

Interpretation approaches of infrared-spectroscopic waste analysis in order to assess biological stability

Maria Tesar and Katharina Meissl

Institute of Waste Management, Dept of Water, Atmosphere and Environment,
University of Natural Resources and Applied Life Sciences, Vienna

Interpretation von Infrarotspektren zur Bestimmung der biologischen Stabilität von MBA-Material

Abstract

Infrared spectroscopic investigations for assessment of biological stability of MBT waste material have been carried out for several years. Degradation and stabilization of waste organic matter are revealed by changes in the mid infrared spectral pattern during the biological process. According to the problem (process control, assessment of stability of material to be disposed) different approaches of spectra interpretation are necessary. The proposed presentation will give an overview and examples. The basic approach is visual spectra interpretation; the occurrence of indicator bands is recorded and correlated with the chemical and/or biological characteristics of the material. For further interpretation of infrared spectra of MBT material multivariate data analysis can be applied. It enables pattern recognition, discrimination and classification – by means of i. e. Principal Component Analysis (PCA), Discriminant Analysis or Cluster Analysis.

Keywords

Infrared spectroscopy, multivariate spectra interpretation, waste analysis, mechanical-biological treatment (MBT), biological stability, respiration activity

1 Introduction

Apart from incineration, mechanical-biological treatment of (municipal) waste is a common measure for stabilising the organic substance prior to dumping. The stabilisation leads to a considerable reduction of the current gaseous and liquid emissions as well as the emission potential. Defining stability of waste containing organic substances and the development of analytic methods of assessment is currently a subject that is much discussed in the EU. At present, stability is determined by means of sum parameters (e.g. total of organic carbon (TOC)) or by biological reactivity tests. Sum parameters do not compulsorily characterise the waste stability; biological tests are time-consuming and thus cost-intensive but also amongst others sensitive to toxic effects. Infrared spectroscopy is based on the detection of characteristic molecular vibration and it gives information on the molecular composition of the waste sample. Analyses so far have shown that the different phases of degradation of the organic substance are reflected in their infrared spectra. Since this method does not bear the above mentioned disadvantages

and allows quick implementations, it motivates to be considered as an alternative to the biological tests.

Although infrared spectroscopy is a routine method in many application areas (pharmacy, food technology etc.), so far it has only been used for the characterisation of complex environment analyses in the context of basic studies. Thereby the description of the organic substance in soils (HABERHAUER, 2000, SANCHEZ-MONEDERO ET AL., 2002; RÉVEILLÉ ET AL., 2003), compost maturity (SMIDT AND MEISSL, 2006; SMIDT ET AL., 2005; CHEN, 2003, OUATMANE ET AL., 2000; TSENG ET AL., 1996) or residue material subject to aerobic changes (TESAR ET AL., 2007) was of interest.

There are different approaches concerning the infrared spectra of waste material. The purpose of this contribution is to give an overview of possibilities for the evaluation of infrared spectra in connection with statements about stability and/or disposal capacity of MBT material.

2 Visual spectra interpretation

2.1 Correlation of band occurrence with conventional parameters

2.1.1 Principles

In the context of various basic analyses, typical bands of reactive groups within an IR-spectrum of waste samples were identified. Table 1 displays these characteristic bands and allocation into functional groups and/or substance classes.

Table 1 Overview of the reactivity indicator bands in the IR-spectrum of waste samples

Wave number (cm ⁻¹)	Vibration	Functional group or component
3400	O-H stretch	bound and non-bound hydroxyl groups and water
2920	asymm. C-H stretch	aliphatic methylene group
2850	symm. C-H stretch	aliphatic methylene group
2520		Carbonate
1740-1720	C=O	Aldehydes, ketones, carbonic acids, ester
1640	C=O	Amides I, carboxylates
	C=C	Aromatic ring modes, alkenes
1635	O-H bending	absorbed water
1580-1540	N-H within the level	Amides II
1515-1505	aromatic structures	Lignin
1425	COO- stretch	carbonic acids
1384	N-O stretch	Nitrate

1320	C-N stretch	aromat. prim. und sec. amines
1260-1240	C-O	carbonic acids
	C-N	Amides III
1250-900	C-O-C, C-O, C-O-P	Polysaccharides Phosphodiester
1080		Quartz
1030	Si-O stretch	Clay
	Si-O-Si	Silica
875	C-O out of plane	Carbonate

2.1.2 Example of application

In order to give information, based on the occurrence of these bands in the spectrum, on the features of the material, as described by various conventional chemical and biological parameters, it was proceeded as follows. The respective samples were gathered in groups showing or not showing a certain band and the distribution of the values in these two groups was described for conventional parameters.

The example of the band with the wave number of $\sim 1540 \text{ cm}^{-1}$ (Amide II) allows showing that the existence or non-existence of a band in the spectrum can be applied as screening method for a general classification with regard to the respiration activity. The following table comprises the results of the correlation of the occurrence of amide II band in the spectrum with the respiration activity (AT_4). It turned out that the MBT samples which showed an existing band did not meet the Austrian limiting value of $7 \text{ mg O}_2 \text{ g}^{-1} \text{ DM}$ for the disposal of MBT material. If the band does not appear in the spectrum, the limiting value then is only slightly exceeded ($8.1 \text{ mg O}_2 \text{ g}^{-1} \text{ DM}$) (see Table 2).

Table 2 Correlation between AT_4 ($\text{mg O}_2 \text{ g}^{-1} \text{ DM}$) and the occurrence of the amide II band in the spectrum

Amide II	n	MV	SD	MED	MIN	MAX
yes	36	21,4	15,2	17,6	7,4	82,5
no	9	6,7	1,0	6,8	5,0	8,1

3 Multivariate spectra interpretation

With the multivariate spectra interpretation the entire information of the IR-spectrum (all data points of the medium IR-range and/or selected spectral ranges) is brought up.

Multivariate spectra interpretation can be used for recognition of pattern and classification (cluster analysis, discriminant analysis, principal component analysis). Furthermore by this it is possible to calculate from the spectrum certain chemical and physical parameters by means of prediction models (e.g. Partial Least Square Regression (PLS-R)).

3.1 Cluster analysis

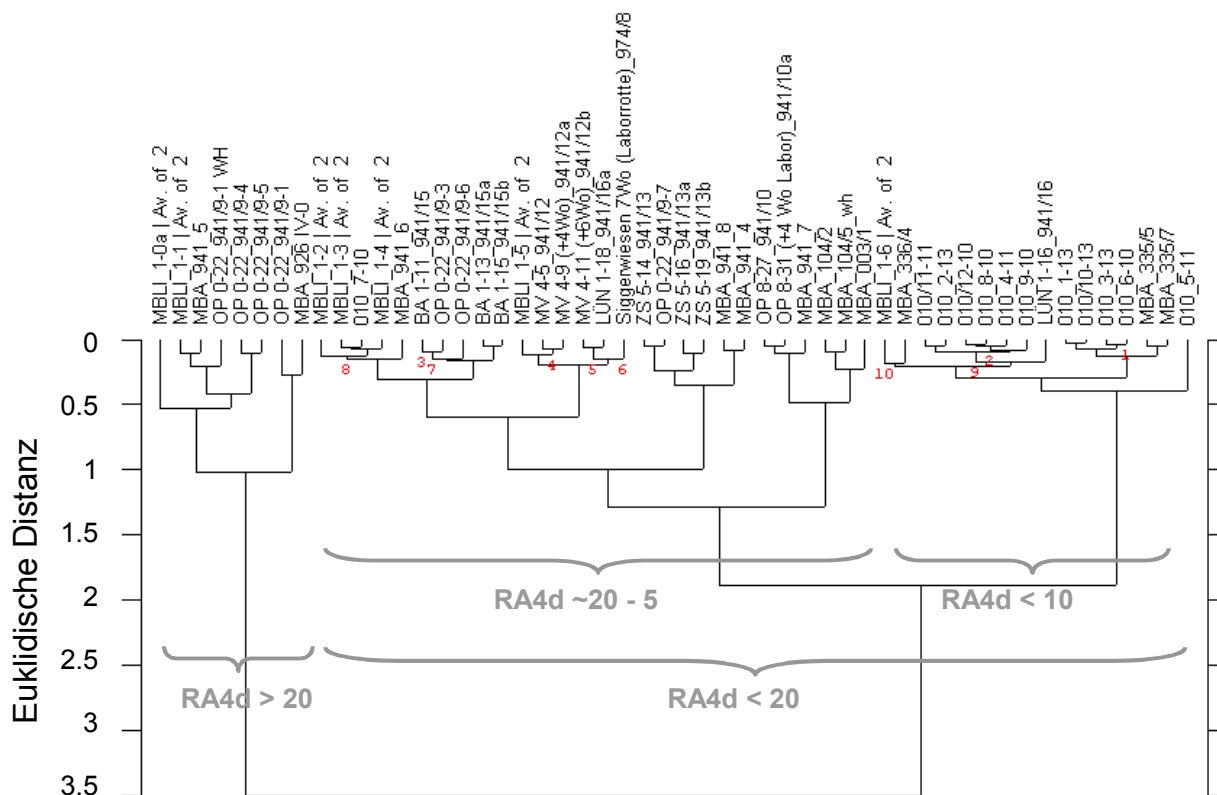
3.1.1 Basis

The cluster analysis is used to detect whether sample groups with similar spectral features are existent. With the help of this analysis the spectral distances between the observed spectra are calculated. The two spectra with the highest similarity (i.e. the spectra with the least spectral distance) are gathered in a cluster. Additionally the distances between this cluster and the remaining spectra are calculated. There are a variety of mathematical methods that can be used (Ward's Algorithm, Single Linkage, Complete Linkage etc.).

3.1.2 Example of application

A cluster analysis was carried out with 53 MBT samples from different Austrian MBT facilities, trying to answer the question whether, based on the features of the IR-spectrum, differences between the samples would be noticeable.

In doing so it became evident that a considerable separation is possible between reactive material (as should cease to occur after intensive composting, $AT_4 > 20 \text{ mg O}_2 \text{ g}^{-1} \text{ DM}$) and material falling below that value. The group of these more stable samples is subdivided into two groups, whereas in one group exclusively samples with a value of $AT_4 < 10 \text{ mg O}_2 \text{ g}^{-1} \text{ DM}$ appear.



(Euklidische Distanz - Euclidean distance)

Figure 1: Dendrogram of a cluster analysis with 53 MBT samples, spectral range: 3000-2800, 1788-1533, 1348-1201 cm^{-1} , vector normalization

3.2 Discriminant analysis

3.2.1 Basis

Based on the IR-spectrum the discriminant analysis can be used in order to determine the belonging of samples to a group with defined features (e.g. compliance/non-compliance with a limiting value for respiration activity). Moreover, those spectral areas can be identified which most contribute to the given classification.

3.2.2 Example of application

The discriminant analysis was also conducted with the same 53 MBT samples. To be able to divide the samples into those complying and not complying with the limiting value of the Austrian Landfill Ordinance of $7 \text{ mg O}_2 \text{ kg}^{-1} \text{ DM}$, the following spectral areas were considered: $3000\text{-}2800 \text{ cm}^{-1}$, $1788\text{-}1533 \text{ cm}^{-1}$ and $1348\text{-}1201 \text{ cm}^{-1}$. Bands, irrelevant for biological reactivity (nitrate: 1384 cm^{-1} , carbonate: 1430 cm^{-1} , 875 cm^{-1} , silicate: 1030 cm^{-1}), were not included in the calculation.

Figure 2 shows the result of the discriminant analysis.

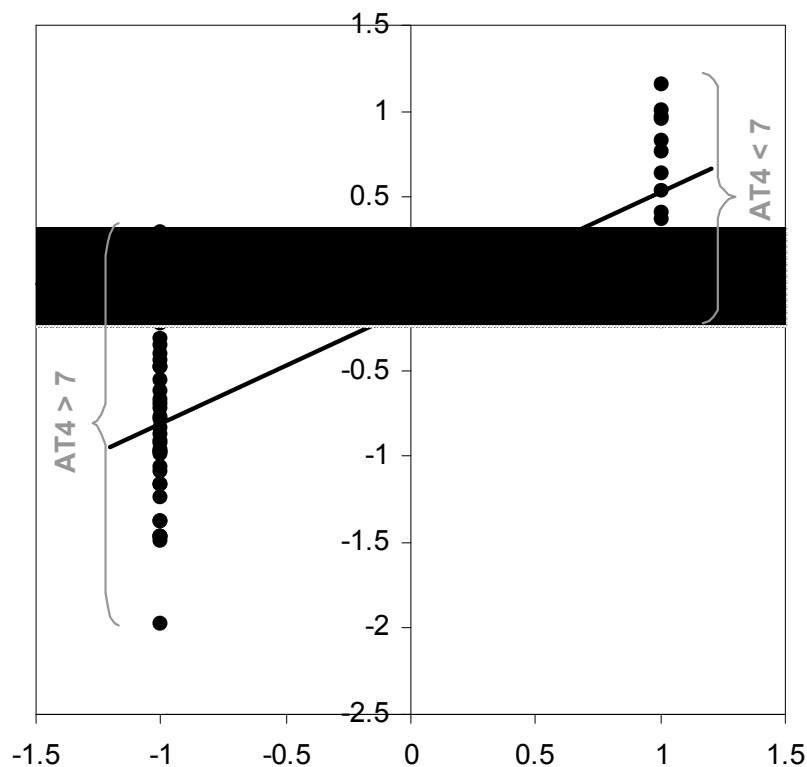
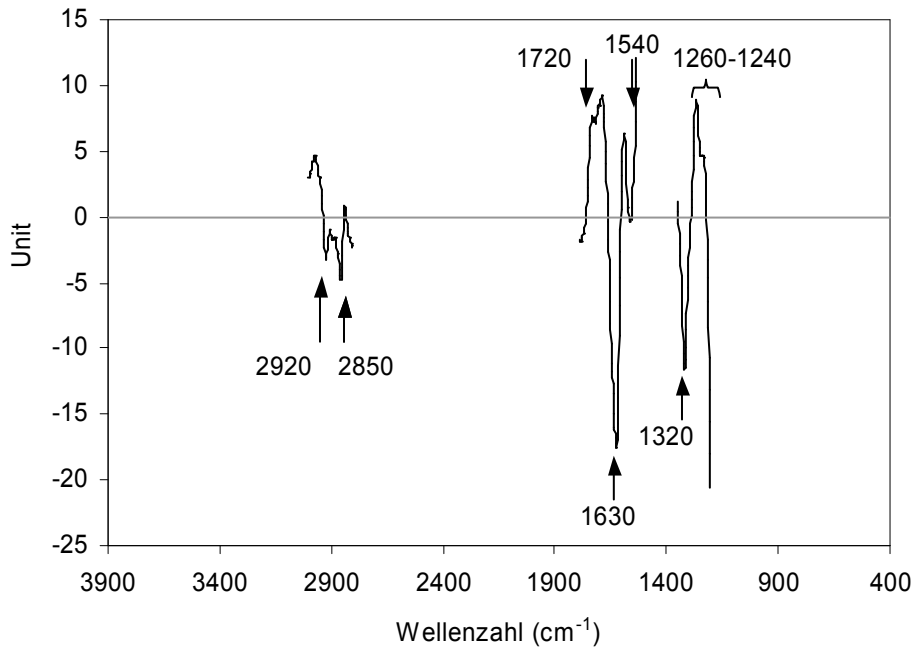


Figure 2 Result of discriminant analysis. Differentiation of samples, which comply with/exceed the limiting value for AT_4 of $7 \text{ mg O}_2 \text{ kg}^{-1} \text{ DM}$.

The Loadings Plot of the 1st principle component of the discriminant analysis (Figure 3) sheds light on what wave number range mostly influences the separation of the samples due to compliance with the limiting value for AT_4 . These bands occur at 1630, a 1720, at 1540, at 1320 and at 1260-1240 cm^{-1} . Though showing a considerable decrease of intensity during the procedure of the whole biological process, the methylene bands at 2925 and 2850 cm^{-1} are of subordinate importance for the separation of those samples complying with/exceeding the limiting value,.



(Wellenzahl – Wave number)

Figure 3 Loadings Plot of the first principle component for the discriminant analysis.

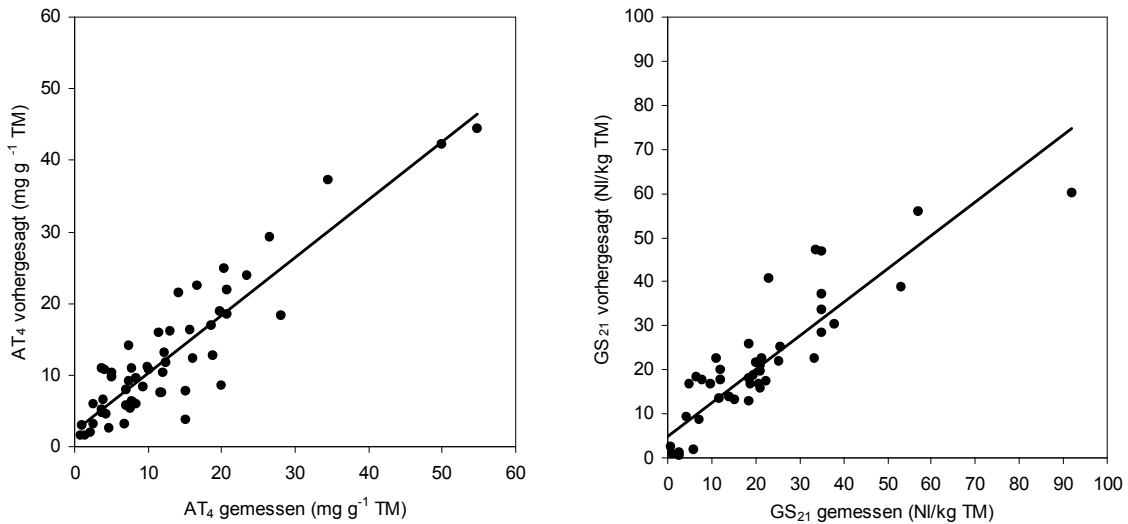
3.3 Partial Least Square-Regression

3.3.1 Basis

The basis for the PLS-R ("Partial Least Squares Regression") models is the principle component analysis. The core idea consists in separately calculating the principle components for the matrices X and Y and to create a regression model between the scores of the principle components. X is to be conceived as the data matrix for the prediction of parameters from the IR-spectrum and Y as the data matrix for parameters to be predicted, such as respiration activity or TOC. The choice of the spectral ranges is based on the chemical principles (cf. 2). Bands, indicating the metabolic products or being subject to severe changes during the biological treatment, are basically appropriate to reflect microbiological activity (e.g. AT₄).

3.3.2 Example of application

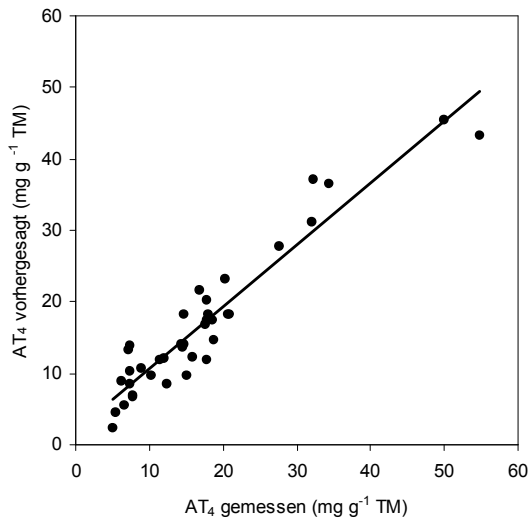
PLS-R models for prediction of AT₄ and GS₂₁ were established for the same samples as were used in the previous analyses. Figure 4 depicts the predicted and measured values for AT₄ und GS₂₁ respectively. The calculation made use of the same spectral ranges as for the discriminative analysis. The model for respiration activity is characterised by $R^2=0.83$ and a mean prediction error of $4.5 \text{ mg O}_2 \text{ g}^{-1} \text{ DM}$ and for arosis by $R^2=0.76$ and a mean prediction error of $8.3 \text{ Mlkg}^{-1} \text{ DM}$ (Figure 4).



AT₄ vorhergesagt (mg g⁻¹ TM) - AT₄ predicted (mg g⁻¹ DM);
AT₄ gemessen (mg g⁻¹ TM) - AT₄ measured (mg g⁻¹ DM)
GS₂₁ vorhergesagt (NI/kg TM) - GS₂₁ predicted (NI/kg DM)
GS₂₁ gemessen (NI/kg TM) - GS₂₁ measured (NI/kg DM)

Figure 4 Correlation of predicted AT₄ and GS₂₁-values and the measured reference values (53 samples of different MBT facilities)

Figure 5 shows that the model parameters improved considerably with regard to the calculation of the models for AT₄ with samples from the same facility: R²=90.1, mean prediction error: 3.5 mg O₂ g⁻¹ DM.



AT₄ vorhergesagt (mg g⁻¹ TM) - AT₄ predicted (mg g⁻¹ DM)

Figure 5 Correlation of predicted AT₄ and the reference values (38 samples of the same MBT facility)

4 Summary and outlook

It can be summarized that both visual spectra interpretation and multivariate spectra assessment are eligible for determining the stability of MBT material. The presented results are initial calculations that were chiefly achieved with samples arising in the scope of routine analytic methods (AT₄).

The following steps are still necessary in connection with the establishment of the method as a routine method:

- In order to make general statements regarding the correlation between features of the IR-spectrum and conventional chemical/biological parameters, it is necessary to include the entire variation range of MBT materials (with/without sewage sludge, with/without biodegradable waste, different sieve cuts)
- Additionally, to obtain high-performance models ampler data sets than presently are required, so that independent test sets for validation would be present.

The Institute of Waste Management of the University of Natural Resources and Applied Life Sciences, Vienna currently carries out a project, supported by the Austrian Science Fund (FWF), with the aim to create such high-performance prediction and classification models for the employment in routine analytics. The project realises comprehensive sampling of Austrian MBT facilities.

5 Literature

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Authors' addresses

Maria Tesar
Institut für Abfallwirtschaft
Muthgasse 107
D-1190 Wien
Phone: +43 01 3189900 310
Email: maria.tesar@boku.ac.at
Website: <http://www.boku.ac.at/abf/>

Katharina Meissl
Institut für Abfallwirtschaft
Muthgasse 107
D-1190 Wien
Phone: +43 01 3189900 345
Email: katharina.meissl@boku.ac.at
Website: <http://www.boku.ac.at/abf/>