# CHARACTERIZATION OF COMPOSTS AND HUMIC ACIDS FROM PULP AND PAPER MILL BIOSLUDGES BY DSC IN ASSOCIATION WITH FT-IR SPECTROSCOPY

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## Abstract

Samples of pulp and paper mill biosludges with different maturation ages (fresh biosludge and composts collected after 3 weeks, 1 year and 2 years of composting) and their corresponding humic acids were analyzed by thermal analysis with DSC in association with FT-IR spectroscopy. The DSC curves obtained exhibited endotherms in the low-temperature region, assigned to dehydration processes, exotherms at around 370°C, attributed to the loss of peptidic structures, and high-temperature exotherms, assigned to the loss of functional groups; the lignins were thermostable, regardless of the maturation age of the compost.

The results obtained provided evidence that, during composting, the organic matter evolved in the direction of higher molecular complexity and stability, leading to a more homogeneous product closely resembling humic-like substances.

**Keywords:** biosludges, composting, humic acids

## Introduction

Organic matter in soils consists of a wide variety of components, which generally include; a) biomolecules of known chemical composition and biological function, which are typical constituents of plant and animal debris or are produced by microbial activity; b) a wide variety of intermediates and partially degraded products arising during the processes of decay of these debris materials; c) a composite pool of chemically recalcitrant, biologically, refractory, physically and/or chemically stabilized organic compounds originating in resynthesis and polymerization processes (humification) during the microbial and chemical transformation of 'raw' organic matter; these are humic substances (HSs). The soil HSs constitute a physically and chemically heterogeneous mixture of macromolecular organic compounds of mixed aliphatic and aromatic nature. The HSs make a substantial contribution to improvement of the overall soil fertility

status. Accordingly, crop residues and animal manure have traditionally been applied to soil, as a mean of maintaining and increasing the organic matter content. This explains the increasing interest in recent years in the possible recycling in agriculture of organic residues derived from a wide variety of human activities. These organic waste materials, however, have to be appropriately processed prior to soil application, in order to obtain mature, stabilized organic matter. This objective can be achieved through a composting process that closely resembles the natural processes in soil, actually comprising an accelerated humification process that produces humic-like materials [1].

The aim of the present paper was to study a number of composts from pulp and paper mill biosludges samples with different maturation ages and their corresponding humic acids (HAs) by thermal analysis (TA) with differential scanning calorimetry (DSC) in association with Fourier transform infrared spectroscopy (FT-IR).

## Materials and methods

Biosludges from waste water treatment in the pulp and paper industry are the most abundant material suitable for composting in Finland, with 360 000 tons of dry matter produced annually. About one half of this material is landfilled, while the other half is burned in mills as a low-grade fuel.

In this work, biowastes in four different phases of the composting process during a 2-year period were studied: fresh biosludge (PP1) and composts collected after 3 weeks (PP2), 1 year (PP3) and 2 years of composting (PP4). PP2 was collected in a 10 m³ drum composter, while PP3 and PP4 were collected in a small household composter. During the composting process, wood chips were added as bulking agent. Samples were ground and then sieved through a 0.5 mm sieve.

The corresponding HAs, HAPP1, HAPP2, HAPP3 and HAPP4, were extracted according to standard procedures of extraction, fractionation and purification [2]. Briefly, the isolation procedure consisted mainly in the extraction of the substrate with sodium hydroxide-sodium pyrophosphate solution, precipitation of the extracted material with HCl to pH ~2, mild purification by two successive NaOH dissolution and HCl precipitation steps, water washing of the precipitated HAs, and final freeze-drying.

Elemental analyses were performed with a Fisons model EA 1108 CHN Elemental Analyzer. Ash content was determined by heating 1 g of sample at 550°C for 3 h in an oven.

DSC was performed with a Perkin-Elmer DSC 7 equipped with an automatic program of TA. Aliquots of 5 mg sample were placed in an aluminum pan of 50 μl capacity and 0.1 mm thickness and then press-sealed with an aluminum

cover of 0.1 mm thickness. DSC curves were measured by heating the sample from 50 to 550°C at a rate of 20°C min$^{-1}$ under a flow of air of 20 cm$^3$ min$^{-1}$. Indium was used as a standard for calibrating temperature. Reproducibility was checked by running the sample in triplicate.

FT-IR spectra were recorded in the range 400–4000 cm$^{-1}$ with a Nicolet 5 PC FT-IR spectrometer, on KBr pellets obtained by pressing under vacuum uniformly prepared mixtures of 1 mg sample and 400 mg KBr of spectrometry grade.

# Results and discussion

Elemental analyses together with the C/H, C/N and O/C ratios for the PP and HAPP samples are presented in Tables 1 and 2.

Table 1 Elemental compositions, atomic ratios and ash contents of PP samples

|        | PP1   | PP2   | PP3   | PP4   |
|--------|-------|-------|-------|-------|
| C/%    | 39.3  | 41.4  | 38.0  | 34.7  |
| H/%    | 4.6   | 4.8   | 4.7   | 4.4   |
| N/%    | 2.7   | 1.9   | 1.1   | 1.2   |
| S/%    | 0.8   | 0.6   | 0.2   | 0.1   |
| O/%    | 52.6  | 51.1  | 55.9  | 59.6  |
| C/H    | 0.71  | 0.71  | 0.67  | 0.66  |
| C/N    | 17.23 | 26.53 | 45.23 | 36.14 |
| O/C    | 1.00  | 0.92  | 1.10  | 1.29  |
| Ash/%  | 25.3  | 20.3  | 26.7  | 31.9  |

Table 2 Elemental compositions, atomic ratios and ash contents of HAPP samples

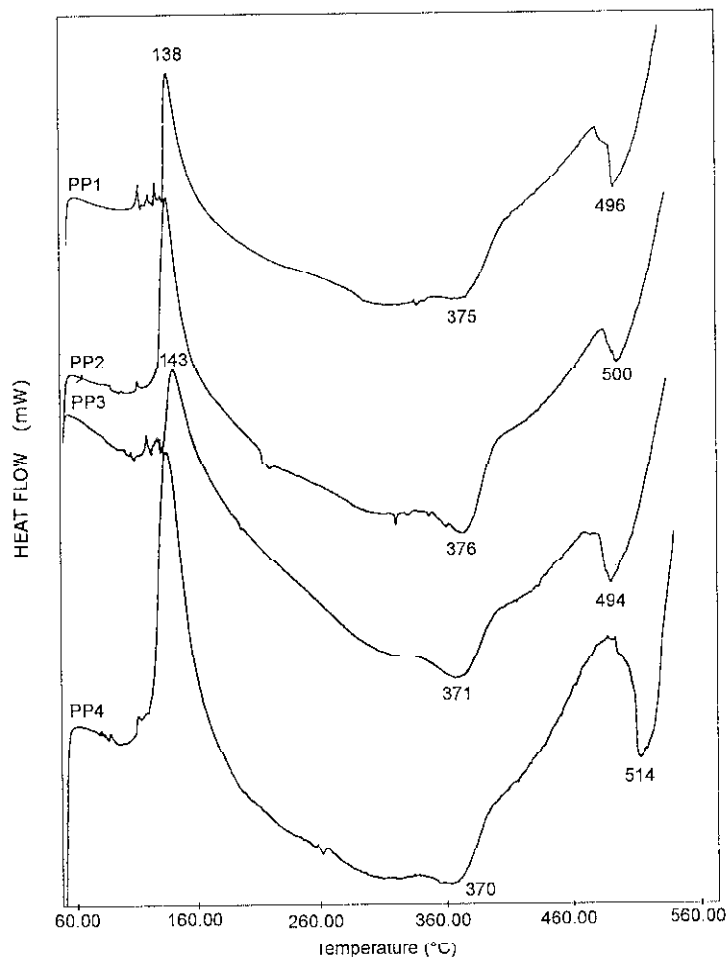|        | HAPP1 | HAPP2 | HAPP3 | HAPP4 |
|--------|-------|-------|-------|-------|
| C/%    | 50.5  | 53.2  | 49.5  | 50.1  |
| H/%    | 5.1   | 6.1   | 5.4   | 5.1   |
| N/%    | 4.8   | 7.1   | 4.4   | 4.0   |
| S/%    | 0.5   | 0.6   | 0.5   | 0.2   |
| O/%    | 39.1  | 33.1  | 40.2  | 40.6  |
| C/H    | 0.8   | 0.72  | 0.77  | 0.81  |
| C/N    | 14.02 | 8.86  | 13.30 | 14.91 |
| O/C    | 0.58  | 0.47  | 0.61  | 0.61  |
| Ash/%  | 10.2  | 12.5  | 6.8   | 5.9   |

**Fig. 1** DSC curves of PP samples

DSC has recently been applied to charaterize HAs and fulvic acids (FAs) of various origins and natures. A typical soil HA DSC curve features a strong endotherm in the low-temperature region (around 140°C), and an exotherm in the high-temperature region (around 500°C). These two thermal effects have been assigned, respectively, to dehydration and/or loss of peripheral polysaccharide chains and to oxidation and polycondensation of the aromatic nuclei of the molecule [3]. In addition to the above thermal effects, the curves of the PP samples (Fig. 1) exhibit a typical exotherm at about 370°C, which appears more strongly in the PP2 and PP3 curves. This exotherm has previously been observed in DSC curves of composts from municipal solid wastes sampled at different composting times, and of HAs extracted from sewage sludges [4, 5] The exotherm at about
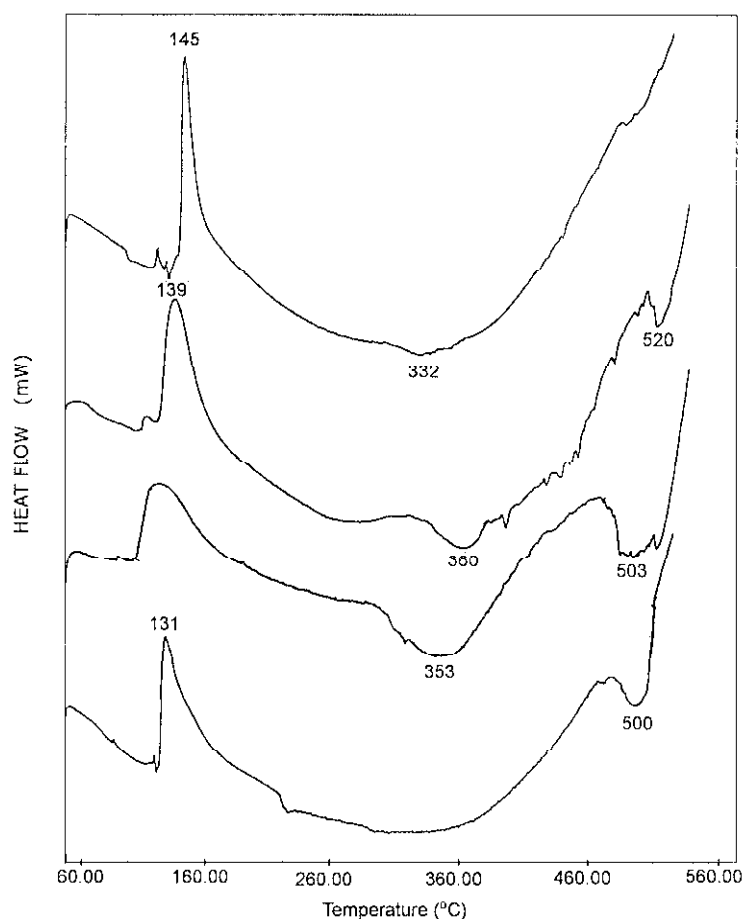
Fig. 2 DSC curves of HAPP samples

370°C can be utilized to distinguish and characterize composted materials of different origins from native soil HAs and FAs.

The DSC curve of HAPP1 (fresh biosludge) (Fig. 2) is characterized by the absence of the high-temperature exotherm assigned to reactions involving the aromatic core of the organic molecule. This result may be related to the very low degree of aromatic condensation of HAs extracted from the fresh biosludge in which the humification process has not started. In addition, HAPP1 shows a very weak exotherm at 330°C, whereas it is present in the DSC curve of HAPP2 (Fig. 2) at 360°C and becomes more intense in the curve of HAPP3 (Fig. 2) at 353°C, showing an intensity which increases with the time of composting. In the curve of HAPP4 extracted from a biosludge composted for 2 years (Fig. 2), this exotherm is not apparent, and the DSC curve closely resembles that of a native soil HA.
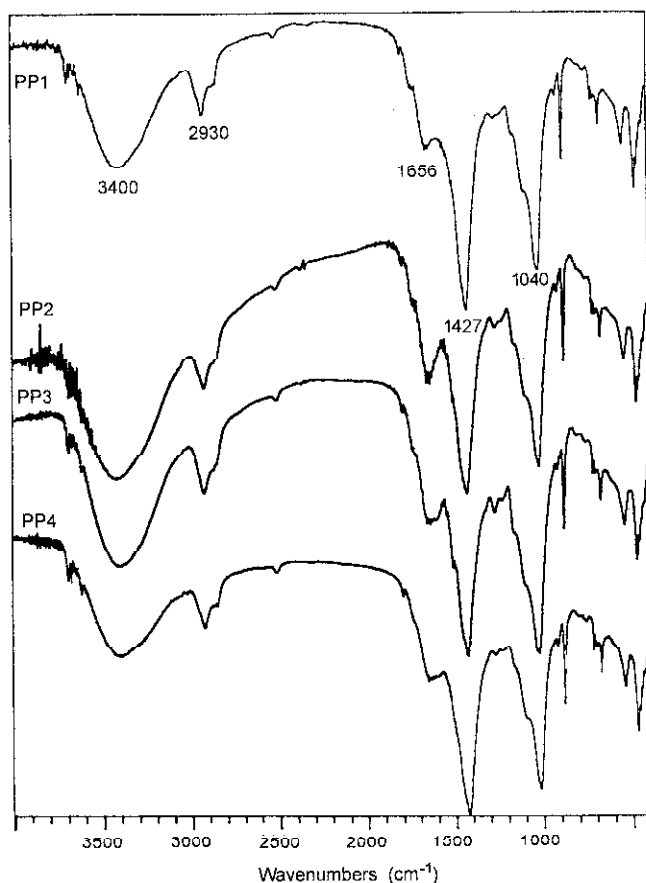
**Fig. 3** FT-IR spectra of PP samples

In order to explain the thermal effects observed and to elucidate the structural transformations occurring during pyrolysis of these materials, FT-IR spectra of samples heated to 200, 400 and 550°C were measured. IR spectra of PP (Fig. 3) samples exhibit typical characteristics of partially-degraded lignins associated with N-containing moieties, known as lignoproteins or lignopeptides, and are markedly different from the FT-IR spectra of solid HAs. They feature the following adsorptions: 3400 cm$^{-1}$ (H–bonded OH); 2930 cm$^{-1}$ (aliphatic C–H stretching); 1656 cm$^{-1}$ (amide I); 1427 cm$^{-1}$ (aromatic skeletal vibrations of lignin); 1269 and 1110 cm$^{-1}$ (various vibrations of graminaceous lignin structures); 1040 cm$^{-1}$ (C–O stretching of polysaccharides, most likely cellulose and residual hemicelluloses).

After heating to 200°C, all PP samples (Fig. 4) display bands of decreased intensity at 3400 cm$^{-1}$, indicating the loss of water. On heating to 400°C, a strong decrease in the peak at 1656 cm$^{-1}$ occurs for all samples, which suggests that the
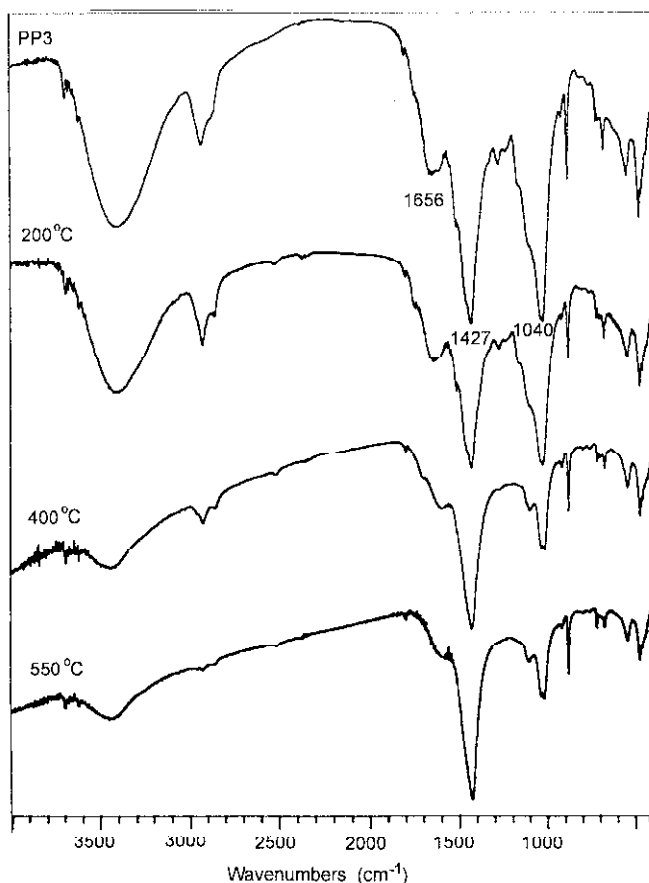
**Fig. 4** FT-IR spectra of PP3 heated to different temperatures

exotherm at around 350°C can be attributed to the loss of amidic groups of polypeptidic structures. Heating to 500°C leads to a strong reduction in adsorp tion due to aliphatic groups, whereas IR adsorptions ascribed to thermostable and recalcitrant lignin structures and polysaccharides are still present. Actually, lignins are three-dimensional network polymers of phenylpropane units with many different linkages between the monomers, leading to a complicated and random structure. This explains the stringent conditions necessary for its depolymerization and the inability to bring about reversion to monomers.

A number of distinctive features are apparent in the FT-IR spectra of HAPP samples (Fig. 5) as compared with those of PP samples. These features, in addition to the 3400 cm$^{-1}$ and 2930 cm$^{-1}$ bands, include: two strong absorption bands at 1656 cm$^{-1}$ (C=C double bond and amide I) and 1527 cm$^{-1}$ (amide II, which is absent for HAPP1); and several weak bands at 1457, 1392 and 1228 (stronger) cm$^{-1}$, assigned to lignin structures; 1040 cm$^{-1}$ (polysaccharides).
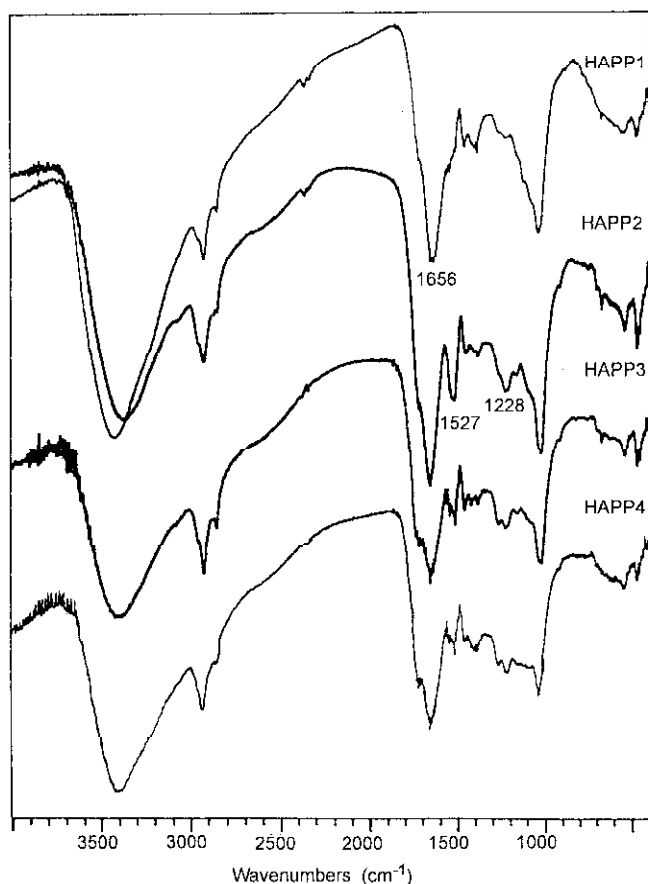
**Fig. 5** FT-IR spectra of HAPP samples

The HAPP1 sample (fresh biosludge) (Fig. 6) after heating to 400°C does not show a significant reduction in the band at 1656 cm$^{-1}$ (amide I). Accordingly, no exotherm at around 360°C is apparent in the HAPP1 DSC curve. In contrast, HAPP2, HAPP3 and HAPP4 (Fig. 7) exhibit dramatic reductions in the band at 1527 cm$^{-1}$, indicating that the exotherm at about 360°C can be assigned to the loss of peptidic structures. The disappearance of this exotherm from the HAPP4 (HA extracted from a 2-year compost) DSC curve may be ascribed to the incorporation and stabilization of peptidic structures in the humic macromolecules.

## Conclusions

DSC analysis in association with FT-IR spectroscopy was applied to study pulp and paper mill biosludges sampled at different maturation ages, and provided the following results:
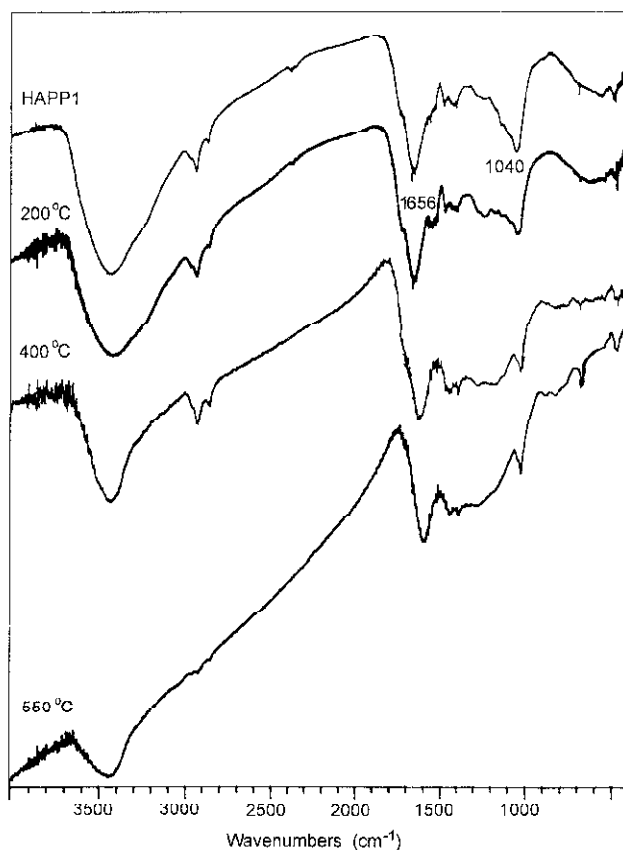
**Fig. 6** FT-IR spectra of HAPP1 heated to different temperatures

PP samples exhibit an endotherm in the low-temperature region, which may be assigned to dehydration processes. The exotherm at around 370°C can be attributed to the loss of peptidic structures. The high-temperature exotherm may be assigned to the loss of functional groups (aliphatic chains) linked to the aromatic network of the molecule, whereas the lignin structures are thermostable, regardless of the maturation age of the compost. For the HA extracted from fresh biosludge, the high-temperature exotherm is absent because of the low degree of aromatic condensation of the molecule, in which humification processes have not started. The exotherm at about 350°C in the HAPP2 and HAPP3 DSC curves may be assigned to the loss of peptidic structures. The DSC curve of HA extracted from a biosludge composted for 2 years closely resembles that of a native soil HA.

These results confirmed that, during composting, the organic matter evolved towards higher molecular complexity and stability, leading to a more homogeneous product, closely resembling humic like substances.
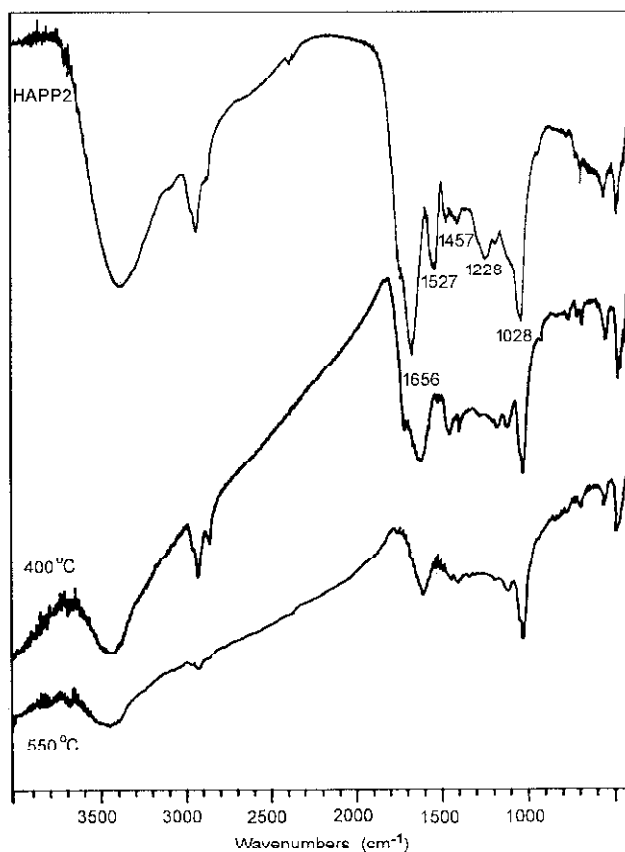
**Fig. 7** FT-IR spectra of HAPP2 heated to different temperatures

# References

1  N. Senesi, Composted materials as organic fertilizers. The Sci. of Total Environ., 81/81, (1989) 521.

2  M. Schnitzer, Organic matter characterization, In Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties, 2nd ed., Agronomy Monograph No. 9, (Edited by B. L. Page, R. H. Miller and D. R. Keeney), 581, Madison, WI (1982).

3  M. R. Provenzano and N. Senesi, Submitted for publication to J. Thermal Anal., (1997).

4  M. R. Provenzano and N. Senesi, Abs. 'Giornate Mediterranee di Calorimetria e Analisi Termica', Cagliari, (1995) 264.

5  M. R. Provenzano and N. Senesi, Abs. 'XVIII Convegno Nazionale della Società Italiana di Calorimetria e Analisi Termica' Pavia 1996, 12.