermediate stages of decomposition and products of a more progressed humification (LOWE, 1974). Thus, forest humic acid represent young or immature humic materials with high resemblance to lignin and with less modification of plant derived precursors. Other soil-humic acids show variable percentages of lignin related peaks.

BRACEWELL and ROBERTSON (1977) also found guaiacyl compounds by gas chromatography only in pyrolysates of the upper soil layer and not in the more humified layers. MARTIN et al. (1978) by studying humic acids pyrolysis-gas chromatography-mass spectrometry, found a high contribution of typical lignin derived phenols only in the non hydrolysed samples. However, when the humic samples were hydrolysed with 6 N HCl for three periods of 24 hours the

lignin phenols disappeared as well as the protein and related compounds. This suggests that lignin or partially altered lignins are coextracted along with humic acids and can be released by the treatment. Furthermore, the humatomelanic acids obtained by ethanol extraction of humic acids showed to be richer in lignins (SAIZ-JIMENEZ et al. 1978).

Figure 3 shows the spectra from fulvic acids from a podzol of N.W. Spain, an andosol of Tenerife Island, a Canadian brown solonetz and a Californian soil-sludge mixture. They have great similarities and few variations in the relative abundance of

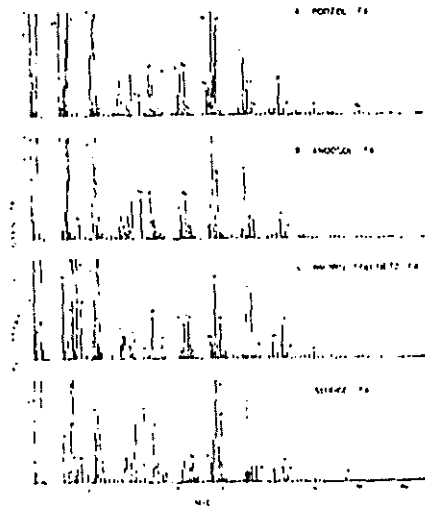


FIG. 3. — Pyrolysis mass spectra of fulvic acids from different soil types.

pyrolysis fragments. The differences are in height of some peaks, e.g. the acetic acid peak at m/e 60, the SO_2 peak at m/e 64, the polysaccharide related peak at m/e 112, and the xylenol peak at m/e 122. The spectra have obvious similarities with those soil polysacchari-

des, except the peaks at m/e 114 and 128, indication of pentose and deoxyhexose units, which are lower in fulvic acids. This should indicate that the polysaccharide component of fulvic acids is not as complex as that of the polysaccharide fraction, but alike to simple polysaccharides as cellulose, to which has also similarities. Peaks from proteinaceous materials are very low in correspondence with their low nitrogen. Simple phenolic peaks, such as those for phenol (m/e 94), cresols (m/e 108), xylenols (m/e 122) and dihydroxytoluenes and/or guaiacol (m/e 124) are comparatively lower than in humic acids.

From these results it can be concluded that polysaccharide-like materials in soils and its humic fractions are more important as presumed till now. Especially noteworthy is the occurrence of those materials in the fulvic acid and humin fractions. Also they are significantly present in the humic acid fraction. Protein derivatives, also present in soils, are significantly enriched in the humic acid and humin, but are low in the fulvic acid fraction. Lignin related phenols are evident in the soil, humic acid and humin fractions, but not in the fulvic acid fraction. While polysaccharide and protein fragments showed a relatively similar contribution to all humic acid samples so far investigated, lignin phenols greatly varied with soil type, soil conditions and most probably with the plant cover. Fulvic acids samples generally showed relatively uniform pattern of polysaccharide-like materials.

The results of this study indicate that the pyrolysis-mass spectrometry method is appropriate for the characterization of soil organic matter fractions and can be used as a « survey » technique, which gives preliminary informations about the composition of humic fractions in a relatively short time and without extensive chemical treatments. However, since compounds of the same mass to charge ratio may contribute to one peak, the more complex and time-consuming method of pyrolysis-gas chromatography-mass spectrometry should be accomplished for a more deeper research about the chemical structure of compounds released during pyrolysis.

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SUMMARY. — Several recent publications showed the usefulness of pyrolysis mass spectrometry for the characterization of the organic matter of total soil samples and of soil organic matter fractions.

Soil humic and fulvic acids were pyrolyzed by the Curiepoint pyrolysis technique and were analyzed with a fast scanning low voltage electron impact mass spectrometer. Humic acids from different soil types and geographical distribution were characterized by series of homologous compounds, which were derived from protein, polysaccharides, alkanes, and lignin phenols.

Fulvic acids showed great similarities and few variations in the relative abundance of pyrolysis products, with major peaks arising from polysaccharides: Aromatics and phenols were scanty or hardly detected.

RÉSUMÉ. — Récemment on a montré l'utilité de la pyrolyse-espectrométrie de masses pour la caractérisation de la matière organique du sol et leur fractions.

Les acides humiques et fulviques furent pyrolysés selon la technique du point de Curie et étudiés avec un spectromètre de masses d'impact électronique à petit voltage. Les acides humiques de différents types de sols et d'origines géographiques furent caractérisés par séries de composés homologues, en trouvant dérivés de protéines, polysaccharides, alcanes et phénols

de la lignine. Les acides fulviques furent très ressemblantes et avec peu de variations dans l'abondance relatif de produits de pyrolyse, étant les pics majeure dérivés de polysaccharides, tandis que par contre les composés aromatiques et phénols furent faibles et difficilement détectés.

ZUSAMMENFASSUNG. — Je mehrere neuerliche Publikationen, die Anwendung des Pyrolyse-Massen Spectrometrie scheint geeignet für die Charakterisierung des gesamten Organischstoffes von Bodenproben und deren Fraktionen. Die Pyrolyse von Humin- und Fulvinsäuren wurde durch die Technik des Curie-Punkt ausgeführt, und die Pyrolyse-Produkte unmittelbar mittels ein Elektronenstoss-Ionisierung Massenspektrometer untersucht.

Huminsäure von Böden aus verschiedene Herkunft wurden durch verschiedene Reihen von Verbindungen, die aus Proteinen, Polysaccharides, Alkanen und Lignin herkommlichen Phenolen stammen, charakterisiert.

Die Fulvinsäuren zeigen grosse Ähnlichkeiten und nur einige Veränderungen hinsichtlich der relativen Reichtung des Pyrolyse-Produkte, von denen die wichtigstens aus Polysaccharides stammen. Phenolen und aromatische Produkts waren knapp oder swierig zu auszuwerten.

RESUMEN. — Publicaciones recientes han mostrado la utilidad de la pirolisis-espectrometria de masas para la caracterizacion de la materia organica del suelo y sus fracciones.

Acidos humicos y fulvicos fueron pirolizados usando la tecnica de la pirolisis por punto de Curie y analizados con un espectrometro de masas de impacto electronico a bajo voltaje. Los acidos humicos de diferentes tipos de suelos y origenes geograficos se caracterizaron por series de compuestos homologos, encontrandose derivados de proteinas, polisacaridos, alcanos y fenoles procedentes de la lignina. Los acidos fulvicos se mostraron muy similares y con pocas variaciones en la abundancia relativa de productos de pirolisis, hallandose que los picos mayores procedian de la pirolisis de polisacaridos, mientras que, por el contrario, los compuestos aromaticos y fenoles fueron escasos y dificilmente detectables.

RIASSUNTO. — Pubblicazioni recenti hanno mostrato l'utilità della pirolisi-spettrometria di masse per caratterizzare la materia organica del suolo e le sue frazioni

Acidi umici e fulvici furono pirolizzati con la tecnica della pirolisi di punti di Curie ed analizzati con spettrometro di masse ad urto elettronico a basso voltaggio. Gli acidi umici, da tipi di suoli ed origine geografica diversa furono caratterizzati per gruppi di composti omologi, trovandosi derivati di proteine, polisaccaridi, alcani e fenoli procedenti dalla lignina. Gli acidi fulvici si mostrarono molto simili e con piccole variazioni rispetto alla abbondanza relativa dei prodotti di pirolisi, trovandosi che i picchi maggiori procedevano dalla pirolisi dei polisaccaridi intanto che i composti aromatici e fenoli furono scarsi e difficilmente rivelabili.