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The influence of waste sample preparation on reproducibility of thermal data

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Abstract

Different milling procedures were applied in waste sample preparation in order to obtain satisfactory reproducibility of thermal investigations (thermogravimetry (TG) and differential scanning calorimetry (DSC)). Due to the complex mixture and the manifold texture involved, municipal solid waste is the most challenging material with regard to obtain representative samples for analysis. The material was subjected to the following milling procedures: ultra-centrifugal mill, cutting mill and vibratory disk mill. Fibrous compounds tend to coil after the milling and sieving process due to hydrogen bonds forming between cellulose materials and electrostatic effects caused by the metallic surface of the sieve. The use of the ultra-centrifugal or cutting mill did not result in an adequate reproducibility. Reproducibility of TG curves, DSC profiles and the effect on resulting enthalpies was evaluated by means of statistical methods. The extensive range of minimum and maximum enthalpies obtained did not allow for correct assessment to be performed. A combination of cutting and vibratory disk mill (agate mill) led to best results. The results are visualized by means of box-plots indicating the minimum and maximum, the 25 and 75% quartile and the median.
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Keywords: Municipal solid waste; Sample preparation; Reproducibility; Thermal analysis

1. Introduction

Over the last decade thermal analysis has been successfully applied by several working groups to characterize waste materials and changes occurring during biological processes. In particular, composting and aerobic treatment of various materials have been the main focus of interest [1–5]. Stabilization of organic matter is reflected by different thermal parameters, e.g. decrease of heat flow and enthalpies, shifting of exothermic peaks [5–7], and changing ratio of mass losses [8]. Identification of degradation and maturity stages, assignment to different processes and materials can be performed by thermal analysis [9,10]. Due to manifold advantages thermal methods are suited to practical application in waste management, in association with adequate supporting evaluation tools based on multivariate data analysis [11,12]. However, preliminary basic investigations on reproducibility are required in order to avoid misinterpretation and to distinguish real effects from random error. Due to the small sample amount investigated, particular care should be taken in sample preparation to ensure satisfactory reproducibility. Representative sampling of waste materials is a prerequisite and is currently an issue undergoing widespread discussion in the European Union. In 2004 recommendations concerning the preparation of laboratory samples from waste materials were published [13]. Waste materials behave in a different way with respect to milling and homogenizing. Abandoned landfill materials with a high content of mineral compounds and sewage sludge lead to remarkably homogenous samples. In biowaste composts fresh wooden components are more recalcitrant against milling than other ingredients, although mixtures obtained are homogenous. Municipal solid waste following mechanical–biological treatment (MBT) is the most challenging matter due to the diversity of materials in terms of physical properties and texture.

The objective of this study was to investigate the influence of different milling procedures, widely used in waste sample preparation, on reproducibility of thermal data.

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2. Materials and methods

Waste samples originated from six MBT-plants which process municipal solid waste. A large part of the biogenic waste fraction (yard and kitchen waste) that is collected separately is missing in municipal solid waste. Representative sampling took place according to Austrian Standards [14]. 10–15 liters of the representative sample from the material under operation in the MBT-plant were chopped by the shredder to obtain particles sizes <20 mm. Approximately 1000 g of the sample were dried at 105 °C. Table 1 illustrates sample names, age and milling procedure applied. All samples were milled in the cutting mill and screened (mesh size 4 mm) in order to obtain smaller particles in a first step. The following milling procedures were performed to get particle sizes <0.2 mm for thermal analysis. Specific milling procedures were assigned to different experiments. 100 g of the 4 mm material for experiment I and the total amount of ∼1000 g for experiments II and III were subjected to further milling processes. For experiment I the material was either milled with the cutting mill or with the ultra-centrifugal mill. For experiment II the cutting mill only, for experiment III the cutting mill and in addition the vibratory disk mill were used. All samples were screened through <0.2 mm which is the required particle size for analyses according to EN15002 [13].

Experiments I–III were carried out with five replicates of each sample. Only sample MBT1-4-U of experiment I was represented by eight replicates. For this sample, separation of sample fractions was performed by rinsing out the granular particles through a sieve. The granular and the fibrous fraction were both freeze dried subsequently.

Equipment: cutting mill SM 2000 Retsch, ultra-centrifugal mill ZM 1000 Retsch, vibratory disc mill RS1 Retsch (100 ml agate jar and agate disks).

Photographs were taken using a Canon EOS 30D.

2.1. Thermal analyses

Thermal analyses were performed using the instrument for simultaneous thermal analysis STA 409 CD Skimmer (Netzsch GmbH). The heating rate was set to 10 K min^{-1} (experiment I) and 20 K min^{-1} (experiments II and III), respectively. Oxidative combustion was carried out with a gas flow of 120 ml min^{-1} (80% He/20% O_2). Temperature and heat calibration were carried out by means of melting characteristics of indium and zinc. A sample amount of 16.00 mg was combusted in an Al_2O_3 pan. Sample DSC curves were corrected by subtraction of the DSC curve of the empty pan.

Enthalpies were calculated by integration of the peak area below the DSC curve drawing a horizontal baseline from 30 to 650 °C (between the second exothermic peak of organic matter combustion and the endothermic peak of the carbonate decay).

2.2. Data analysis

The distribution of data was visualized by box-plots including the maximum, the 75% quartile, the median, the 25% quartile, and the minimum. The mean distances (D_M) of each replicate ($D_{(i)}$) to the average curve ($\bar{y}$) of all replicates (n) and each data point ($a_{(k)}$) was calculated. This calculation was performed for all samples listed in Table 1. The mean distance is given in arbitrary units.

$$\bar{y} = \frac{\sum_{k=1}^{n} y_k}{n}, \quad D_{(i)} = \sqrt{\sum_k (a_{(k)} - \bar{y}_{(k)})^2}, \quad D_M = \sum \frac{D_{(i)}}{n}$$

The coefficient of variation (CV) was determined for mass losses (30–650 °C) and enthalpies resulting from TG curves and DSC profiles.

Table 1
Summary of experiments (experiment) and sample names according to waste origin (MBT-plants: MBT1–MBT6), age (weeks), and combined milling procedures (applied/not applied = +/−); U = ultra-centrifugal mill; C = cutting mill

Sample	Experiment	Age (weeks)	Cutting mill	Ultra-centrifugal mill (U)	Cutting mill (C)	Vibratory disk mill
			Screen ≤4 mm	Screen ≤0.2 mm	Screen ≤0.2 mm	Screen ≤0.2 mm
MBT1-4-U	I	4	+	+	−	−
MBT1-4-C			+	−	+	−
MBT1-6-U		6	+	+	−	−
MBT1-6-C			+	−	+	−
MBT1-12-U		12	+	+	−	−
MBT1-12-U			+	−	+	−
MBT2-4-U		4	+	+	−	−
MBT2-4-C			+	−	+	−
MBT2-15-U		15	+	+	−	−
MBT2-15-C			+	−	+	−
MBT3-0	II	0	+	−	+	−
MBT4-0		0	+	−	+	−
MBT5-70		70	+	−	+	−
MBT6-120		120	+	−	+	−
MBT3-0	III	0	+	−	+	+
MBT4-0		0	+	−	+	+
MBT5-70		70	+	−	+	+
MBT6-120		120	+	−	+	+

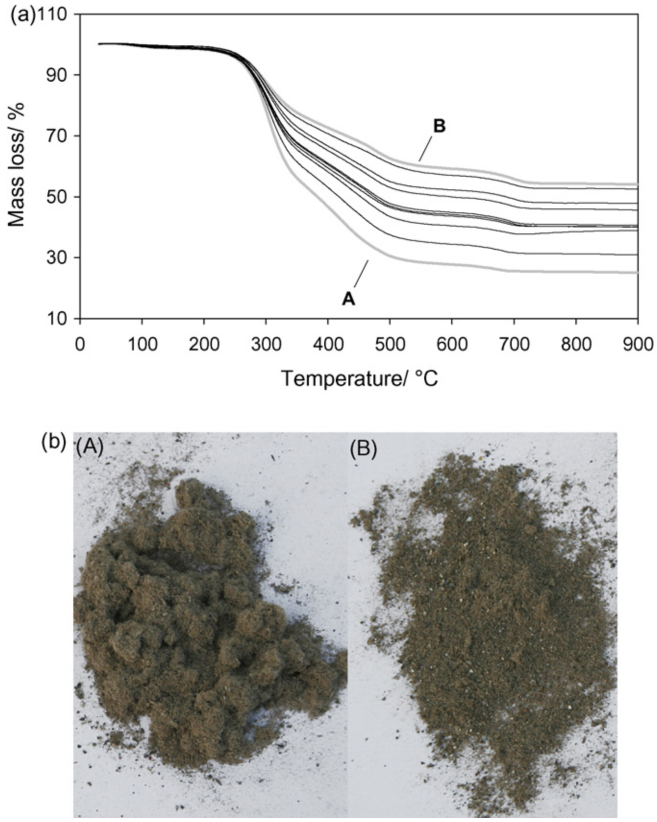

Fig. 1. Thermograms (a) of eight sample MBT1-4-U replicates (ultra-centrifugal milling) and of the separated fractions assigned to fibers (A) and particles (B) and (b) photographs of the separated fractions (A) and (B).

3. Results and discussion

Thermal analysis of experiment I was performed with samples having been subjected to chopping by the ultra-centrifugal mill or the cutting mill. The use of the ultra-centrifugal mill is common in MBT waste preparation. Fig. 1a displays the thermograms of eight replicates of sample

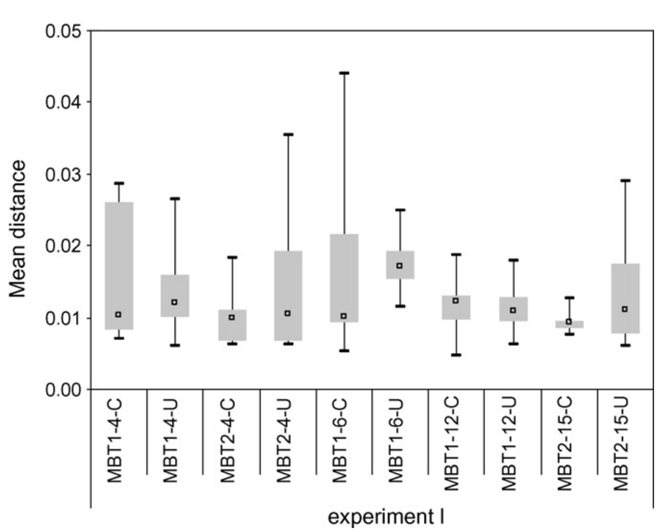

Fig. 2. Box-plots of minima and maxima, median and 50% quantile of TG curves of different MBT waste samples (C: cutting mill; U: ultra-centrifugal mill).

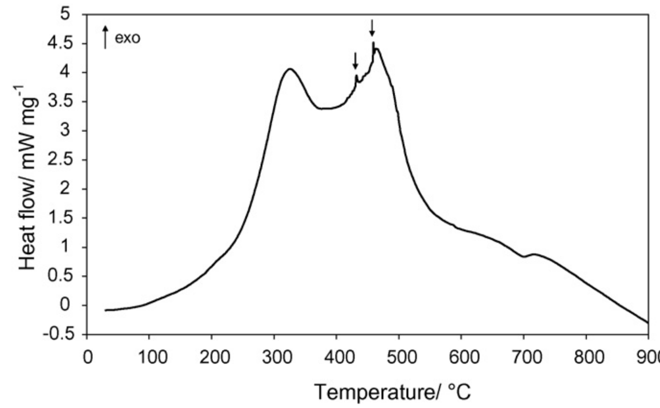

Fig. 3. DSC curve of MBT1-4-U displaying two small sharp exothermic peaks (arrows) caused by tiny plastic particles.

MBT1-4-U, milled by means of the ultra-centrifugal mill. It is clearly visible that the deviation of the replicates is considerably high due to the difficulty of representative sample removal. Cellulose belongs to the organic matter fraction that is combusted between 200 and 350 °C. Varying portions of cellulose in the laboratory sample due to coiling effects influence the incline of the mass loss slope. Due to the succeeding generation of the data points the gradient of the curve between 200 and 350 °C influences all following data points and leads to diversification. The ultra-centrifugal milling affects the geometry of the material and leads to fractionation of organic matter. In particular, cellulose fibers tend to coil after passing through the metallic sieve (<0.2 mm), likely due to the presence of hydrogen bonds and electrostatic effects [15]. Granular particles of different chemical composition (mineral compounds, organic matter and plastic particles) are enclosed in these coils. In an additional sieving and washing procedure these fractions were both separated as completely as possible. This "coiling" phenomenon is less distinct

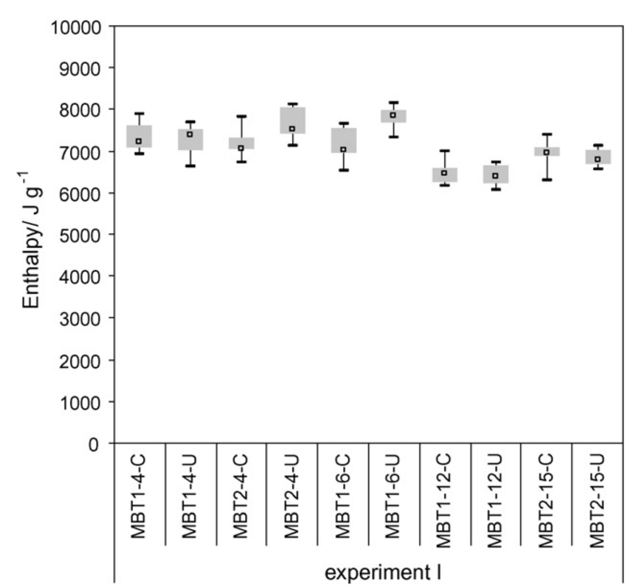

Fig. 4. Effects of milling procedures (C: cutting mill; U: ultra-centrifugal mill) on calculated enthalpy in terms of minimum and maximum, median and 50% quantile.

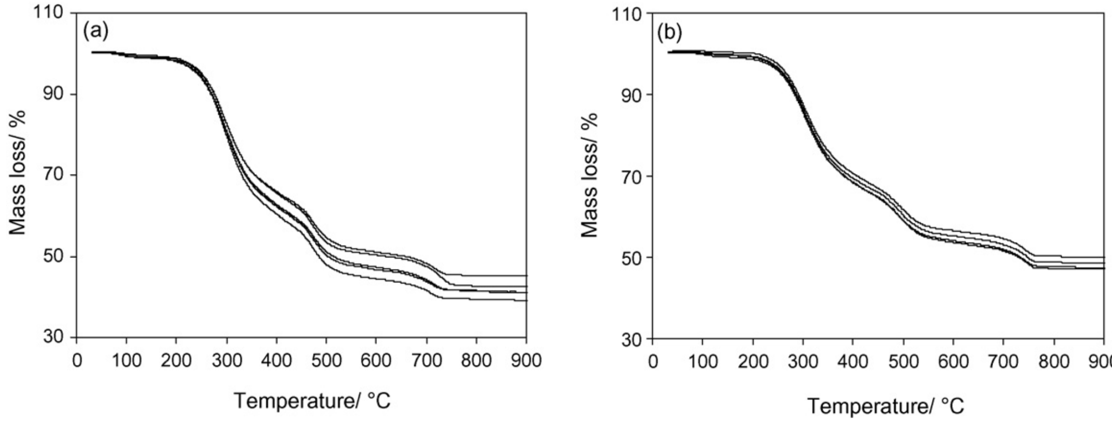

Fig. 5. Effect of milling procedures on reproducibility of TG curves (sample MBT4-0): (a) experiment II and (b) experiment III.

when applying cutting milling procedures, although still present to a certain degree. However, due to the closecut fibers the "coils" can easily be destroyed.

Curves A and B show the separated fractions of fibers (A) and granular particles (B) representing the extremes. The eight replicates of sample MBT1-4-U are located in between. Fig. 1b illustrates the "fiber" and the "granular particle" fraction by means of a photograph.

The mean distances between the TG curves are displayed in Fig. 2. The mean distance is represented by the distance of each TG curve to the average of all TG curves. The box-plots include the minima and maxima, the median and the 50% quantile. All TG curves feature high distances irrespective of origin and age. No obvious difference was observed between the milling procedures. Cutting mill and ultra-centrifugal mills both produce high deviation.

DSC curve profiles are influenced by small sharp peaks that can be attributed to tiny plastic particles. Enthalpies of the marked plastic peaks (arrows Fig. 3) are 0.08% of the total enthalpy. Due to the marginal contribution they are not separately considered in the calculation of enthalpies.

However, in order to ascertain how deviation affects the corresponding enthalpies the box-plots, indicating the minimum and maximum, the median and the 50% quantile, were calculated (Fig. 4). Enthalpies provide important information on stability of the sample. Degradation of waste organic matter causes a decrease of enthalpy in the whole system [16]. Furthermore, according to the Austrian Landfill Ordinance MBT-materials are required to meet a limit calorific value of 6600 kJ kg^{-1} DM before landfilling [17]. According to German Standards DIN 51900-1 [18], the correlation of calculated enthalpies with the calorific value may provide the basis for a prediction model in the future.

All samples featured considerable differences between the minimum and maximum of enthalpy values. As shown in Fig. 3, tiny granular plastic particles influence the shape of the heat flow curve, though their contribution to the enthalpy of the sample is marginal. The material examined at times may become more homogenous with age, although in the sample sets examined (MBT1 and MBT2) this was not the case. The poorly operated processes (MBT1 and MBT2) might explain the marginal changes observed. Apart from a slight decrease of enthalpies from "younger" to "aged" samples no obvious differences were observed. This fact was also confirmed by conventional parameters.

Accordingly, a second set of samples from different MBT-plants (MBT3–MBT6) was used for experiments II and III, covering a wider range of degradation stages. In addition more material (1000 g) was milled in order to improve the throughput. Milling procedures focused on the cutting mill. Three samples were extremely fibrous due to their age (MBT3-0 and MBT4-0) or to the particular composition (MBT5-70) with a high content of paper diapers that are treated in association with municipal solid waste. For experiment III an additional milling step (vibratory disk mill) was performed. This procedure caused a dispersion of fibrous coils and led to a more homogenous mixture of the sample material. Fig. 5 displays the effect of milling procedures in experiments II (a) and III (b).

Fig. 6 illustrates the results of experiments II and III, regarding the mean distances of the TG curves. Minima and maxima, median and 50% quantile are shown in the box-plots. Modified sample preparation in experiment III produced a decrease in mean distances of the TG curves.

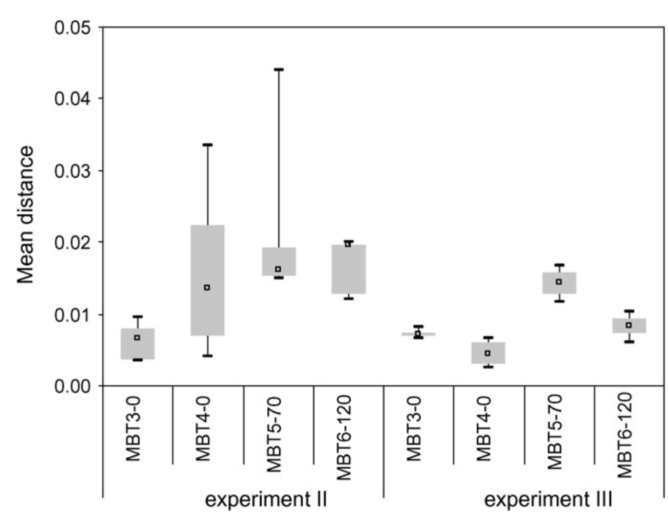

Fig. 6. Box-plots of the TG curves (experiments II and III) indicating the minima and maxima, the median and the 50% quantile.

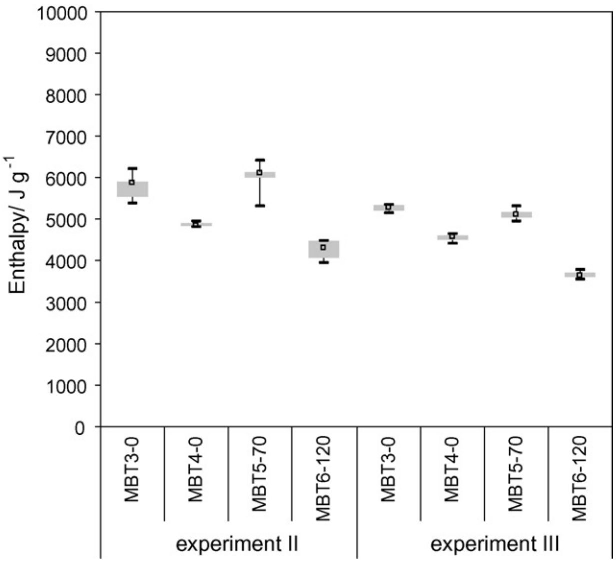

Fig. 7. Effects of milling procedures (cutting mill = experiment II; cutting mill and vibratory disk mill = experiment III) on calculated enthalpy in terms of minimum and maximum, median and 50% quantile.

For practical use it is important to assess how the calculated enthalpies are affected by the milling procedure. The additional use of the vibratory disk mill (experiment III) led to minor deviations (Fig. 7). In particular, the minima and maxima values were much closer, an indispensable requisite for the accurate evaluation of waste stability. Enthalpy values of experiment III are located at the bottom of the experiment II values. Due to coiling effects fibrous particles are disproportionately represented which is reflected by the TG profiles and the mass losses, respectively (Fig. 8). Mass losses of experiment III were comparable to the lowest mass losses of experiment II.

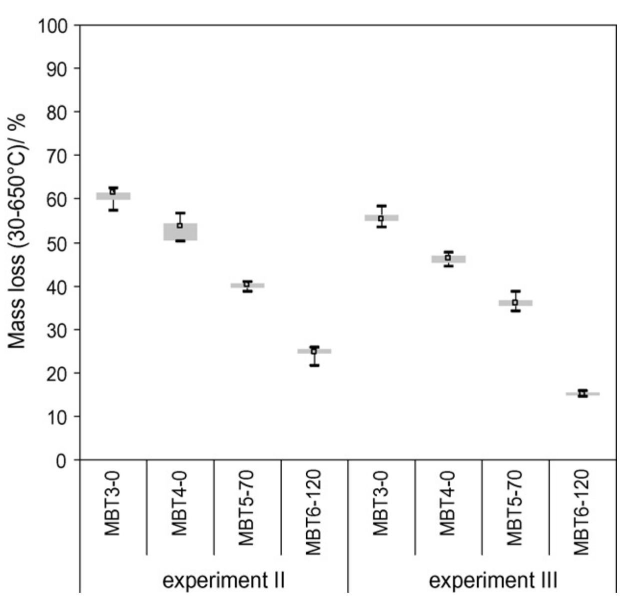

Fig. 8. Effects of milling procedures (cutting mill = experiment II; cutting mill and vibratory disk mill = experiment III) on mass loss of 30–650 °C in terms of minimum and maximum, median and 50% quantile.

Table 2
Mean coefficient of variance (CV) of mass losses (30–650 °C) and enthalpies determined for experiments I–III

Experiment	Mean CV (%)	
	Mass loss (%) (30–650 °C)	Enthalpy ($J\,g^{-1}$)
I	8	5
II	4	4
III	3	2

The decreasing coefficient of variation (CV), calculated for mass losses and enthalpies, indicates the improvement of reproducibility by the milling procedure applied in experiment III (Table 2).

4. Conclusions

The satisfactory reproducibility of thermal pattern and results obtained is largely influenced by the means of sample preparation and milling procedures applied. Fibrous compounds tend to coil and are represented disproportionately causing organic matter contents and enthalpies to increase. Therefore, fibrous compounds reduce the degree of reproducibility. Materials for analysis should feature a uniform shape and geometry of waste particles. Best results to reach this target were obtained by milling procedures using a cutting mill in association with a vibratory disk mill. The latter is effective against coiling of fibers. The decreasing coefficient of variation confirms the improvement of reproducibility from experiments I–III regarding mass losses ($CV_I = 8\%$, $CV_{II} = 4\%$ and $CV_{III} = 3\%$) and enthalpies ($CV_I = 5\%$, $CV_{II} = 4\%$ and $CV_{III} = 2\%$).

Due to the comprehensive information provided by thermal analysis the implementation of this method in waste management practice is a target to be reached. Austrian Standards dictate limit values for municipal solid waste intended for landfilling, with regard to biological reactivity and calorific values. These parameters are reflected by the thermal behavior. Future research focuses on data evaluation tools based on multivariate statistical methods, supporting practical application in waste management. For this purpose, the obtaining of satisfactory reproducibility is a fundamental requirement.

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