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# Study on the degradation and stabilization of organic matter in waste by means of thermal analyses

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## Abstract

During the biological treatment of waste organic matter undergoes considerable changes. Degradation and transformation, mineralization and humification take place. These processes correspond to different energy contents, which are reflected by the characteristic thermal behavior of the samples. Waste materials such as compost, municipal solid waste and waste from abandoned landfills have been investigated in this study to demonstrate the applicability of thermal methods in waste management. The use of the total sample, thus avoiding chemical extraction, has proved to be advantageous in the management of complex materials. Nevertheless, waste compounds were also characterized. TG/DTG and the curves of the $CO_2$ ion current have been recorded in order to shed light on changes occurring in humic acids during composting.

Thermal characteristics were attributed to different stages of decomposition of landfill materials. Further to the assessment of unknown landfills process control was carried out to evaluate the efficiency of aeration.

A simple procedure that it not based on the comparison of a series of data but rather enables assessment of an individual sample is described for use in the evaluation of organic matter present in municipal solid waste.
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*Keywords:* Waste organic matter; Stabilization; Thermogravimetry/MS; Differential thermogravimetry (DTG); $CO_2$ ion current

## 1. Introduction

Knowledge of the stage and stability of organic matter contained in waste is a fundamental prerequisite when faced with a decision concerning application of the most appropriate form of treatment in waste management. In line with recent European regulations stability has to be reached before landfilling to avoid harmful environmental impacts caused by reactive organic matter. Further to mineralization and humification, stabilization also comprises enrichment of less degradable molecules and interactions with mineral compounds.

Process and quality control, and the assessment of abandoned landfills are tasks facing the field of waste management. In situ remediation, i.e. in situ aeration that aims at organic matter stabilization should be verified using suitable methods.

Stability is assessed on the basis of several parameters [1]. Decreasing organic matter and organic carbon contents, the C/N ratio, the content of mineralization products and early metabolic components such as ammonium, nitrate and volatile fatty acids and respiration activity are established methods to assess stability and maturity of waste materials. Degradation and stabilization are manifested by a changing energy content. These features are reflected by a modified thermal behavior. Therefore thermal methods provide a fast means of assessment of the decomposition stage. In addition the entire sample can be analyzed avoiding chemical extraction steps that very often affect the nature and the ambience of organic matter. For complex samples this approach proves advantageous and provides additional information.

Different stages of compost maturity have been characterized by Dell'Abate et al. [2,3] using differential scanning

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calorimetry (DSC) and thermogravimetry (TG). Calorimetric investigations have been carried out to describe the thermal behavior of biomass combustion [4]. Otero et al. [5] monitored the stabilization progress of sewage sludge from wastewater treatment plants by means of differential thermogravimetry. Advanced sludge stabilization due to aerobic digestion was indicated by a shift to higher combustion temperatures. Melis and Castaldi investigated the evolution of municipal solid waste/vegetal waste in a composting process using thermogravimetry and differential scanning calorimetry [6]. Different stages of compost have been characterized using pyrolysis field-ionization mass spectrometry [7–9] and pyrolysis techniques [10,11]. The mass spectrum of pyrolysis products represents the “chemical fingerprint” in a general way. The evolution of municipal solid waste treatment has been determined by differential scanning calorimetry [12]. The shift of the exothermic reaction at 350 °C towards higher temperatures was observed with increasing composting time. Thermal methods have been widely used to characterize soil organic matter. Gonzalez et al. [13], by means of analytical pyrolysis and additional methods, have revealed how several preserved biomacromolecules are accumulated in the humus fraction. Changes in organic matter in the soil subsequent to agricultural activities have been monitored by Stuczinski et al. [14]. The presence of minerals affect the thermal stability of organic matter and organic-mineral bonds have been detected by high-temperature volatilization of biomolecules [15].

The objective of the present study was to demonstrate the applicability of thermal analyses to assess stability and maturity of different waste materials originating from real industrial processes or existing landfills. Humic acids that are built up during the biological treatment were also analyzed. Thermogravimetry (TG/DTG) and differential scanning calorimetry (DSC) were combined with the information from the mass spectrum. The main interest focused on the $CO_2$ ion current curve versus increasing temperature.

## 2. Materials and methods

### 2.1. Materials

#### 2.1.1. Compost

Yard waste from private gardens and parks and organic waste from households (except leftovers) and markets are collected separately in Vienna. Composting of “pure” biogenous fractions results in high quality products that are used in horticulture and agriculture. Following the removal of plastics and metallic components organic waste with high water content due to fruits, plants, and vegetables, was mixed with yard waste (i.e. wood, branches) as bulk material to ensure aerobic conditions. The mixture thus obtained was composted in an open windrow system. The material was rotated mechanically daily during the most reactive phase (2 weeks), then twice a week. Within this time temperatures up to 72 °C were reached. After 4 weeks the compost was piled up for the curing phase over a period of 8 months. During this period, characterized by a decrease in temperature and reactivity, transformation processes dominated [1]. Rotation took place once a month. Samples were taken according to the required sampling procedure [16].

For thermal analyses four samples (4, 25, 50, 260 days) were selected from a sample set of 47 samples collected during the composting process. After the aerobic composting process 30 kg of compost were stored under anaerobic conditions in a lab scale reactor. Sampling took place after 1 year.

Humic acids from the collected compost samples (25, 260 days, 260 days + 1 year under anaerobic conditions) were extracted according to Gerzabek et al. [17]. The precipitated humic acid fraction was dialyzed (exclusion: molecular weight of 12 000) and freeze-dried.

#### 2.1.2. Municipal solid waste (mechanical–biological treatment)

After the mechanical treatment municipal solid waste was screened and rotated in the cylindric aerated reactor for 24 h. The rotting process took place in an open windrow system for 9 weeks. The material was rotated mechanically once a week. For the curing phase of 20 weeks the material was piled up.

#### 2.1.3. Abandoned landfills A1, A2 and B (municipal solid waste and construction waste) from the 1980s

Samples A1 and A2 originated from the layers underlying the surface (depth 0.2–1 m) of two different sections in landfill A. The material in section A1 was sealed between two tight layers of clay minerals. The layer of A2 was well aerated.

The material originating from landfill B (Ba) was aerated (20 L $h^{-1}$) in a lab scale reactor of 100 L volume (Bb).

### 2.2. Sample preparation

Biological tests and ammonium-N determinations were carried out immediately from the fresh material screened through 20 mm. For other analyses the material was air-dried, ground in an agate mill, screened through 0.63 mm, and milled with an agate mortar.

### 2.3. Analyses

#### 2.3.1. Thermal analyses

Thermal analyses were performed with an STA 409 CD Skimmer (Netzsch GmbH and Balzers mass spectrometer) that enables the recording of thermograms, DSC curves, and mass spectra of combustion gases simultaneously and of combustion gases. All samples were combusted with oxygen/He (gas flow: 150 ml $min^{-1}$ containing 20% of oxygen and 80% of helium) within a temperature range from 30 to 950 °C. Employed conditions: heating rate 10 K $\text{min}^{-1}$, sample weight 16.00 mg, $Al_2O_3$ pan, self-controlled calibration.

For data evaluation Netzsch Proteus/Balzers Quadstar Software were employed.

### 2.3.2. *Chemical analyses*

The total content of organic matter (OM) was determined by incineration at 545 °C. Total carbon (TC), total inorganic carbon (TIC) and total nitrogen contents (TN) were analyzed by combustion in a Variomax CNS analyzer. Total organic carbon (TOC) was calculated by the difference between TC and TIC. Two replicates were performed. The results of conventional parameters complied with the requirements of Austrian standards regarding deviation.

Humic substances were extracted using a 0.1 M sodium pyrophosphate solution (pH 10.5). Fulvic and humic acids were separated according to their behavior in acidic solution [17]. The humic acid fraction, precipitated at pH 2, was used for further investigations. Quantification was carried out by photometric determination at 400 nm. For the actual increase of humic acids mineralization was included by the factor $f = (100 - \text{LOI}_4)/(100 - \text{LOI}_t)$, where $\text{LOI}_4$ is the loss of ignition on day 4 and $\text{LOI}_t$ the loss of ignition on day $t$.

### 2.3.3. *Biological tests*

Respiration activity (RA) and gas forming potential (GFP) were determined according to Binner et al. [18]. For respiration activity the oxygen uptake was registered and referred to dry matter (DM). Gas forming potential was measured in the incubation test reactor.

## 3. Results and discussion

### 3.1. *Compost and humic acids*

The loss of ignition (LOI) and TOC show a slight decrease during composting. Due to the high content of mineral compounds degradation proceeded slowly. Previous investigations [1] of common parameters (organic carbon, total nitrogen, C/N, infrared spectroscopic characteristics) indicated that stabilization according to limit values was achieved after 9 weeks. Data of the selected samples for thermal analyses are summarized in Table 1. However, transformation continued under anaerobic conditions. The samples show a slight increase of extractable humic acids. If mineralization is taken into account no further increase of humic acids is observed.

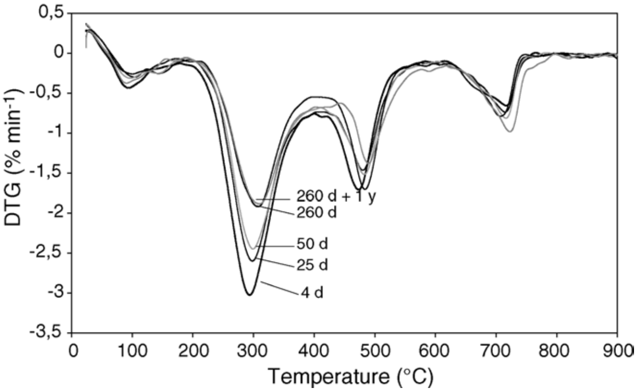

Fig. 1. DTG curves of progressive stages in the composting process (4, 25, 50, 260 days, 260 days + 1 year anaerobic).

Four obvious steps can be distinguished in the compost thermograms. Fig. 1 shows the derivative of the thermograms (DTG curve). A slight decrease within the temperature range from 70 to 150 °C, is mainly caused by the loss of residual water. Dehydration within this temperature range was also reported by Dell'Abate et al. [3] and Melis and Castaldi [6]. In addition it is confirmed by the peak of the ion current (mass 18) at this temperature. Between 200 and 350 °C, respectively, 400 and 550 °C two prominent peaks indicate the main losses of organic matter. This is in accordance with findings by the authors mentioned above [3,6]. Aggarwal et al. assigned this thermal pattern to cellulose and lignocellulosic substances [19] that are a main component of plant materials. The first peak decreases considerably with time. However, other organic molecules that are degraded during composting also contribute to this peak. The occurrence of DTG, DSC and $CO_2$ ion current peaks at differing temperatures supports this assumption. Intensities of the first peak decrease during composting. As stability of organic matter increases metabolic products that are combusted preferentially within this temperature area disappear. Temperatures of the second peak are very similar for all curves. Peak 2 intensities are less affected by the degradation process than peak 1 although a decrease with time is also observed. The peak can be attributed to scarcely degradable molecules, i.e. aromatic compounds such as wood and humified matter that are enriched during composting. Table 2 represents temperatures of the DTG, DSC and the $CO_2$ peaks.

Table 1

Loss of ignition (LOI), TOC, respiration activity (RA 7 days), humic acid contents (HA) and humic acid increase of the samples during the composting process (DM: dry matter, oDM: organic dry matter)

| Composting time (days) | LOI (% DM) | TOC (% DM) | RA 7 days (mg $O_2$ $g^{-1}$ DM) | HA (% oDM) | HA (% oDM × $f$) |
|---|---|---|---|---|---|
| 4 | 48.9 | 26.2 | 64.0 | 5.0 | 5.0 |
| 25 | 45.3 | 23.9 | 25.3 | 8.7 | 8.1 |
| 50 | 42.4 | 22.2 | 20.9 | 14.5 | 12.9 |
| 260 | 40.7 | 21.8 | 7.1 | 30.5 | 26.2 |
| +1 year anaerobic | 39.1 | 20.2 | n.d. | 31.0 | 26.0 |

Table 2
Temperatures (°C) of the peak maximum ($CO_2$ ion current, DTG and DSC curves)

| Composting time (days) | $CO_2$ ion current | | DTG | | DSC | |
|---|---|---|---|---|---|---|
| | Peak 1 | Peak 2 | Peak 1 | Peak 2 | Peak 1 | Peak 2 |
| 4 | 315.8 | 472.2 | 293.7 | 473.3 | 320.0 | 476.1 |
| 25 | 315.8 | 479.6 | 298.1 | 480.3 | 318.7 | 483.3 |
| 50 | 315.8 | 481.5 | 299.1 | 482.8 | 317.7 | 484.8 |
| 260 | 319.5 | 483.3 | 307.3 | 484.2 | 319.7 | 486.1 |
| 260 + 1 year | 319.5 | 488.9 | 309.5 | 489.8 | 322.0 | 491.1 |

The shift towards higher temperatures with increasing stabilization is obvious. This fact was also reported by Melis and Castaldi [6] for municipal solid waste/vegetal waste compost and by Otero et al. [5] for sewage sludge.

Intensities of DSC peaks 1 and 2 were related to the peaks of $CO_2$ ion current. Oxidative combustion of organic compounds causes exothermic reactions. The energy release is higher in the undecomposed material than in the degraded one according to the declining energy content during decomposition. The decrease of organic compounds results in a decrease of the $CO_2$ ion current and causes therefore a reduction of DSC peak intensities. An increase of the second exothermic DSC peak as described for other compost mixtures has not been observed [6,3]. The composition of the composted material which comprised a considerable portion of resistant substances (bulk material) from the start could account for the almost constant intensity of the second peak.

A weaker peak at about 716 °C can be attributed to the decay of carbonates that is confirmed by the endothermic reaction.

The pattern of mass losses (%) versus temperature is demonstrated in Fig. 2. More stabilized samples require higher temperatures to achieve the same mass losses. Mass losses of 15–30% are obtained at lower temperatures for the compost stored under anaerobic conditions compared to the last sample of the aerobic process. This shift towards lower temperatures could be attributed to mobilization processes that took place under anaerobic conditions. Degradation is also indicated by a slight decrease of the LOI (Table 1).

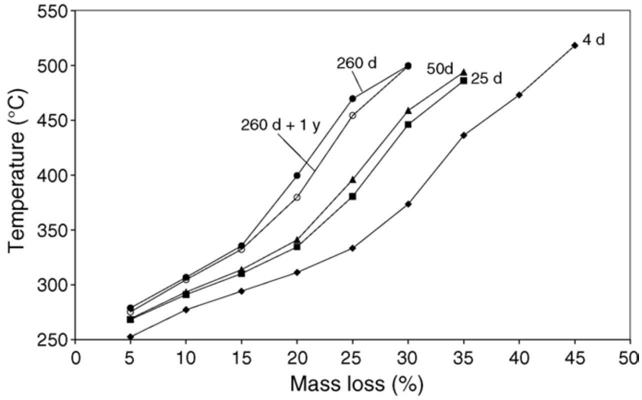

Fig. 2. Mass losses vs. temperature of progressive stages in the composting process (4, 25, 50, 260 days, 260 days + 1 year anaerobic).

Nevertheless, peak shift towards higher temperatures (DTG, $CO_2$ ion current) argues for stabilization as well. It can be hypothesized that besides progressing stabilization a small portion of the material is remobilized.

This ambivalent development is also reflected by the thermal behavior of the precipitated humic acid fraction. The TG/DTG curves shed light on the high temperature that is necessary to combust humic acids (Fig. 3). Weight loss takes place up to 700 °C.

The ion current of the mass 44 ($CO_2$) reveals further details of the modifications undergone by humic acids during composting (Fig. 4). A peak at 207 °C can be attributed to carbohydrates that are confirmed by infrared spectroscopic

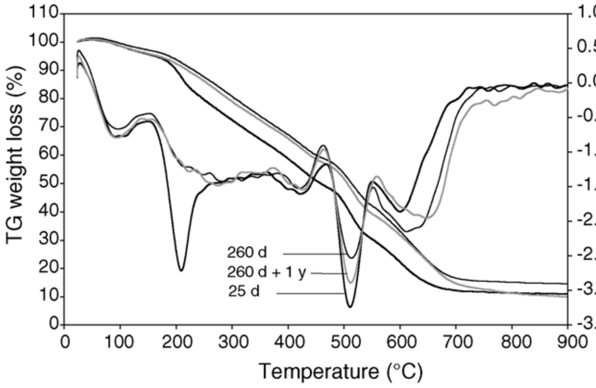

Fig. 3. TG and DTG curves of precipitated humic acids originating from progressive stages in the composting process (25, 260 days, 260 days + 1 year anaerobic).

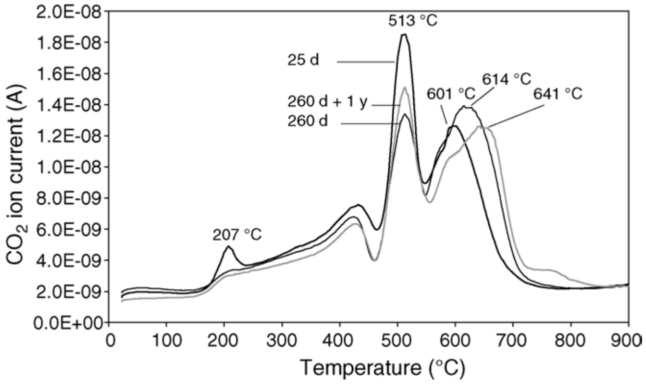

Fig. 4. $CO_2$ ion current of precipitated humic acids originating from progressive stages in the composting process (25, 260 days, 260 days + 1 year anaerobic).

Table 3
Loss of ignition (LOI), TOC, total N, ammonium-N, respiration activity (RA 4 days), and gas forming potential (GFP) at different stages of the process (DM: dry matter)

| Biological treatment (days) | LOI (% DM) | TOC (% DM) | $N_t$ (% DM) | $NH_4$-N (ppm) | RA 4 days (mg $O_2$ $g^{-1}$ DM) | GFP (NL $kg^{-1}$ DM) |
|---|---|---|---|---|---|---|
| 1 | 52.2 | 26.6 | 1.17 | 1203 | 80 | 132 |
| 17 | 50.8 | 25.4 | 0.98 | 2472 | n.d. | n.d. |
| 51 | 40.7 | 20.0 | 1.19 | 1006 | n.d. | n.d. |
| 63 | 38.4 | 19.7 | 1.34 | 664 | n.d. | n.d. |
| 92 | 34.3 | 17.8 | 1.30 | 144 | n.d. | n.d. |
| 129 | 31.7 | 16.7 | 1.25 | 38 | n.d. | n.d. |
| 197 | 29.5 | 15.3 | 1.21 | 6 | 1.7 | 7 |

characteristics [1]. The latter is only found in the humic acid of the 25-day-old compost. A weak (at around 430 °C) and two prominent peaks at 513 and > 600 °C are representative for the humic acid fraction. The peak at 513 °C does not elicit a change in position but only modifies intensity and decreases with age. An increase is observed in the humic acid fraction from composts stored under anaerobic conditions. The second prominent peak shifts from 601 °C (25 days) to 614 °C (260 days) and to 641 °C (260 days + 1 year anaerobic). These results reveal a "splitting" effect during the ageing process under anaerobic conditions (curve 260 days + 1 year). On the one hand some compounds of humic acids contribute towards an increase of the $CO_2$ peak at 513 °C, on the other hand the 2nd prominent peak shows a slight decrease of intensity but a considerable shift towards higher temperatures. These results indicate that stabilization of humified matter is still ongoing.

### 3.2. *Municipal solid waste (MSW)*

Mineralization was much higher in the municipal solid waste (MSW) than in the compost. Table 3 illustrates data pertaining to different stages of the biological treatment. Respiration activity and gas forming potential were determined for the initial and the final sample.

The DTG curves reflect the considerable decrease of organic matter. The most important finding is represented by the substantial shift of the TG curve towards higher temperatures indicating increasing stabilization. Fig. 5 shows the DTG curves of the different stages of decomposition during biological treatment of municipal solid waste. The derivative of the thermograms indicate the temperatures characterized by the main weight losses. As previously reported for biowaste compost, four distinct steps of weight losses can be distinguished. Dehydration takes place in the range from 60 to 150 °C. Due to intensive mineralization of municipal solid waste the decrease of the two prominent peaks (DTG curve) representing the loss of organic matter is more substantial. Compared to the compost described above peaks 1 and 2 of MSW are found at lower temperatures (282.2–302.7 and 451.6–486.0 °C, respectively), especially at an early stage of decomposition. The peak shift is more distinct. Due to different components peak 2 intensity of MSW is much more affected by the degradation process than peak 2 intensity of the compost. The characteristic thermal pattern of biologically treated waste could provide a method to distinguish different materials according to their composition and quality. The peak at about 700 °C that is attributed to carbonates increases due to the relative increase of inorganic components during composting. The different chemical composition of organic matter in municipal solid waste influences the peak positions and the shift towards higher temperatures.

The pattern of the $CO_2$ ion current (Fig. 6) originating from organic molecules is similar to the DTG curve with respect to shift and intensity. Whereas the samples from day 1 to 92 differ notably with regard to peak intensities and peak shift a constant level is observed for samples 92, 129, and 197 days indicating stabilization. This finding is confirmed

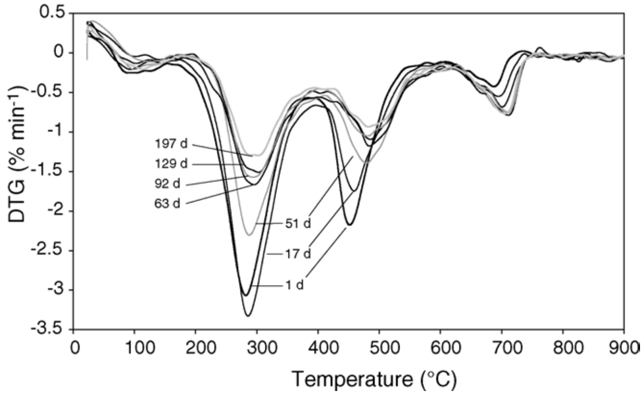

Fig. 5. DTG pattern of municipal solid waste by days of the biological treatment.

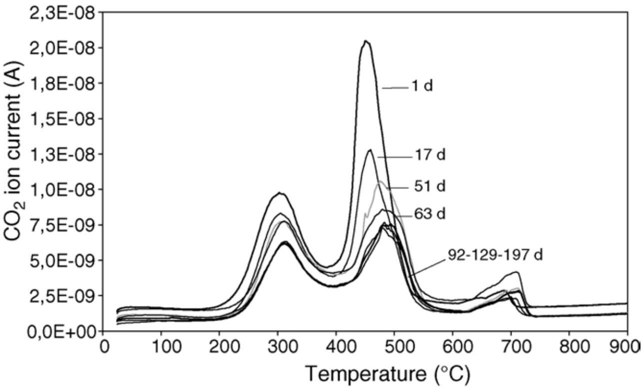

Fig. 6. Changes of the $CO_2$ ion current of municipal solid waste by days of the biological treatment.

Table 4
Loss of ignition (LOI), TOC, respiration activity (RA 4 days), and gas forming potential of the landfill samples A1, A2, Ba and Bb

| | LOI (% DM) | TOC (% DM) | RA 4 days (mg $O_2$ $g^{-1}$ DM) | GFP (NL $kg^{-1}$ DM) |
|---|---|---|---|---|
| A1 | 32.0 | 16.4 | – | n.d. |
| A2 | 4.3 | 1.7 | 0.0 | n.d. |
| Ba | 13.5 | 7.0 | 9.6 | 27.5 |
| Bb | 10.9 | 5.3 | 0.8 | 1.0 |

by conventional parameters (Table 3). A higher amount of $CO_2$ develops from carbonates in the stabilized sample due to the relative increase of inorganic compounds. The peak of carbonates decay is not observed at constant temperatures. It can therefore be concluded that interactions between organic matter and inorganic compounds take place.

It is noteworthy that the temperature of the DTG peaks does not correspond exactly with the peak maximum of the $CO_2$ ion current in the aged sample, especially the peak at 302 °C/312 °C. This might be due to several other fragments, e.g. $C_xH_y$ that are generated in this temperature range and contribute towards weight loss. The development of different carbon species during combustion may provide additional information on the stability of organic matter and should be investigated accordingly in further studies.

Practical application of the TG curves requires evaluation of the individual waste sample. In this study the evaluation of equal mass losses versus temperature differences is suggested. Depending on the degree of stability increasing temperatures are required to combust an additional mass unit. The temperature range corresponding to a mass loss of 5–15% seems to be appropriate. Fig. 7 demonstrates the curves of all samples mentioned above. Step1 signifies the temperature difference required to obtain a weight loss from 5 to 10%, step 2 from 10 to 15%.

The required gradient of the “stability” curve should be determined for the specific treatment plant.

### 3.3. Abandoned landfill materials

The thermograms of landfill materials provide a fast means of assessment of the degradation stage. In landfill A two totally different sections (A1 and A2) can be distinguished (Fig. 8). The loss of ignition is 32.0% in sample A1 and 4.3% in A2. Sample A1 shows four characteristic steps of weight losses as observed in municipal solid waste. Due to drought and tight clayey layers mineralization was inhibited despite the location adjacent to the surface for two decades. The constantly slow weight loss of A2 is similar to soil organic matter combustion.

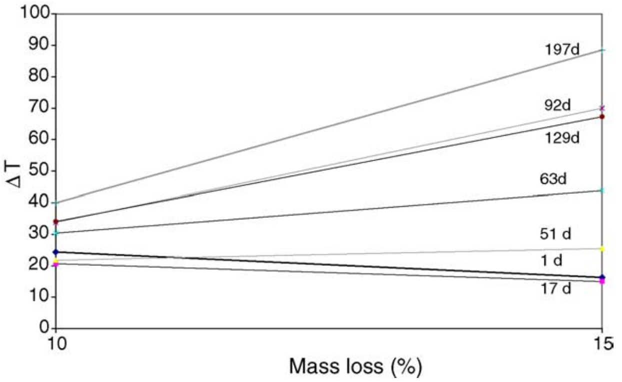

Fig. 7. Temperature differences to achieve mass losses from 5 to 10% (1st point) and from 10 to 15% (2nd point).

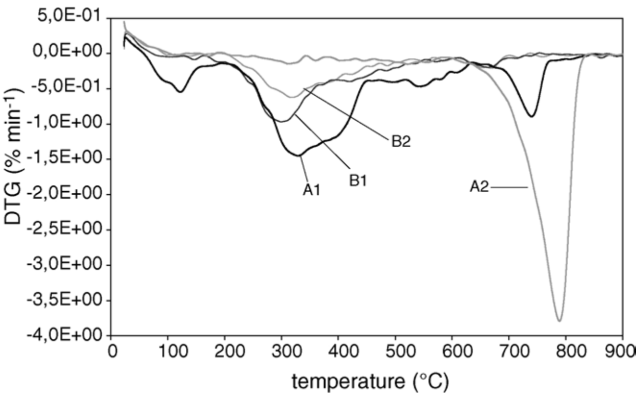

Fig. 8. DTG characteristics of two abandoned landfills A and B; A1 and A2 represent different sections, B1 and B2 are assigned to landfilled waste before and after aeration.

Mineralization of landfill B material, more degraded than A1, is supported by aeration in a lab reactor. Table 4 summarizes basic data obtained for the landfill materials. Due to stabilization by drought that causes a longer lag phase the respiration activity test (RA 4 days) of sample A1 failed despite the considerable amount of organic matter and TG characteristics of a scarcely degraded waste sample. The moderate continuous weight loss of sample A2 is similar to the thermogram of mineral soil samples. However, the high content of carbonates indicated by the considerable weight loss >650 °C points to the characteristics of construction waste rather than excavation residues.

## 4. Conclusions

Thermal methods have proved to be an appropriate tool in assessment of the stage of degradation and stabilization in waste materials. Further to evaluating the status of organic matter, information concerning the fraction of inorganic compounds are also made available. Stabilization is indicated by the shift of TG/DTG peaks towards higher temperatures. This trend is confirmed by the $CO_2$ ion current. The $CO_2$ ion current reveals interesting details of humic acid development in composts.

In practice, the application of thermal methods merely requires a simple procedure for data interpretation. The present paper illustrates how thermal methods are suited for use in the monitoring the degree of stabilization of municipal solid waste. Interpretation schemes will constitute a crucial issue in further investigations for practical use. Due to the specific composition of “biowaste” compost and biologically treated municipal solid waste different thermal characteristics could provide a quick assessment of high quality composts in the future, based on statistical evaluation (e.g. cluster analysis). The influence of material composition, humification and mineral compounds on stability, thermal behavior, and exothermic reactions still remain to be properly investigated.

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