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The Application of FT-IR Spectroscopy in Waste Management

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1. Introduction

This synopsis of FT-IR spectroscopic applications in waste management covers relevant issues regarding monitoring, process and quality control. Quality in this context means low reactivity, low gas forming potential and compliance with limit values of materials to be landfilled, appropriate compost ingredients and improvement of the stable carbon pool by humification of compost organic matter. The division into sections was carried out according to specific materials and processes and the related questions to be answered.

Waste materials have not posed a problem in the past, as long as they were returned to the natural cycle. The higher degree of utilisation, the long lasting life cycle of goods and their re-use caused minor waste amounts and contributed to the balance of input and output streams. As natural materials were the basis for good production, waste was integrated in the natural cycle. Organic waste materials only escaped degradation if they were preserved under particular conditions. Inorganic residues from ore mining have led to local contamination by heavy metals. In contrast, fragments of ancient pottery or ruins have gained in importance as historical witnesses. The economical and social increase in prosperity and urban development has been paralleled by strongly rising amounts of organic and inorganic waste and the acceleration of turnover rates. These have led primarily to sanitation problems, especially in expanding urban areas. Disposal of these wastes by spreading them over the surrounding countryside or filling dumps were only temporary "solutions". Natural waste such as foliage falling in autumn can be considered as an intermediate product in a closed circle. Except for natural disasters, turnover rates and the related contents of substances are subjected to regulations. Anthropogenic waste is in most cases the end of a one-way street that causes system imbalances. Therefore new approaches and waste management strategies aim at copying natural cycles.

The amount, changes in the chemical composition of our goods, the use of hazardous substances and the careless landfilling of waste in dumps have caused serious environmental problems and demonstrated the need for action. The awareness of this issue emerged when soils and groundwater were contaminated by leachate emissions. Due to the missing separation of hazardous waste, landfill remediation has often implied a complete excavation of the landfilled material. Discussions on climate change, the role of waste management in the global carbon cycle and its contribution to the carbon budget have drawn attention to relevant gaseous emissions from landfills with a global warming potential, especially of methane.

Analytical approaches in the past differed in that the main analytical interest focused on the effect of gaseous emissions on the environment and on soil and water pollution. Environmental analytical methods were applied to find out the effects in these spheres caused by waste materials. Waste materials themselves were not investigated. The first attempts to encapsulate waste materials were aimed at prevention of contact with the environment. Analytical investigations in the past concentrated on pollution control and on the chemical and physical quality of landfill liners with regard to their density, tightness and stability.

Later on the interest in the waste material itself came to the fore as it represents the source of future emissions. The environmental impact and the economic implication caused the government to react in terms of regulations regarding the handling of waste materials. During the last decades waste management has become an important industrial sector in countries with a high environmental awareness and adequate standards. The approach of waste encapsulation was abandoned due to the missing knowledge about the durability of landfill liners and technical facilities. Moreover, it was evident that the encapsulation would have promoted the preservation of the material and postponed the problem of reactivity.

The concept of a "multi-barrier system" that includes pre-treatment of municipal solid waste in terms of stabilisation besides the technical equipment and an adequate geological basement was implemented. The reduction of waste reactivity within a manageable space of time should avoid the long lasting after care period of several decades that does not comply with the objective of the Austrian Waste Act (BMLFUW, 1990) not to burden the next generations with environmental problems from the past.

Among the wide range of current research topics in waste management the development of appropriate analytical tools is an overall concern at the national and the European level. Waste materials represent an analytical challenge due to their widely varying composition and structure contrary to all principles of natural order. The implementation of limit values by national rules and the need for environmental compliance have stimulated the discussion on adequate methods, their reliability and usefulness. Their availability is a prerequisite to achieving the protection of the environment according to the principles of social welfare and sustainability as required by the aims of the Austrian Waste Act (BMLFUW, 1990). For waste management practice analytical methods should be fast, cheap, easy to handle, and marginally error-prone. Many requirements in view of the complex matrix!

There are two main problem areas in waste management to be dealt with: toxic effects and reactivity of the material. Heavy metals, organic pollutants such as hydrocarbons, polycyclic hydrocarbons and chlorinated substances are quantified individually. The complex matrix of waste materials makes the determination and quantification of single substances difficult. Interferences of different compounds affect their extraction and separation for quantification. The complex mixture of different materials regarding chemical components, texture and behaviour implies the application of new analytical tools. With respect to pollutants the determination of single compounds remains indispensable in many cases. Analytical advances concentrate on improved extraction and disintegration methods and on modern instruments for determination. For an overall waste characterisation including chemical properties and behaviour more holistic approaches have gained in importance.

1.1 Fourier transform infrared (FT-IR) spectroscopy and data evaluation

FT-IR spectroscopy has proved to be a powerful tool to comply with the purpose of comprehensive characterisation. The unique characteristic of the material presented by the

spectrum sheds light on material properties, its behaviour as well as on specific components represented by their functional groups. The substantial progress regarding the infrared spectroscopic measurement is achieved by the recording of the interferogram, the fast detection systems and the Fourier transformation. This combination provides many advantages and has caused a high interest in this method for process and quality control in many areas (Mantsch & Chapman, 1996; Moron & Cozzolino, 2004; Pollanen et al., 2005; Zhang et al., 2005). Infrared spectroscopy is based on interactions of infrared radiation with matter. Infrared light causes functional groups to vibrate. The uptake of energy is indicated by absorption bands in the spectrum. Measured band intensities depend on the content of the substance to be determined and on the individual interaction of the functional group with infrared radiation at a distinct energy level (Hesse et al., 1995; Smith, 1999; Socrates, 2001). The near-infrared (NIR) region from $14,000\text{ cm}^{-1}$ - 4000 cm^{-1} and the mid-infrared (MIR) region from 4000 cm^{-1} - 400 cm^{-1} are commonly applied for process and product control in many industrial fields. The spectral pattern of substances reveals inherent features and allows the proof of their identity. These characteristics support the solution of frequent problems in industry. Infrared spectroscopic investigations of waste materials presented in this chapter have focused on the KBr (potassium bromide) pellet and the attenuated total reflection (ATR) technique in the MIR area. Most experiences and insight regarding spectra interpretation, assignment and behaviour of bands during waste degradation or stabilisation have been gained from the KBr technique (Smidt et al., 2002; Smidt & Schwanninger, 2005; Smidt & Meissl, 2007). Subsequently, investigations were extended to the NIR area and the reflection mode using a fibre probe and the integrating sphere, as well as to the ATR technique in the MIR area (Meissl et al., 2008a). During the last decade the applicability for waste characterisation and assessment has been proved and gives impetus to new ways in waste management practice (Chen, 2003; Michel et al., 2006; van Praagh et al., 2009). In association with multivariate statistical methods these techniques provide an additional benefit for application in practice in terms of time saving and handling. Multivariate statistical methods extract a maximum of latent information from a huge data pool (Brereton, 2002; Esbensen, 2002) and transform the complex spectral pattern into a generally understandable result. The presented results for classification and prediction of the applied multivariate statistical methods focus on Principal Component Analysis (PCA), Soft Independent Modelling of Class Analogy (SIMCA), Partial Least Squares - Discriminant Analysis (PLS-DA), and Partial Least Squares Regression (PLS-R). PCA is used to analyse large data sets. This procedure extracts the information of the original data matrix which leads to a smaller number of dimensions, called principal components (PCs). The required number of PCs depends on the complexity or dissimilarity of the data-set. The variance explained by each PC decreases with increasing number of PCs. PCA reveals the inherent data structure and underlying features which supports the identification of similarities and differences between materials. The loadings spectra, corresponding to the PCs, provide information on the contribution of the spectral regions to the differentiation between samples visible in the scores plot. Based on the PCA, classification and prediction models can be developed. SIMCA is a well known pattern recognition method which describes each class separately in a principal components space. New objects are considered to belong to the class if their distance (e.g. Euclidean) to the constructed PC space is not significantly larger than the distance of the class objects to their PC space. In a further classification method PLS-DA, samples are distinguished by means of the partial least squares regression according to their membership that is defined by the dummy variable (+1) and (-1).

PLS-R relates the variation in one variable (questioned parameter = Y-variable) to the variation of spectral data (X-variables). Based on this correlation models were calculated and further used for prediction. It is a prerequisite that the questioned parameter is reflected by the spectral pattern (Michel et al., 2006; Meissl et al., 2007). The quality of classification and prediction models is expressed by several characteristics (model parameters). R^2 is the coefficient of determination. The root mean square error of cross validation (RMSECV) reflects the error of the model. Cross validation is a validation method where samples out of the sample set are alternately excluded from calibration and used for prediction. This procedure is repeated until all samples have been kept out once. The bias indicates the systematic difference between the measured and the predicted values. The ratio of standard deviation to standard error of performance (RPD) provides information on the precision of analyses for a specific purpose (Williams & Norris, 2004).

This study shows in many cases the development or changes of spectral characteristics, therefore the spectra were shifted in parallel for a clear presentation. Most spectra were recorded from KBr pellets except the ATR spectra shown in section 2.3. For multivariate data analysis spectra were vector normalised.

1.2 Interpretation of infrared spectral data originating from waste materials

Waste is a complex material and heterogeneous regarding the chemical composition and texture. Due to the low amount of sample needed for MIR spectroscopic measurement adequate sample preparation is a prerequisite to obtain reliable and reproducible results. A convenient procedure of sample preparation was described by Meissl et al. (2008b).

Pure substances are characterised by sharp distinct absorption bands that can be assigned to functional groups. By contrast, waste materials display broad overlapping bands due to the complex mixture and manifold interactions between degrading organic molecules. During the last decade MIR and NIR spectroscopy has been applied with increasing success to complex samples. New approaches have gained in importance due to the association with multivariate statistical methods. The proof of identity and the classification of unknown waste materials are based on similarities or differences of the spectral pattern. Identification of functional groups and assignment to substances are an essential target to follow and to understand the chemical changes during degradation and stabilisation processes. Due to the complexity of the material and overlapping bands the identification is limited to a few but significant indicator bands.

Spectra interpretation of waste materials is primarily based on theoretical locations of functional groups cited in literature for pure substances as well as for waste materials or components of waste materials (Hesse et al., 1995; Smith, 1999; Socrates, 2001; Smidt et al., 2002). Due to interactions of degrading organic molecules band shifts in waste spectra occur frequently. Several bands that are assigned to organic functional groups, such as aliphatic methylene bands (Table 1) have a stable band position in waste spectra. The location of many other bands may vary due to the stronger influence of the whole molecule and the waste matrix. Bands of inorganic compounds are mostly sharp and support identification by their characteristic shape and relatively stable position. For many functional groups wavenumber regions are indicated. Band assignment is supported by recording the spectral signature of waste ingredients or by addition of a specific component to waste materials of which the presence should be verified. The most relevant indicator bands that provide information on the stage of degradation are compiled in table 1. The list is limited to bands that are clearly visible in the spectrum of the complex waste matrix even though many substances are

represented by several bands. Intensities of bands that are assigned to organic functional groups decrease with progressing degradation until a nearly constant level is reached that indicates the slow-down of metabolic activities. Bands of some metabolites appear temporarily and disappear. Degradation of organic matter leads to a relative increase of mineral compounds that is reflected by the increase of the corresponding absorption bands (Hesse et al., 1995; Naumann et al., 1996; Haberhauer et al., 1998; Grube et al., 1999; Smith, 1999; Ouattmane et al., 2000; Socrates, 2001; Reig et al., 2002; Smidt et al., 2002; Zaccheo et al., 2002; Chen, 2003; Madejova, 2003; Tan, 2003; Smidt & Schwanninger, 2005; Smidt & Meissl, 2007).

Location wavenumber (cm ⁻¹)	Vibration	Functional group or component
Organic compounds		
2920	C-H stretching (as)	aliphatic methylene group
2850	C-H stretching (s)	aliphatic methylene group
2590-2520	S-H stretching	thiols
1740-1700	C=O stretching	aldehyde, ketone, carboxylic acids, esters
1685-1630	C=O, COO ⁻ stretching C=C stretching	amide I, carboxylates aromatic ring modes, alkenes
1600-1590	C=C	aromatic skeleton
1570-1540	N-H in plane bending	amide II and secondary amines
1515-1505	aromatic skeletal	lignin from lignocellulosic materials
1430-1420	COO ⁻ stretching	carboxylic acids
1350-1250	C-N stretching	primary and secondary aromatic amines
1265-1240	C-O-C stretching C-N stretching	esters amide III
1250-900	C-O-C, C-O C-O-P	polysaccharides phosphodiesteres
Inorganic compounds		
3700-3200	SiO-H stretching	silica
3700-3400	O-H stretching	bonded and non-bonded hydroxyl groups and water
1635	O-H bending	water
1450-1410	C-O stretching	carbonate
1384 (1400-1340)	N-O stretching	nitrate (leachate)
1140-1080	S-O stretching	sulphate
1080	Si-O stretching	quartz
1030	Si-O stretching Si-O-Si stretching	clay minerals silica
875	C-O out of plane bending	carbonate
713	C-O in plane bending	carbonate
680-610	S-O bending	sulphate

Table 1. Location of indicator bands, corresponding vibration and assignment to functional groups and components (as = antisymmetric, s = symmetric)

The nitrate band at 1384 cm⁻¹ in solid waste materials has been proved by addition of KNO₃ (potassium nitrate) (Fig. 1a). The appearance of the nitrate band in the compost spectrum at

an advanced stage of composting corresponds to the evolution of nitrate in the biological process (Fig. 1b). The sharp band shape is an additional indicator of an inorganic compound that does not interact with other molecules as degrading organic molecules do. Both facts support identification of nitrate characterised by a stable band position in solid waste samples (Smidt et al., 2002). It is evident that all background information available contributes to band assignment and spectra interpretation. It should be mentioned that the position of the nitrate band in liquid samples vary in a wider range (cp. freeze-dried leachate in Fig. 5).

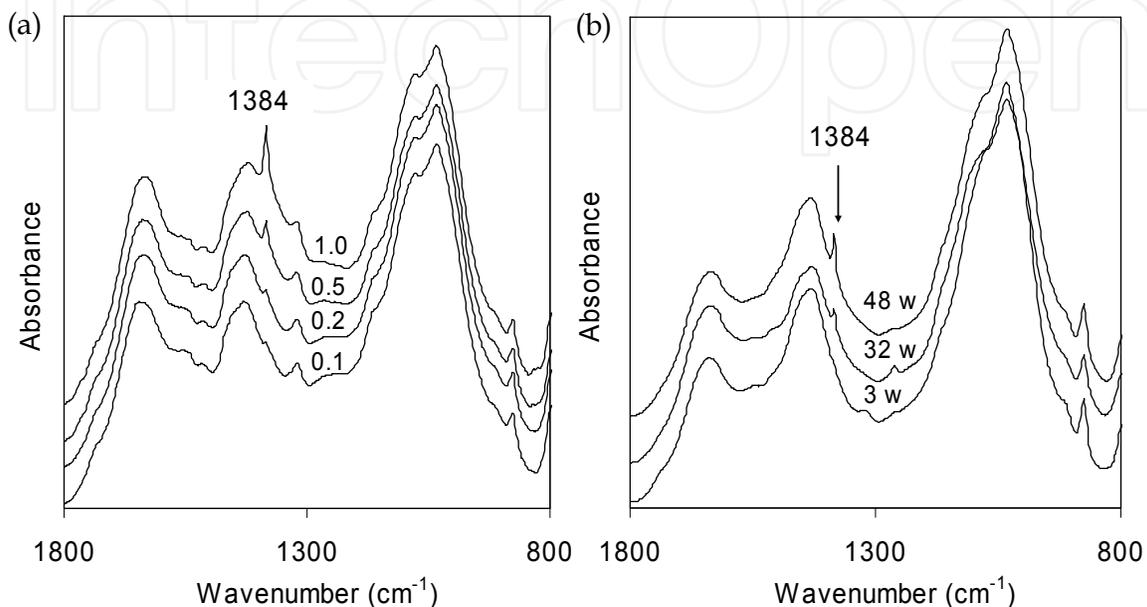


Fig. 1. (a) Increasing nitrate band at 1384 cm^{-1} due to addition of KNO_3 , corresponding to mass fractions of 0.1, 0.2, 0.5, and 1% nitrate; (b) emerging nitrate band during a composting process (3, 32, 48 weeks)

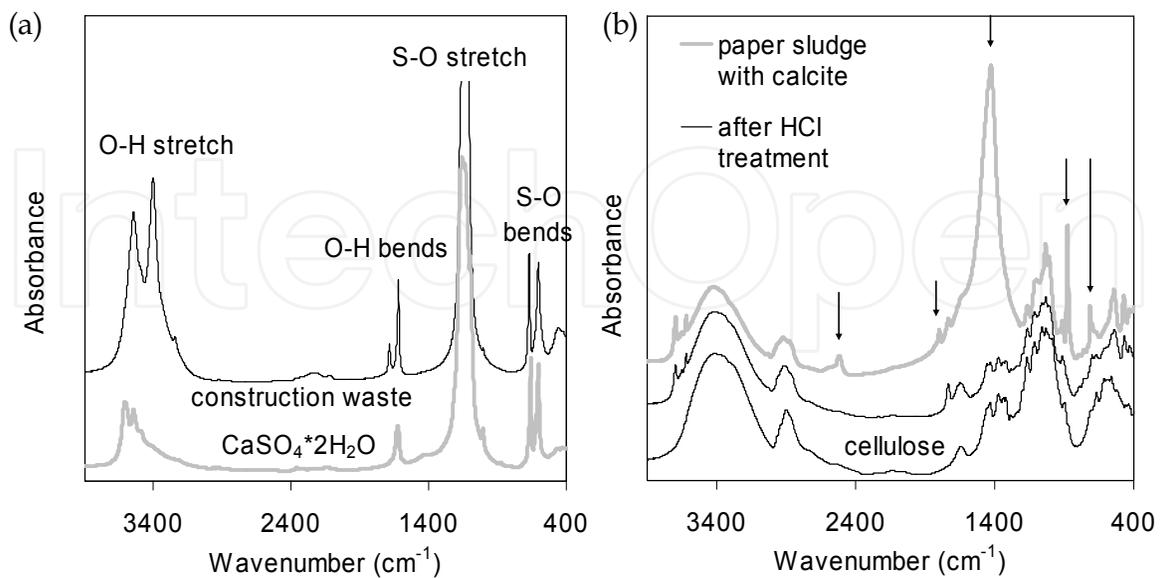


Fig. 2. (a) Infrared spectra of mineral lumps from a construction waste landfill and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; (b) spectral characteristics of the original industrial landfill sample (carbonate bands indicated by arrows), the HCl treated sample and cellulose as reference

Figure 2 shows approaches of band assignment by comparison of waste ingredients with a pure substance and by sample treatment. Figure 2a displays spectra of mineral lumps from a construction waste landfill and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (calcium sulphate) to reveal the specific bands assigned to sulphate that plays a relevant role in leachate. Apart from the sulphate (S-O) stretching and bending vibrations at 1136 cm^{-1} and 620 cm^{-1} , respectively, the mineral lumps also show strong O-H stretching vibrations. Figure 2b illustrates an example of waste material originating from an abandoned landfill with unknown composition. The sample was treated with HCl ($c = 0.1 \text{ mol/L}$) to convert carbonates into carbon dioxide and water, and to reveal bands of other compounds that are overlapped and covered by strong bands of carbonate. Cellulose was identified by comparison with a spectrum of pure cellulose. The material was found to be industrial paper sludge mixed with carbonate for stabilisation before landfilling.

2. Abandoned sites and old landfills

The environmental damages resulting from abandoned landfills and dumps have revealed the problems of careless disposal. At the beginning of a well-regulated and organised waste management system pollutants and toxic substances were in the foreground due to their immediate impact on water and soil. They covered the more subtle contribution of unsuspecting goods of daily use to relevant emissions and their effect on the imbalance in the global carbon budget. The registration of abandoned landfills is part of exploration programmes in terms of risk assessment and adequate remediation measures. The majority of abandoned landfills under investigation contain municipal solid waste and construction waste originating from the sixties and seventies of the last century. The measurement of landfill gas emissions is still state of the art and part of monitoring programmes. Long-path spectroscopic instruments developed for air pollution control are also applied for landfill monitoring. Long-path FT-IR spectroscopic investigations provide several advantages such as fast scanning of large surfaces at long distances without contact and online measurement of emissions from areas that are difficult to access. Due to infrared absorption of many air pollutants they can be detected and quantified by FT-IR long-path instruments (Bacsik et al., 2005). Quantification of gaseous compounds is carried out according to Lambert-Beer's law (Weber et al., 1996; Galle et al., 2001; Hegde et al., 2003). Methane and nitrous oxide are the main components to be measured in the context of landfill monitoring. The measurement of gaseous emissions only provides information on the current microbial activity that depends on environmental conditions such as water supply. The gas forming potential according to the present chemical compounds that could be degraded under appropriate conditions cannot be determined in this way. Preferential gas flows make the quantification of emissions difficult. Due to the missing base seal, the leachate that provides additional information is not available in most cases. Therefore investigations of the solid waste are indispensable.

2.1 Classification of waste materials

The classification of landfilled materials should be a first step. The knowledge about the landfilled material supports the interpretation of data as the composition influences the behaviour, especially biological tests of reactivity. Municipal solid waste (MSW) comprises all components of consumer goods and features a typical spectral pattern. Different pre-treatment and landfilling conditions of MSW lead to divergent spectral characteristics of the

waste material. Old landfills (old-LF) are characterised by the high portion of construction waste. The 5-year-old recent reactor landfill (reactor-LF) differs from the landfill with mechanically-biologically treated waste (MBT-LF) due to the missing pre-treatment. The waste bank represents a special kind of deposit where scarcely biologically treated MSW was piled up to form a constructional wall of about 6 m. Despite the differences in composition and degradation conditions similarities are distinctive. Industrial waste (ind-LF), by contrast, features a more one-sided composition. The following PCAs are based on the mean-centred MIR spectra that cause zero-lines in the scores and loadings plots, indicating the averages of all samples. The PCA supports the discovery of differences and similarities that are visualised by long or short distances between the samples in the scores plot (Figs. 3a, c). They illustrate the differences between landfills containing MSW and an industrial landfill containing carbonate stabilised paper sludge. The loadings plots elucidate how much the spectral regions contribute to the first (PC1, explained variance 69%) and the second (PC2, 15%) principal component (Figs. 3b, d). The PCA calculated with the whole spectrum (Figs. 3a, b) reveals the strong influence of inorganic components, especially of carbonate and clay minerals that dominate the loadings spectrum of PC1. The position of the ind-LF samples found at the positive side of PC1 in the scores plot corresponds to the positive loadings (e.g. at 1420 cm^{-1}). The position of most of the MSW landfill samples found at the negative side of PC1 in the scores plot corresponds to the negative loadings (e.g. at 1030 cm^{-1}). To sum it up: positive loadings plus positive scores = ind-LF with more carbonate (1420 cm^{-1}), negative loadings plus negative scores = MSW landfills with more clay minerals (1030 cm^{-1}). This means that ind-LF and MSW landfills differ basically in composition especially in carbonate and clay minerals. Different types of MSW landfills are distinguished along PC2 that reflects the development from reactor-LF to old-LFs. Apart from inorganic compounds (clay minerals) spectral regions that can be assigned to organic functional groups (2920 and 1640 cm^{-1}) become more relevant in the loadings spectrum (Fig. 3b). The characteristics are in accordance with higher organic matter contents and reactivity in the reactor-LF compared to old-LFs that display higher mineral contents due to mineralisation and a portion of construction waste. However, the transition from one landfill type to another one is not distinct as old-LFs can still feature more reactive sections. Vice versa, the reactor-LF also contains sections of low organic matter content and moderate reactivity. Most of the material from the 15-year-old waste bank is located in the scores plot between the reactor-LF and the old-LFs. The variance within the bank samples is caused by different environmental conditions and development during the 15-years of disposal. More details were reported by Smidt et al. (2007).

Figs. 3c and 3d present the scores plots and the loadings spectra of a PCA that was based on the organic indicator bands represented by C-H and C=O vibrations. Separation of MSW landfill types due to organic compounds is performed along PC1. MSW landfill types and the ind-LF are differentiated along PC2. In terms of these characteristics several old-LF samples move closer to ind-LF samples in the scores plot. This indicates a weaker discrimination power of the selected spectral regions.

The PCA is an appropriate tool to obtain a general idea on the similarities and differences of waste materials and the contributing spectral regions. For practical application the development of classification models is indispensable in order to immediately attribute waste materials to defined classes depending on the problem to be solved. A classification model according to SIMCA was reported by Smidt et al. (2008b) to distinguish different waste materials.

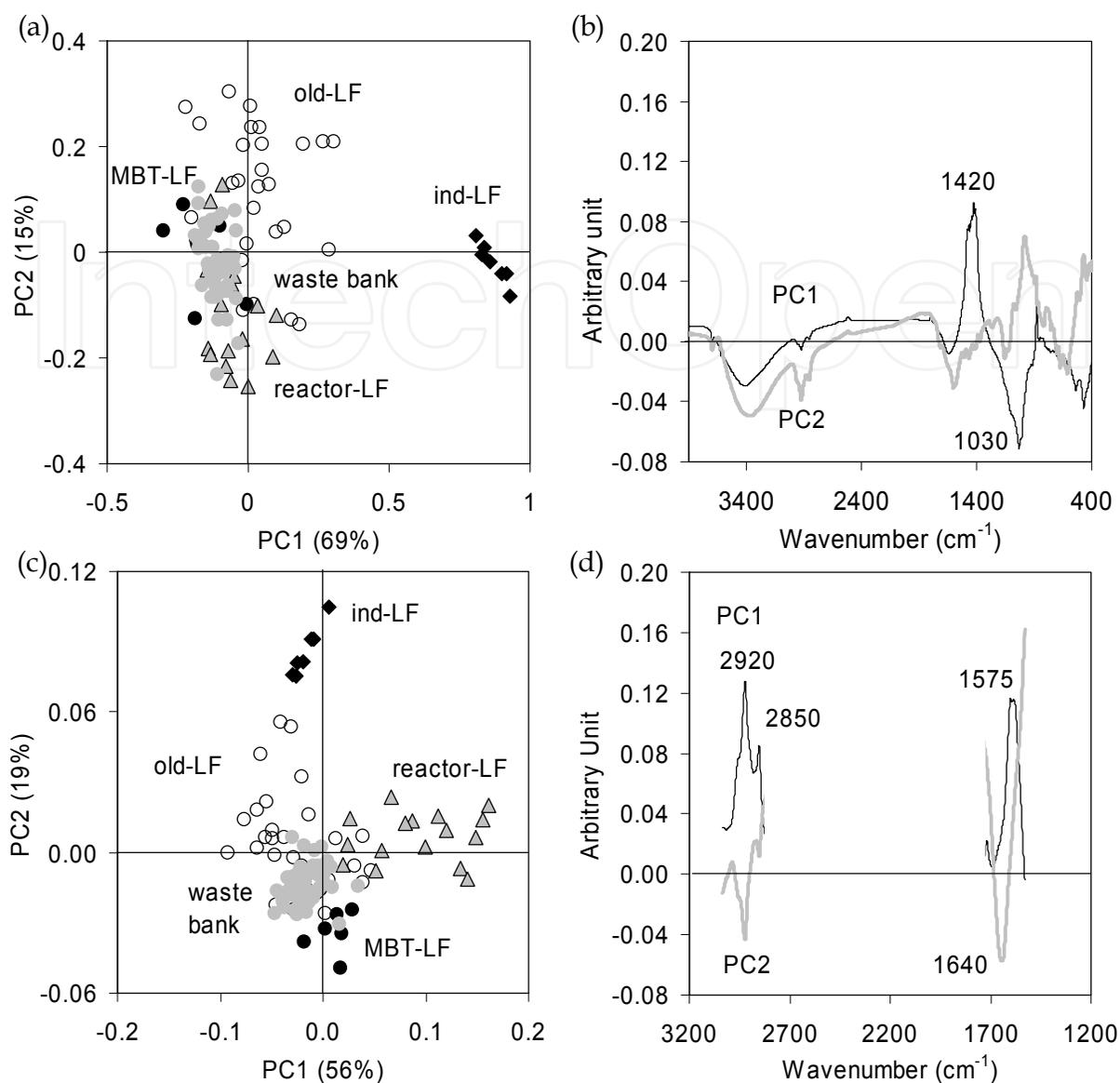


Fig. 3. Scores plots and loading spectra of samples from landfilled wastes based on the whole spectra (a, b) and on selected wavenumber regions from 3030 to 2800 cm^{-1} and from 1795 to 1530 cm^{-1} (c, d)

2.2 Risk assessment of abandoned landfills and dumps regarding the reactivity

The careless landfilling of waste in the past has caused extensive investigations to assess the remaining risk and the necessity of remediation measures. In this context the stability of waste organic matter is a fundamental criterion (Binner & Zach, 1999; Tesar et al., 2007; van Praagh et al., 2009). The proof of stability can be carried out by means of time-consuming biological tests that provide information on the current microbial activity under aerobic conditions and the gas forming potential under anaerobic conditions. These tests were primarily established for MBT waste to verify its stability prior to landfilling (Binner & Zach, 1999; Adani et al., 2004). The dissolved organic carbon (DOC) and the total organic carbon (TOC) are relevant parameters for the assessment of abandoned landfills according to the Austrian Landfill Ordinance (BMLFUW, 2008). The DOC provides information on

soluble organic compounds. Their portion decreases with progressing stabilisation. The stipulated limit values of TOC restrict the organic matter content in all landfill types. Only for MBT waste the TOC limitation is not valid. Figure 4 shows the correlation between predicted and measured (references) parameters using selected regions of the MIR spectrum and PLS-R. The model parameters are summarised in table 2.

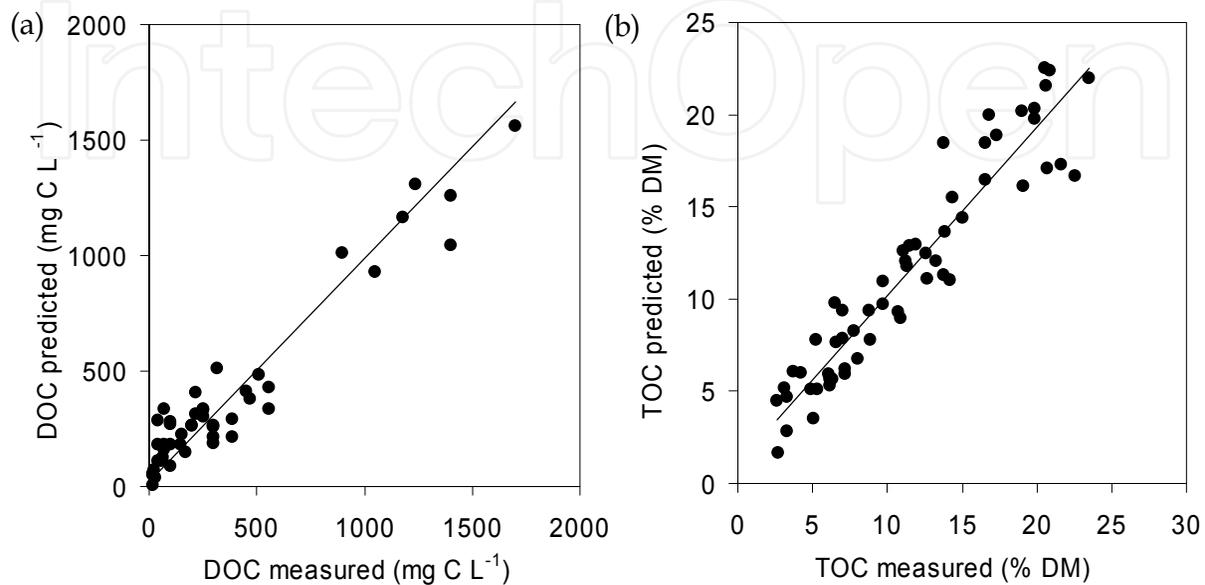


Fig. 4. Correlation between (a) the predicted and the measured DOC and (b) the predicted and the measured TOC, both based on the spectral ranges from 3003 - 2816 and 1770 - 400 cm^{-1} and PLS-R

Model parameters	DOC	TOC
Wavenumber ranges (cm^{-1})	3003 - 2816 and 1770 - 400 cm^{-1}	
Calibrated range	15 - 1700 mg C L^{-1}	2.6 - 23.5 % DM
R^2	89%	90%
RMSECV	158 mg C L^{-1}	1.9 % DM
RPD	3.0	3.1
No. of PLS components	6	7
Bias	-5.94	-0.0719

Table 2. Parameters for the PLS-R models dissolved organic carbon (DOC) and total organic carbon (TOC) content

2.3 Success control of remediation measures

In situ aeration of old reactive landfills is one measure to avoid methane emissions and to accelerate mineralisation in that anaerobic conditions are exchanged for aerobic ones. The spectral pattern of the solid waste matrix reflects the chemical changes mainly by decreasing band heights of organic functional groups (Tesar et al., 2007). Aeration of the solid waste is paralleled by oxidation of soluble components in the leachate. The most conspicuous changes in the spectral pattern are caused by transformation of N-H and S-H groups containing compounds to the mineralisation products nitrate and sulphate that are

presented in the spectrum by strong bands of the N-O and the S-O vibrations (Smidt & Schwanninger, 2005; Smidt & Meissl, 2007). ATR spectra (4000 – 600 cm^{-1}) of freeze-dried leachate from aerated landfill material and leachate from landfill material under anaerobic conditions were classified by means of PLS-DA (Fig. 5). The corresponding loadings spectrum of the 1st PLS component (Fig. 5b) shows the relevant regions, especially the S-O, N-O, C-H, S-H and N-H vibrations (Table 1) that contribute to the discrimination of leachate obtained from materials under different aeration conditions. Three PLS components explain 97% of the total variance, whereas the 1st one already explains 94%, indicating a distinct differentiation and the efficiency of aeration.

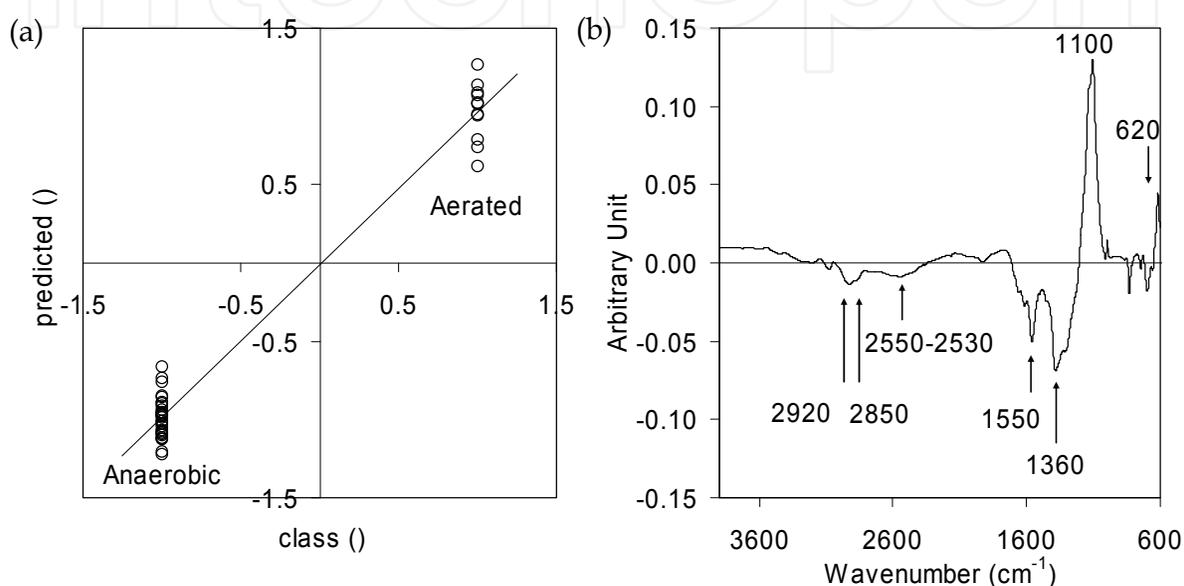


Fig. 5. PLS-DA results based on spectral data of freeze-dried leachate from landfill material under anaerobic and aerated conditions: (a) correlation between predicted and class (dummy variable) and (b) loadings spectrum of the 1st PLS component

2.4 Long-term behaviour of deposits

The long-term behaviour of landfills and dumps is a relevant issue with respect to remediation activities and the re-use of these areas. Although organic matter degradation leads to similar metabolic and mineralised products, the individual composition causes a specific spectral pattern as shown in figure 3. MSW that had been piled up to a waste bank (Fig. 3) showed different characteristics after 15 years corresponding to depths and air supply. Aerobic conditions in the upper layer of the profiles accelerated degradation and corresponding changes in the spectral pattern (Smidt et al., 2007). The classification of samples according to specific stages of degradation by means of spectral characteristics is a fast method for the risk assessment of abandoned landfills, besides the precise determination of relevant parameters as shown in section 2.2. The long-term behaviour is strongly influenced by both the chemical composition and environmental conditions.

The scores plot and loadings spectra in figure 6 illustrate the distance of samples and the responsible spectral regions. The samples originated from an old landfill. They were taken as a composite sample along the depth profile. Two samples (black dots) that were collected between tight clayey layers, where degradation was inhibited, differ considerably from the other ones. The loadings spectra of PC1 and PC2 reveal the strong influence of mineral

compounds ($1430 - 400 \text{ cm}^{-1}$). The loadings spectrum of PC1 additionally shows the contribution of organic components (1630 cm^{-1}). Besides the poor mineralisation the enclosed material was protected against degradation and subsequent mixing with construction waste.

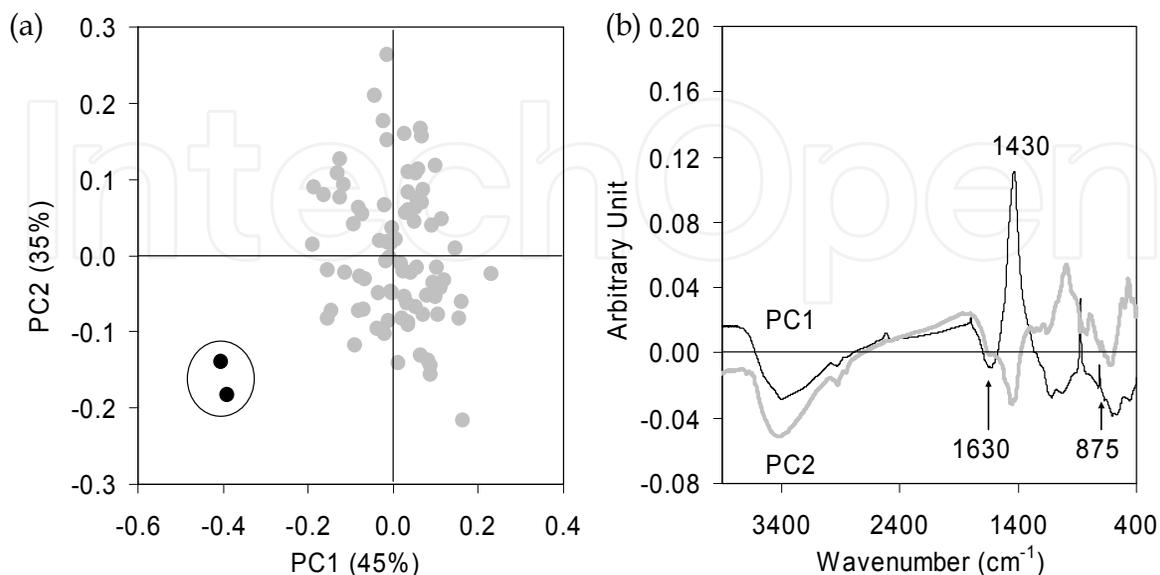


Fig. 6. PCA based on spectra of samples from an old landfill; (a) scores plot with 2 samples (black dots) between tight clayey layers, (b) loadings spectra of PC1 and PC2

3. Separation of recyclables and mechanical-biological or thermal pre-treatment of municipal solid waste prior to landfilling

The maximum possible separation of recyclables is a crucial issue. In addition to the individual separation by the waste producer, the recovery of recyclables is improved by mechanical sorting systems in the plant. The pre-treatment of municipal solid waste prior to landfilling comprises two main strategies: the mechanical-biological and the thermal treatment. Both processes aim at reducing reactivity, either by mineralisation and stabilisation or by incineration of organic matter.

3.1 Identification and separation of recyclables by NIR spectroscopy

The development of mechanical separation and sorting systems has become an important technical approach in the improvement of the recycling proportion and the required quote respectively. Identification of different materials is a prerequisite in order to achieve an efficient and correct separation. NIR spectroscopy is an appropriate tool for a comprehensive characterisation of wastes (Bonifazi et al., 2009) and differentiation of polymers. In this field of application the measurement in the near infrared area ranks first (Feldhoff et al., 1997; Van Den Broek et al., 1998; Kulcke et al., 2003; Leitner et al., 2003; Li et al., 2005; Dou et al., 2006; Luiken & Bos, 2010).

3.2 Mechanically-biologically treated (MBT) waste - process control and compliance with limit values according to the Austrian Landfill Ordinance

National and international regulations and limit values for MBT waste require verification of compliance before final disposal. For MBT waste reactivity and stability are relevant

properties. Process kinetics, the release of organic components and their long-term behaviour are fields of intensive research in waste management (Barlaz et al., 1990; Barlaz, 1998; Tintner et al., 2010). Despite the scientific interest, the performance of industrial processes strongly depends on this basic knowledge. Waste organic matter primarily consists of non-hazardous organic molecules responsible for the reactivity of the material and emerging gaseous and liquid emissions. Chemical and physical sum parameters are preferably applied for waste characterisation in practice. Waste organic matter is usually quantified by the determination of loss of ignition, TOC and nitrogen content. The significance of these parameters is limited as they do not differentiate the particular behaviour of the molecules subsumed therein. Mineralisation products of organic matter such as ammonium and nitrate provide information on progressing biological degradation. High ammonium contents are assigned to early stages of degradation, whereas nitrate indicates the late phase when ammonium has been oxidised. Nevertheless, a wide range of contents is observed during the biological treatment. The coexistence of ammonium and nitrate and the repeated increase and decrease of ammonium contents make unambiguous assessment difficult. Last but not least these parameters depend on the uniformity of metabolic processes in the rotting unit. The equal progress is strongly related to process operation in terms of mechanical mixing and evenly distributed aeration and moisture.

Biological tests provide more comprehensive information on reactivity in that chemical properties of all compounds contribute to the behaviour of waste materials under aerobic and anaerobic conditions. Biodegradability of organic compounds is revealed by the oxygen uptake or CO₂ release due to microbial activity, indicating mineralisation of organic molecules. The gas sum over a period of 21 days, generated under anaerobic conditions, is measured by means of the incubation test (Austrian Standards Institute, 2004). For MBT materials to be landfilled biological tests replace the determination of the total organic carbon content (TOC) because the limit value of 5% dry matter for this landfill type cannot be achieved by biological degradation only. However, biological parameters are time-consuming and require considerable expertise. In addition to biological tests limitation of the calorific value by 6600 kJ kg⁻¹ dry matter was stipulated for MBT waste. The calorific value indicates the efficiency of plastic separation and progressing degradation of organic matter by its decline (BMLFUW, 2008). Chemical changes during the biological treatment of MSW are reflected by spectral characteristics that allow a fast process control, evaluation and optimisation. The progress of organic matter degradation is influenced by the technical system and process operation. The development of spectral characteristics is illustrated in figure 7. Fresh input materials feature strong aliphatic methylene bands at 2920 and 2850 cm⁻¹. Absorption bands of organic components (cp. Table 1, cellulose) decrease or disappear as far as they indicate temporarily present metabolic products (1740, 1320 cm⁻¹). This process showed extensive mineralisation after 9 weeks. It can be assumed that the chemical composition of MSW is related to the biological behaviour. PLS-R models based on MIR spectra were developed for the prediction of the biological parameters "respiration activity" and "gas generation sum" to get information on reactivity of MBT waste faster (Böhm et al., 2010a). Bands that feature considerable changes during the biological treatment such as the aliphatic methylene bands and the fingerprint region (1788 - 1532 cm⁻¹, 1350 - 1028 cm⁻¹), were selected for the prediction models.

The loadings spectrum of the first PLS component out of 8 (Fig. 8b) indicates that organic (methylene bands) and inorganic (carbonate bands at 1430 and 875 cm⁻¹) compounds contribute to the thermal behaviour of the waste sample. Whereas waste organic matter

causes the calorific value to increase, water and carbonates affect its decrease due to the endothermic reactions of water evaporation and carbonate decay.

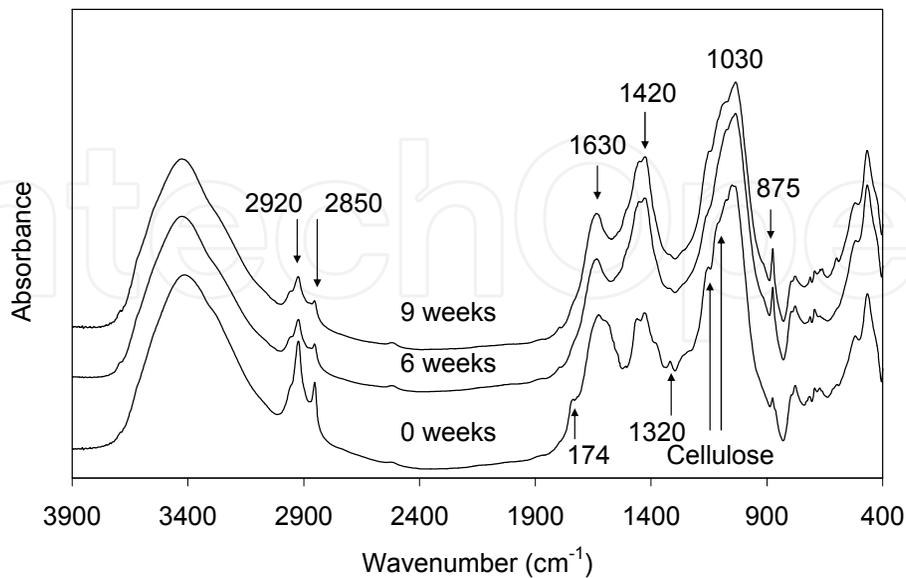


Fig. 7. Changing spectral characteristics of MSW during the biological treatment

Figure 8 illustrates the correlation between the predicted and the measured calorific value of the PLS-R model (Model parameters: $R^2 = 76\%$, $RMSECV = 711 \text{ kJ kg}^{-1}$ dry matter (DM), $RPD = 2.1$; bias = 2.1).

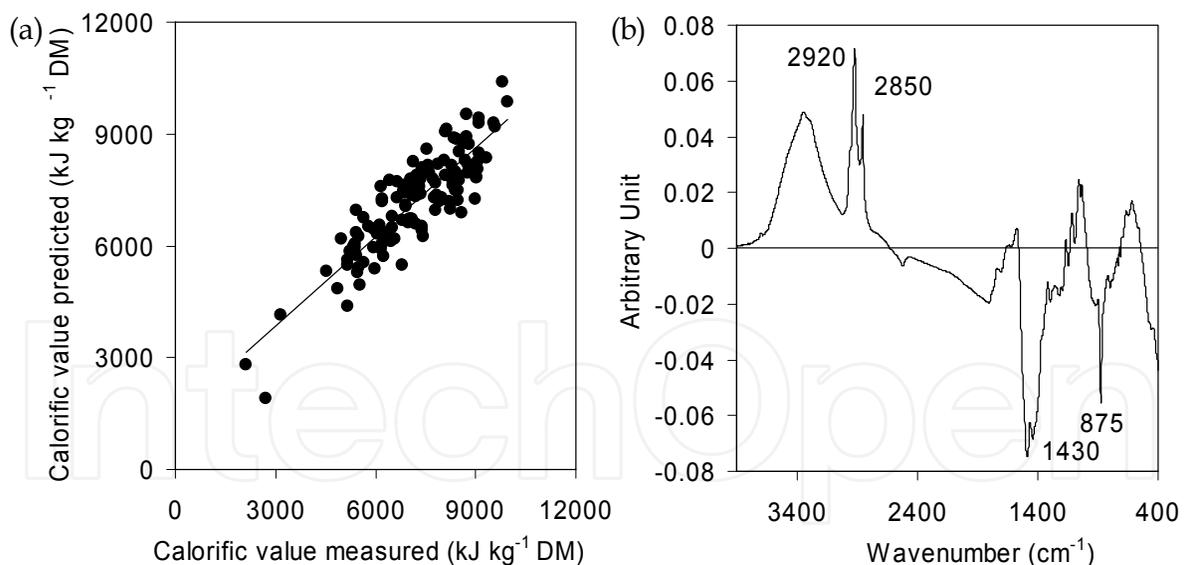


Fig. 8. (a) Correlation between the predicted and the measured calorific values based on the whole MIR spectrum, (b) the corresponding loadings spectrum of the 1st PLS component

3.3 Thermal treatment of MSW - natural and accelerated ageing (carbonation) of MSW incinerator bottom ash

Inorganic residues from incineration have gained in significance during the last decades due to the increase of the thermal treatment of waste for energy recovery. The long-term behaviour of landfilled bottom ash, the process of carbonation and the fate and release of

heavy metals all dependent on the ageing process, have become relevant topics. In figure 9a the main differences between spectra of MSW (I) and MSW incinerator bottom ash (II) are elucidated. Spectra of incineration residues differ from MSW by the loss of bands that are assigned to organic functional groups. Figure 9b illustrates two spectra of MSW incinerator bottom ash before (III) and after CO₂ exposure (IV), two spectra of a bottom ash deposit from a depth of 50 cm (V), from the surface (VI), and a spectrum of the calcite reference. It is evident that the progress of carbonation in abandoned deposits depends on the available surface and the access of air. Carbonates that are part of MSW decay during incineration above 650 °C. The reaction of CaO with water leads to Ca(OH)₂ which causes the pH-value of the inorganic residues to increase.

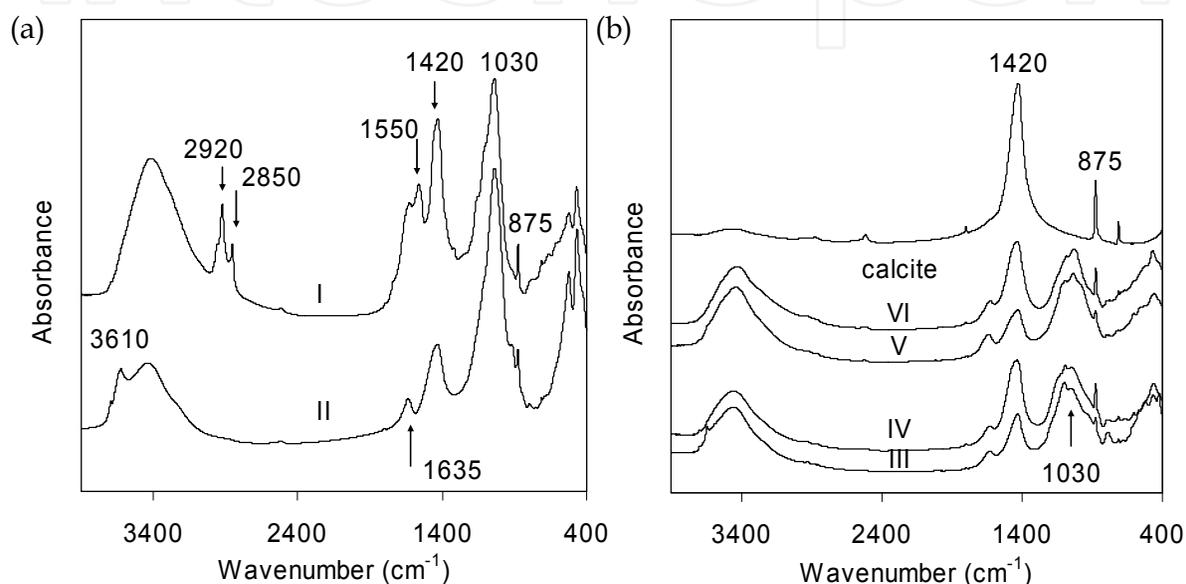


Fig. 9. Spectra of (a) MSW (I) and MSW incinerator bottom ash (II) and (b) MSW incinerator bottom ash (III) before and (IV) after CO₂ exposure, two samples from different depths (V = 50 cm and VI = surface layer) of a bottom ash deposit and the spectrum of the reference (calcite)

The uptake of CO₂ from air effects carbonation. This process in the opposite direction leads to stabilisation, immobilisation of heavy metals and the decrease of the pH-value to a neutral level (Chimenos et al., 2000; Poletini & Pomi, 2004; Rendek et al., 2006). This process can be accelerated by forced CO₂ supply (Mostbauer et al., 2008).

The ageing and stabilisation of incinerator bottom ash are solely chemical processes compared to the stabilisation of waste organic matter that is promoted by microbial activity. Carbonation is reflected by the increase of typical “carbonate bands” (Table 1) in the spectrum. Quantification of carbonates in MSW incinerator bottom ash by means of FT-IR spectra leads to reliable results (Smidt et al., 2009). The standard method is based on the measurement of the CO₂ release from carbonates by acid treatment which can be affected by the complex matrix.

4. Recovery of biogenic waste materials, secondary products

In the context of resource recovery biogenic waste materials have become important ingredients for valuable composts that are applied as soil conditioners. Composting has been practiced for many centuries all over the world at different technical levels (Ahmad et

al., 2007). The variety of biogenic waste materials available from the public separate collection and from industrial processes requires quality criteria and suitable input materials for specific applications. This purpose has been stipulated by the Austrian Compost Ordinance (BMLFUW, 1992). The limitation of heavy metals and pollutants is in the focus of legislation. Nutrients (Courtney & Mullen, 2008), humic substances (Meissl et al., 2007; Smidt et al., 2008d) and phytosanitary properties (Bruns et al., 1996; Erhart et al., 1999) are additional quality criteria that emphasise the positive effects on plants and soils and improve the reputation of composts. Biogenic waste and sewage sludge are usually processed in composting plants whereas manure compost is produced locally by farmers.

4.1 Differentiation of various input materials and assignment of composts to specific biogenic waste materials

Figure 10 displays five composting processes in different plants, grouped by a PCA.

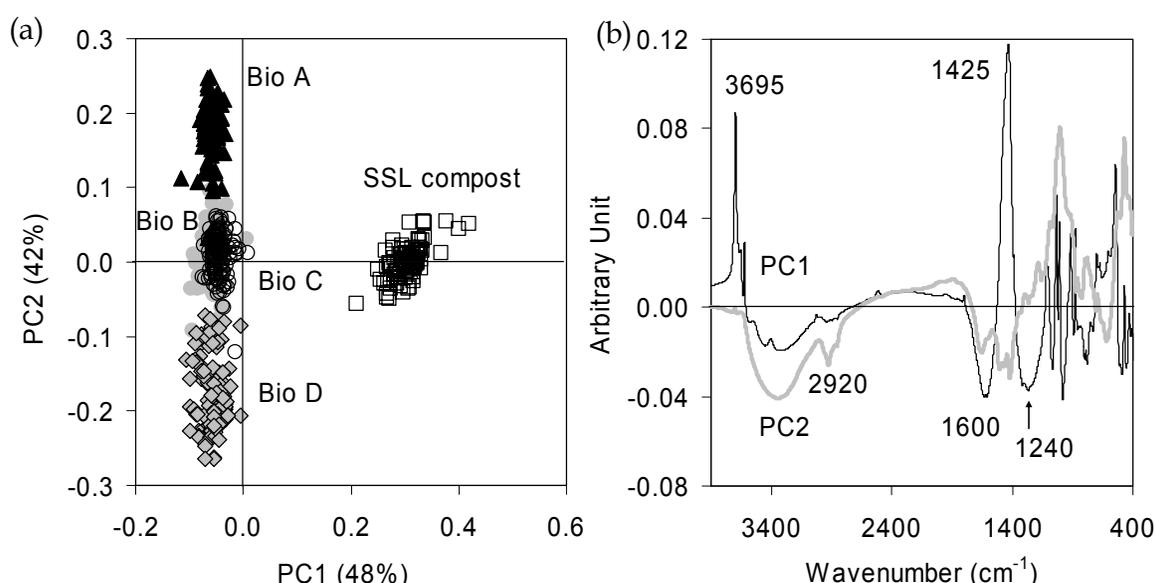


Fig. 10. (a) Scores plot and (b) loadings spectra (PC1 and PC2) of a PCA based on spectral characteristics of five different composting processes (Bio = biowaste, SSL = sewage sludge)

Input materials are distinguished by their characteristic spectral pattern. Along PC1 the particular composition of biowaste and sewage sludge compost contributes to the separation. Biowaste composting processes (Bio A-D) are separated along PC2 according to specific features such as anaerobic pre-treatment (Bio D) or addition of mineral compounds (Bio A). Bio B and Bio C represent the typical mixture of yard and kitchen waste that is processed in open windrow systems.

The loadings spectra of PC1 and PC2 indicate the relevant bands that contribute to the differentiation of composts: mineral components, O-H vibrations of kaolin at 3695 and 910 cm⁻¹ (additive to sewage sludge compost) and organic components at 1600 cm⁻¹ (aromatic compounds such as humic substances) and at 1240 cm⁻¹ (C-O vibrations).

4.2 Process control during the aerobic treatment (composting) of biowaste (yard waste, market waste) and sewage sludge

The degradation of organic matter during composting goes through several phases. The most intensive rotting phase is paralleled by high microbial activity indicated by the high

oxygen demand and the release of metabolic products such as ammonium and volatile fatty acids responsible for odour emissions. During the maturation phase the respiration activity reaches a nearly constant low level. The increasing pH-value affects losses of ammonia. Oxidation of ammonium causes nitrate contents to increase. Compost maturity is characterised by a C/N ratio of 10 - 12 (Ouatmane et al., 2000), low microbial activity and plant compatibility that has to be verified by plant tests according to the Austrian Compost Ordinance (BMLFUW, 1992). Figure 11 and 12 show different stages of three composting processes by spectral characteristics. The indicator bands (cp. Table 1) that are identifiable by visual inspection are the same as indicated for MSW. Nevertheless, the complete pattern of composts differ sufficiently to separate MSW from biogenic waste as shown by the SIMCA classification model (Smidt et al., 2008b). Figure 11a illustrates a typical biowaste composting process over a period of 121 days. Apart from organic matter mineral compounds such as carbonates and clay minerals are usually occurring constituents in biowaste from the separate collection. Their relative increase due to mineralisation of organic substances is obvious. Figure 11b demonstrates the degradation of straw mixed with liquid manure in a fast composter device during a period of nine days. The spectra are dominated by straw characteristics. It is evident that straw is only partially degraded during the short period of composting. Besides the disappearing band at 1720 cm^{-1} and the decreasing band at $1260 - 1230\text{ cm}^{-1}$ that can be assigned to esters in e.g. hemicelluloses (Stewart et al., 1995) and the decreasing bands at 1165 and 1060 cm^{-1} (cellulose marked by arrows in the spectrum) intact cell structures are indicated by sharp and distinct bands in the wavenumber region $1520 - 1200\text{ cm}^{-1}$. Figure 12 demonstrates the development of primary sludge and anaerobically stabilised sludge from a wastewater treatment plant to sewage sludge compost. The latter originates from a composting plant. The FT-IR spectrum of the primary sludge is dominated by bands that can be assigned to cellulose, hemicelluloses (1740 and 1240 cm^{-1}) and to the microbial biomass that is identified by aliphatic methylene and amide bands. The mature sewage sludge compost features low methylene bands and a considerable nitrate band at 1384 cm^{-1} . Due to the specific mixture in the composting plant the portion of clay minerals is higher, the carbonate content lower.

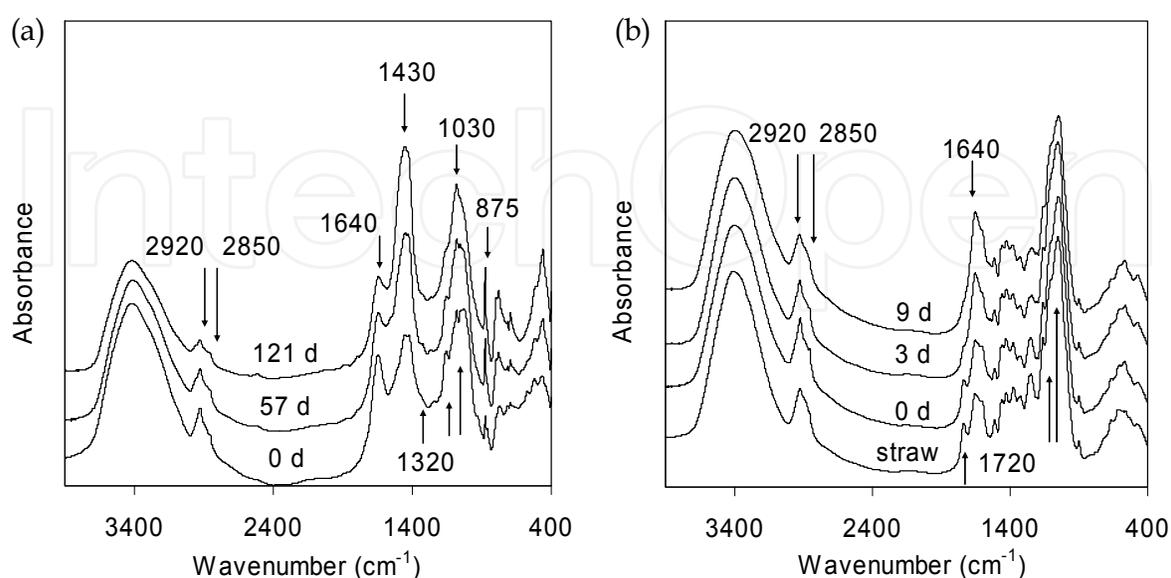


Fig. 11. Development of spectral characteristics during composting processes of (a) biowaste and (b) straw/liquid manure

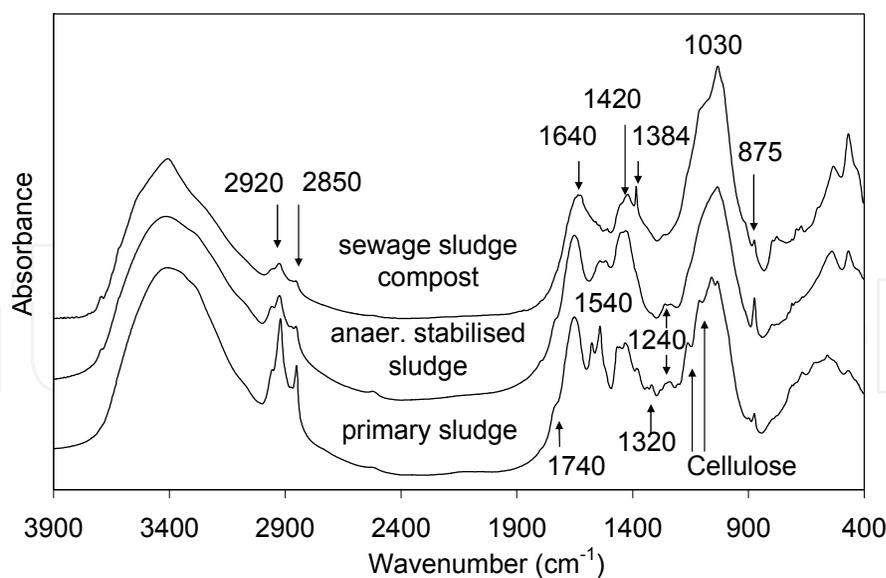


Fig. 12. Spectra of different process stages of sewage sludge treatment and composting

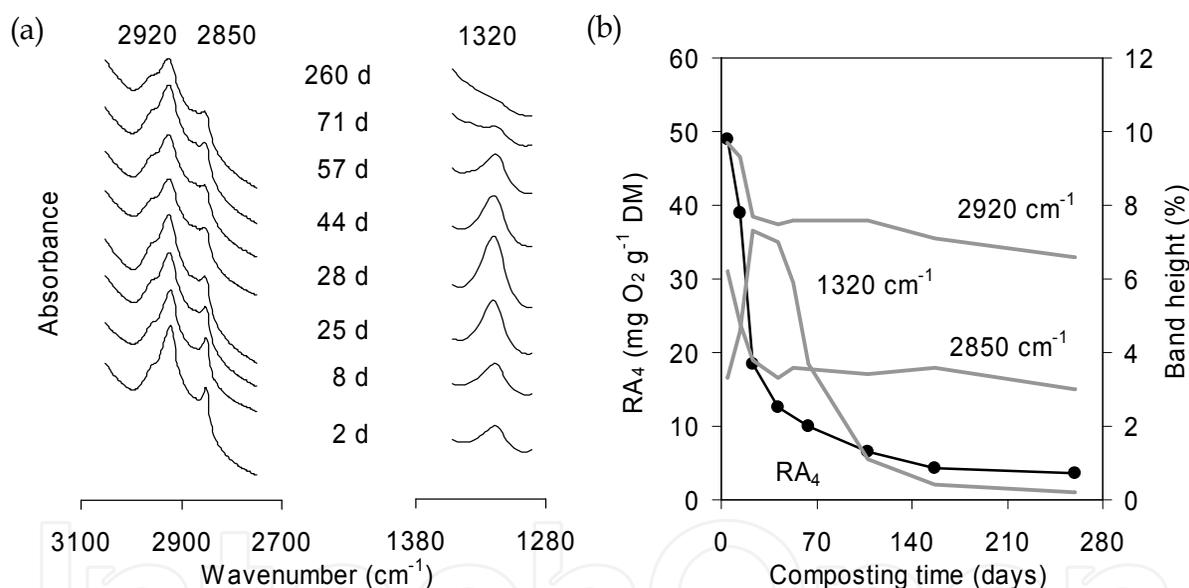


Fig. 13. (a) Decreasing aliphatic methylene bands at 2920 and 2850 cm^{-1} , emerging and disappearing band at 1320 cm^{-1} ; (b) development of corresponding relative band heights and respiration activity (RA_4) during a biowaste composting process (2-260 days)

Data evaluation can be performed in different ways. Changing heights or areas of bands indicate the progressing mineralisation. Haberhauer et al. (1998) suggested the ratio of band heights (2920 cm^{-1} /1640 cm^{-1}) as an indicator of stability. Figure 13a shows the development of selected bands (2920, 2850, and 1320 cm^{-1}), figure 13b the corresponding band heights during a biowaste composting process over a period of 260 days. The individual band height is expressed in per cent of ten measured band heights in the spectrum (Smidt et al., 2002). Aliphatic methylene groups are part of many biomolecules with different degradability. Degradation of easily degradable substances is indicated by the decreasing band height at 2920 and 2850 cm^{-1} that reached a low constant level (Fig. 13). Recalcitrant

molecules such as long chain fatty acids and waxes are responsible for the remaining weak bands. They are still found in soil organic matter (Jandl et al., 2002). The emerging and disappearing band at 1320 cm^{-1} that can be assigned to amines shows the typical behaviour of metabolic products that are temporarily visible in the spectrum. The corresponding microbial activity of the composting process is indicated by the respiration activity over a period of 4 days (RA_4). The interaction of microbial activity and changing chemical composition is revealed by the conformity of the curves, each of them reflecting process kinetics.

4.3 Quality assessment of the final product - prediction of parameters using PLS-R

For products such as compost, quality criteria have been defined and require analytical control. Various parameters are involved depending on the waste material to be investigated. Waste organic matter is affected by different mechanisms of degradation and transformation. Composts that comply with quality standards according to the Austrian Compost Ordinance (BMLFUW, 1992) leave the waste management regime and become products for soil amelioration. Mineralisation and humification contribute substantially to stabilisation. Whereas mineralisation causes enrichment of scarcely degradable substances, humification leads to synthesis of new biomacromolecules. Therefore humification counteracts carbon losses by CO_2 release in that it is fixed in humic substances. Extractable humic acids are a suitable parameter for assessing the increase of stable humic substances in composts. Prediction of humic acid contents and respiration activity (RA_4) by FT-IR spectroscopy and PLS-R is an adequate approach for avoiding the time consuming procedure of humic acid (HA) and RA_4 determination. Prediction models being valid for biowaste composts were developed by Meissl et al. (2007; 2008a). Additional PLS-R models for TOC and total nitrogen (TN) were established by Böhm et al. (2010b). Table 3 compiles the parameters for the TOC, TN, RA_4 , and HA prediction models. The quality of the models depends on the precision of the reference analyses. Considering this fact all developed MIR based PLS-R models are suitable for practical application, especially for time-consuming parameters such as the determination of humic acid contents and respiration activity.

Model parameters	TOC	TN	RA_4	HA
Wavenumber ranges (cm^{-1})	3000-2800, 1790-1492, 1373-1030			1745-1685, 1610-1567
Calibrated range	9.4 - 27.3 % DM	0.9 - 2.6 % DM	1.0 - 60.6 $\text{mg O}_2\text{ g}^{-1}$ DM	4.5 - 45.6 % ODM
R^2	89%	83%	88%	88%
RMSECV	1.3 % DM	0.14 % DM	2.9 $\text{mg O}_2\text{ g}^{-1}$ DM	2.4 % ODM
RPD	3	2.4	2.9	2.9
No. of PLS components	6	9	7	7
Bias	0.005	0.001	-0.01	0.004

Table 3. Parameters of the models for total organic carbon (TOC), total nitrogen (TN), humic acids content (HA), and respiration activity (RA_4); ODM = organic dry matter

Prediction of commonly used parameters in waste management has been reported by several authors, especially for composts (Reeves & Van Kessel, 2000a; Reeves & Van Kessel, 2000b;

Michel et al., 2006; Huang et al., 2007). Apart from organic matter, TOC, TN and nutrient contents, both physical and biological parameters were predicted by FT-NIR spectroscopy.

4.4 Compost application on soils; development of soil organic matter by compost application – characterisation of humic acids by FT-IR spectroscopy

The loss of organic matter in soils by agricultural activities has become a serious problem in many countries (Montanarella, 2002). The application of composts is an appropriate measure for improving the stable organic matter content long-term (Franko et al., 1997; Jensen et al., 1997; Li et al., 1997) as confirmed by field experiments. Figure 14a visualises the increase of humic acid contents (% ODM) in three different plots of agricultural soil where well humified biowaste compost has been applied since 1994, 1999 and 2004 (C). These plots were compared to the reference soils (R) without any amendment. The spectral region of aromatic compounds where humic acids are expected ($1610 - 1567 \text{ cm}^{-1}$) were selected (Meissl et al., 2007; Meissl et al., 2008a). The increase is visualised by the highlighted area in figure 14b ($1610 - 1567 \text{ cm}^{-1}$) between the spectra of the reference soil (R) and of the soil with compost application (C). It corresponds to the duration of compost application (Smidt et al., 2008c). Humic acids belong to the stable organic matter fraction in soils with low turnover rates. Regarding the age of soil humic acids and the diversity of these molecules the question arises, if compost humic acids are similar regarding the composition and stability. Figure 15a demonstrates the changing spectral pattern of compost humic acids after 4, 25 and 260 days of composting. In the scarcely composted material humic acids feature strong aliphatic methylene bands and bands that can be assigned to polysaccharides ($1150 - 950 \text{ cm}^{-1}$). In the mature compost, spectral characteristics become similar to soil humic acids. The intensity of the band at 1030 cm^{-1} is caused by impurities of clay minerals that were not completely separated by the extraction procedure of soil humic acids (Smidt et al., 2008d).

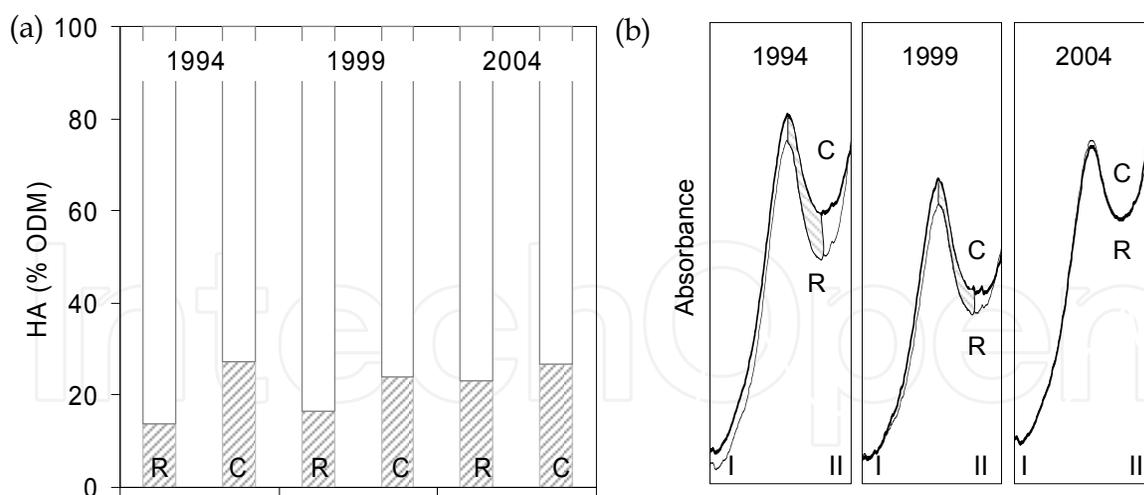


Fig. 14. Increasing contents of stable organic matter in agricultural soil due to compost application since 1994, 1999 and 2004, verified by (a) increasing humic acid (HA) contents (shaded bar) and (b) corresponding spectral characteristics (C = compost amended soil, R = reference soil, presented wavenumber region $1795 \text{ (I)} - 1505 \text{ (II)} \text{ cm}^{-1}$)

Lignin is known to serve as a precursor in humic substance formation (Tan, 2003). A lab scale composting process with biogenic waste was carried out to reveal the effect of lignin on humic acid synthesis. Addition of 5% lignin from an industrial process could improve

the humic acid content in the mature compost compared to the reference without lignin application. Figure 15b shows the spectra of freeze-dried humic acids extracted from the fresh biogenic waste with lignin addition (1 d), from the 42-day-old compost with lignin (42 d) and from the reference without lignin (R-42 d). Whereas spectral characteristics of lignin are clearly visible at the beginning (1 d), they disappear during the progressing process (42 d). Humic acids become similar to the reference. Based on FT-IR spectra it can be assumed that lignin building blocks were integrated in the humic acid molecule (Smidt et al., 2008a).

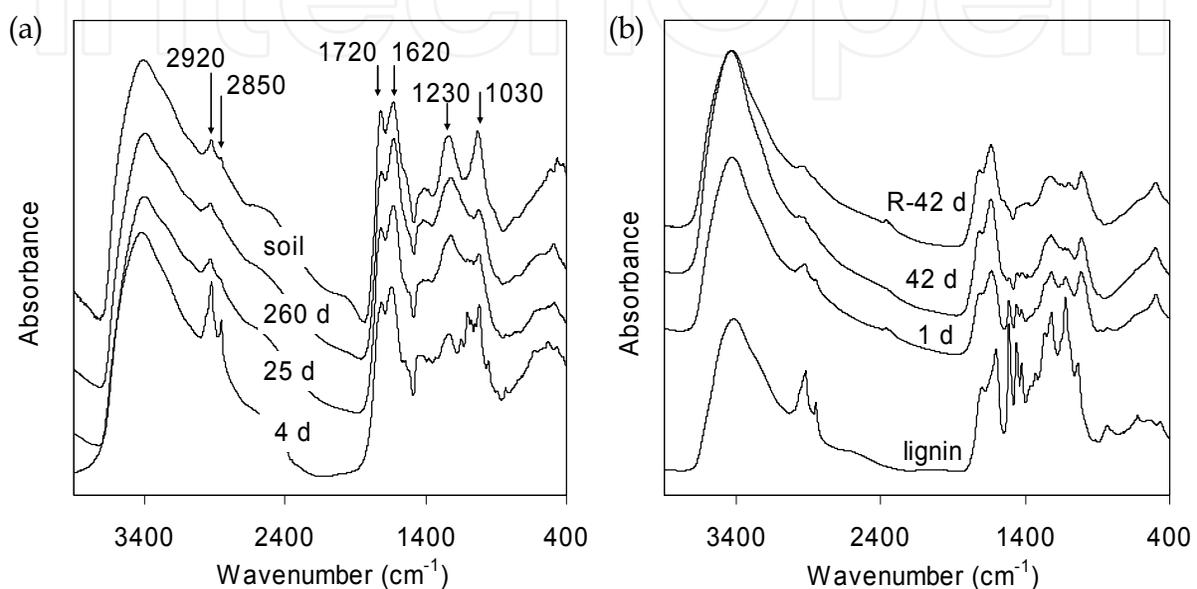


Fig. 15. (a) Spectral pattern of humic acids originating from a biowaste composting process (4, 25, 260 days) and from soil; (b) integration of lignin in compost humic acids

5. Conclusion

The application of FT-IR spectroscopy in waste management provides fast, cheap and reliable process and product control. Moreover, environmental monitoring can be based on spectral characterisation. Besides conventional methods of spectral data evaluation multivariate statistical methods enable the extraction of the inherent information. The development of classification and parameter prediction models is a prerequisite for using this analytical tool in waste management practice. There are many perspectives for the adoption of the method in this area. Depending on the questions to be answered tailor made models can be developed in order to replace time-consuming analyses. The strength of FT-IR spectroscopic investigations is the comprehensive characterisation of complex materials by their unique signature. Due to the small sample amount used for infrared spectroscopic measurements careful sample preparation is a crucial issue in view of the heterogeneous mixture of waste materials.

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