Process and Quality Control of MBT-Waste by Means of Thermal Analysis

Ena Smidt and Johannes Tintner

Institut für Abfallwirtschaft, Department für Wasser, Atmosphäre und Umwelt, Universität für Bodenkultur, Vienna

Thermische Analyse zur Prozess- und Qualitätskontrolle bei der mechanisch-biologischen Behandlung

Abstract

The present study reports on the application of thermal analysis for investigation and characterization of MBT – materials. The thermal behaviour of waste materials depends on physical and chemical properties of all waste components. The thermal behaviour suggests a specific composition and stage of decomposition. By means of thermogravimetry (TG) the mass loss of the sample is measured in dependence of the temperature. By means of differential scanning calorimetry (DSC) the heat flow of the material is recorded. Municipal solid waste displays a characteristic DSC – profile that reflects the stage of mineralization and waste composition. Apart from the visual evaluation, the determination of mass losses, temperatures of maximum heat flows and peak shifts, is performed by the instrument software. Multivariate data analysis also supports evaluation of many data points generated by these analytical techniques. Evaluation tools based on multivariate data analysis are developed for practical application.

Keywords

Mechanical-biological treatment, process control, thermogravimetry (TG), differential scanning calorimetry (DSC), multivariate data analysis

1 Introduction

The daily practice of mechanical-biological waste treatment requires appropriate control whether the goals in terms of reducing the reactivity have been attained. Measures to improve existing technologies and new processes also have to be evaluated by examining the waste during the process or at important interfaces. While modern analysis methods are used to determine pollutants, mainly cumulative parameters like ignition loss, organic carbon or calorific value are available for the evaluation of the organic substance. Though they are suitable to make statements within a process about the progress of the degradation, they permit comparisons between different plants only with some reservations. The biological tests in the aerobic and anaerobic environment for the examination of reactivity and gas formation potential have more meaning. However, these analyses take long and quick information about the status of the process is therefore not available. Especially in case of incidents when there is need for action, quick but meaningful testing methods are advantageous.

It is therefore important to introduce modern testing methods in the field of wastes analysis in order to evaluate the degradation of organic substances in the biological treatment.

Several testing methods were applied in the field of research to characterize the organic substance in residual waste during the mechanical-biological treatment. Methods like NMR spectroscopy and IR-spectroscopy were suggested for the evaluation of the development of the organic substance in domestic waste by several authors (CASTALDI ET AL., 2005; SMIDT UND MEISSL, 2006). Thermoanalytical methods were also used to characterize the organic substance in wastes (MELIS UND CASTALDI, 2004; SMIDT UND LECHNER, 2005).

Several essential requirements apply for the practical use of modern analysis methods:

- Short analysis duration
- Low costs
- Simple handling
- Simple evaluation
- Comprehensive information

IR-spectroscopy and thermal analysis meet these requirements. This paper is about thermoanalytical tests of mechanically-biologically treated residual waste. The possibilities offered by thermal analysis for practical use are explained with several examples. The presented examples include the use of thermogravimetry/mass spectrometry (TG/ MS) and differential scanning calorimetry (DSC). The evaluation of the results is carried out by means of the device-software (Proteus) and additionally by means of multivariate data analysis.

2 Thermoanalytical methods TG/ MS and DSC

2.1 Principle of the methods

Physical and chemical properties of a material influence its thermal characteristic. The fact that the combustion process runs differently for different substances is verified by our observations. Therefore materials, their composition and their degree of degradation can be concluded from the thermal characteristic. In complex mixtures like wastes, the thermal characteristic results from the sum of the physico-chemical properties of all individual components. The result of a thermoanalytical test is – like in spectroscopic analyses - a curve with many data points characterizing the material. The interpretation and evaluation of the results is supported by the multivariate data analysis.

In thermogravimetry (TG) the mass loss of the sample is measured with a thermobalance and in dependence of the temperature. With an existing coupling device with a mass spectrometer, the combustion gases occurring in his process can be recorded as well. With the differential scanning calorimetry (DSC) the heat flow of the sample is measured and recorded. The integration of the area below the curve gives the energy content of the sample.

2.2 Sample pretreatment

One advantage of thermoanalytical methods is that the whole treated sample is used and characterized for analysis. The sample pretreatment includes the drying at ambient temperature or at 105°C, the grinding and sieving to a size of < 0.5 mm. With this particle size a good repeatability is obtained. Due to the light initial weight of the sample the representative sampling, a sufficient sample quantity and the homogeneity of the material has to be looked after.

2.3 Execution of the analyses

The incineration of the material is carried out under defined conditions (oxidative or pyrolytic) within a certain temperature range. The following incineration parameters were chosen for the presented examples: combustion atmosphere O_2/ He (20 % / 80 %), gas flow 120 ml min^{-1}, heating rate 10 K min^{-1}, temperature range 30 to 950 °C. With the given incineration conditions the analysis duration is 90 minutes. A sample quantity of 16.0 mg is incinerated in an Al_2O_3 crucible that is suitable for the measures. All tests were carried out with a device for the simultaneous thermal analysis (STA 409 CD Skimmer by the company Netzsch GmbH).

3 Questions and examples from practical use

3.1 Thermogravimetry/ MS

The reactivity of the sample and the concentration of organic substance in MBT-material are part of the essential parameters of process control. Figure 1 shows the first derivative of the thermograms (DTG-curves) of a typical residual waste from mechanical-biological waste treatment. The mass loss in four stages is characteristic of residual waste fractions. The first stage (1) marks the loss of the residual water (with air-dry samples), the second and third stage correspond the incineration of the two organic fractions and the fourth corresponds the decomposition of the carbonate. The incineration of the organics in two stages (2 and 3) reflects the different degradability of the organic compounds. Carbonate (stage 4) is mostly part of residual waste and depends among other things on the geogenic background of the region. The MBT-samples represent a biological detention time of differing length. The shifts are clearly recognizable by the fall of the peaks (first derivative of the TG-curve). Between the 6-weeks-old and the 9-weeks-old sample there is, however, only an insignificant degradation.

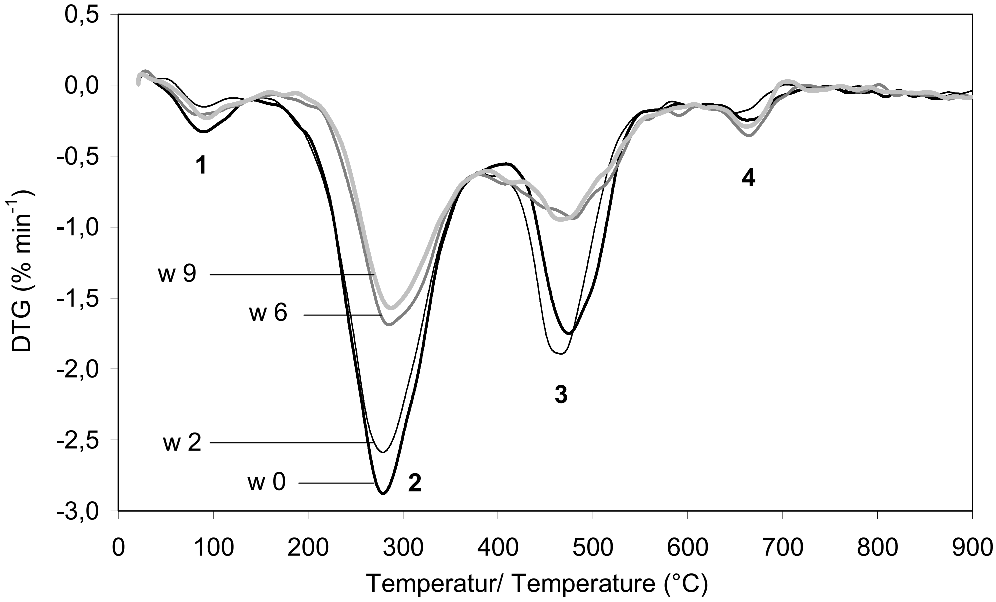

Figure 1 First derivation of the thermogram curves (DTG) of different degradation stages of residual waste during the biological treatment (week 0, 2, 6 and 9)

In Figure 2 two different processes of the mechanical-biological residual waste treatment are compared by means of their thermograms. The samples come from Austria (Pr I) and Germany (Pr II). It is obvious that the processes are running in a very similar way. The figure shows the thermograms of the original sample (week 0) and of the samples after 9 weeks of rotting. There is more carbonate in the sample from Austria due to the geogenic background, which is visible in the bigger weight loss of > 650 °C (decomposition of the carbonate).

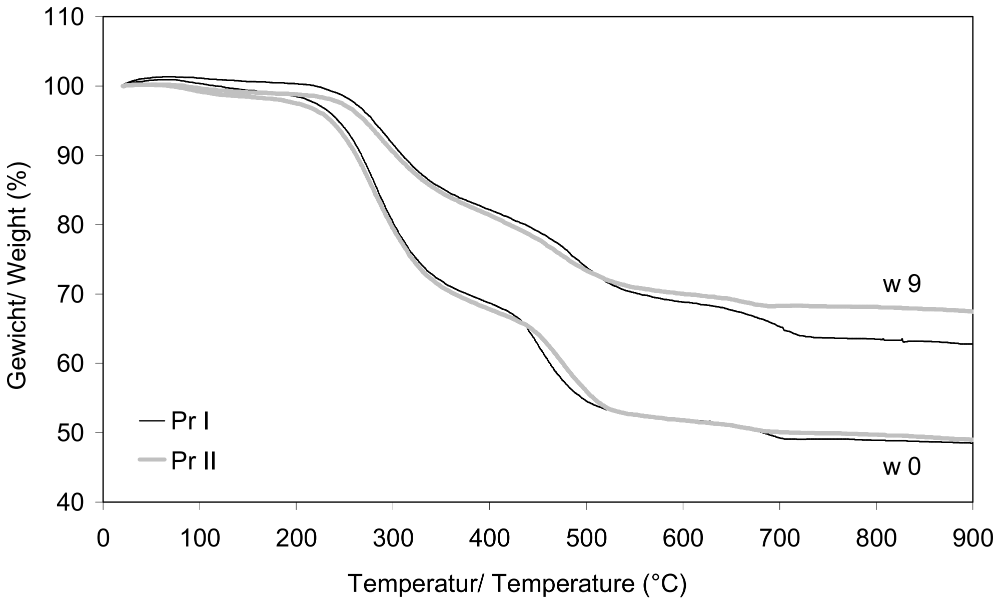

Figure 2 Thermograms of samples from different development stages (week 0 = w 0 and week 9 = w 9) and processes (Pr I and Pr II) of the biological residual waste treatment

The comparison between different plants or different processes of a plant is possible due to the characteristic incineration curves. A “reference“-process of a plant can be defined by its thermograms or DSC-profiles and can serve as an assessment factor for further processes. Figure 3 shows two different processes of a plant. The thermograms of the original samples (w 0) are almost identical. The thermograms of the 12-weeks-old material (w 12), however, differ from each other significantly. Due to disturbances the degradation in process IV was delayed. The mass loss at 550 °C corresponds the definition of the ignition loss. Comparing the two processes it is clearly visible that the mineralization in process IV is less advanced than in process III.

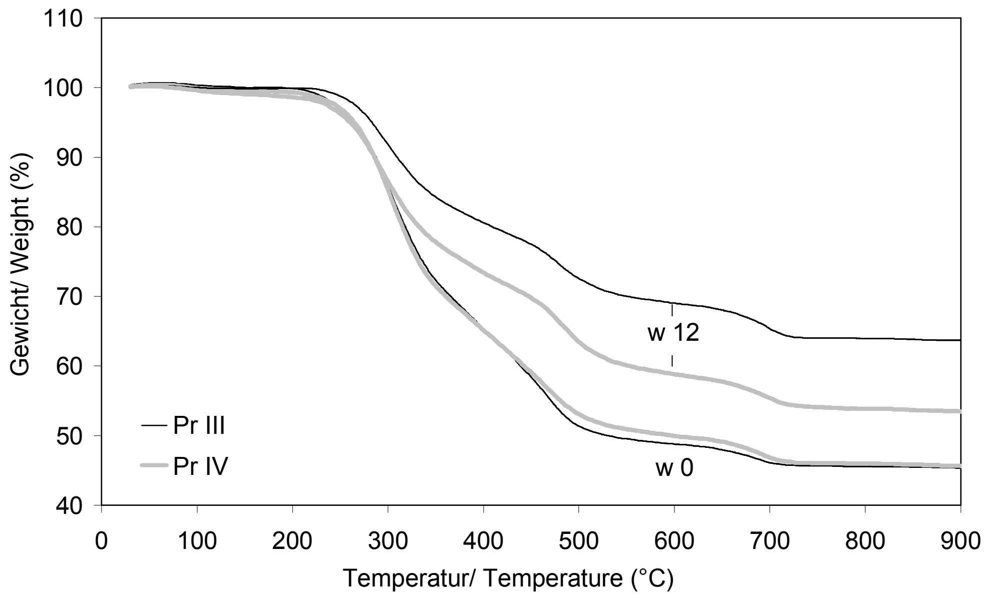

Figure 3 Thermograms of samples from different development stages (week 0 = w 0 and week 12 = w 12) and processes (Pr III and Pr IV) of the biological residual waste treatment

If in the course of incineration also incinerator gases are recorded, the ion currents of individual components or the whole mass spectrum can be evaluated. Figure 4 shows the mass spectra of the original sample and the final sample (28 weeks) of residual waste from a mechanical-biological process.

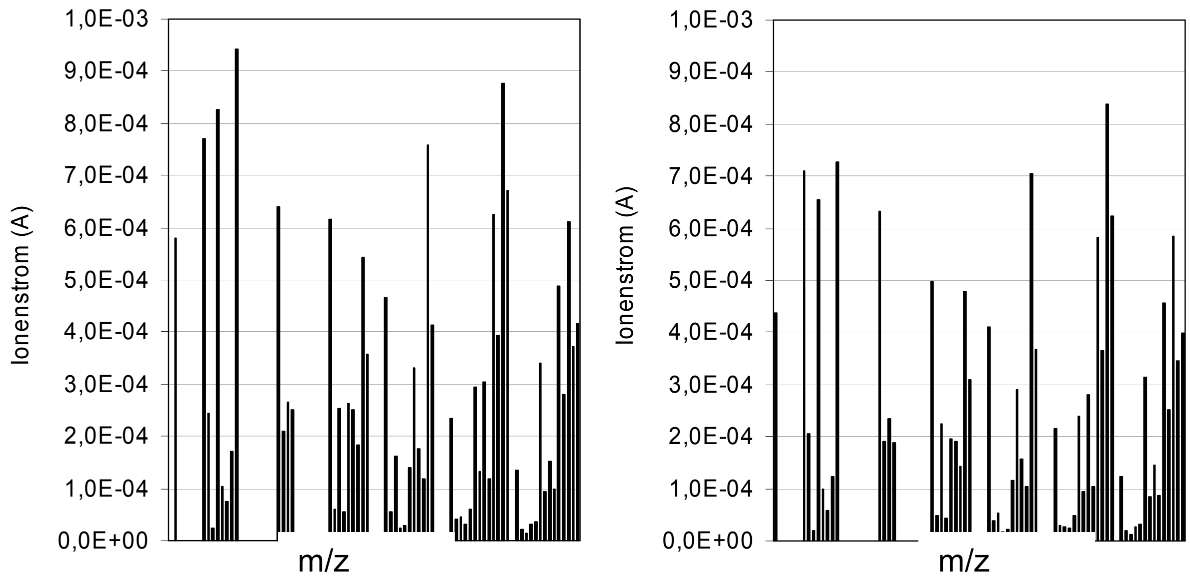

Figure 4 Mass spectra of the original and final sample (28 weeks) of mechanically-biologically treated residual waste

Explanation of the German terms contained in the figure: *- Ionenstrom – ion flow*

The ion currents recorded in the mass spectrometer come from the combustion products of the waste sample. The change of the ion currents of the recorded masses in the course of mechanical-biological treatment corresponds the increasing mineralization and stabilization of the organic substance. The mass spectra are like a “fingerprint“ of the sample. An evaluation for practice can be carried out by means of multivariate data analysis, which checks the conformity of the mass spectra or single meaningful masses (“Pattern recognition“).

3.2 Differential Scanning Calorimetry (DSC)

The heat flow of a material depends on the one hand on its components, but also on its development stage. The oxidative incineration of the organic material is shown by the two exothermic peaks. Figure 5 clearly shows the change of the heat flow of the bulk sample with increasing mineralization and stabilization of the material. There is a decrease in heat flow with the samples from the original residual waste sample (MBT 1) via the 8-weeks-old sample from the mechanical-biological treatment (MBT 2) to the landfills 1 and 2, which represent differently degradated domestic waste from the 1980s. The DSC-profile of a soil from the region of the landfills is shown as reference. The decrease in the heat flow is connected with a decline of the enthalpy of the sample, which can be calculated by integrating the area below the DSC-curve. This value given in joule per gram does not correspond exactly the calorific value, as the incineration process in thermal analysis differs fundamentally from the determination of the calorific value.

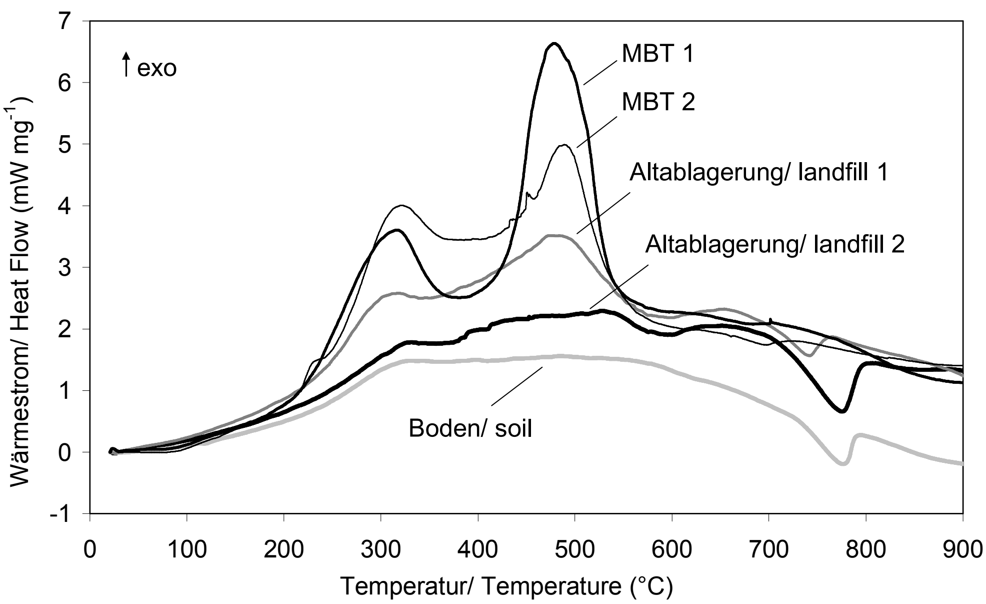

Figure 5 DSC-profiles of differently degradated residual waste samples (MBT 1, MBT 2) and domestic waste samples (landfills 1 and 2) and a soil

Figure 6 indicates that the composition of the material influences the DSC-profile considerably. Whereas Figure 5 shows typical domestic waste in the different stages of mineralization, in Figure 6 domestic waste with a high proportion of plastic (a), to which further plastic particles were added (b) is shown. Whereas the organic fractions of the domestic waste are characterized by two wide exothermic peaks, plastics produce sharp narrow peaks. Due to the low weight loss these reactions are easier to identify in the DSC-curve than in the thermogram.

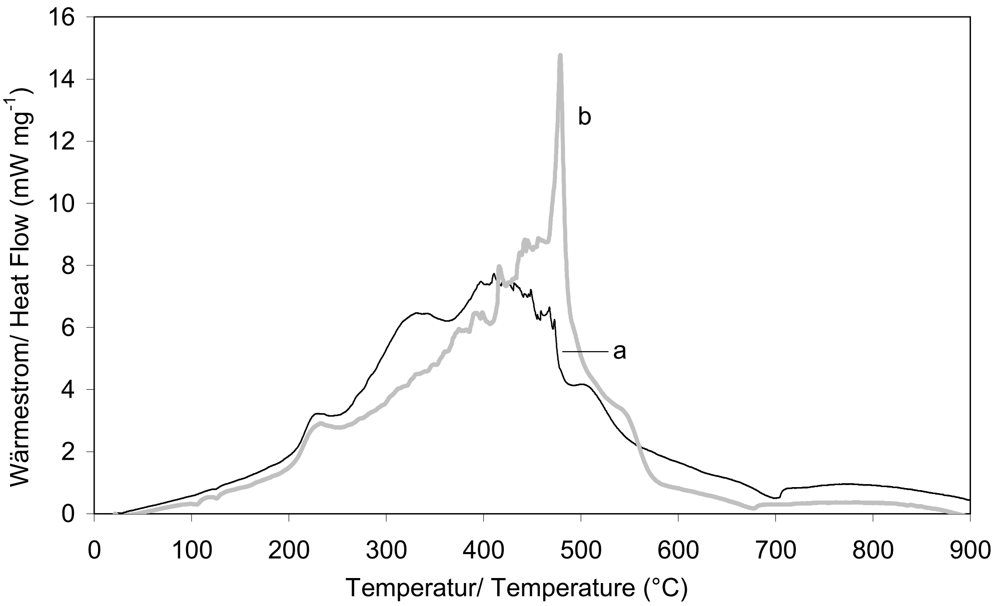

Figure 6 DSC-profile of residual waste samples with a high proportion of packaging material and plastics (a) and with a proportion of plastics of 3 % w (b)

3.3 Evaluation with multivariate data analysis

The presented examples are supposed to reflect the diversity of information about a waste material that can be obtained by means of thermoanalytical methods. It is, however, necessary for practical application of these methods to have appropriate evaluation tools. In TG and DSC large quantities of data are generated, which are no longer manageable in detail and for the evaluation of which multivariate data analysis is the right method (ESBENSEN, 2002; STATHEROPOULOS ET AL., 2002). An important basis is the Principal Component Analysis (PCA). With the PCA large data pools are reduced to their essential main components. This mathematical transformation permits to recognize the inherent structure of the data. In this way the similarity of samples and the influence of the variables become visible. Based on the PCA, models can be developed for the use in practice that permit a quick assignment of the material or a prediction of parameters.

Figure 7 shows a PCA of DSC-profiles of different types of waste. It is clearly visible that wastes whose composition differs notably from residual waste are grouped elsewhere. Landfill material from old municipal solid waste landfills is situated on the low end of the MBT-materials due to its composition and age. The composition of the material which is 78 % responsible for the variance has an essential influence on the separation along the first main component. The shift due to the degradation of the organic substance or respectively the increase of the mineral proportion in the sample is depicted along the second main component which has an influence of 21 % on the variance.

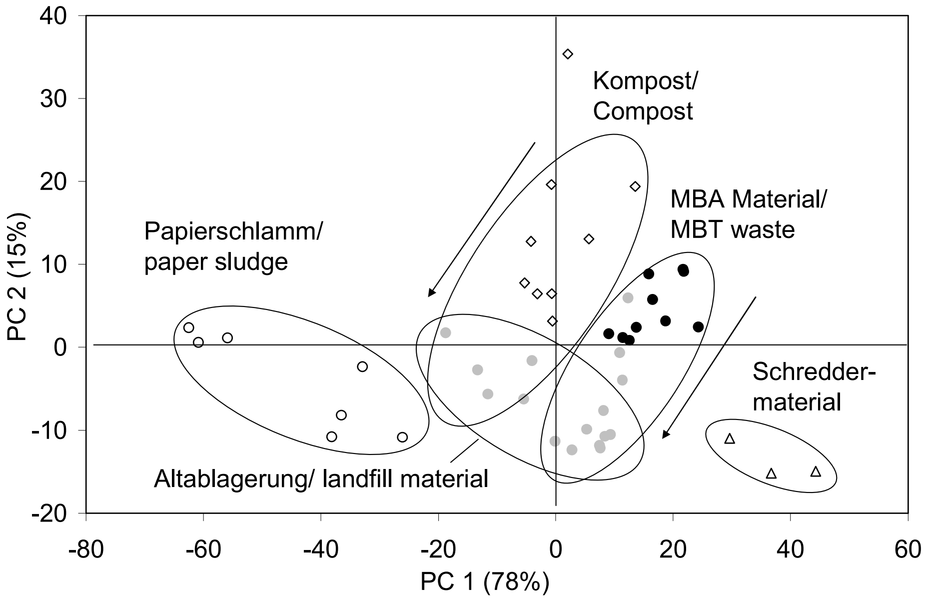

Figure 7 Principal Component Analysis (PCA) of the DSC-profiles of different waste materials

4 Conclusion and prospects

Thermoanalytical methods permit an extensive characterization of waste samples due to the numerous data points generated in an analysis. Apart from individual parameters (peak temperature, mass loss etc.), which can be detected by means of the integrated device software, the evaluation takes place by multivariate data analysis. On the basis of these methods appropriate evaluation tools for practice are developed for defined questions. One topic is the classification of wastes owing to their composition. Wastes that differ from the usual composition of residual waste do not belong to the group of residual wastes because of their different thermal behaviour. This distinction can be necessary for the evaluation of testing parameters or the application of specific methods. A second important question is the prediction of parameters which are reflected in the thermal behaviour. For the determination of the reactivity or stability of waste samples, for which at present there are only time-consuming biological parameters, quicker methods for practical application are desirable. The development of such models is being currently worked on.

5 Literature

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Author's address

Dr. Dipl. Ing. Ena Smidt, Dipl. Ing. Johannes Tintner
Institut für Abfallwirtschaft
Universität für Bodenkultur
Muthgasse 107
A-1190 Wien
Phone: +43-1/ 318 99 00-343
Email: ena.smidt@boku.ac.at
Email: johannes.tintner@boku.ac.at
Website: http://www.wau.boku.ac.at/abf.html