Lösungsansätze zur Vermeidung von Fehlbefunden bei der Bestimmung der Reaktivität von MBA-Materialien

Katharina Meissl, Erwin Binner, Ena Smidt, Johannes Tintner

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

Reactivity of MBT-Waste - A new approach to identify failures of biological tests

Abstract

The "Austrian Landfill Ordinance" (BGBl. II Nr. 39/2008) (BMLFUW, 2008) provides requirements for the disposal of wastes. Limit values regarding reactivity such as respiration activity and gas generation sum (by incubation test) or gas evolution (by fermentation test) have to be met before landfilling. In Austria respiration activity $AT_4 < 7$ mg O_2 g^{-1} DM (dry mass) and gas generation sum GS_{21} (gas evolution GB_{21}, respectively) < 20 Nl kg^{-1} DM are stipulated. In 2004 Austrian Standards for these parameters were established. Sometimes reactivity is underestimated by biological tests when the microbial community is affected by environmental conditions during the test (e.g. dryness, insufficient oxygen supply, production of metabolic products). Gas generation sum and respiration activity in general feature a good correlation. Due to this fact, lower findings can be identified by determination of both parameters. On the one hand this approach serves as security and on the other hand these tests are very time consuming (4 and 21 days resp.). Thus, it was aimed for, to develop new analytical tools for the determination of reactivity parameters. Fourier Transform Infrared (FT-IR) spectroscopy was used as a non-destructive method to predict reactivity parameters and to identify errors resulting from inhibiting effects on biological tests. The development of prediction models that allow an accurate interpretation of FT-IR spectra, was based on multivariate data analysis. For parameter determination a partial least squares regression (PLS-R) was applied. A series of MBT-materials was subjected to infrared spectroscopic investigations and biological tests. This paper presents the comparison of the results obtained by the developed prediction models and by biological tests (respiration activity and gas generation sum). The procedure of error identification is demonstrated.

Inhaltsangabe

Die mechanisch-biologische Behandlung von Restmüll ist eine mögliche Behandlungsmaßnahme zur Stabilisierung der Abfälle vor ihrer Ablagerung. In Österreich sind als Kriterien zur Beurteilung der Stabilität die Atmungsaktivität (AT4) und die Gasbildung (GS21 bzw. GB21) vorgeschrieben. Die Deponieverordnung begrenzt die AT4 mit 7 mg O2 g-1 TM und die GS21 mit 20 Nl kg-1 TM. In Österreich muss die Einhaltung beider Grenzwerte nachgewiesen werden. Aufgrund von Störungen der biologischen Tests sind Unterbefunde möglich. Die beiden Parameter AT4 und GS21 stehen in direktem Verhältnis zueinander. In der Praxis hat sich daher gezeigt, dass die Forderung nach der Analyse beider Parameter sehr wichtig ist, um Fehlbeurteilungen durch Unterbefunde bei einem der beiden Tests ausschließen zu können. Da beide Parameter jedoch sehr zeitaufwändig sind, wurde nach neuen, schnelleren Bestimmungsmethoden gesucht. Dabei fiel die Wahl auf die Infrarotspektroskopie, die in zahlreichen Branchen als Routineanalytik in der Qualitätskontrolle eingesetzt wird. Sie zeigt die chemische

Zusammensetzung des Materials und lässt die Beurteilung der Reaktivität aufgrund der chemischen Zusammensetzung, unabhängig von biologischen Tests zu. Zur einfachen Bestimmung der Reaktivitätsparameter mittels FT-IR wurden Vorhersagemodelle entwickelt. Dafür wurden alle österreichischen MBA-Anlagen beprobt und von den Proben sowohl die Atmungsaktivität als auch die Gasbildung bestimmt, sowie parallel dazu ein Infrarotspektrum aufgenommen. Für die Modellerstellung wurde eine Partial Least Squares Regression (PLS-R), ein Verfahren der multivariaten Datenauswertung, verwendet. Sowohl die Atmungsaktivität als auch die Gasbildung können mittels des erstellten PLS-R Modells über das Infrarotspektrum bestimmt werden. Die Modellparameter der Modelle sind für die Atmungsaktivität unter Berücksichtigung von 220 Proben ein Korrelationskoeffizient r² von 0,92 und ein Vorhersagefehler von 3,9 mg O2 g-1 TM. Für die Gasbildung wurden im derzeitigen Modell für 62 Proben ein Korrelationskoeffizient r² von 0,82 und ein Vorhersagefehler von 8,4 Nl kg-1 TM erreicht. Es konnte gezeigt werden, dass Unterbefunde in den biologischen Tests durch die Bestimmungen mit der Infrarotspektroskopie (Vorhersagemodelle) vermieden werden können.

Keywords

Mechanisch-biologisch vorbehandelter Abfall (MBA), Atmungsaktivität, Gasbildung, Fourier Transform Infrarot Spektroskopie, Multivariate Datenauswertung, Partial Least Square Regression (PLS-R)

Mechanically-biologically pretreated waste (MBT), respiration activity, gas generation sum, Fourier Transform Infrared Spectroscopy, multivariate data analysis, Partial Least Square Regression (PLS-R)

1 Introduction

The Austrian Landfill Ordinance requires limit values for respiration activity (AT_4) < 7 mg O_2 g^{-1} DM and gas generation sum GS_{21} (gas evolution GB_{21} resp.) < 20 Nl kg^{-1} DM. In 2004 Austrian Standards (OE-NORM S2027-part 1 to 3) for these parameters were established. A good correlation between GS_{21} and AT_4 has been demonstrated by BINNER ET AL. (2007). The correlation coefficient for 70 samples was r = 0.94. In Austria both, respiration activity and gas generation sum (or gas evolution) have to be determined to assess the quality of the MBT-output. In practice biological tests sometimes underestimate the reactivity due to unfavorable conditions for the microbial community. Thus, determination of both parameters confirms the conformity of the results obtained. Several effects that have a negative impact on biological tests have been observed in the past. Due to acidification very reactive materials often feature long lag-phases during the anaerobic test. In these cases, GS_{21} does not allow a correct interpretation. On the other hand during the respiration activity test metabolic products are generated and antagonize aerobic decomposition. Anaerobic conditions, insufficient oxygen supply or running dry during the biological treatment process can lead to lower findings too (BINNER, 2007). Adoptions of the OE-NORM-methods help to prevent such errors. Pre-aeration of samples after wetting results in shorter lag phases and higher degradation rates during the aerobic test (BINNER, 2003).

However, the number of incorrect results obtained by biological tests can be minimized, but not completely avoided (BINNER, 2006). Thus it is aimed for to apply new alternative methods that are capable to assess the reactivity of MBT-output directly via the chemical composition, avoiding the time-consuming biological tests. Accordingly, Fourier Transform Infrared (FT-IR) spectroscopy has been carried out.

Infrared spectra illustrate the plot of absorbed infrared radiation versus wavenumbers caused by interactions of infrared radiation with matter. Infrared spectroscopy has shown to be a valuable tool for the characterization of waste with several applications in waste science (POLLANEN ET AL., 2005; SMIDT ET AL., 2002; SMIDT AND MEISSL, 2006). An infrared spectrum reflects the chemical composition of the whole sample. Infrared spectroscopy has been applied to describe changes at a molecular level (ZHANG ET AL., 2005) during the biological treatment of organic waste (SMIDT ET AL. 2005, ZACHEO ET AL., 2002). Each infrared spectrum consists of many data points providing information on the material. Multivariate statistical methods are necessary to handle such huge data sets. Furthermore it should be pointed out that recording of an infrared spectrum takes only about 15 minutes compared to the “Sapromat” test that lasts at least 4 days or the anaerobic test that requires 21 days. The objective of the study was to develop a new analytical tool for reactivity determination of MBT-waste by means of FT-IR spectroscopy and multivariate data analysis (Partial Least Squares Regression). Prediction models for respiration activity and gas generation sum should allow verification of equivocal data obtained by biological tests.

2 Material and Methods

2.1 Materials, sampling and sample preparation

Samples originated from different Austrian MBT-plants. Sampling took place according to Austrian Standards OE-NORM S 2123-1. Representative fresh samples were shredded to a particle size of 20 mm. Respiration Activity was determined using these fresh samples. For spectroscopic investigations a representative subsample (about 1 kg of the original fresh sample) was oven dried (105°C), and in a first step prepared by a cutting mill (Retsch SM 2000), then ground by a centrifugal mill Retsch ZM 1000 and by a vibratory disc mill and screened through 0.63 mm to provide an appropriate particle size according to Austrian Standards for chemical analyses.

2.2 Biological tests

Respiration activity was measured for a 4-day-period (AT_4) in a Sapromat (Voith Sulzer). According to OE-NORM S 2027-1 the oxygen uptake (mg O_2) was recorded and referred to one gram of dry mass (g DM). GS_{21} was determined by the "Incubation Test" according to OE-NORM S 2027-2.

2.3 Infrared spectroscopic investigations

FT-IR absorbance spectra were recorded by a Bruker (Ettlingen, Germany) FT-IR spectrometer (EQUINOX 55) equipped with a DTGS detector. Two mg samples were mixed with 200 mg KBr (Aldrich; 22,186-4; FT-IR grade) and homogenized by pestle and mortar. The 13 mm KBr pellets were prepared under vacuum in a standard device under a pressure of 75 kN cm^{-2} for 3 minutes. Thirty-two scans per sample were collected in the wavenumber range 4000-400 cm^{-1} in transmission mode at a spectral resolution of 4 cm^{-1}. The collected spectra were ratioed against air as background.

For multivariate data analysis spectra were vector-normalized.

2.4 Multivariate data analysis

Multivariate data analysis was carried out using the OPUS 5 Quant software package (BRUKER Optics, Germany). For parameter prediction a partial least squares regression (PLS-R) was used.

For the PLS-R the preprocessed (vector-normalized) infrared data were regressed against the calibration components, and by means of full cross-validation with one sample omitted a significant number of PLS components was obtained.

3 Results and Discussion

3.1 Infrared spectroscopic investigations

Figure 1 shows the development of FT-IR spectra during decomposition of municipal solid waste. Changes during the process are marked by arrows. The band assignments have been published by several authors (CHEN, 2003; SMITH, 1999; SOCRATES, 2001; SMIDT AND SCHWANNINGER, 2005; SMIDT AND MEISSL, 2006). The indicator bands of the FT-IR spectrum reflect the reactivity of the sample and can reveal "lower findings" obtained by the biological test. Multivariate data analysis, especially parameter prediction, is a promising way to use FT-IR for practical purposes due to the fast and easy handling and maximum information. By means of partial least squares regression (PLS-R) a multivariate regression model from a known corresponding X and Y data set is established. Based on an established model prediction of new data (Y-values) is possible only by measuring X-values.

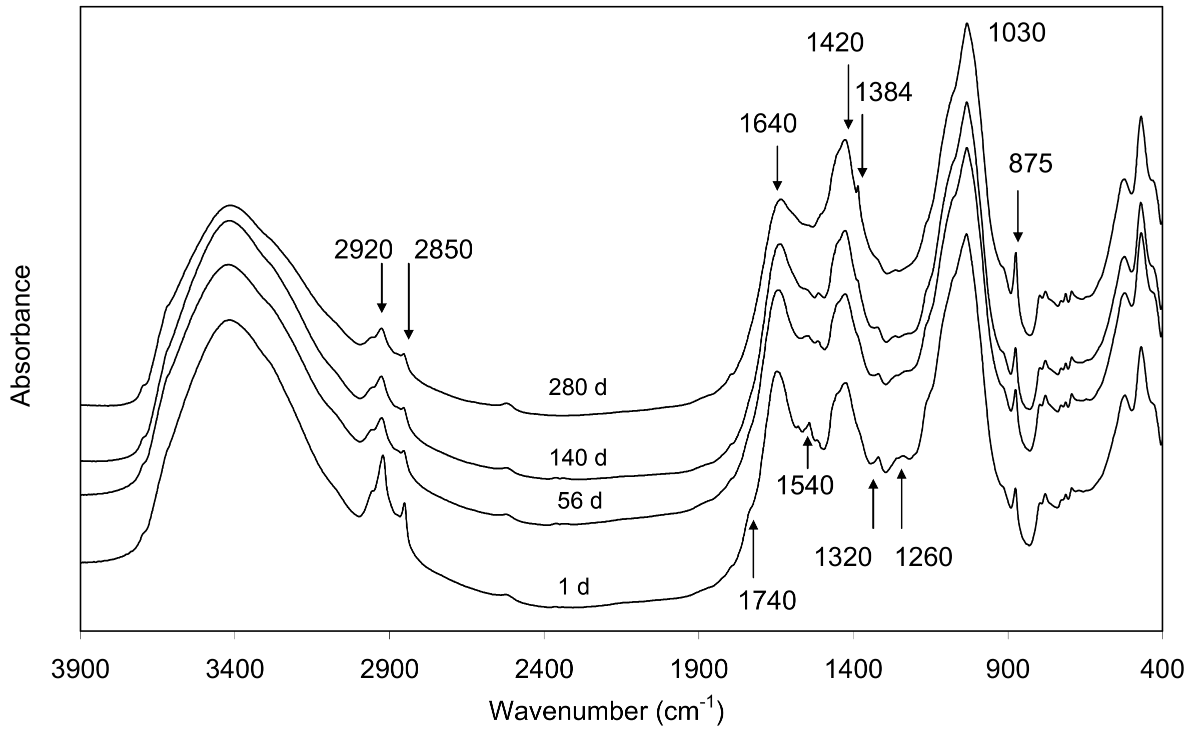

Figure 1 Development of infrared spectra during decomposition of municipal solid waste

3.2 Development of prediction models for stability parameters such as respiration activity and gas generation sum

3.2.1 Gas generation sum

Gas generation sum by incubation test is used to determine reactivity of MBT-waste under anaerobic conditions. The possibilities of errors by incubation test are acidification of materials, or H_2S formation during the test, which is toxic for anaerobic microbes. Thus, it was aimed for, to develop new analytical tools for the determination of reactivity parameters Therefore, FT-IR spectroscopy by means of multivariate data analysis was selected. In Figure 2a the correlation for gas generation sum by incubation test and by FT-IR spectra up to gas generation sum of 120 Nl kg^{-1} DM is carried out. The correlation is not satisfactory. There are only few very reactive samples with a correct gas generation sum. The samples above 70 Nl kg^{-1} DM seem to be underestimated by the model. Thus, a model without these 5 samples was developed illustrated in Figure 2b. This model shows a good correlation for prediction of gas generation sum. It is hypothesized that FT-IR spectra and the gas generation sum show a linear correlation only up to 70 Nl kg^{-1} DM. For the prediction model 62 samples were used ranged from 0.1 to 70 Nl kg^{-1} DM. The coefficient of determination was 0.82 with a mean error of prediction of 8.4 Nl kg^{-1} DM.

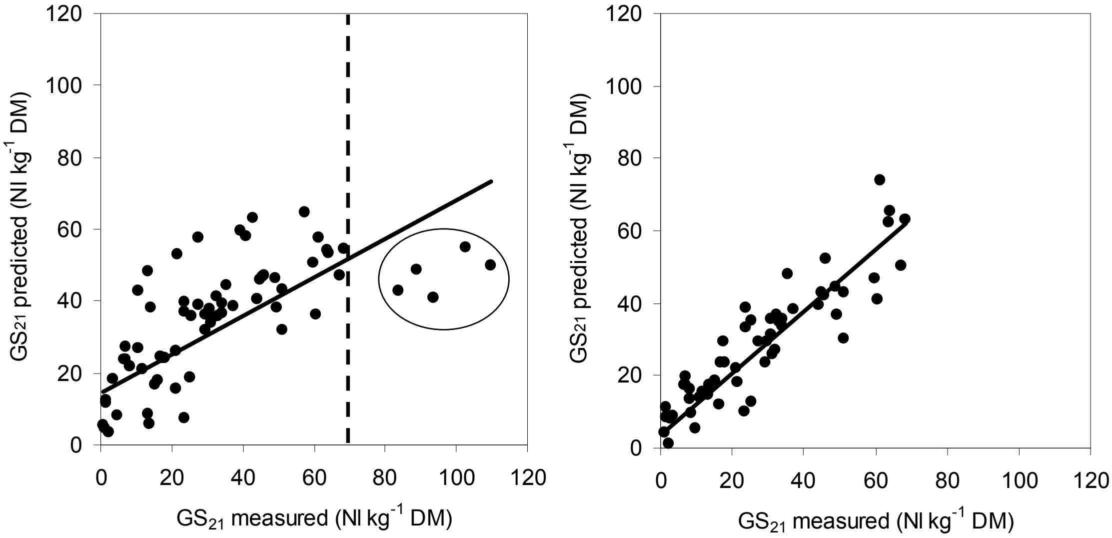

Figure 2 PLS-R model for gas generation sum (a) 0-120 Nl kg^{-1} DM and (b) 0-70 Nl kg^{-1} DM

3.2.2 Respiration activity

Respiration activity is used to determine the reactivity of MBT-waste under aerobic conditions. The possibilities of errors during the test are falling dry of material during the biological treatment process and air supply restrictions. Again FT-IR spectroscopy was used to determine the reactivity. The developed PLS-R model for respiration activity (AT_4) by means of FT-IR spectroscopy and multivariate data analysis is shown in Figure 3. The PLS-R of respiration activity was carried out using 220 calibration samples distributed in the range 0.1 to 55 mg O_2 g^{-1} DM with a mean error of prediction of 3.9 mg O_2 g^{-1} DM.

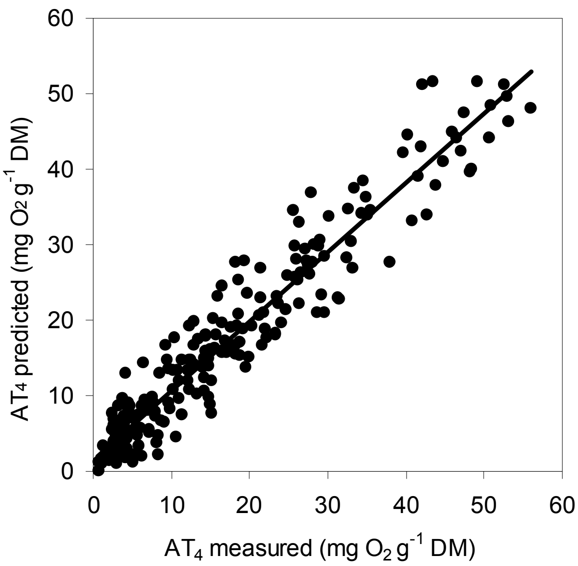

Figure 3 PLS-R model for respiration activity

3.2.3 Model validation

Furthermore the models were carefully validated and their stability and robustness were proven by an independent test set. For validation the data was divided randomly in a calibration set and a test set. The sets additionally were used vice versa. If the developed models are valid and stable they show equal model parameters. For the presented models it was successfully proven. Details of validation are not shown in this paper.

3.3 Identification of questionable results obtained by biological tests and provision of reliable results using FT-IR spectroscopy

3.3.1 Identification of failed biological tests

To prove the correlation between respiration activity and gas generation sum (BINNER ET AL., 2007) for FT-IR spectroscopy, the same 62 samples were predicted by the developed models and analyzed by Sapromat and incubation test. For comparison reason the values measured by Sapromat and incubation test of these 62 samples are also shown in Figure 4. It can be seen that the correlations are similar to each other.

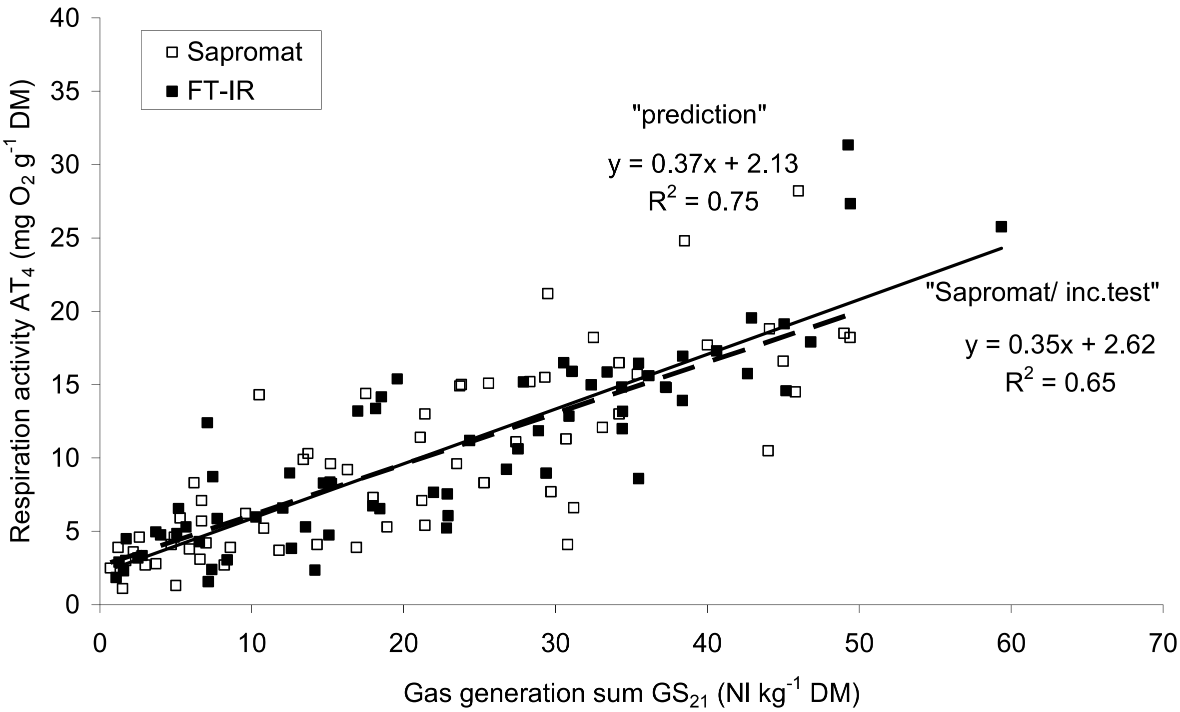

Figure 4 Correlation of respiration activity and gas generation sum by "Sapromat" and "incubation test" resp. predicted by the PLS-R models.

To illustrate the potential of the method, the models were applied to several samples supposedly underestimated by the Sapromat or incubation test in order to predict respiration activity and gas generation sum. It was assumed that there were lag phases or biological restrictions to degradation (falling dry during MBT process, formation of metabolic byproducts) during the tests. In Figure 5 the correlation of respiration activity and gas generation sum is shown. The biological tests were carried out using the conventional analytical methods as Sapromat and incubation test. Marked samples showed problems during one of the biological tests.

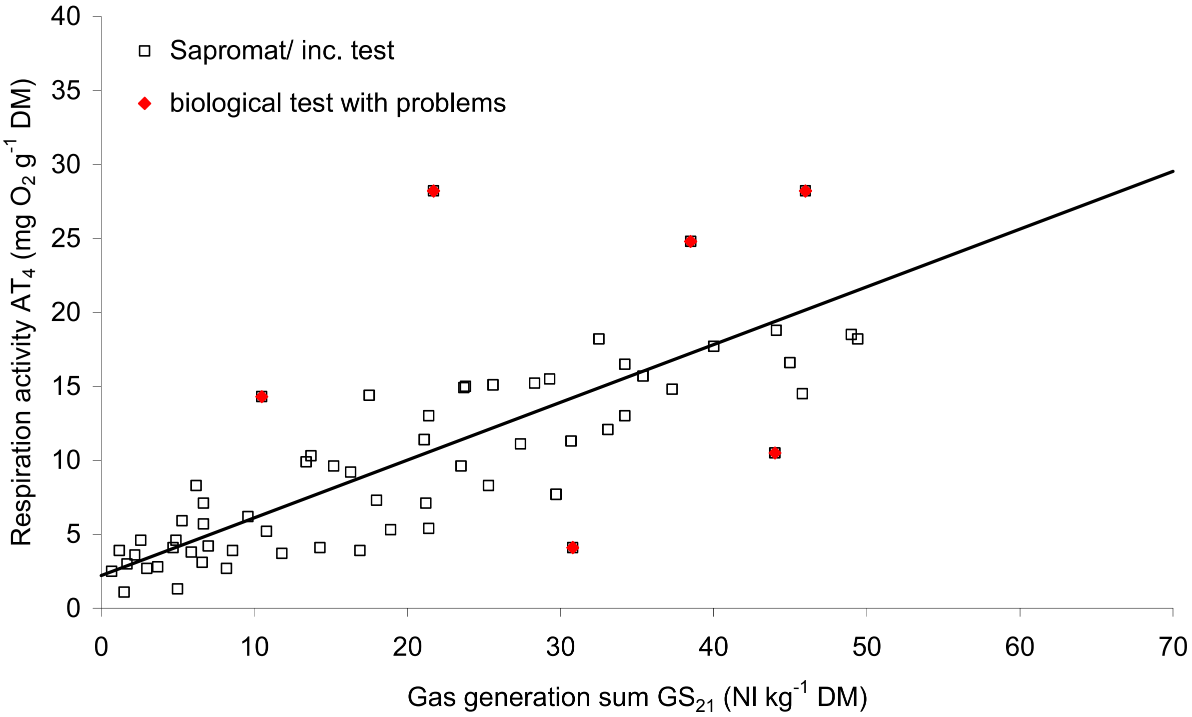

Figure 5 Correlation between gas generation sum (GS_{21}) and respiration activity (AT_4); samples with problems during the biological test are marked

3.3.2 Application of the developed prediction models

Due to the fact that samples marked in Figure 5 do not show good correlation of gas generation sum and respiration activity it is hypothesized that one of the biological test failed. Therefore, first the respiration activity was determined using FT-IR spectroscopy by means of the developed model. The results are illustrated in Figure 6. The two samples below the correlation line were underestimated by the Sapromat test. It is hypothesized that the respiration activity is underestimated by the Sapromat because material fell dry during MBT-process. The other samples compared to the Sapromat show similar results (marked by cycles). It is supposed that the gas generation sum of these samples is underestimated due to acidification. Thus, the gas generation sum was also predicted using the FT-IR model. The results are shown in Figure 7. All samples above the correlation line shift to a higher value of gas generation sum. All presented samples predicted by FT-IR models show good correlation between respiration activity and gas generation sum. These results demonstrate the applicability of FT-IR for determination of respiration activity (AT_4) and gas generation sum (GS_{21}).

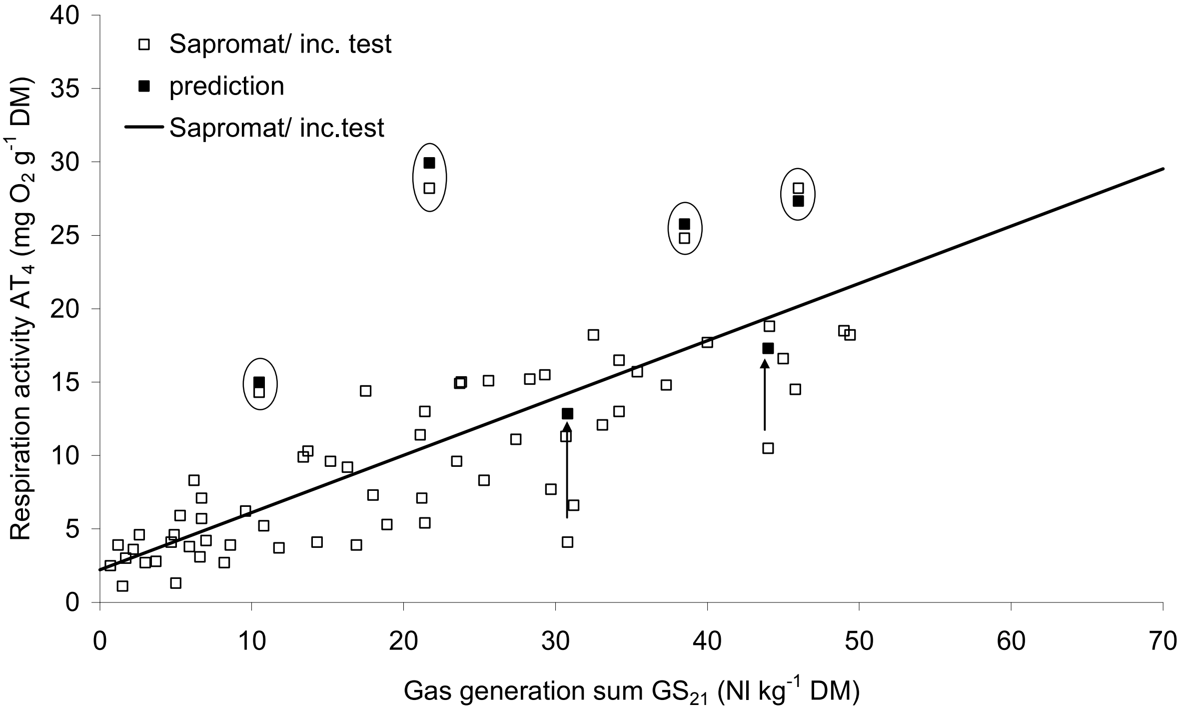

Figure 6 Prediction of the respiration activity of the sample set showing problems during the biological test

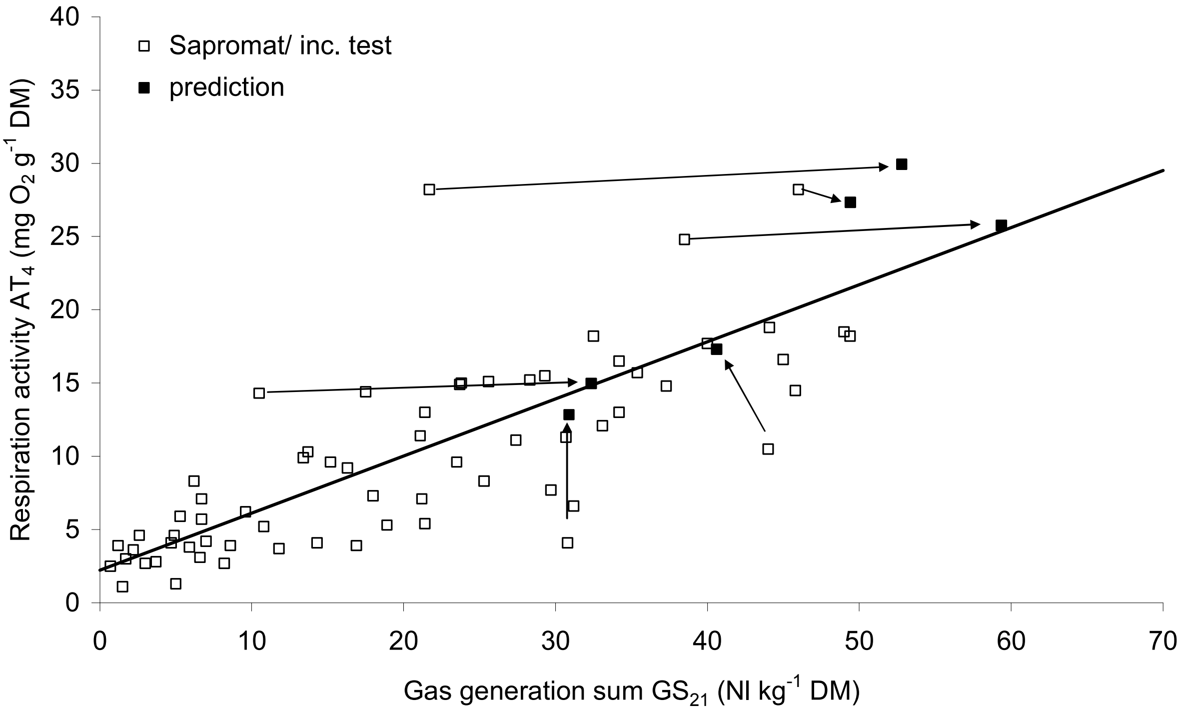

Figure 7 Recalculation of the sample set using prediction models for AT_4 and GS_{21}

4 Conclusion

The biological parameters gas generation sum within 21 days (GS_{21}) and respiration activity within 4 days (AT_4) are regulated by the "Austrian Landfill Ordinance" (BMLFUW, 2008) for reactivity determination of MBT-waste. Extreme lag phases during respiration activity test produce lower findings, occurring mainly in untreated wastes or those undergoing only brief biological treatment, as well as in the presence of disadvantageous environmental conditions (poor oxygen supply, falling dry) during the MBT process. The pre-aeration of samples (prior inserting samples in the reaction bottles and exposure to air for 4-6 hours) allows microbes to get adapted to the actual conditions (this shortens lag-phases). On the other hand aeration in between the test period of 4 days, allows repressing metabolic products to leave the test system, which increases activity. These adoptions may help to minimize lower findings but it does not ensure to avoid them completely. Thus a new analytical method the Fourier transform infrared spectroscopy (FT-IR) by means of multivariate data analysis (PLS-R) was developed. The results obtained demonstrate that this approach provide further support to biological tests due to the lack of effect produced by lag phases or toxic effects on the FT-IR spectrum. Furthermore it should be pointed out that the time consuming biological tests respiration activity and gas generation sum could be carried out efficient and rapid by means of FT-IR spectroscopy only in a few minutes. The results demonstrate that using a combination of different determination methods reliable results for biological reactivity of MBT-waste can be achieved.

5 References

BMLFUW	2008	Austrian Landfill Ordinance: Verordnung des Bundesministers für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft über Deponien (Deponieverordnung 2008) BGBl. II Nr. 39/2008
Binner E., Meissl K., Tesar M.	2007	Assessment of MBT-Waste – A new approach to avoid failures by measuring respiration activity. In: Proceedings of SARDINIA '07 – 11th International Landfill Symposium, Vol. I, Cagliari, Sardinia, Italy
Binner E.	2006	Beurteilung der Reaktivität von Abfällen - Anwendbarkeit der für mechanisch-biologisch behandelten Restabfall entwickelten Methoden bei anderen Abfällen. In: Matthias Kühle-Weidemeier (Eds.): Abfallforschungstage 2006 „Auf dem Weg in eine nachhaltige Abfallwirtschaft", Cuvillier Verlag, Göttingen, Germany
Binner E.	2003	Assessment of MBP-Waste - Misinterpretations of Respiration Activity. In: Proceedings of SARDINIA '03 – 9th International Landfill Symposium, Vol. I, Cagliari, Sardinia, Italy

Chen Y.	2003	Nuclear Magnetic Resonance, Infra-Red and Pyrolysis: Application of spectroscopic methodologies to maturity determination of composts. Compost Science and Utilization 11, 152–168
Meissl K., Smidt E., Schwanninger M.	2007	Prediction of Humic Acid Content and Respiration Activity of Biogenic Waste by Means of Fourier Transform Infrared (FTIR) Spectra and Partial Least Squares Regression (PLS-R) Models, Talanta 72, pp. 744-799
Pollanen K., Hakinnen A., Reinikainen S.P., Rantanen J., Karajalainen M., Louhikultanen M., Nystrom L., Pharamaceut J.	2005	Spectroscopy Together with Multivariate Data Analysis as a Process Analytical Tool for In-line Monitoring of Crystallization Process and Solid-state Analysis of Crystalline Product, Journal of Pharmaceutical and Biomedical Analysis 38, pp 275-284
Smidt E. and Schwanninger M.	2005	Characterization of waste materials using FT-IR spectroscopy – Process monitoring and quality assessment. Spectroscopy Letters 38, 247–270.
Smidt E. and Meissl K.	2006	The applicability of Fourier transform infrared (FT-IR) spectroscopy in waste management, Waste Management 27, pp. 268-276
Smidt E., Eckardt K.U., Lechner P., Schulten H.R., Leinweber P.	2005	Characterization of Different Decomposition Stages of Biowaste Using FT-IR Spectroscopy and Pyrolysis-field Ionization Mass Spectrometry, Biodegradation 16, pp 67-79
Smidt E., Lechner P., Schwanninger M., Haberhauer G., Gerzabek M.H.	2002	Characterization of Waste Organic Matter by FT-IR Spectroscopy: Application in waste science, Applied Spectroscopy. 56, pp 1170-1175
Smith B.	1999	Infrared Spectral Interpretation. CRC Press, London, New York, Washington; DC, Boca Raton.
Socrates G.	2001	Infrared and Raman Characteristic Group Frequencies. Tables and Charts. John Wiley & Sons Ltd, Chichester.
Zacceo P., Ricca G., Crippa L.	2002	Organic Matter Characterization of Composts From Different Feedstocks, Compost Science and Utilisation 10, pp 29-38

Anschrift der Verfasser(innen):

Dipl.-Ing. Katharina Meissl

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

Muthgasse 107, A-1190 Vienna

Phone: (+43-1) 318 99 00-345

Email: katharina.meissl@boku.ac.at

Website: http://www.wau.boku.ac.at/abf.html