# Speciation of organic matter in sandy soil size fractions as revealed by analytical pyrolysis (Py-GC/MS) and FT-IR spectroscopy

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## Introduction

One of the main techniques used to analysis of soil organic matter (SOM) is gas chromatography. Nevertheless, due to the complexity of the SOM composition, numerous treatments are usually needed. For instance, samples should be treated with different solvents for each type of target-homologues: lipids (Ma´Shum et al., 1988), PLFA (Bucheli et al., 2014), lignin (Bjorkmann, 1954), etc.

The main problem in these analyses is that the extraction residue contains a fraction of organic compounds which has not been analysed. This research tries to answer this question:

**Which organic homologues are still remaining after the extraction procedure?**

Aiming to this, we have studied original soil samples and the extraction residues by using analytical pyrolysis (Py-GC/MS) and infrared spectroscopy techniques (FT-IR).

## Methods

Soil samples were collected in sandy soils, Arenosols (WRB 2006) from the Doñana National Park (SW Spain) under different vegetation covers: cork oak (*Quercus suber*, QS), eagle fern (*Pteridium aquilinum*, PA), pine (*Pinus pinea*, PP) and rockrose (*Halimium halimifolium*, HH). Two size fractions, coarse (C: 1-2 mm) and fine (F: 0.05-0.25 mm), were studied at each case. In addition, the two fractions from each soil were exhaustively Soxhlet extracted with a Dichlorometane-Methanol (3:1) mixture to obtain the lipid-free fractions (LF) from each size fraction (LFC and LFF).

## Results and Discussion

Soil size fractions showed contrasting differences in SOM content (C 4-7 % and F > 40 %; Jiménez-Morillo et al., 2014) and conspicuous differences were found in the pyrolysis products released by the studied fractions. The main families of pyrolysis compounds have well defined macromolecular precursors, such as methoxyphenols, polypeptides, polyssaccharides and lipids (González-Vila et al., 2001).

The organic C fractions yielded higher relative abundance of lignin- and polysaccharides-derived pyrolysis compounds. In contrast, the F fractions released mainly lipids and aromatic compounds of unspecific origin. A low decrease of lignin- and polysaccharides-derived pyrolysis compounds was observed in F fractions at all cases. This might be due to high microbial activity in this fraction. Regarding the composition of LF soil fractions, the pyrolytic behavior of LFC fractions was quite similar to the not extracted corresponding C soil fraction, showing a high proportion of lignin- and sugar-derived pyrolysis compounds. LFF fractions also showed the same behavior than the C fraction, but with no lipid derived compounds, what effectively indicates the occurrence of a selective and efficient removal of soil free lipids.

The FT-IR analysis of all the C fraction samples revealed signals of OH-stretch (3200 $cm^{-1}$), C = O of acid, aldehydes and ketones (stretch) (1750 $cm^{-1}$), or even, C-O (stretch) and OH (bending) of COOH. C-O (stretch) of phenols; lignin (1260 $cm^{-1}$), they are characteristics of "fresh organic matter. In contrast, the F fraction spectra of PP and HH showed an alteration of its organic matter (loss of OH-stretch band among others). QS and PA samples showed similar FT-IR spectra.

The FT-IR spectra of LF fractions analyses were consistent with the results of pyrolysis, both indicating a relatively slight increased presence of lignin compounds for LFF soil fractions under PA, PP and HH. For soil under QS, no differences were found between the LFF fractions and the whole SOM in the F fraction, probably due to the high SOM content in this fraction.

## Conclusions

1) Analytical pyrolysis results and FT-IR spectral features were highly consistent.
2) The organic matter present in coarse and fine sieve size fractions under different vegetation covers showed some differences: the coarse sieve size fractions were composed mainly by "fresh organic matter" (lignocellulosic plant residues), while the fine sieve size fractions presented a more mature/evolved organic matter.
   Latter results resembled the characteristics of customary wet extracted humic materials as characterized elsewhere (Stevenson, 1994; González-Pérez et al., 2013).
3) Lipid compounds were still present in samples after extraction.

### Acknowledgments

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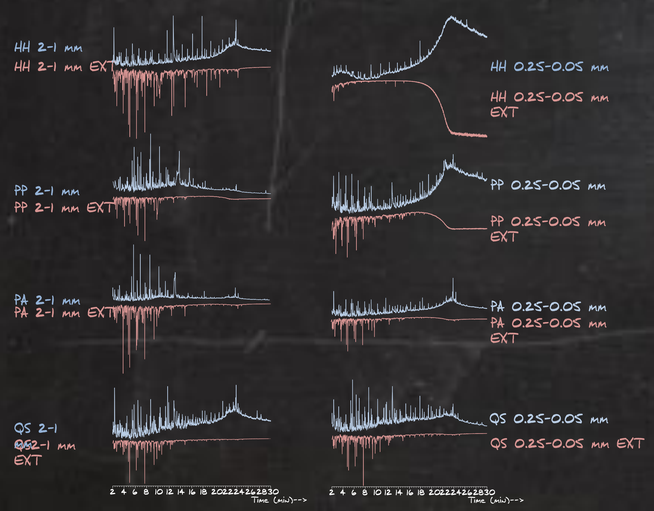
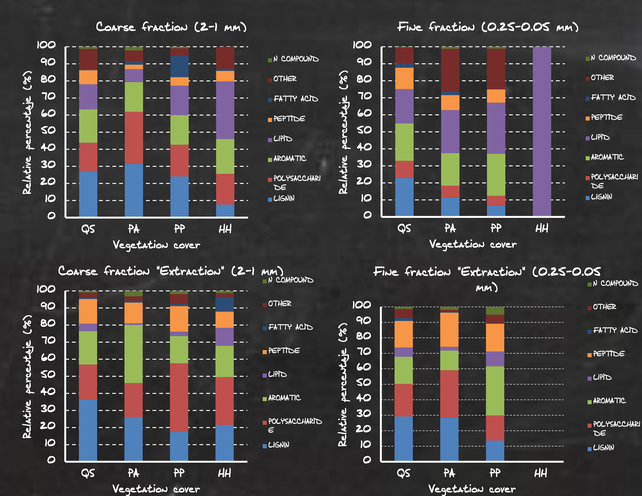
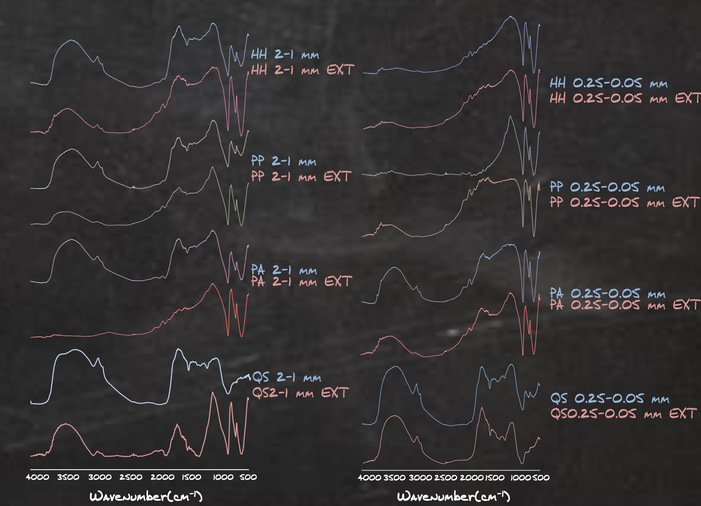
## Figure 1




## Figure 2




## Figure 3




| Frecuency ($cm^{-1}$) | Assignation |
|---|---|
| 3400 | OH (stretch) |
| 2950-2840 | C-H aliphatic (stretch) |
| 1725-1705 | C = O of COOH, aldehydes and ketones (stretch) |
| 1640-1600 | C = O of amides (amide I) (stretch) |
| 1540-1500 | C = C aromatic (stretch); symmetric stretch of $COO^-$ |
| 1460-1450 | C-H (bending) and C = N (amide II) (1540) (stretch), C = C aromatic (1500) (stretch) |
| 1440-1410 | C-H aliphatic (asymmetric bending) |
| 1420 | C-H aromatic (asymmetric bending) (stretch) |
| 1400-1380 | O-H (bending) and C-O (stretch) of OH phenolics, asymetric stretch of $COO^-$ |
| 1340-1320 | C-O (stretch) and OH (bending) of COOH; C-O (stretch) of phenolic lignin |
| 1170-1120 | C-OH (stretch) of C-H alphatic |
| 1080-1050 | C-O (stretch) of polysaccharides; Si-O of mineral |
| 915-775 | Twist out of plane of C-H aromatic |

## References: