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Evaluation of the aerobic composting process of winery and distillery residues by thermal methods

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Abstract

The possibility of using thermal analysis for a quick characterization of chemical changes was tested in the organic matter from composting materials. Differential thermal analysis (DTA), thermogravimetry (TG) and the first derivative of the TG (DTG) were calculated in oxidizing conditions on compost samples obtained from three composting piles. The composting piles were made by mixing winery and distillery residues with sewage sludge (pile 1), with cow manure (pile 2) and hen droppings (pile 3). The temperature values in the pile 1 showed a different evolution during the thermophilic stage of the composting process in relation to the piles 2 and 3. The thermophilic stage for pile 1 was 17 days, meanwhile for the piles 2 and 3 were around 80 and 110 days, respectively, and probably pile 1 was not well composted. The curves of ion current of CO_2 have been recorded in order to shed light on changes occurring in organic matter during composting. Particularly DTG curves allowed us to distinguish between well (piles 2 and 3) and poor (pile 1) stabilized organic matter. The energy released was calculated for each sample by integrating the DTA curves and these results are agreed with the previous hypothesis. Information deriving from weight losses, registered by the TG and DTG curves, enables to follow the evolution state of the organic matter and therefore changes in its stability. These data could determine the final point of the composting process of winery and distillery residues and then reduce the time for compost harvest.

Keywords: Winery residues; Compost; Aerobic digestion; Differential thermogravimetry; Differential thermal analysis

1. Introduction

Composting of agricultural and urban residues such as winery and distillery residues (WDR) is an useful method for producing a stable material, which can be used as a source of nutrients and as a soil conditioner in the field [1]. Part of the organic matter is mineralized into carbon dioxide, ammonia and water during composting, and part is transformed into refractory humic substances. In the agriculture field a process for rapid conversion of fresh organic matter into humus is available for commercial purposes [2]. The composting technique is an accelerated version of the processes involved in the natural transformation of organic debris in soil, and can be obtained through the provision of the most favorable conditions for microbial activity [3]. This process needs controlled conditions, particularly moisture and aeration, to reach favorable temperatures for thermophilic microorganisms, to decompose the organic substrate and to transform it into stabilized organic matter. It is a complex microbial process that comprises self-heating, multistage temperature conditions and different microorganisms [4]. The understanding of organic matter transformation throughout the composting process and the proper evaluation of compost stability and maturity are essential for a successful utilization of compost [5]. Compost quality is defined by its stability and maturity. Stability is related to the level of biological activity of the compost and depends on the degree of degradation achieved during the composting process and maturity is related to the lack of phytotoxicity on vegetation growing in the soil treated with compost [6,7].

New analytical methods and well established methods with new applications get insight into the compost samples, such as thermal methods, contributing to a better understanding of the

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decomposition and stabilization processes that take place. Thermal degradation techniques, such as thermogravimetry (TG), derivative thermogravimetry (DTG) and differential thermal analysis (DTA), have been applied for many years to elucidate structural features of decayed natural heterogeneous organic matter [8,9], providing important information about the chemical characteristics of the sample [10].

The objective of the present study is to verify the previously assessed applicability of thermal analyses in order to determine the stability and maturity of compost elaborated with WDR from real agricultural activities in industry. Thermogravimetry (TG/DTG) and differential thermal analysis (DTA) are combined with the information from the mass spectrum of evolved gases.

2. Materials and methods

2.1. Composting procedure

Three different piles were prepared by the Rutgers static pile composting system, using in all of them wastes from the winery and distillery industry. Pile 1 was initially prepared with mixtures of grape stalk (GS), grape marc (GM) and exhausted grape marc (EGM) and after 17 days sewage sludge (SS) was added as source of microorganisms and nitrogen (about a 29% of fresh weight of the pile). Pile 2 and pile 3 were elaborated using exhausted grape marc (EGM) and cow manure (CM) and poultry manure (PM), respectively (Table 1). SS came from a treatment plant of urban wastewater placed in Torrevieja (Alicante, Spain). CM was collected from a cattle farm placed in Santomera (Murcia, Spain) with a productivity of 35,000 heads per year. PM was collected from a poultry farm with 30,000–40,000 laying hens located in Orihuela (Alicante, Spain). GS and GM were collected from a winery placed in Jumilla (Murcia, Spain) and EGM from an alcohol distillery placed in Villarrobledo (Albacete, Spain).

The mixtures (about 1800 kg weight each) were composted in a pilot plant, in trapezoidal piles (1.5 m high with a 2 m × 3 m base); thereafter, a forced aeration conducted through three basal PVC tubes (3 m length and 12 cm diameter) was applied. Aeration system was imposed for 30 s every 30 min, at 55 °C as ceiling temperature for continuous ventilation. Turning treatments for improving both homogeneity and fermentation processes were applied when necessary (Table 1). After 17 days, the pile 1 was amended with 735 kg of sewage sludge (SS) (228 kg of dry matter).

The bio-oxidative phase of composting was considered finished when the temperature of the pile was stable and near to that of the surrounding atmosphere. Then, the piles were allowed to mature for 2 months. The moisture of the piles was controlled weekly by adding the necessary amount of water to maintain a moisture content around 40%. Excess of water leached from the piles was collected and added again to the piles. Samples were obtained by mixing subsamples from seven different zones of the piles. The sampling was made at the beginning of the process (I), during the thermophilic phase (T), at the end of the bio-oxidative phase (E) and during the maturing phase (M) in order to analyze physical and chemical parameters.

Table 1
Characteristics of the composting heaps

Waste[a]	Composition[b]		
	Pile 1[c]	Pile 2	Pile 3
GS	63 (56)	–	–
EGM	25 (28)	70 (80)	70 (79)
GM	12 (16)		–
CM	–	30 (20)	–
PM	–	–	30 (21)
Turning (days)	18–53–86	92	144

[a] GS: grape stalk; EGM: exhausted grape marc; GM: grape marc; CM: cow manure; PM: poultry manure; SS: sewage sludge.

[b] Data expressed as percentage on a fresh weight basis (dry weight basis in parentheses).

[c] Initial proportions, after 17 days sewage sludge was added (about a 29% of fresh weight of the pile).

2.2. Chemical methods

Total organic carbon (C_{org}) was determined by automatic microanalysis [11], as were the 0.1 M NaOH-extractable organic carbon (C_{EX}) and fulvic acid-like carbon (C_{FA}), the latter after precipitation of the humic acid-like carbon (C_{HA}) at pH 2.0, [12]. The C_{HA} was calculated by subtracting the C_{FA} from the C_{EX}. The humification ratio (HR), the humification index (HI) and the percentage of humic acid-like carbon (P_{HA}) were calculated as $(C_{EX}/C_{org}) \times 100$; $(C_{HA}/C_{org}) \times 100$ and $(C_{HA}/C_{EX}) \times 100$, respectively. The cation exchange capacity (CEC) was determined with $BaCl_2$-triethanolamine [13]. All parameters were determined in triplicate and significant differences among the values of each humification index studied during composting were calculated by the LSD (least significant difference) test at $P < 0.05$.

2.3. Sample preparation and thermal analysis

Samples were air-dried, ground in an agate mill, then sieved through a 0.125 mm mesh, and milled again with an agate mortar. Thermal analyses were performed with a METTLER TOLEDO (TGA/SDTA851e/LF/1600) and PFEIFFER VACUUM (THERMOSTAR GSD301T) mass spectrometer that enables the recording of thermograms and mass spectra of combustion gases simultaneously. All samples were combusted with a mixing stream of oxygen/He (20/80%), a gas flow 100 ml min^{-1} within a temperature range from 25 to 1000 °C, a heating rate 10 °C min^{-1}, a sample weight about 5 mg, Al_2O_3 pan, and self-controlled calibration. All the assays were carried out in triplicate. The enthalpy of combustion, ΔH, of the samples was calculated from the DTA curves, as the area between the baseline and the exothermic combustion peak, using a calibration curve plotting with the fusion enthalpy of different metals: In (3.28 kJ mol^{-1}), Pb (4.80 kJ mol^{-1}), Al (10.67 kJ mol^{-1}) and Au (12.55 kJ mol^{-1}).

3. Results and discussion

3.1. Temperature evolution of the compost piles and humification parameters

The temperature is one of the main parameters to evaluate the composting process, since its value determines the rate at which many of the biological reactions take place as well as the Sanitation capacity of the process [14]. Mainly, there are three temperature intervals that govern the different aspects: firstly, temperatures above 55 °C that maximize sanitization, secondly temperatures between 45 and 55 °C that improve the degradation rate and thirdly that ones between 35 and 40 °C that increase microbial diversity [14].

Fig. 1 shows the temperature curves of each pile together with the surrounding temperature. Piles 2 and 3 showed a longer thermophilic phase than pile 1, maintaining the temperature above 40 °C for 76 and 122 days in piles 2 and 3, respectively. Moreover, the temperature within these piles reached higher values (above 50 °C). Nevertheless, a rapid increase in the temperature was recorded for pile 1, so that on the first days the maximum temperature values were reached. However, the temperature decreased suddenly and the pile needed to be enriched with sewage sludge (SS) after 17 days in order to improve the composting process (Table 1). Addition of SS did not stabilize the thermophilic phase for the pile 1. This decrease of the temperature values after a short thermophilic phase was also observed in an experiment of composting grape stalk with sludge [15].

The presence of grape stalk in pile 1, a material that is characterized by its high polyphenolic content, was probably responsible for these differences. Polyphenolic compounds, especially tannins, could influence the composting process because of their antimicrobial effect [16]. On the other hand, the composting process in pile 1 took place in winter. This fact could also explain that the temperature values reached in this pile were lower and the thermophilic phase shorter than in piles 2 and 3, which were performed in summer. At cold environmental conditions, the large difference of temperature between the pile and the surroundings which favors an energy flux through the surrounding atmosphere [17], which makes difficult to reach high temperatures into the pile.

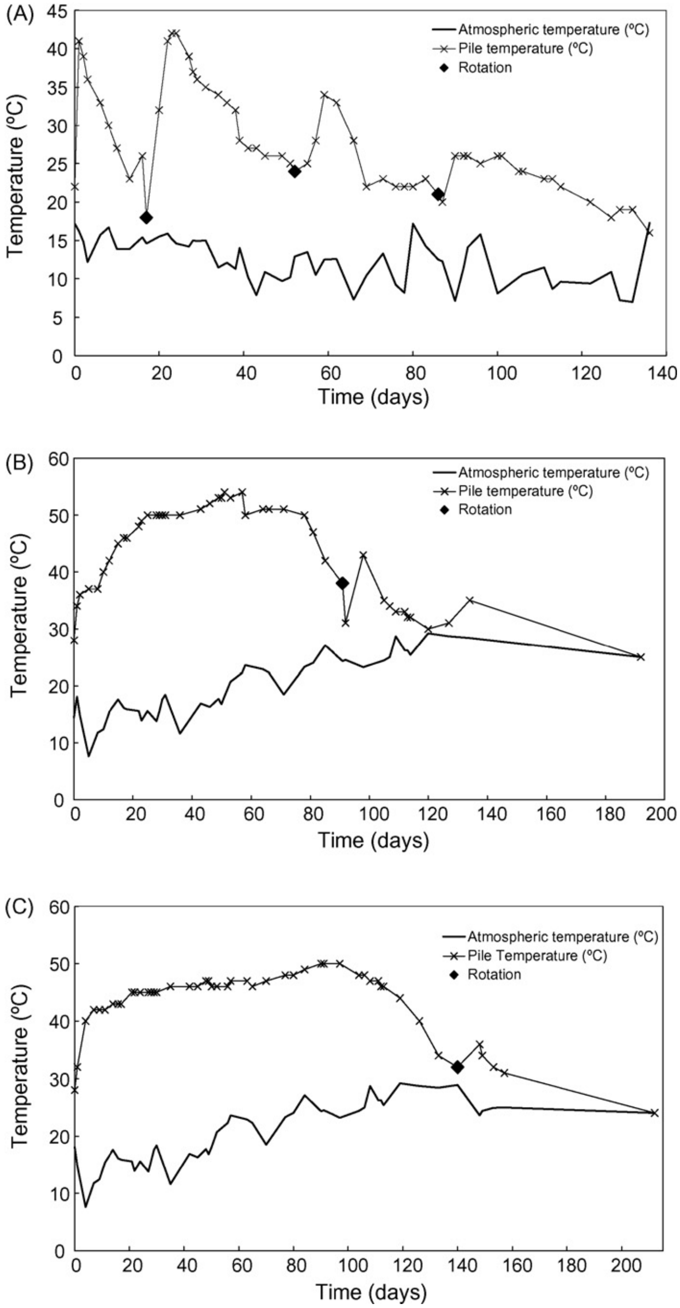

Fig. 1. Evolution of the atmospheric temperature and the temperature within the different piles during the composting process: (A) pile 1 (grape stalk + grape marc + exhausted grape marc + sewage sludge); (B) pile 2 (exhausted grape marc + cow manure); (C) pile 3 (exhausted grape marc + poultry manure).

The humification ratio (HR), expressed as $(C_{EX}/C_{org}) \times 100$, and the humification index (HI), calculated as $(C_{HA}/C_{org}) \times 100$, fell in all the mixtures. The percentage of humic acid-like carbon ($P_{HA} = (C_{HA}/C_{EX}) \times 100$) and C_{HA}/C_{FA} did not show a clear tendency during the composting process of piles 2 and 3 and these parameters decreased throughout the composting process of pile 1 (Table 2). So, these parameters could not indicate the evolution of the humification process in this experiment. The humification process was best revealed by the increase in CEC/C_{org} ratios throughout the composting process. This finding could be due to the alkaline co-extraction and partial acid co-precipitation of incompletely or not humified components of organic matter, such as the polyphenols of the winery and distillery wastes [18], which hid the real evolution of the humic fraction. The concentration of polyphenols is higher in grape stalk and marc than in exhausted grape marc [19] and this could explain the effect of these compounds in humification parameters was lower in piles 2 and 3. The values of HR, HI, P_{HA} and C_{HA}/C_{FA} accepted as indicating compost maturity [18,20], were exceeded, in general, at the beginning of the experiment in all the composts, and therefore they cannot be used here as maturity indicators. Similar findings were observed by [21], in a study of maturity parameters for composts of different origin, and by [22], in an experiment with composts of olive mill waste water with agroindustrial and urban wastes. Therefore, definite values of these parameters for mature composts cannot be stated. However, their evolution during composting is a good indicator

Table 2
Evolution of humification index and cation exchange capacity (CEC) during composting process (dry weight basis)

Composting time (days)	HR (%)	HI (%)	P_{HA} (%)	C_{HA}/C_{FA}	CEC[a]/C_{org} (mequiv. g^{-1})
Pile 1: grape stalk + grape marc + exhausted grape marc + sewage sludge					
0	27.5	16.5	59.9	1.50	1.48
17[b]	12.6	5.0	39.5	0.66	2.18
24	13.3	6.6	49.5	0.98	–
45	13.6	6.6	48.7	0.95	2.33
59	12.3	4.9	40.0	0.67	2.28
234	8.9	2.9	32.6	0.48	3.00
LSD	1.0	0.9	4.9	0.14	0.41
Pile 2: exhausted grape marc + cow manure					
0	10.9	7.1	65.4	1.91	1.63
15	16.7	12.9	77.2	3.39	1.67
29	12.4	8.8	71.3	2.48	1.64
50	11.7	8.3	71.2	2.47	–
71	9.0	5.7	63.5	1.78	2.06
91	8.5	5.3	62.5	1.67	–
134	8.80	5.7	64.7	1.83	2.47
192	8.65	5.7	66.2	1.96	2.72
LSD	1.5	1.5	5.7	0.57	0.26
Pile 3: exhausted grape marc + poultry manure					
0	12.1	7.6	62.7	1.68	1.46
14	14.1	10.3	73.3	2.75	1.58
28	9.1	5.4	59.5	1.47	1.71
42	9.2	5.6	60.7	1.55	1.63
70	8.0	5.0	63.3	1.72	2.06
106	11.3	7.8	69.0	2.24	2.39
140	8.7	5.7	65.4	1.89	–
212	7.8	4.9	63.5	1.74	2.36
LSD	0.6	0.7	4.3	0.40	0.26

HR: humification ratio (HR = (C_{EX}/C_{org}) × 100), HI: humification index (HI = (C_{HA}/C_{org}) × 100), P_{HA}: percentage of humic acid-like C (P_{HA} = (C_{HA}/C_{EX}) × 100), C_{HA}/C_{FA}: ratio of humic acid-like C/fulvic acid-like C, C_{org}: total organic carbon, LSD: least significant difference ($P < 0.05$).

[a] Ash-free material. –: Not determined.

[b] Pile 1 was initially made by mixing only grape stalk + grape marc + exhausted grape marc, and after 17 days was enriched with sewage sludge.

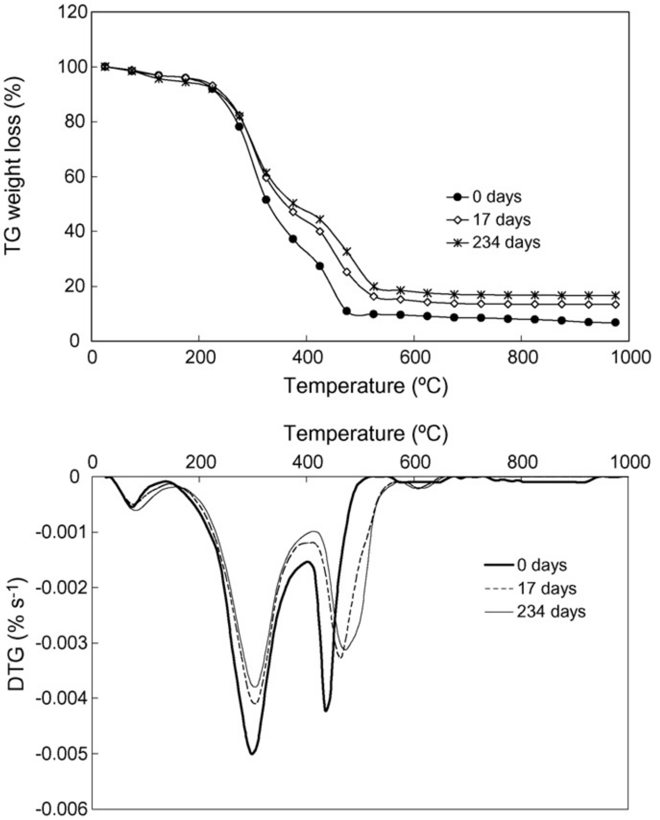

Fig. 2. TG and DTG curves of the samples collected at different times of the composting process for pile 1 (grape stalk + grape marc + exhausted grape marc + sewage sludge).

of the OM humification process. In all mixtures reached final values of CEC/C_{org} ratio > 1.9 mequiv. g^{-1} (value accepted as indicating compost maturity [18]), which suggested that all the composts had and acceptable degree of maturation according to this parameter.

3.2. *Thermal analysis*

The interpretation of the chemical analysis as HR or HI is difficult as it was discussed above. Only the CEC/C_{org} ratio can be useful in order to follow the maturity process of the organic matter in the compost piles. Thermal analysis provides information about the chemical characteristics of the sample without any extraction step. This information of the whole sample can help to determine the maturity state of the organic matter during the composting process.

Compost thermograms show four clear steps (Figs. 2–4). TG and DTG profiles display a weight loss in the 50–150 °C, mainly caused by loss of residual water (again Figs. 2–4). Dehydration within this range of temperature was also reported by different authors [9,23–25], that is confirmed by the peak of the ion current (mass (18)) at this temperature range (data not shown). In the DTG profiles, two peaks can be distinguished between 200 and 580 °C, which indicate the highest losses of organic matter. The first peak lies in between 200 and 400 °C and the second one appears between 400 and 580 °C (Figs. 2–4). This is in accordance with the findings reported by the authors former mentioned before [9,23–25]. The first peak, in the 200–400 °C range, can be attributed to the combustion of carbohydrates such as cellulose and lignocellulosic substances [26], which are the main components of the plant material present in the winery and distillery residues. The first peak decreases with time for the piles 2 and 3, however, for pile 1 only a minor decrease is observed after 17 days of the composting process when the pile was enriched with SS. Note that carbohydrates are combusted preferentially within this range (200–400 °C) and they decrease due to microbial degradation during the composting. The second peak between 400 and 580 °C increases during the degradation process for piles 2 and 3. This increase in the peak could be attributed to the humified matter that increases during composting [9,25], although the dominant role in the composting process could be the mineralization and enrichment of recalcitrant compounds.

TG and DTG profiles for piles 2 and 3 display a similar behaviour, while the TG and DTG profiles for pile 1 show

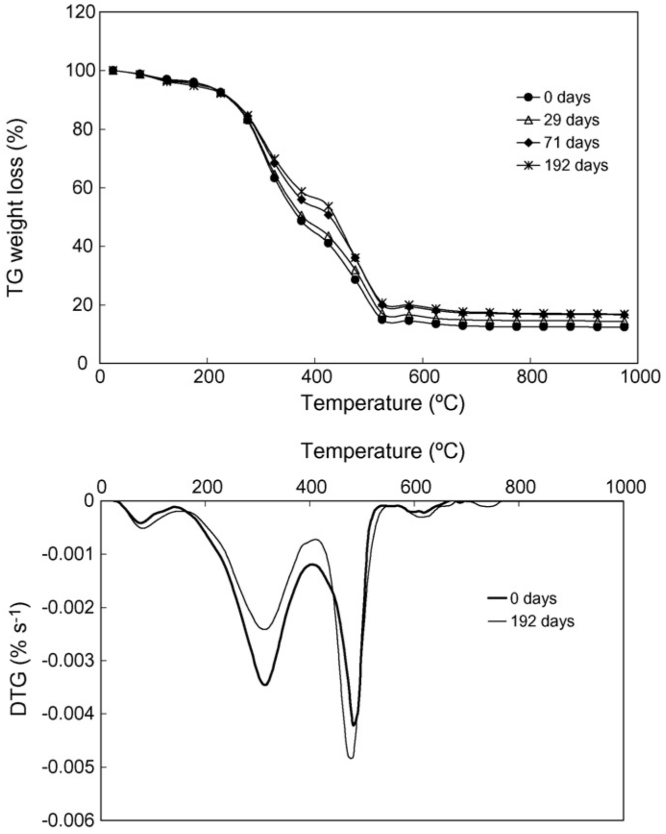

Fig. 3. TG and DTG curves of the samples collected at different times of the composting process for pile 2 (exhausted grape marc + cow manure).

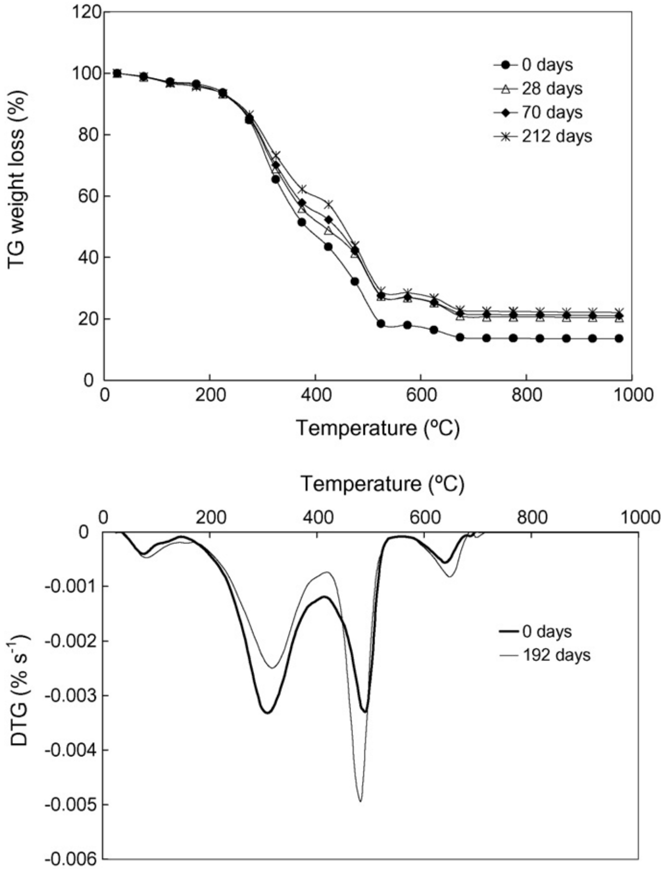

Fig. 4. TG and DTG curves of the samples collected at different times of the composting process for pile 3 (exhausted grape marc + poultry manure).

certain peculiarities as it is described below. TG curves of the initial sampling of piles 2 and 3 show a weight loss of 52.0 and 48.7% respectively, in the range between 200 and 400 °C, that decrease in the last sampling to 39.0% (192 days) and 36.6% (212 days), respectively (Table 3). Between 400 and 580 °C temperature range, the thermal degradation of the aromatic compounds takes place [23]. In this range, the weight loss for the first sampling (0 days) is 29.9 and 31.5%, piles 2 and 3, respectively. This percentage increases to 35.2% for pile 2 at the end of the experiment. According to the literature this trend suggests a progressive transformation of the biomass in the polyelectrolyte macromolecules known as humified matter and thus, the increase in molecular weight, stability, and aromatization degree during the composting process [23,25,27,28]. However, for the pile 3, the weight loss decreases to 30.3% in 400–580 °C temperature range. Between the first sample (0 days) and the second sample (14 days) the weight loss decreases to 24.1%. This decrease of the weight loss suggests that there are important changes in the original organic matter in the first days of the composting time in pile 3. It is important to consider that in this first time (2 weeks), the temperature of the compost pile increase quickly by the microbial activity and this biological activity can degrade biomolecules that are combusted in the 400–580 °C temperature range. A preferential degradation of these biomolecules present in pile 3 by microorganisms could explain differences between the initial (0 days) and the second (14 days) weight loss values.

It has been observed with other compost that the DTG peaks shift toward higher temperatures (more difficult to oxidize the organic matter), corresponding to more stabilized samples [23]. However, with the WDR samples this is not the case (see Figs. 2–4). Presumably, the DTG peak delay is related to the compost origin and to the changes in the organic matter during the composting process. Dell’ Abate et al. [25], working with wastes coming from various agricultural products (fruit-sludge, grape-wood, wood-chips and chestnut rind), observed a shift of both first and second exothermic peaks towards lower temperatures during the composting process. Our compost piles, elaborated with WDR, have also agricultural origin. These agricultural products are made up of a very complex biomolecules with high thermal stability. Changes in the organic matter, as humic-like colloids formed in the course of composting, could modify the thermal stability of the samples. On the other hand, it has been reported the role of the different inorganic salts in the DTG curves of the organic matter combustion process [29]. Salts as ammonium carbonate, sodium bicarbonate or calcium carbonate can be shifting toward lower temperatures the exothermic peaks [29]. The accumulation of inorganic materials during the composting process may in part make the delay observed in the exothermic peaks in the DTG profiles (Figs. 2–4).

TG and DTG thermograms of the pile 1 show minor changes in the combustion of the samples during the composting time after the enrichment with SS (Fig. 2). This feature could be

Table 3
Mass losses (% of total sample) corresponding to the main peaks displayed in the thermograms (Figs. 2–4) and content (%) of sample residue at 950 °C

Composting time (days)	Mass loss (%) 1° step	Mass loss (%) 2° step	Residue (%)	R1
Pile 1: grape stalk + grape marc + exhausted grape marc + sewage sludge				
0	65.0	22.0	6.7	0.339
17[a]	52.8	28.4	13.6	0.537
24	52.5	27.1	15.2	0.516
45	51.4	27.4	15.8	0.533
59	51.3	27.8	15.3	0.541
234	47.3	29.3	17.0	0.619
Pile 2: exhausted grape marc + cow manure				
0	52.0	29.9	12.6	0.574
15	49.5	30.2	14.6	0.610
29	50.0	30.1	14.3	0.602
50	45.0	33.2	15.1	0.738
71	43.8	33.6	16.0	0.768
91	43.1	33.9	16.0	0.787
134	39.7	33.7	18.8	0.849
192	39.0	35.2	18.2	0.903
Pile 3: exhausted grape marc + poultry manure				
0	48.7	31.5	12.6	0.648
14	46.9	24.1	19.3	0.515
28	45.1	24.3	20.6	0.539
42	45.5	25.0	20.1	0.549
70	42.1	27.1	21.1	0.644
106	37.3	29.8	22.4	0.797
140	38.3	28.3	22.9	0.739
212	36.6	30.3	22.4	0.827

R1 refers to the 2° step mass loss to the 1° step mass loss ratio. The temperature range for the first step is between 200 and 400 °C and for the second step is between 400 and 580 °C.

[a] Pile 1 was initially made by mixing only grape stalk + grape marc + exhausted grape marc, and after 17 days was enriched with sewage sludge.

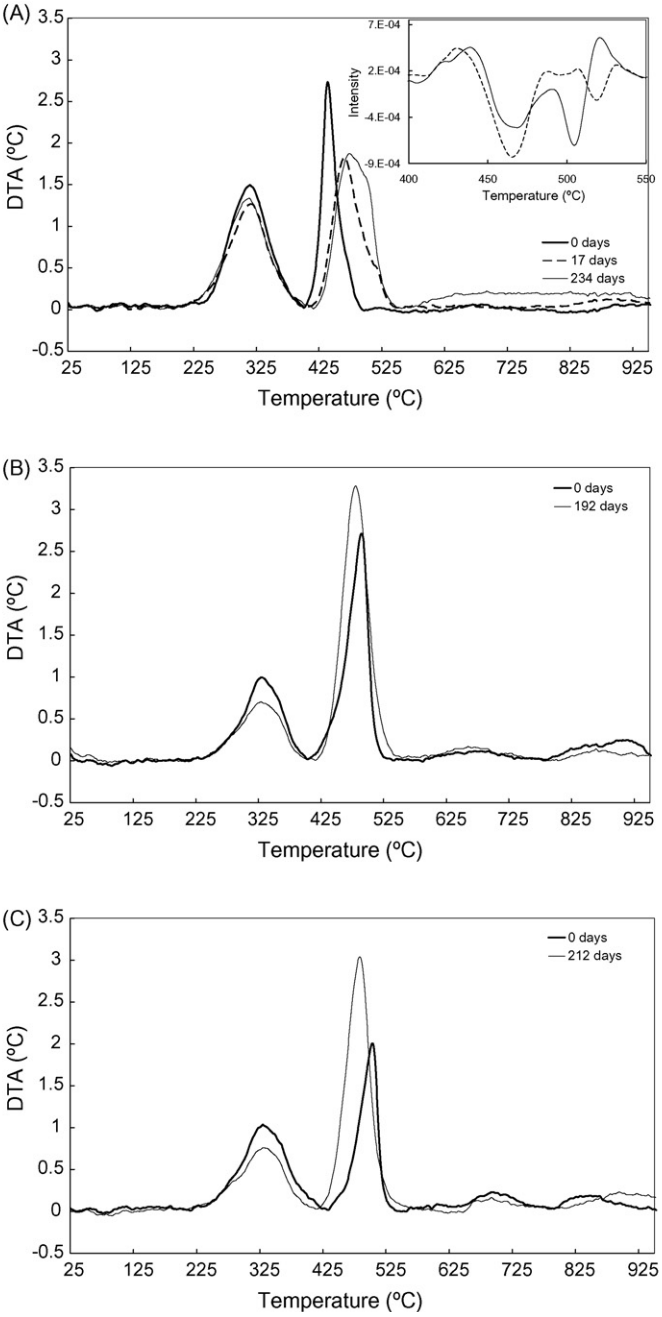

Fig. 5. DTA curves of the samples collected at different times of the composting process: (A) pile 1 (grape stalk + grape marc + exhausted grape marc + sewage sludge); (B) pile 2 (exhausted grape marc + cow manure); (C) pile 3 (exhausted grape marc + poultry manure). The insert in (A) shows the second-derivative DTA curves from pile 1.

displayed little changes in the organic matter in this pile and, consequently, a poor stabilization of the organic matter. A weight loss in the range of 50–150 °C is also attributed to the loss of residual water [9,23–25]. In the 200–400 °C temperature range, corresponding to the thermal degradation of carbohydrates and other substances [23], the first sample after the enrichment with SS (17 days) shows a weight loss of 52.8%, which does not change significantly in the final sample (47.3%). At the same time, the weight loss recorded between 400 and 580 °C was of 28.4% in the first sample after the enrichment with SS (17 days) and of 29.3% in the final sample, indicating a weak decomposition process. A shoulder can be observed in the second exothermic peak (400 and 580 °C range) in the DTA profiles from pile 1 (Fig. 5A). The temperatures at which the shoulders were recorded were 520 °C at 17 days and 505 °C at 234 days of the composting process. The intensity of this shoulder increases with the composting time, as it is showed in the second derivative of the DTA profiles (insert in Fig. 5A). The shoulder displays the same shifting toward lower temperatures that the second exothermic peaks for pile 2 and pile 3 (Fig. 5B and C). However, the first exothermic peak and the maximum in the second exothermic peak do not show shifting toward lower temperatures or intensity variations (Fig. 5), providing an indication of the poor humification degree. The DTA profile from the initial mixture for pile 1, only with WDR, does not display any shoulder in the second exothermic peak (Fig. 5). The initial mixture in the pile 1 was enriched with SS in order to reactive the thermophilic stage (Section 2) and the shoulder can be due to a contribution of the SS components. The evolution of this shoulder could be suggesting that the composting process is more efficient in the SS than in the original WDR.

Finally, the thermograms for piles 1, 2 and 3 were characterized by a weight loss in the 620–750 °C range, attributed to the carbonate thermal degradation [9]. This peak shows a slight increase that it can be ascribed to the mineralization process during composting (Figs. 2–4).

Weight loss in the 200–580 °C temperature range can be considered as the combustion of the organic matter. The initial values in this range are 81.2, 81.9 and 80.2% for pile 1 (after the enrichment with SS), pile 2 and pile 3, respectively. The final values are 76.6, 74.2 and 66.9% for pile 1, pile 2 and pile 3, respectively. These total organic matter weight loss are similar to the values obtained for other compost from wasted coming from various agricultural residues [25], from wheat straw [29] and from cotton and yard wasted [30]. Compost with different origins can reach higher mineralization values [23].

Usually, the DTA profiles of organic matter display a small endothermic peak near 98 °C, representative of dehydration reactions, and two distinct exothermic peaks (250–400 and 400–580 °C, respectively) that indicate the thermal reactions of organic components characterized by different thermal stability [9,23–25]. DTA profiles from WDR (pile 1, pile 2 and pile 3) show this characteristic pattern in peaks. However, the endothermic peak (around 98 °C) is imperceptible in DTA curves from our samples. A decrease in the relative intensity of the first exothermic peak is observed in DTA profiles (Fig. 5). This peak corresponds to the thermal degradation of the carbohydrates and the dehydration of aliphatic structures. Concomitantly, an increase in the second peak intensity is observed in sequential samplings of the compost piles (piles 2 and 3) (Table 4). These exothermic reactions are associated with the two peaks in the DTG curves (Figs. 2–4). Peak area values in the DTA profiles are proportional to the energy released during the combustion process (Table 4). The first peak shows a slight diminution of the area for piles 2 and 3, indicating a possible decrease in the carbohydrate content in the compost. On the contrary, the area for the second peak increases as the energy released in the combustion increases (Table 4). These results suggest an enhancement of the number of stable molecules through two ways either by a concentration effect by the loss of the less stable molecules in the composting process or/and by the *novo* synthesis of more stable molecules. Presumably, both processes occur simultaneously for the microbial activity during the composting time.

Table 4
Mean values of exothermic peak temperatures (°C) and enthalpy of the combustion process (J mg^{-1}) for the exothermic peak

Composting time (days)	1° exotherm peak (°C)	2° exotherm peak (°C)	ΔH (J mg^{-1}) 1° step	ΔH (J mg^{-1}) 2° step
Pile 1: grape stalk + grape marc + exhausted grape marc + sewage sludge				
0	316.6	442.0	4.1	3.5
17[a]	319.3	466.8	3.7	4.3
24	322.2	475.1	3.6	3.3
45	316.3	474.1	3.9	3.9
59	316.2	475.1	4.0	3.7
234	314.3	474.7	3.9	5.0
Pile 2: exhausted grape marc + cow manure				
0	332.0	491.5	2.9	4.9
15	337.0	489.8	2.8	5.1
29	335.1	492.8	2.8	6.2
50	330.8	485.1	2.9	6.2
71	331.9	486.9	3.1	6.7
91	330.8	482.2	2.9	6.7
134	330.6	482.0	2.7	6.6
192	330.6	483.1	2.3	7.3
Pile 3: exhausted grape marc + poultry manure				
0	330.8	495.3	2.3	5.2
14	331.0	504.7	3.3	3.1
28	335.1	499.4	3.2	3.4
42	334.0	496.4	3.2	3.7
70	335.9	491.3	3.0	5.0
106	333.7	489.0	2.6	6.0
140	330.7	485.8	2.8	5.6
212	330.7	485.8	2.6	6.3

The temperature range for the first step is between 200 and 400 °C and for the second step is between 400 and 580 °C.

[a] Pile 1 was initially made by mixing only grape stalk + grape marc + exhausted grape marc, and after 17 days was enriched with sewage sludge.

The pattern of the DTG and DTA profiles are related to the CO_2 ion current, simultaneously obtained under oxidizing atmosphere. The release of CO_2 during the combustion reaction follows the same pattern of the DTG profiles (Fig. 6). Two distinct peaks can be observed in the curves. A decrease in the release of CO_2 in the first peak is observed (250–400 °C temperature range) (Fig. 6). As it was previously discussed, this peak corresponds to the thermal degradation of the carbohydrates and the dehydration of aliphatic structures. An increase in the release of CO_2 in the second peak is observed in sequential samplings of the compost piles (400–580 °C temperature range) (Fig. 6).

In order to evaluate the composting process, we can use the ratio between the mass loss associated with the first and the second exothermic reactions (R1) (Table 3). The R1 was previously identified as a reliable parameter for evaluating the level of maturation of organic matter in composts [25,30]. This value indicates the relative amount of the most thermally stable fraction of the organic matter with respect to the less stable one. The R1 ratio increases during composting (Table 3), thus revealing a high sensitivity of this parameter to the chemical changes induced by the bio-transformation of organic materials. In fact, the ratio is 1.6 times higher for the sample after 212 days of composting than in sample 0 (pile 2). The R1 value for the first sample (at 0 days) of the pile 3 is 0.648 and after 2 weeks (second sample) the R1 value decreases to 0.515. During the rest of the composting process, the R1 values increase to 0.827 (Table 3). The ΔH value for the initial sample (0 days) is 5.2 J mg^{-1}, decreasing to 3.1 J mg^{-1} after 2 weeks (Table 4). Initial mixture of pile 3 must contain different components with high thermal stability corresponding to second exothermic peak. However, these components are quickly degraded in the first 2 weeks of the composting time. The residues (%) after the thermal run increase from 12.6% (0 days) to 19.3% (14 days) for the pile 3 (Table 3). This difference in the residues (%) between 0 days and 14 days, suggests also the quick degradation of a component in the initial mixtures of the pile 3. Residue (%) values after the programmed combustion increase until 22.4% (212 days) during the composting time (Table 3). The variation in the R1, ΔH and residues (%) after the thermal run for pile 1 has similar behaviour that pile 3, in the first days of the composting process after the enrichment with SS. However, these parameters for pile 2 increase during the composting process (Table 3). These features denote the impor-

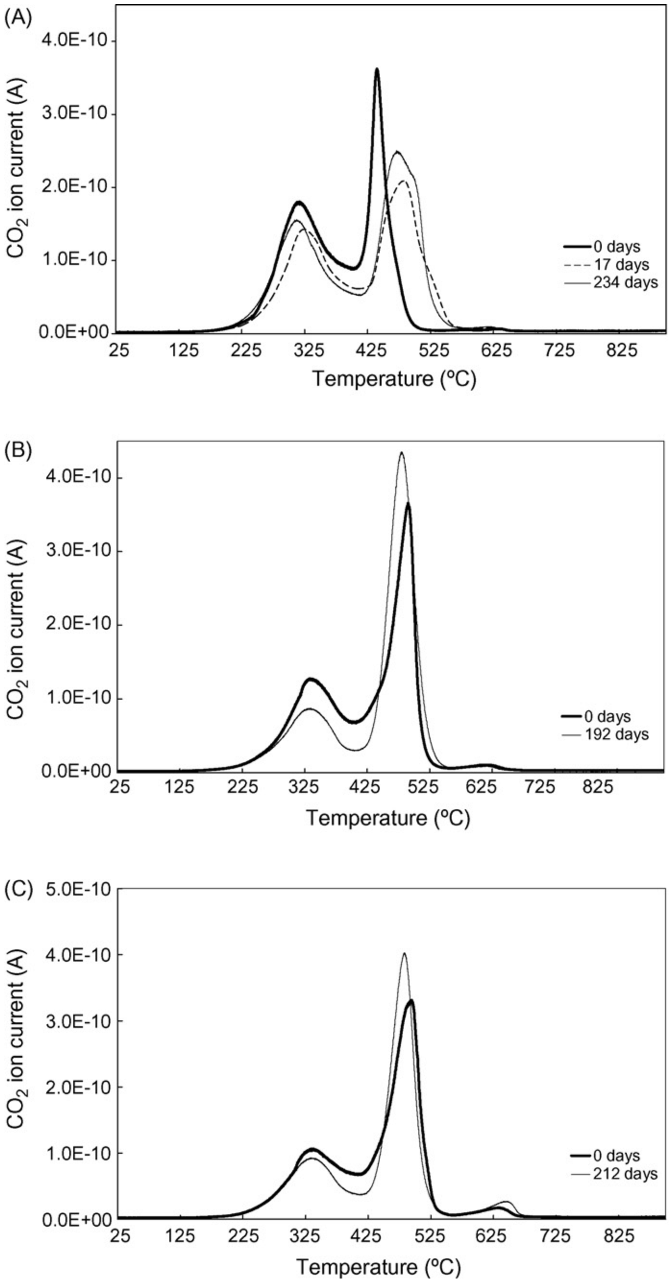

Fig. 6. CO_2 ion current for samples collected at different times of the composting process: (A) pile 1 (grape stalk + grape marc + exhausted grape marc + sewage sludge); (B) pile 2 (exhausted grape marc + cow manure); (C) pile 3 (exhausted grape marc + poultry manure).

tance of the input material in the thermogravimetry analysis of the compostsing process. On the other hand, the thermogravimetry analysis can show very well this quick modification in the organic matter during a composting process.

In addition to that, the pattern of mass losses (%) versus temperature is shown in Fig. 7. More stabilized samples require higher temperatures to achieve the same mass losses, i.e. a mass loss of 50% is achieved at 374 °C for the first sample and at 453 °C for the last sample (pile 2). On the one hand, this feature indicates the stabilization of the organic matter in the composting process, and on the other hand, the poor composting process is

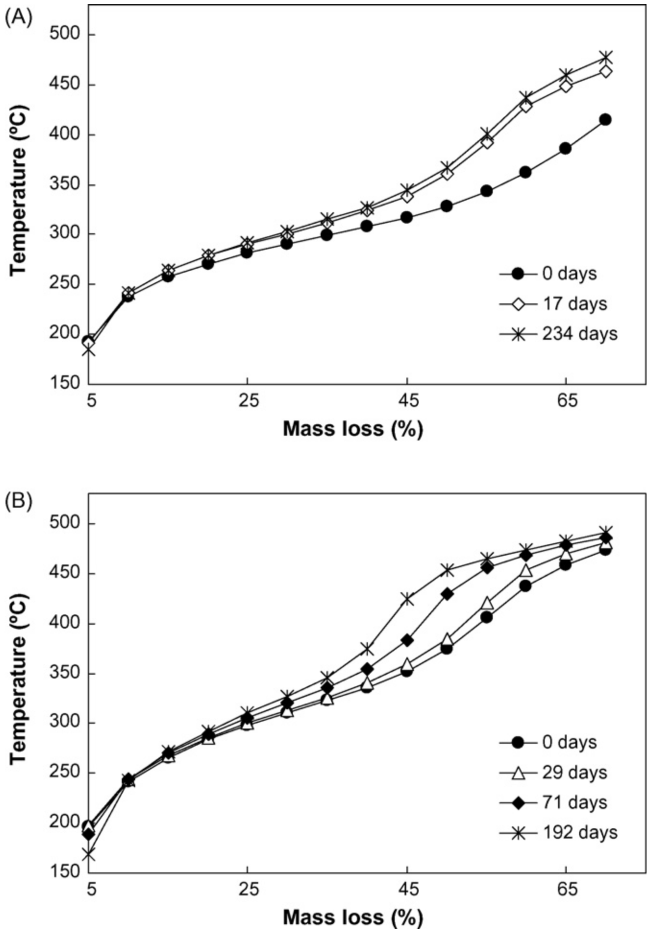

Fig. 7. Mass losses vs. temperature of progressive stages in the composting process: (A) pile 1 (0, 17 and 234 days); (B) pile 2 (0, 29, 71 and 192 days).

evident by considering the mass loss (%) for the pile 1. There is little difference between the necessary temperatures to achieve a mass loss of 50% for the pile 1: 361 °C for the first sample after the enrichment with SS (17 days) and 387 °C for the last sample.

4. Conclusions

One of the main advantages of thermal methods is to analyze the whole samples with a minimal pre-treatment (dry and mill only). Thermal methods can be used to follow the composting process along time: the thermal stabilization of the organic matter in the compost is observed in the TG and DTG curves of samples taken at different composting times. The thermogravimetry can reveal preferential degradation in a fraction of the organic matter such as it is found in pile 3. In order to interpret the results of the thermal methods it is very important having into account the origin of the raw material in the composting piles.

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