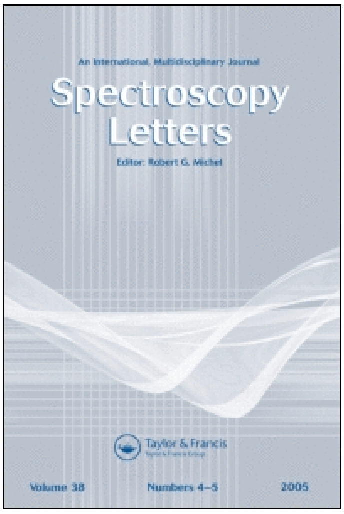

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Characterization of Waste Materials Using FTIR Spectroscopy: Process Monitoring and Quality Assessment

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Characterization of Waste Materials Using FTIR Spectroscopy: Process Monitoring and Quality Assessment

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Abstract: Stages of organic matter decomposition in waste materials are reflected by their IR spectral pattern. Indicator bands undergo changes during the biological treatment of the waste material. Based on the alteration of band intensities, process control can be carried out. Different spectral patterns of yard-waste composting processes were related to divergent compost features. Mechanical–biological treatment of municipal solid waste results in a final product that can be disposed in a land fill. Several missing bands that indicate metabolic activities reveal final product quality. Identification of unknown materials can be carried out by comparison with pure substances or landfill components. The assessment of waste organic matter in

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abandoned landfills is based on the spectral pattern that is assigned to a specific stage of decomposition. Maturity and stability, which are considered important properties of waste organic matter, are reflected by their spectroscopic characteristics.

Keywords: FTIR spectroscopy, identification, process monitoring, quality assessment, waste materials

INTRODUCTION

During the past two decades, the environmental impact of untreated waste materials has been intensely investigated. The main interest has focused on the determination of gaseous and liquid emissions, especially methane that contributes to the greenhouse effect and leachate compounds that contaminate soil and water. In the past, the enclosure of waste material was considered the solution to prevent interactions with the environment. The development of landfill liners and suitable landfill covers was emphasized. However, in the past decade there was an increasing awareness that we have a gap in our knowledge about the long-term behavior of landfill covers. At the same time, regulations claimed responsibility for the following generations. On the other hand, the positive aspects of sludge and biowaste recycling have been emphasized. Recycling is a comprehensive approach to resource management. Due to the organic matter content of composted sludge and biodegradable waste, the application of such materials is considered a way of maintaining or restoring the quality of agricultural or urban soils. Organic matter maturity and stability are a prerequisite to realize this purpose.

The characterization of waste material and the assessment of degradation or stabilization by treatment have come to the fore. Due to the complexity of waste samples, the application of new analytical methods that provide more comprehensive information is necessary. Maturity and stability are complex properties that are described by chemical, biological, and physical parameters. In this context, the terms "maturity" and "stability" characterize a stage of organic matter in waste materials when biological activities and turnover rates have reached a low level. Further degradation takes place over long periods up to the equilibrium with the environment.[1] "Maturity" is rather applied for composts, "stability" for materials that have to be disposed in landfills. According to environmental legislation, this stage is defined by several parameters like respiration activity, the gas-forming potential under anaerobic conditions, organic carbon, different nitrogen compounds, and plant compatibility for composts.

Whereas chemical data provide information about individual compounds, IR spectral shapes of the waste material describe the chemistry of the system in a general way. The spectral fingerprint that is reflected by the size, shape, presence or absence of several indicator bands can be assigned to specific stages of decomposition. Based on these spectral characteristics, process control and assessment can be carried out. The behavior of indicator bands over a period of time reveals the process kinetics.

Band identification is based on literature and supported by the comparison to pure substances or waste components, by mathematical spectral treatment (e.g., the second-derivative mode), and chemical data. Addition of pure substances or sample treatment (E1) confirms in some cases the band identity and reveal matrix effects.[2]

There are several experiences over the past two decades concerning IR spectroscopic investigations of complex samples. Characteristics of organic matter in soils and their changes through deforestation,[3–5] and the impact of fertilizers and agricultural activities on soils[6] were revealed by their IR spectra. Spectroscopic characterization of natural organic matter fractions has shed light on structural and functional properties.[7] Waste materials and humic acids from soils, peat, and waste materials were investigated using Fourier-transform infrared (FTIR) spectroscopy.[8–22] Chen reported about the application of spectroscopic methodologies to maturity determination in composts.[23] The interaction of humic acids with lead, which causes structural changes of the macromolecule, was investigated using FTIR spectroscopy and a multivariate curve resolution.[24] The application of FTIR spectroscopy has been enhanced to identify microorganisms[25,26] and to characterize tissues.[26] In geochemistry, FTIR spectroscopy is a helpful tool as well.[27,28]

The objectives of the presented investigations are:

1. to demonstrate the applicability of FTIR spectroscopy in waste science and waste management, for process and product control and for the assessment and identification of abandoned landfills,
2. to demonstrate the approach to spectral interpretation for complex waste samples,
3. to get a better insight into the decomposition processes of waste materials.

Chemical and biological data that describe the stage of waste materials were compared to spectroscopic patterns. Several examples of different waste treatment processes and waste materials from abandoned landfills are presented. All samples originated from both real industrial processes and existing landfills.

EXPERIMENTAL

Sampling and Sample Preparation

To each representative sampling of complex materials, a good sampling design is demanded according to accepted procedures for chemical analyses in waste treatment plants. A composite sample from 6 singular samples, screened through 20 mm, is required per 2000 m^3.[29,30] The composite samples were air-dried, milled in an agate mill (Retsch GmbH & Co. KG, Haan, Germany), and screened through 0.63 mm. The sample prepared in such a manner was the basic material for chemical and IR spectroscopic investigations.

Materials

Yard and Kitchen Waste Compost (A and B)

The mixture of yard/kitchen waste (A) and yard waste (B) originated from two composting plants. The plants both operate an open windrow process. In process A, the yard/kitchen waste was rotated mechanically, daily for 1 week, then twice a week for 3 weeks. The curing phase took place over 8 months in a pile with rotation once a month. In process B, aeration was strengthened by daily repeated rotation over 2 weeks. The curing phase proceeded in a pile over 6 months.

Mechanical–Biological Treatment of Municipal Solid Waste (C)

Municipal solid waste (MSW) was mechanically–biologically pretreated and mixed with an unknown amount of sewage sludge. The initial biological treatment happened in a rotating vessel for 1 day, subsequently on a rotting platform with forced aeration for 10 weeks (inside). The curing phase of the material took place outside in a pile.

Sewage Sludge in a Wastewater Treatment Plant and After Landfill Disposal (D)

Samples were taken at different phases of the wastewater treatment: primary sludge (SL1), excess sludge (SL2), mixture (50:50) of excess sludge and primary sludge after 30 days of anaerobic digestion (SL3). SL1, SL2, and SL3 were repeatedly washed with deionized water to take out the water-soluble wastewater compounds. The remaining sludge was freeze-dried. The 2-year-old sample of land-filled sewage sludge (SL4) is a mixture of anaerobically digested sewage sludge with $Ca(OH)_2$.

Primary sludge is the particulate fraction of the wastewater, intended for treatment in the plant; excess sludge is the activated sludge that leaves the aerobic tank.

Abandoned Landfills (E)

Sample E1 originates from a depth of 1 m covered by a 0.8 m earthy layer. For IR spectroscopic investigations, the sample was treated 3 times with hydrochloric acid [$c(\mathrm{HCl}) = 0.1\,\mathrm{mol/L}$] to remove the high amount of calcite and washed with deionized water until the filtrate remained neutral.

Sample E2 originates from a 15-year-old deposit profile (bank) of a shortly composted municipal solid waste/sewage sludge mixture. The surface layer is covered by plants (nettle, grass, moss, etc.).

For lab-scale experiments, landfill material (E3; density, 1.18) was put into two columns (height, 56 cm; diameter, 25 cm; mass, 20 kg). Three hundred milliliters of deionized water were added. One column was aerated from the bottom for 4 weeks (airflow = 1.4 L/h). The second column (reference) was not aerated. After 4 weeks, samples of both collected leachates were taken and freeze-dried.

Cellulose powder (SIGMA-ALDRICH Handels GmbH, Vienna, Austria) for comparison with primary sludge and unknown landfill material was used as obtained.

Prof. Franz Ottner from the Department of Structural Engineering and Natural Hazards (BOKU–University of Natural Resources and Applied Life Sciences, Vienna, Austria) made calcite (Ernstbrunner Kalk, Austria, with 99.7% calcite) available.

Methods

FTIR Spectroscopic Investigations

For spectroscopic investigations, the material (fraction $<0.63\,\mathrm{mm}$) was ground with a pestle in order to obtain good reproducibility of the recorded spectra. Two milligrams of the sample were pressed with (FTIR grade) KBr (1:100) to a pellet. The pellet was immediately measured after preparation in the spectrometer under ambient conditions using the transmission mode. The measurements were carried out in the mid-infrared range from $4000\,\mathrm{cm}^{-1}$ to $400\,\mathrm{cm}^{-1}$ with a Bruker Equinox 55 FTIR spectrometer (Bruker Austria GmbH, Vienna, Austria). The resolution was set to $4\,\mathrm{cm}^{-1}$, 32 scans were recorded, averaged for each spectrum, and corrected against ambient air as background. Spectra were shifted parallel to the wavenumber axis in most of the figures.

Band-heights were measured to a chosen baseline with the Perkin Elmer software (Spectrum lite) or the Bruker software (OPUS). For the comparison of different stages of decomposition, relative intensities of distinct bands were calculated to emphasize the relative change.[5]

To determine the differences in the profile, band-heights of sample E2 were measured as described by Smidt et al.[13] The relative absorbance [%] is the corrected band-height of one distinct band multiplied by 100 and divided by the sum of all compared corrected band-heights.

Spectra in the second derivative mode were calculated by applying the algorithm of Savitzky and Golay[31] for selected samples.

Chemical Investigations

The total content of organic matter (OM) was determined gravimetrically after incineration at 545°C. The spectrum of the remaining material (ignition residue) of sample C was recorded to distinguish organic from inorganic bands. Total carbon (TC), total inorganic carbon (TIC), and total nitrogen contents (N_t) were analyzed by combustion in a Variomax CNS analyzer (Kendro Laboratory Products GmbH, Vienna, Austria). Total organic carbon (TOC) was calculated by the difference between TC and TIC. All analyses were carried out twice. OM, TOC, and N_t refer to dry matter (DM).

Humic substances were extracted with a sodium pyrophosphate solution ($c = 0.1\,\mathrm{mol/L}$, pH 10.5). Different fractions were separated according to their solubility in acidic or alkaline solutions.[32] Their optical densities were measured photometrically at 400 nm.

Nitrate–nitrogen (NO_3–N) and ammonium–nitrogen (NH_4–N) were determined photometrically according to the German Standard[33,34] using the fresh material.

Biological Investigations

For respiration activity (RA), fresh material was used. The oxygen uptake was measured in a Voith Sulzer sapromat[35] (H + P Labortechnik GmbH, Germany) during a period of 7 days. The oxygen demand for 4 days (RA 4d) and 7 days (RA 7d) was calculated as mg O_2/g dry matter (DM) and mg O_2/g organic dry matter (oDM).

The gas sum (GS21) was determined under anaerobic conditions (incubation test) over 21 days[35] and calculated as liter (0°C, 1013 mbar)/kg DM, resp. oDM.

RESULTS AND DISCUSSION

General Findings

The most important bands found in the spectra of waste materials and their usual behavior during degradation are compiled in Table 1. The arrows indicate the development of bands during the rotting or composting process. Differences of the general spectroscopic pattern enable the identification of composts, municipal solid waste, and sewage sludge.

The stretching vibration of bonded and nonbonded hydroxyl groups and water causes the broad band at about 3400 $\mathrm{cm^{-1}}$ in each waste material. OH-bending vibrations from water (1635 $\mathrm{cm^{-1}}$), which is adsorbed by functional groups in organic matter like lignocelluloses[36] and inorganic constituents, can overlap vibrations from some functional groups.

Table 1. Indicator bands and their development during a rotting process

Wavenumber (cm^{-1})	Vibration	Functional group or compound	Development (weeks)	
			<16	>16
3400	O–H stretching	Bonded and nonbonded hydroxyl groups and water[41]		
2920	C–H stretching	Methylene[37]	↓	→
2850	C–H stretching	Methylene[37]	↓	→
2520		Carbonate[22]	↑	→
1740–1720	C=O	Aldehyde, ketone,[15] carboxylic acids, esters [26,37]	↓	
1640	C=O	Amide I, carboxylates[3,15,26,37]	↓	→
	C=C	Aromatic ring modes, alkenes[21,37,38]	↑	→
1635	O–H bending	Adsorbed water[41]		
1560, 1546	N–H in plane	Amides II[15,25,26,37]	↓	→
1515–1505	Aromatic skeletal	Lignin[15,36]		
1425	COO^- stretch	Carboxylic acids[37,39]	↓	→
	C–O stretch	Carbonate	↑	→
1384	N–O stretch	Nitrate[13,37,40]		↑ ↓
1320	C–N stretch	Aromatic primary and secondary amines[37]	↑ ↓	
1260–1240	C–O	Carboxylic acids	↓	
	C–N	Amide III[37]		
1250–900	C–O–C, C–O	Polysaccharides[25,26,42]	↓	→
	C–O–P	Phosphodiesters[26]		
1080		Quartz[27,28,37]		
1030	Si–O stretch	Clay minerals[27,37]	↑	→
	Si–O–Si	Silica		
875	C–O out of plane	Carbonate[28,37]	↑	→

The decrease of the aliphatic methylene bands at 2920 and 2850 cm^{-1} is an indicator of the degradation process. When the material becomes stable, a constant level of band-heights is maintained. Aliphatic methylene groups are part of many organic molecules. Their degradability varies in a wide range. Mineralization, volatilization or transformation of easily degradable molecules and metabolites cause the most significant decrease of these bands within the first weeks. After 10–16 weeks band-heights usually reach a constant level, indicating stabilization of the rotting processes.

The band at about 1740 cm^{-1}, assigned to the C=O stretch of aldehydes, ketones, and esters, is generally weak in waste materials. This band disappears very rapidly, indicating decomposition of early metabolic products.

The band at 1645 cm^{-1} that is attributed to the C=O stretching vibration of carboxylates[37] and amides[26,37] and to the C=C stretching vibration of alkenes and aromatic rings[37–39] shows a divergent behavior. Degradation and synthesis (e.g., microbial biomass) take place at the same time and can be responsible for divergent changes in the band intensity. The amide II band found between 1570 and 1540 cm^{-1} is strong in those sewage sludge and waste materials with a high content of microbial biomass. A weak band at 1512 cm^{-1} is assigned to lignin from lignocellulosic material.[15,36] Despite the small size, the aromatic C=C band at about 1512 cm^{-1} characterizes yard waste with a high content of lignocellulosic materials. In addition, this band is hardly overlapped by other bands. The lignin ring vibration/C=O stretch at 1238 cm^{-1}, and the C–C/C–O/C=O stretch at 1230 cm^{-1}[36] which confirm the indicator band at 1512 cm^{-1}, covers the C–O and the C–N vibration of carboxylic acids and amides in this region. However, "lignin bands" are not a suitable indicator of the rotting process, as a considerable part of wood serves primarily as bulk material. Particles >20 mm are excluded at sample preparation and eliminated at the end of the process.

Different substances contribute to the band at 1425 cm^{-1}. Apart from organic molecule groups (e.g., the COO^{-} stretch of carboxylates, the O–H in-plane bending vibration of carboxylic acids), the C–O stretch of carbonates is found at this wavenumber.[37] The relative increase of inorganic compounds causes this band to increase. Nitrates that absorb at 1384 cm^{-1} [13,37,40] are found at a later stage of decomposition. The sharp carbonate band at 875 cm^{-1}, which is not covered by overlapping bands, indicates a more notable relative increase than the 1425 cm^{-1} band. The band of aromatic amines at 1320 cm^{-1} [37] increases and decreases during the first 6–10 weeks of composting. A fast decrease of this band at the beginning of the composting process indicates diminishing microbial activity and lower transformation rates to more resistant molecules. This band is a reliable indicator of the process kinetics. Compost maturity according to biological and chemical criteria is reached when the band has disappeared. A shoulder at 1260–1240 cm^{-1} can be attributed to the C–O stretching vibration of carboxylic acids and the C–N stretching vibration of amides.[37]

Clay minerals at 1030 cm^{-1} and quartz at 1080 cm^{-1} are main compounds of the inorganic fraction in waste materials. The huge band dominates the region between 1100 cm^{-1} and 900 cm^{-1}[41] in the majority of waste spectra.

The ring vibrations (C–O–C, C–O) of polysaccharides are also found in the region between 1200 cm^{-1} and 900 cm^{-1}.[25,42] Due to low concentration and matrix effects, only two shoulders (1080 cm^{-1} and 1160 cm^{-1})

at the left side of the silica band are visible in most cases. Industrial wastes with higher concentrations of specific components often show the characteristic fingerprint (see sample E1). Plant cells and the microbial biomass can contribute to the symmetric and asymmetric stretch vibrations of phosphodiesters that are also found in the region from 1250 cm^{-1} to 900 cm^{-1}.[26]

Biological Treatment (Composts A and B, Municipal Solid Waste C, Sewage Sludge D)

Composts A and B

Figure 1 demonstrates the divergent behavior of the composting processes A and B. Although the decrease of organic matter is not as important, a continuous increase of humic acids took place in process A. The shift toward stable humic substances requires a certain level of microbial activity, which is revealed by the respiration activity (Table 2). Dynamics of process A are also reflected by the behavior of the 1320 cm^{-1} band. Polysaccharides (e.g., cellulose) are a main component in yard/kitchen waste materials. Grassinger[43] found 10–12% of cellulose for similarly composed yard/kitchen waste. The shoulders at 1160 cm^{-1} and 1080 cm^{-1} (arrows) can be assigned to polysaccharides as described by Grube et al.[25] for glycogen in mycelia. Furthermore, the band at about 1080 cm^{-1} can also be assigned to quartz,[41] which is supported by the double band at 798 and 779 cm^{-1}.

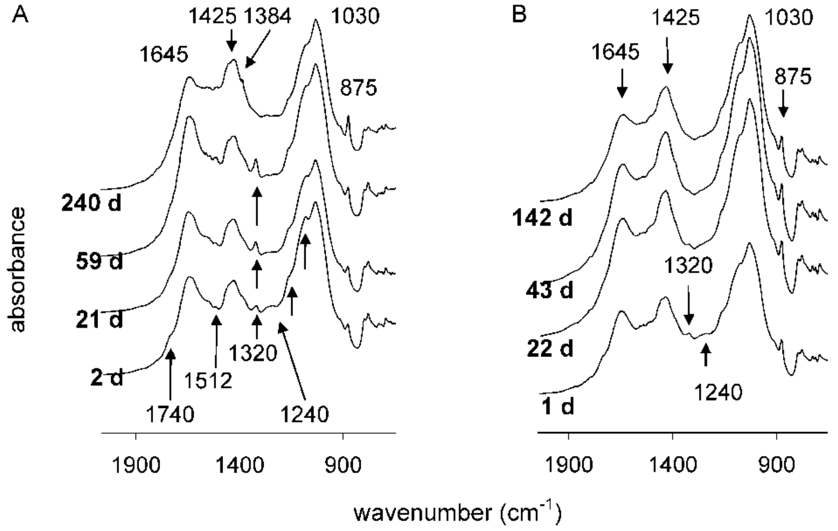

Figure 1. Fingerprint region of different stages of (A) a yard/kitchen and (B) a yard waste composting process.

Table 2. Chemical and biological data of the processes A, B, and C

Time (days)	OM (% DM)			TOC (% DM)			HA (% oDM)		GS21 (L/kg DM)/ (L/kg oDM)	RA		
										(4d)		(7d)
	A	B	C	A	B	C	A	B	C	A	B	C
1		35.4			18.3			8.9			115/325	
2	45.1			23.7			6.6			70/155		
14			45.9			22.8			70/152			49/107
21	43.3			22.7			7.7			31/72		
22		32.9			16.9			10.8			16/49	
43		32.0			16.3			11.4			8/24	
59	39.4			21.6			15.9			15/37		
70			41.7			20.6			21/52			21/52
90			38.9			18.6			18/46			15/39
142		31.2			16.6			11.5			4/12	
240	38.6			20.9			28.7			5/13		

OM, organic matter; TOC, total organic carbon; HA, humic acids; RA, respiration activity; DM, dry matter; oDM, organic dry matter.

Investigations into matrix effects confirmed the band positions for starch and cellulose in waste materials.[2]

In process B, no considerable changes are visible in the IR spectra. Neither an essential mineralization nor humic substance formation were observed (Table 2). Easily degradable substances were metabolized quickly, and the respiration activity reached a low level within 4 weeks. Due to the composition of the material and the resulting low microbial activity, no further degradation or transformation took place. The 1320 cm^{-1} band is weak at the beginning, and only a slight increase was observed within the first two weeks. The insignificant change of this band indicates less metabolic activities in process B.

Municipal Solid Waste (Process C)

The spectra of MSW (Fig. 2) are characterized by a higher amount of carbonate (1425 and 875 cm^{-1}). Addition of sewage sludge becomes visible by the amide II band at 1560 cm^{-1}. After 90 days, the sample still shows characters of immaturity as the bands at 2920 cm^{-1} and 2850 cm^{-1} are strong and the 1320 cm^{-1} band is still visible as a shoulder. Spectroscopic characteristics are also reflected by the TOC and respiration activity (Table 2).

Sewage Sludge (Process D)

The organic matter fraction in wastewater and treated wastewater was characterized by Dignac et al.[44] using FTIR spectroscopy. These investigations

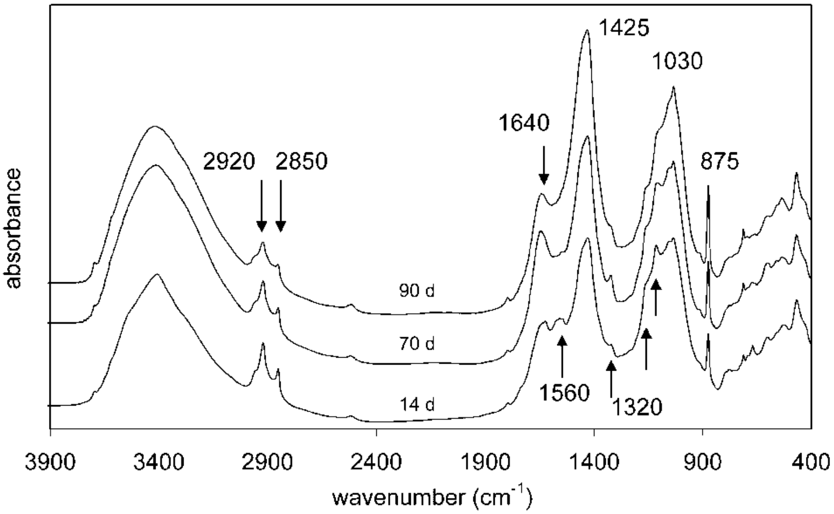

Figure 2. Different decomposition stages (14, 70, 90 days) of the biological process after mechanical pretreatment (municipal solid waste).

concentrated on the particulate fraction due to the relevance with regard to land filling. The spectrum of primary sludge is dominated by the characteristic bands of cellulose. The comparison with the cellulose spectrum reveals the high similarity (Fig. 3). In the spectrum of primary sludge, the amide II band at 1560 cm^{-1} and the contribution of the amide I band at 1650 cm^{-1} are clearly visible due to protein-containing compounds in the particulate wastewater fraction.

Spectroscopic characteristics of excess sludge (SL2) (Fig. 4, spectrum a) differ completely from primary sludge. Available wastewater compounds are used to build up microbial biomass in the aerobic tank (about 30–40% of DM) or are transformed by respiration activities to inorganic compounds and volatile products. Although there are also particulates that are hardly degradable (about 30%) and inorganic (about 20%) wastewater components, a considerable part of the sludge consists of bacteria cells. The total nitrogen content of 7% and the low C/N ratio of 5.3 confirm the presence of microbial biomass. Spectra of excess sludge show three strong amide bands: the C=O stretch of the amide I band at 1655 cm^{-1}, the N–H in-plane bending of the amide II band at 1545 cm^{-1}, and the C–N stretching of the amide III band at 1260 cm^{-1}.[26,37] The stretching vibration of aliphatic methylene bands at 2925 and 2855 cm^{-1} can be assigned to fatty acids in biomolecules.[26]

The IR spectrum of anaerobically digested sludge (Fig. 4, spectrum b) still shows strong amide bands that are sharpened in the second-derivative mode (Fig. 5). Although there is a visible decrease of amplitudes after the anaerobic treatment, the bands are still present, and the respiration activity of the material is still high (Table 3).

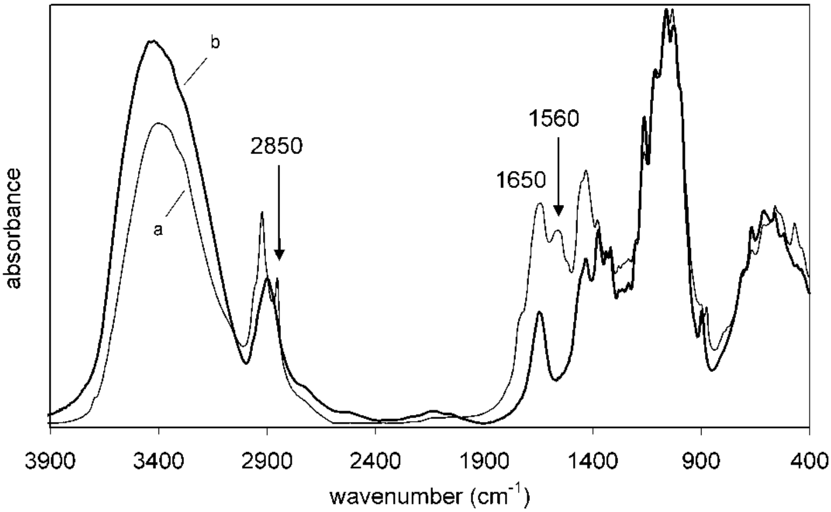

Figure 3. Spectra of (a) primary sludge (SL1 = a) and (b) cellulose.

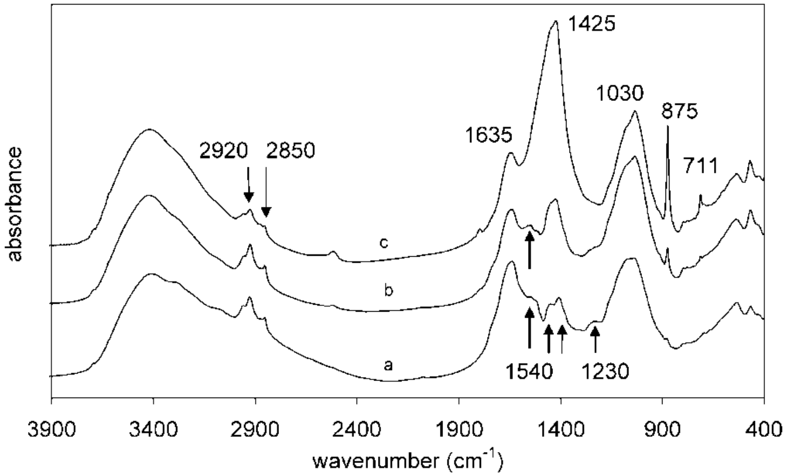

Figure 4. (a) Excess sludge (SL2), (b) anaerobically digested sludge (SL3), (c) 2-year-old landfilled sludge with slaked lime (SL4).

The spectrum of the anaerobically digested sludge (SL3) is more similar to the excess sludge (SL2) spectrum. This finding indicates the degradation of polysaccharides (primarily cellulose) originating from primary sludge (SL1), whereas the microbial biomass that was built up in excess sludge resists more to degradation due to chemical compounds that are undegradable under anaerobic conditions, as lipids from membranes. Therefore, different

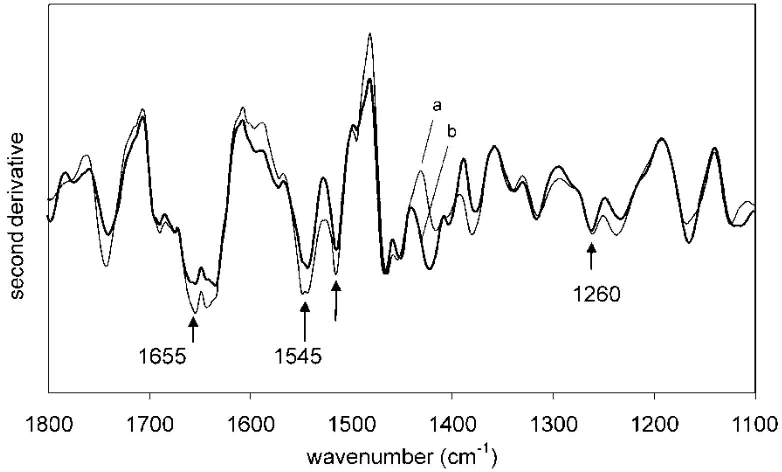

Figure 5. Fingerprint region of the spectra a (excess sludge SL2) and b (anaerobically digested sludge SL3) in the second derivative mode.

Table 3. Chemical and biological data of different stages of sewage sludge formation, treatment, and deposit

	OM (% DM)	TOC (% DM)	N_t (% DM)	C/N	GS21 (L/kg DM)/ (L/kg oDM)	RA 4d (mg O_2/g DM)/ (mg O_2/g oDM)
SL1	73.6	39.0	2.8	14	139/189	285/387
SL2	72.9	37.6	7.1	5	148/203	113/155
SL3	53.8	27.9	3.1	9	44/82	77/143
SL4	22.1	10.1	ND	—	5.4/24	1.2/5.4

SL1, primary sludge; SL2, excess sludge; SL3, anaerobically treated sludge; SL4, landfilled sludge mixed with $Ca(OH)_2$; OM, organic matter; TOC, total organic carbon; N_t, total nitrogen; C/N, carbon nitrogen ratio; GS21, gas sum over 21 days; RA 4d, respiration activity during 4 days.

techniques for sludge disintegration have been tested to get a higher yield of biogas and to reduce the content of organic matter of the residues.[45] It is evident that the anaerobic treatment can partly reduce the carbon content of wastewater sludge by transformation to methane and CO_2, but a considerable amount is still present. Chemical and biological data listed in Table 3 illustrate the decrease of organic matter, organic carbon, respectively, and the development of the nitrogen content. Ammonium and nitrate are in the liquid phase of sludge and therefore not visible in the spectrum of washed sludge. Additional measures are necessary for land filling due to the high organic matter content and the biological activity of anaerobically "stabilized" sludge that do not reach limit values, according to the Austrian landfill regulation from 2004 (RA 4 days = 7 mg/g DM, GS21 = 20 L/kg DM). Addition of $Ca(OH)_2$ causes mechanical stability for land filling and stops microbial activity due to the alkaline $pH > 12$. Spectrum c (Fig. 4) shows the sewage sludge mixed with $Ca(OH)_2$ after 2 years of land filling. The transformation to carbonate is reflected by the prominent carbonate bands (2520, 1430, and $875\,cm^{-1}$). Despite a decrease of the pH to 7.4 and the organic matter content of 22.1%, respiration activity remains very low. The presence of $CaCO_3$ leads to organic matter stabilization as demonstrated by several investigations in soil science.[46,47] In addition, the recalcitrant organic matter fraction prevents considerable decomposition.

Abandoned Landfills (E)

In former times, municipal solid waste was disposed in landfills without any treatment. Depending on air and moisture content, degradation or preservation took place. Samples of landfill materials reflect only the stage of organic matter degradation at the moment of sampling. However, investigations of profiles (landfill E2) can elucidate the development of organic matter over time. Indicator bands mentioned above reveal the stage of organic matter.

Identification of an Unknown Landfill (E1)

The spectrum of the landfill material (Fig. 6A) is dominated by the strong calcite bands despite the high content of organic matter (32.9% of DM).

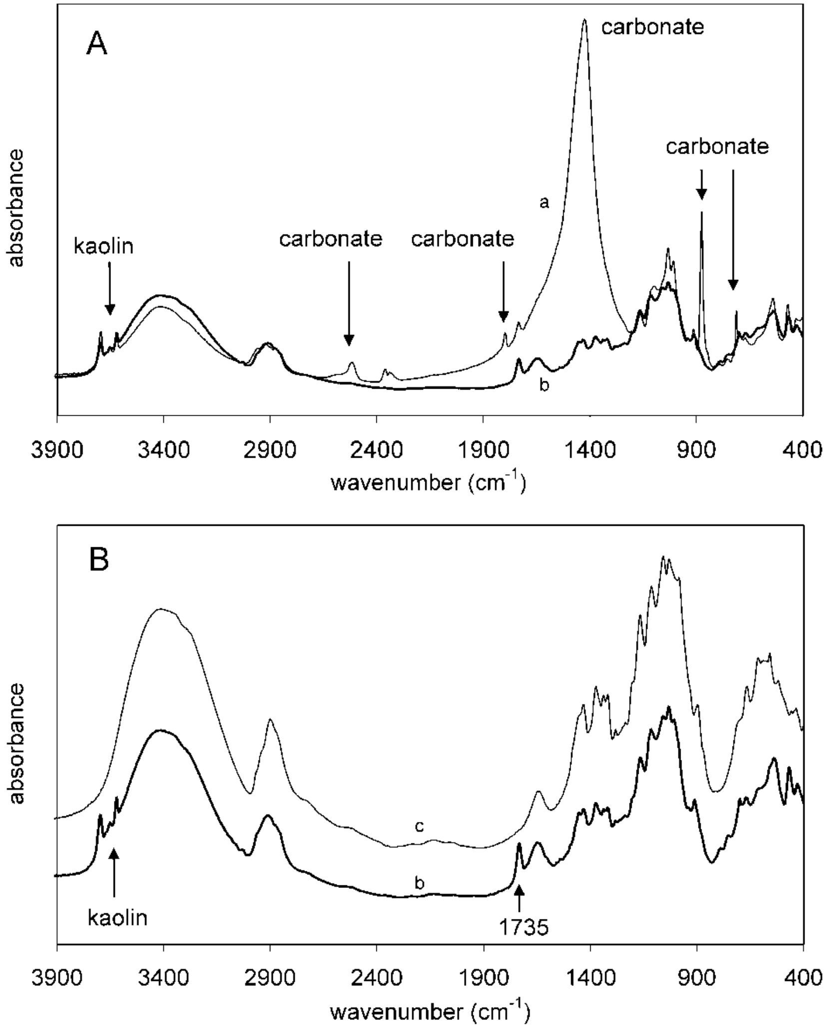

Figure 6. (A) Spectra of the landfilled material (a) and of the HCl-treated sample (b). (B) Spectra of the HCl treated sample (b) and cellulose (c).

Organic bands are visible at about 2900 cm^{-1} and in the 1200–900 cm^{-1} area. The hydrochloric acid (HCl) treatment removes the carbonate from the sample, uncovering other organic bands that derive from cellulose. Figure 6B shows the comparison of the HCl-treated sample and celluose.

Spectroscopic characteristics of the HCl-treated sample and cellulose reveal the concordance. The bands at 3695, 3650, and 3620 cm^{-1} can be assigned to kaolin, which is an additive in paper production. The band at 1735 cm^{-1} is assigned to aldehydes, ketones, and esters. As no band can be seen at about 1235 cm^{-1}, which is characteristic for acetic acid esters in hemicelluloses,[48] the presence of the band at 1735 cm^{-1} indicates the degradation of the cellulosic material. The unknown material was identified to be sludge from the former paper industry. Paper sludge had been mixed with calcite and disposed in a landfill.

Profile of a 15-Year-old Deposit (E2)

The comparison of the organic matter content, humic acids content, and the height of the aliphatic methylene band shows the divergent development of the waste material depending on depth and aerobic or anaerobic conditions. The highest humic acids content was found at a depth of 0.5 m (Fig. 7) and decreases to a low level with increasing depth. Under anaerobic conditions, no humic acids were built up. The organic matter content in 0.5 m was as high as in 3 m (30.8% DM). However, the different quality of organic matter is reflected by the ratio of the relative intensities 2920/1640 cm^{-1} (aliphatic methylene band and unsaturated or aromatic C=C vibrations).

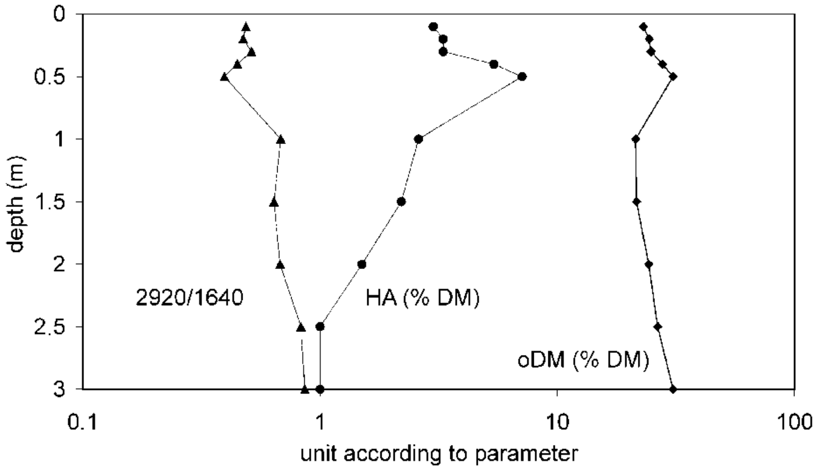

Figure 7. Profile of a 15-year-old deposit (municipal solid waste/sewage sludge): ratio of the relative absorbances at 2920 cm^{-1} and 1640 cm^{-1}, humic acid (HA) content, and organic dry matter (oDM) content referred to dry matter (logarithmic scale).

The ratio decreases and reaches a minimum in 0.5 m. The low ratio indicates the decreasing aliphatic feature of the material in 0.5 m. Despite the same organic matter content as in 3 m, the shift to the stable fraction of humic acids or enriched recalcitrant components causes a change in organic matter quality. The higher ratio in the surface layer can be caused by the impact of fresh plant materials.

Spectroscopic Characteristics of Leachate (E3)

Aeration is a common method to stabilize organic matter in abandoned landfills. The IR fingerprint of the leachate can support the monitoring of landfill remediation. Spectra of leachates from an untreated and an aerated landfill sample are illustrated in Fig. 8. The leachate (spectrum a) from the untreated, anaerobically stored material shows several bands of organic nitrogen and sulfur compounds. Amines are reflected by the symmetric and asymmetric N–H stretching vibration $>3000\,\mathrm{cm}^{-1}$, the N–H in-plane bend at $1600\,\mathrm{cm}^{-1}$, the C–N stretching vibration at $1295\,\mathrm{cm}^{-1}$, the N–H out-of-plane bend at 834 and $706\,\mathrm{cm}^{-1}$, and the S–H stretching vibration at $2575\,\mathrm{cm}^{-1}$. The spectrum of the leachate from the aerated material (Fig. 8, spectrum b) is characterized by three strong bands that can be assigned to the S–O stretch at $1100\,\mathrm{cm}^{-1}$, the S–O bend at $616\,\mathrm{cm}^{-1}$ of sulfates, and to the N–O stretching vibration of nitrate at $1400\,\mathrm{cm}^{-1}$.[37] The bands at $1100\,\mathrm{cm}^{-1}$ and $616\,\mathrm{cm}^{-1}$ correspond to the spectral characteristics of K_2SO_4 or Na_2SO_4.[41] Spectroscopic investigations of the ignition

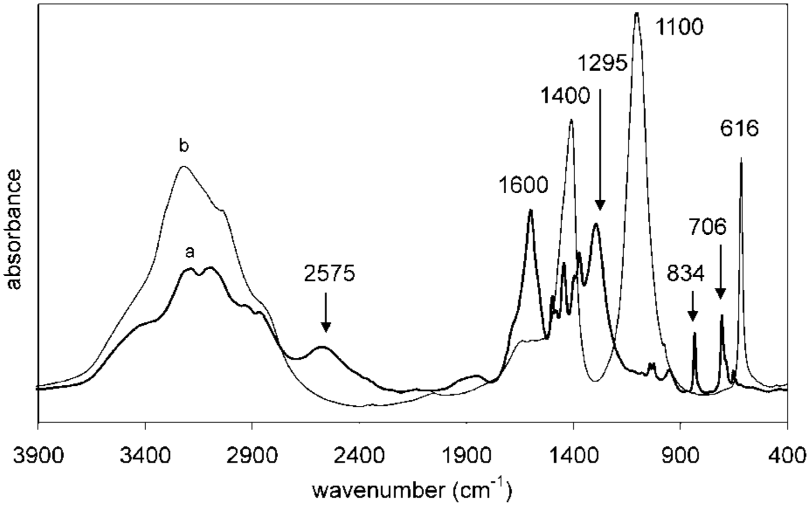

Figure 8. Leachate from (a) nonaerated landfill and (b) aerated landfill material after 4 weeks (lab scale experiments).

residue confirmed the sulfate bands at 1100 cm^{-1} and 616 cm^{-1}, whereas the band at 1400 cm^{-1} has not been found. Due to the promotional effect on combustion, present organic compounds can reduce nitrate. To clarify this effect, and to ensure the band identity, a mixture of the freeze-dried leachate and KNO_3 (3:1) was incinerated at 545°C. The spectrum of the ignition residue (not shown) did not show the nitrate band. Several shoulders in the 2820–3050 cm^{-1} area (C–H and N–H stretching vibration) indicate that the oxidation or mineralization process is not finished yet (Fig. 8b). Changes in the spectra show that the spectral characteristic is a suitable indicator of successful aeration treatment. Wu et al.[49] found a decreasing intensity of double or triple bonds between carbons after ozonation of leachate. Nanni and Ratasuk[38] shed light on the different composition of the humic/fulvic acid like fractions in leachates compared to terrestrial and aquatic humic substances that are more oxidized.

Process Monitoring, Process Control, and Quality Assessment

Several papers have been published on the progression of bands in the infrared spectra of biowaste,[15] municipal solid waste,[16] and organic matter in wastewater treatment.[44] Most of them gave attention to humic acid characterization and to soil-related aspects. In waste management, FTIR spectroscopy is not yet applied as a monitoring tool and for the assessment of abandoned landfills, although it provides several advantages: a fast practicability and comprehensive information about the stage of organic matter. The monitoring of waste treatment plants comprises parameters that are indispensable for process operation: water and organic matter contents and temperature.[50] Only the temperature can be measured immediately. This parameter gives several hints about the phase of the process, but it does not characterize the material itself. Toxic effects and temporary desiccation can inhibit microbial activity that causes temperature to decrease and pretends stability of the material.

Sampling as the first crucial step during analysis is always a question of "fitness for purpose". The procedure for chemical analyses in waste treatment plants[29,30] uses a composite sample from 6 singular samples per 2000 m^3, which is primarily based on the detection of locally distributed heavy metal contaminations.[51] However, the proper sampling procedure is a current topic in the European Union (drafts of the European Committee for Standardization CEN, Technical Committee 292, working groups 1–5). If the overall process has to be evaluated, a composite sample is appropriate. If the variations within the process are of interest, the investigation of singular samples is preferred. Compared to other techniques, FTIR spectroscopy is a fast method, and a spectrum can be collected within a few minutes, which makes the investigation of several samples possible. Moreover, new developments will allow reducing sample preparation time.[52]

Variations in the system are mostly caused by process conditions like water content, aeration, temperature, and the heterogeneity (particle size, different chemical composition) of the input material, as well as the interdependency of these. Consistent water content and aeration are a supposition for uniform degradation of organic matter. In general, a larger variability within a batch is expected in an open windrow process than in a closed reactor system. Seasonal variations of biowaste and addition of sewage sludge to municipal solid waste cause differences between batches.[50]

Besides sampling, sample preparation is a critical step during analysis. It is known from other biological materials like wood that milling has a major impact on the sample that could cause disappearance of bands in the infrared spectra.[53] On the other hand, intensive milling could lead to an overestimation of components like calcite due to their milling behavior (easy to mill).[54] Despite the divergent behavior of materials, a good reproducibility was achieved with the described method.

The repeatability of the spectra, and therefore of the calculated second derivatives, using biological material like wood and cellulose was investigated by Schwanninger et al.[54] No band shifts were observed, and the "band-heights" of the spectra in the second-derivative mode varied a few percent. The subtraction of two or more spectra, or difference spectroscopy, is a straightforward way of simplifying an experimental spectrum and/or extracting overlapping bands. Difference spectroscopy is a spectroscopic method that is sensitive to all types of band changes and an ideal tool for spectral interpretation. Nevertheless, there are some limitations and peculiarities that have to be taken into account.[55,56] Furthermore, self-deconvolution and curve fitting can be used to enhance the resolution, gaining additional information about bands representing indicators of degradation. According to Tseng et al.,[22] these techniques were not satisfactory for a composting process. Each of the noted procedures has advantages and drawbacks. In complex systems, like waste materials, the calculation of the second derivatives is an easy, robust, and reliable method to draw qualitative conclusions.

The stage of organic matter (composting and biological treatment of municipal solid waste) is based on a qualitative general assessment of the spectrum.[2] Especially the aliphatic methylene bands (2920 and 2850 cm^{-1}) and the amide II (1560 cm^{-1}), the 1320 cm^{-1}, the 1260–1240 cm^{-1}, and carbonate bands (1425 and 875 cm^{-1}) provide information about reactivity or stability of the material. Biological treatment processes are monitored by the curve progression of relative absorbances of the indicator bands mentioned above. A constant band-height over time and the absence of several bands (1560, 1320, 1260–1240 cm^{-1}) indicate stabilization. The stability assessment based on spectroscopic features corresponds to the assessment resulting from stability parameters mentioned in the introduction section.

Respiration activity is a time-consuming parameter to determine stabilization. Temperature determination is a fast method. However, both methods only provide reliable results if inhibiting factors of microbial activity are absent. The organic matter content, total organic carbon and nitrogen are sum parameters that give some information about the stage of decomposition in well-known processes. The different behaviors of carbon-containing molecules with regard to stability is not taken into account. In addition, all mentioned analyses are more time consuming than IR spectroscopic investigations. An enhancement or replacement of several soil parameters by IR spectroscopy are suggested by Janik et al.[57]

For practical use, characteristics of an individual "optimized" process have to be established as a reference, depending on the target to reach (humification or mineralization). Difference spectra reveal the divergences. Severe failures are detected immediately by the exceptional presence of bands (e.g., a strong increasing amide II band in biowaste) or a strange behavior during the process (e.g., increasing aliphatic methylene bands). For the first time, frequent sample collection is useful to characterize an unknown process and to find out its kinetics.[13] Quality control of the final product with regard to stability parameters is based on the specific spectroscopic pattern, especially on the missing bands mentioned above.

The assessment of organic matter degradation in abandoned landfills can be carried out very fast using FTIR spectroscopic features. It is based on the relevant "indicator bands". Due to the high content of inorganic compounds, sample treatment or investigations of leachate might be advantageous. Process control and the proof of successful remediation (e.g., *in situ* aeration), are an additional application area in waste management. Landfills originating from industrial wastes often contain huge amounts of a specific material. A spectra library supports identification.

CONCLUSIONS

FTIR spectroscopy has been proved to be a powerful tool for process monitoring and quality assessment in waste management. Kinetics are reflected by several indicator bands. Individual bands that change considerably during the composting process (e.g., the aliphatic methylene bands and the band at $1320\,\mathrm{cm}^{-1}$) are helpful indicators. The assessment of abandoned landfills and the current stage of organic matter are rather based on the total spectral pattern of the sample and on the presence of bands indicating reactivity. Spectra interpretation was supported by chemical and biological data. It is evident that a spectral pattern can be assigned to a specific stage of decomposition processes. However, band assignment remains a current issue. More information has to be discovered from band shift during degradation.

Stabilization of organic matter due to interaction with mineral surfaces is an additional issue to be investigated by FTIR spectroscopy. Interesting findings about mechanisms of humus coatings on mineral surfaces have been reported by Wershaw et al.[58] The presented results focus on qualitative spectral features of waste materials. Further investigations should concentrate on quantitative interpretation. The correlation between band-heights and their changes with time could provide some information about individual processes. Processes can be matched with the slope of an optimized process. In the future, the IR spectrum could replace chemical and biological investigations for the assessment of organic matter maturity in waste materials.

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