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Methodological considerations for using thermal analysis in the characterization of soil organic matter

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Abstract Thermal analysis is primarily used in the field of materials science, but has a long history in the geosciences. Soil organic matter (SOM) has received a great deal of recent scientific interest because of its role in the global carbon cycle. Conventional methods of characterizing SOM quality are unsatisfactory because they do not adequately capture the complete quality continuum that SOM comprises or the various mechanisms that act to stabilize it in the soil matrix. Thermal analysis techniques have the potential to capture this quality continuum, but are dependent on numerous experimental conditions that limit the comparability of results among different studies. Published methodology on thermal analysis of soils and sediments has largely focused on the characterization of the mineral component, while the organic component has received little attention. We tested several experimental conditions for their effects on the exothermic region of curves generated by thermal analysis of easily dispersed soil clay fractions and non-protected light-density particulate organic matter fractions isolated from the surface horizon of a forest soil. Results were found to be highly repeatable but strongly sensitive to crucible material, heating rate, and sample amount, and relatively insensitive to the use of a reference material. Thermal analysis is an important addition to the set of analytical tools used to characterize SOM quality because it provides direct, quantitative information of the energy potentially available for microbial metabolism. However, users will need to balance the needs of specific scientific objectives with the need for standardized methods and comparability between studies.

Keywords Soil organic matter · Thermogravimetry · Differential scanning calorimetry · Crucible material · Heating rate

Abbreviations

SOM	Soil organic matter
TG	Thermogravimetry
DSC	Differential scanning calorimetry

Introduction

Current estimates are that 1500–2000 Pg (1 Pg = 10^{15} g) of carbon are stored in the top meter of the Earth's soils, making soil organic matter (SOM) the third largest global C pool after the oceanic and geologic pools, and the largest of the active terrestrial pools [1, 2]. Despite the large contribution of SOM to the global C cycle and its determinant influence over a number of soil properties, knowledge about SOM composition and dynamics is still nascent. SOM is a heterogeneous, composite material consisting of fresh biological inputs, products of biological activity within soil, and in some circumstances organic matter of geologic or pyrogenic origin (e.g., coal, char). SOM quality is defined as a set of properties meant to characterize the continuum of materials comprising SOM in terms of how easily organic carbon present in the soil can be mineralized

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by the microbial community [3]. Characterization of SOM quality is critical because of its implications in SOM permanence which can directly affect key issues related with climate change such as carbon sequestration or the vulnerability of current SOM stocks to disturbance [4–6]. Due to the heterogeneous nature of SOM, quantifying its quality has remained elusive, as reflected by the large number of current methods used to describe it. The demand for a quantitative means to assess the complete SOM quality continuum, therefore, remains high [7].

While thermal analysis techniques have long been used in the study of soils, particularly clay mineralogy [8–10], the exothermic reactions associated with the thermal oxidation of SOM have received much less attention until recently. However, there are important reasons to consider adding thermal methods to the set of analytical techniques used to characterize SOM quality [11]: thermal methods can potentially help elucidate fundamental mechanisms of SOM stability, they can be used to distinguish pyrogenic C from other SOM in terrestrial ecosystems exposed to fires, and, contrary to many of the current methods, thermal techniques are inexpensive, rapid, require little sample preparation, and give reproducible results.

In recent years, several researchers have used thermal analysis techniques, such as differential thermal analysis (DTA), differential scanning calorimetry (DSC), and thermogravimetry (TG), to characterize organic matter in bulk soils, isolated soil fractions, humic substances, and other organic materials such as forest litter and composts. While the results obtained are quite promising, a wide range of experimental conditions have been used (Table 1) because few methodological issues have been reported for the specific use of thermal analysis in SOM studies. As with many other techniques, results obtained by thermal analysis depend not only on the properties of the sample, but also on the specific experimental conditions that can influence the resulting curves. Smykatz-Kloss [12] proposed a set of standard experimental conditions for the DTA of minerals, but these conditions were specifically designed for the study of the mineral component of soils rather than the organic component, for which no such standards currently exist.

Now that the number of thermal analyses of SOM reported in the literature is increasing, it is necessary to provide information to answer some new important methodological questions. This information will help inform the selection of experimental conditions to achieve valid, reproducible, and comparable results when thermal techniques are specifically applied to the study of SOM. The objective of this research is, therefore, to explore the effect of several experimental conditions on the exothermic region of DSC and TG curves of two representative soil fractions. We seek to provide valuable information about how thermal analysis results and their comparability

Table 1 Experimental conditions used in published studies of thermal analysis of bulk soils, isolated fractions, humic substances, or composts

Sample	Measurement	Heating rate/°C min^{-1}	Final T/°C	Crucible	Mass/mg	Atmosphere	Reference	Instrument	Study
Compost	DTA/TG	10	1000	Alumina	35	Air	Calcinated kaolinite	Netzsch STA 409	[35]
Compost	DSC/TG	10	1000	Alumina	32	Air	Calcinated kaolinite	Netzsch STA 409	[36]
Humic substances	DSC/TG	10	900	Alumina	5	Air	Calcinated kaolinite	Netzsch STA 409	[27]
Humic substances	DSC/TG	10	800	Alumina	8	Air	Calcinated kaolinite	Netzsch STA 409	[37]
Humic acids	DTA/TG	10	700	Alumina	10	Air	Calcinated kaolinite	TG-DTA92	[38]
Soil clay fractions	DSC/TG	10	700	Pt	30	Air	Calcinated kaolinite	Netzsch STA 409	[39]
Soil	DSC	20	600	Aluminum	15 (0.3 mg C)	Air	Empty pan	DSC100	[32]
Compost	DSC/TG	10	900	Al	11–12	Air	Calcinated kaolinite	Netzsch STA 409	[40]
Soil	DSC/TG	2	1000	Alumina	100	Air	Calcinated kaolinite	Netzsch STA 409EP	[41]
Soil	DSC/TG	20	990	Alumina	30	20% O_2 in He	Not reported	Netzsch STA 449C	[42]
Bulk soil and fractions	DSC/TG	20	1000	Alumina	30	20% O_2 in He	Not reported	Netzsch STA 449C	[43]
Pine litter	DSC/TG	10 (<105° C) 3 (>105 °C)	600	Not reported	10	Air	Not reported	Metter-Toledo Thermobalance and calorimeter	[19]
Plant material and soil light fraction	DTA/TG	10	800	Not reported	15 (1:9 sample: alumina)	Air	Calcinated α-alumina	Perkin Elmer Diamond TG/DTA	[44]

between studies can be affected by these factors. For this aim, several experimental conditions are examined and discussed, with special attention to the influence of: heating rate, crucible material, and sample mass. Various combinations of these three experimental settings were tested on two isolated soil fractions representing a predominantly organic soil fraction and a predominantly mineral soil fraction. To the best of our knowledge, this represents the first time that such methodological issues are reported in the literature. While it is beyond the scope of this study to provide universal standards for experimental conditions, our results represent an important step in establishing recommendations for obtaining valid and comparable data for the thermal analysis of SOM.

Materials and methods

Samples analyzed

Trials were conducted using aliquots of an easily dispersed clay fraction (clay, total organic C = 65 g C kg^{-1}) and a non-protected light fraction (LF, total organic C = 190 g C kg^{-1}).

These fractions were previously isolated from surface-horizon (0–5 cm) soil samples collected from an Orthic Gray Luvisol (in the Canadian soil classification system) [13] or Typic Haplocryalf (in U.S. Soil Taxonomy) [14] in an undisturbed aspen woodlot adjacent to the Breton Classical Plots site near Breton, Alberta Canada (53°07′N, 114°28′W). Soil fractions were isolated by partial dispersion and physical fractionation by fractionating air-dried 2-mm sieved soil in a microaggregate isolator [15]. The easily dispersed clay fraction was separated from water-stable aggregates and from the easily dispersed silt fraction by wet sieving and subsequent centrifugation. The unprotected light fraction was isolated from the microaggregate fraction by density flotation using 1.85 g cm^{-3} sodium polytungstate [16]. Further details of the site, soil, and fractionation procedure are reported in detail in Plante et al. [17] and Stewart et al. [18]. These fractions were chosen as two of the most representative forms in which organic matter can be found in soils. LF is mainly compose of particulate organic matter with a high content in labile organic matter and a rapid turnover, and the clay fraction is typically rich in stable organo-mineral compounds due to the high capacity of clay minerals of stabilizing organic matter in soils [19].

Table 2 Tested combinations of experimental conditions with suggested standard experimental conditions reported in the second column

Tested parameters	Fixed parameters	
Crucible material: Pt–Rh, Al, Al_2O_3	Heating rate: 10 °C min^{-1}	Sample weight: 10 mg LF; 30 mg clay
Heating rate: 2, 5, 10, 20, and 40 °C min^{-1}	Crucible material: Pt–Rh	Sample weight: 10 mg LF; 30 mg clay
Sample weight: 1, 2, 5, 10, 20, 30, and 40 mg	Crucible material: Pt–Rh	Heating rate: 10 °C min^{-1}

All analyses were performed using a temperature range of 25–700 °C, with an empty crucible used as reference, and a posteriori baseline correction applied

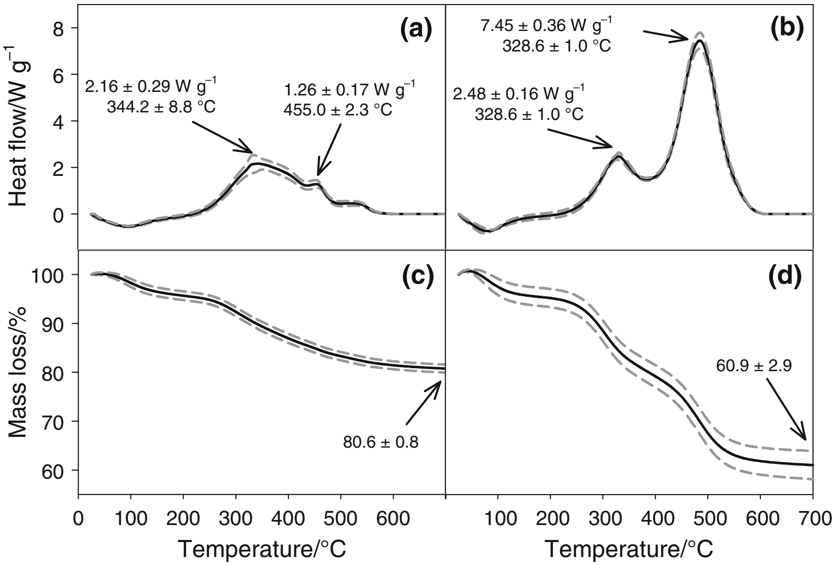

Fig. 1 Repeatability of differential scanning calorimetry (Exo up) of **a** dispersable clay and **b** light fractions, and of thermogravimetry of **c** dispersable clay and **d** light fractions, showing mean (*black, solid line*) and standard deviation envelope (*gray, dashed line*) of six analyses performed over the span of a year

Instrumentation and experimental design

The instrument used in this study was a Netzsch simultaneous heat flux thermal analyzer (STA 409PC Luxx) equipped with a type-S (Pt/PtRh) TG–DSC sample carrier supporting a PtRh10-Pt thermocouple (Netzsch-Gerätebau GmbH, Selb, Germany). The experimental conditions for this instrument consisted of using an 85 μL sample crucible with a lid and an identical empty crucible as a reference. Samples were heated from ambient (~25 °C) to 700 °C in a furnace atmosphere consisting of synthetic air (80% N_2 and 20% O_2) flowing at 30 mL min^{-1} and N_2 protective gas flowing at 10 mL min^{-1}. Multi-point calibrations for temperature and enthalpy sensitivity were performed using a range of standard inorganic salts (i.e., $RbNO_3$, $KClO_4$, Ag_2SO_4, CsCl, and K_2CrO_4) or metals (i.e., In, Sn, Bi, Zn, Al, and Au). Separate calibrations are required for each different experimental condition, particularly for crucible material and atmosphere, but typically not for heating rate.

The experimental conditions tested (Table 2) were various combinations of heating rate (2, 5, 10, 20, and 40 °C min^{-1}), sample quantity (1, 2, 5, 10, 20, 30, and 40 mg), crucible material (Pt, Al, and Al_2O_3), and the presence or absence of calcinated kaolinite as a reference material. Initial analyses of the clay (30 mg) and LF (10 mg) samples were conducted six times over the span of a year under the standard conditions described above to assess sample and analytical variability. Otherwise, all analyses were performed in triplicate over the span of a few days.

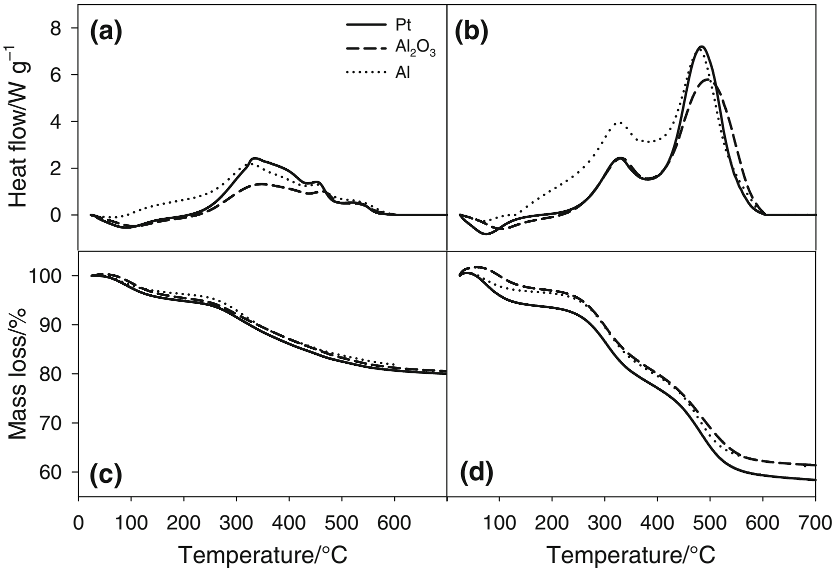

Fig. 2 Crucible material comparisons of differential scanning calorimetry (Exo up) of **a** dispersable clay and **b** light fractions, and of thermogravimetry of **c** dispersable clay and **d** light fractions

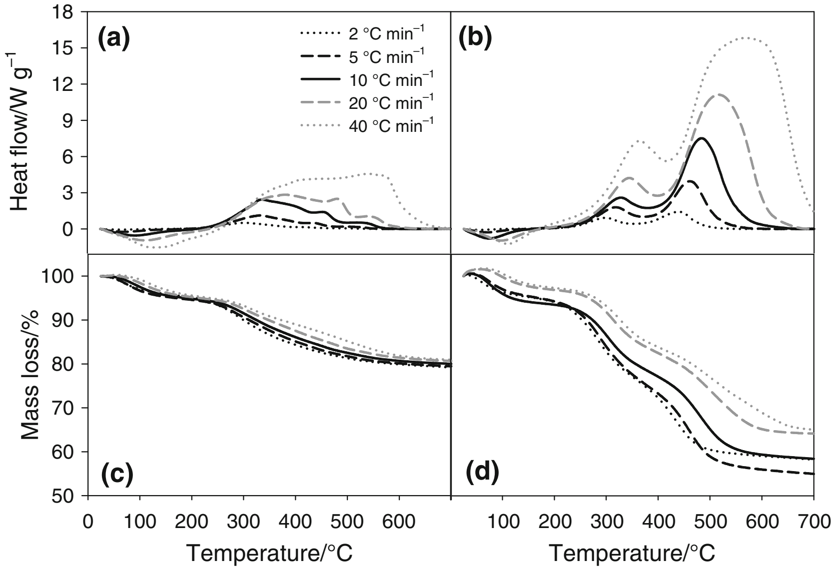

Fig. 3 Heating rate comparisons of differential scanning calorimetry (Exo up) of **a** dispersable clay and **b** light fractions, and of thermogravimetry of **c** dispersable clay and **d** light fractions

Table 3 Changes in peak position (°C) and height (W g^{-1}) for samples of clay (30 mg) and LF (10 mg) analyzed with different heating rates using Pt–Rh crucibles in the temperature range of 25–700 °C with an empty crucible used as reference and a posteriori baseline correction applied

	Peak position/°C					Peak height/W g^{-1}				
	2 °C min^{-1}	5 °C min^{-1}	10 °C min^{-1}	20 °C min^{-1}	40 °C min^{-1}	2 °C min^{-1}	5 °C min^{-1}	10 °C min^{-1}	20 °C min^{-1}	40 °C min^{-1}
Clay 1st peak	303.4 ± 3.7	332.4 ± 0.5	336.3 ± 0.4	379.7 ± 4.7	397.0 ± 3.5	0.5 ± 0.0	1.1 ± 0.0	2.4 ± 0.1	2.8 ± 0.1	3.9 ± 0.1
Clay 2nd peak	410.3 ± 1.9	434.7 ± 0.5	453.0 ± 0.5	480.8 ± 2.1	543.4 ± 6.9	0.2 ± 0.0	0.5 ± 0.0	1.4 ± 0.1	2.5 ± 0.1	4.6 ± 0.1
LF 1st peak	297.1 ± 1.5	318.2 ± 1.6	328.3 ± 0.5	343.9 ± 0.3	363.9 ± 2.1	0.9 ± 0.1	1.8 ± 0.1	2.6 ± 0.0	4.2 ± 0.2	7.3 ± 0.1
LF 2nd peak	438.5 ± 2.7	460.4 ± 0.6	483.5 ± 0.8	516.2 ± 2.1	578.6 ± 21.3	1.4 ± 0.1	3.9 ± 0.2	7.5 ± 0.2	11.1 ± 0.6	15.9 ± 0.7

Modern thermal analysis instruments provide the means to create baseline corrections by running an empty crucible under the same conditions of sample analysis. The correction is then automatically subtracted from the resulting sample DSC curve to adjust the baseline. However, in our experience, results obtained in this way are not always satisfactory. We elected to perform additional a posteriori baseline corrections of sample DSC curves. Peakfit v.4.12 (Systat Software Inc, San Jose CA) was used to subtract baselines from DSC curves using a non-parametric adjustment from the terminal region of the curve (generally at temperatures >600 °C). We compared DSC curves with and without instrumental or additional baseline correction.

Results and discussion

Instrumental considerations: repeatability and use of a reference sample

Repeatability

While the first thermal analysis instruments used decades ago were known to have problems with repeatability of measurements, modern instruments generally have high repeatability. DSC and TG curves of six aliquots analyzed over the span of a year showed high reproducibility and small standard deviation envelopes (Fig. 1). As thermal analysis is destructive, differences between measurements reflect instrumental variability as well as variability between sample aliquots. Repeated analyses of reference materials such as calcium oxalate suggest that instrumental variability is minimal (data not shown), and therefore, the majority of the observed variability can be attributed to variation in the composition of sample aliquots.

Reference sample

Until recently, the use of a reference sample was a common practice (Table 1). However, most modern instruments do not require the use of reference materials, and an empty crucible is usually sufficient. For TG measurements not using a reference material eliminates any concern about potential mass losses from the reference material since, contrary to DSC measurements, the instrument has a single balance that measures changes in the entire system and not between crucibles. For DSC, only slight differences, which did not interfere with interpretation, were observed in the exothermic regions of clay and LF analyses obtained using an empty crucible versus calcinated kaolinite as a reference (data not shown). In general, an empty crucible may be sufficient as a reference and the preferred option, but this should be tested for each instrument because of potential effects on baseline stability.

Experimental conditions

Temperature range

Thermal analyses of soil samples typically begin at room temperature (~20–25 °C), but end at various temperatures (~600–1000 °C) (Table 1). The interval of interest for characterizing SOM quality is typically between 180 and 650 °C, where the main exothermic reactions associated with thermal decomposition and oxidation of organic compounds take place [20]. The region <180 °C is dominated by endothermic reactions associated with water evaporation and desorption. Rovira et al. [21] suggested programming an isothermal stop of 15 min at 105 °C to minimize the effect of sample water on the transition from endo- to exo-thermic reactions. Most of the hygroscopic water is estimated to be eliminated at 105 °C temperature, though sometimes the dehydration can be incomplete and some salts (e.g., gypsum) may be present in the soil and can release water at temperatures above 105 °C [22]. For soils dominated by hydrated clays, Schulte and Hopkins [23] recommended using 150 °C as the pre-heating temperature for determination of SOC by the loss-on-ignition (LOI) method. Meanwhile, the region >700 °C is dominated by mineral reactions including carbonate decomposition [24] and clay mineral degradation [25]. In non-calcareous soils, the end of the exothermic region can generally be assessed by the end of mass loss at around 550 °C, which was also suggested by some authors as the optimal temperature for the LOI method [26, 27]. In general, a temperature range between 25 and 700 °C is adequate for analyzing most soil samples. However, the presence of highly recalcitrant forms of carbon (e.g., black carbon) can occasionally involve exothermic reactions at temperatures greater than 650 °C [28], in which case the upper temperature limit will need to be increased to 900 °C. In this case, it was not necessary to increase the temperature range since none of the samples showed evidence for the presence of this kind of material (i.e., no significant mass loss at >600 °C), and thus the upper temperature limit was kept at 700 °C.

When soil samples are analyzed under identical experimental conditions, some common thermal patterns due to differences in the thermal stability of SOM can be observed. Typically, the presence of peaks at the low-temperature part of the exothermic region around 300–350 °C has been associated with the combustion of carbohydrates and other aliphatic compounds while reactions around 400–450 °C are thought to result from the loss of aromatic compounds such as lignin or other polyphenols [29, 30]. In addition, some highly recalcitrant forms of organic matter such as polycondensed aromatic carbon can show peaks at temperatures higher than 500 °C [28]. These differences are essentially a function of SOM chemical composition, degree of humification, and the degree of mineral association. These patterns are usually better defined in samples dominated by less altered and less mineral-associated SOM as is observed here with the clear bimodal DSC pattern generated by LF samples. In contrast, SOM that is more altered by decomposition and humification and more closely associated with soil minerals by various sorption mechanisms typically results in a shouldered single peak, such as that obtained from the clay samples.

Though some thermal reactions attributable to organic matter can occur at similar temperatures as mineral thermal reactions, the contribution from thermal reactions of the

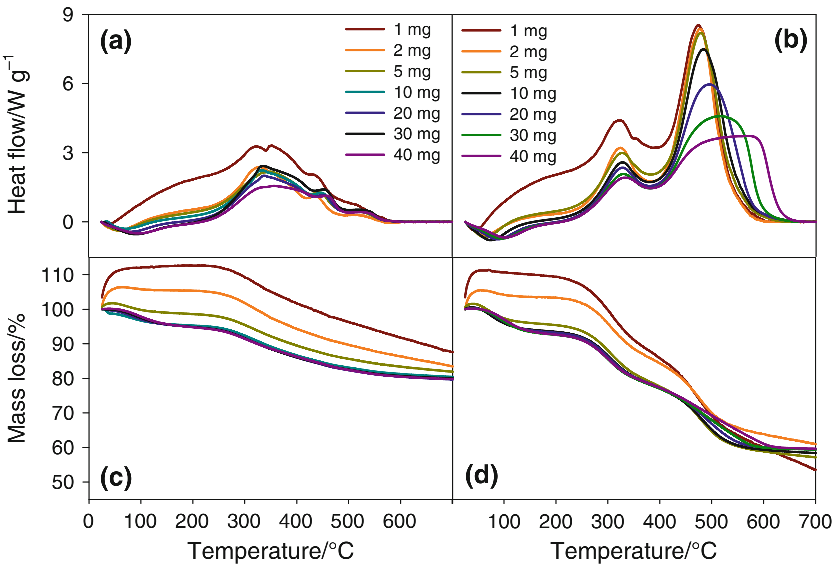

Fig. 4 Sample mass comparisons of differential scanning calorimetry (Exo up) of **a** dispersable clay and **b** light fractions, and of thermogravimetry of **c** dispersable clay and **d** light fractions

Table 4 Changes in peak position (°C) and height (W g^{-1}) for different quantities of clay and LF samples analyzed with a 10 °C min^{-1} heating rate and Pt–Rh crucibles in the temperature range of 25–700 °C with an empty crucible used as reference and a posteriori baseline correction applied

	Peak position/°C						Peak height/W g^{-1}					
	2 mg	5 mg	10 mg	20 mg	30 mg	40 mg	2 mg	5 mg	10 mg	20 mg	30 mg	40 mg
Clay 1st peak	330.3 ± 1.5	349.0 ± 1.6	332.9 ± 0.6	337.9 ± 1.2	336.3 ± 0.4	351.7 ± 11.7	2.4 ± 0.2	2.2 ± 0.0	2.5 ± 0.5	2.0 ± 0.0	2.4 ± 0.1	1.6 ± 0.1
Clay 2nd peak	435.5 ± 0.7	444.1 ± 0.8	447.1 ± 0.5	451.7 ± 0.8	453.0 ± 0.5	464.7 ± 10.0	1.1 ± 0.1	1.3 ± 0.0	1.3 ± 0.0	1.2 ± 0.0	1.4 ± 0.1	1.0 ± 0.3
LF 1st peak	322.9 ± 4.2	327.0 ± 0.6	328.3 ± 0.5	327.6 ± 1.6	329.4 ± 1.3	333.1 ± 1.3	3.2 ± 0.2	3.0 ± 0.1	2.6 ± 0.0	2.4 ± 0.1	2.1 ± 0.1	1.9 ± 0.1
LF 2nd peak	476.8 ± 1.3	478.8 ± 1.7	483.5 ± 0.8	495.4 ± 2.9	516.9 ± 2.2	564.5 ± 13.8	8.4 ± 0.4	8.2 ± 0.6	7.5 ± 0.2	6.0 ± 0.1	4.6 ± 0.1	3.7 ± 0.1

mineral phase is usually relatively small compared to the contribution from SOM [31], with exception of samples from subsoils or low-C samples. Thermal reactions contributed by soil minerals can generally be distinguished by re-running samples a second time under the same conditions (applicable only to reversible reactions),or by running a second aliquot of sample under a non-oxidative atmosphere (e.g., N_2).

Crucible material

Al, Al_2O_3, and Pt–Rh crucibles are the most commonly used for SOM analyses. DSC curves of 10 mg of clay and 30 mg of LF samples obtained using different crucibles at the same heating rate (10 °C min^{-1}) showed significant differences (Fig. 2). In general, DSC peaks from samples in Al_2O_3 crucibles appeared at slightly higher temperatures compared to metallic crucibles, and were also smaller.

To a large extent, the degree to which experimental conditions of thermal analyses affect the size and shape of the exothermic region is a result of deviations from thermal equilibrium within and throughout the sample during the heating program. The ideal set of experimental conditions will generate the same temperature throughout the entire sample at the same moment during the heating process. Divergence from ideal conditions can occur when using different crucible materials to analyze similar samples because of differences in the thermal conductivity of the crucible materials. Heat is transferred rapidly through metallic materials while ceramic materials, such as Al_2O_3, have lower thermal conductivity [32]. This would explain why peaks were broader and occurred at higher temperatures for the Al_2O_3 crucibles (Fig. 2). The selection of the most adequate crucible material will depend on the nature of the sample and the temperature at which the analysis is to be performed. There are several incompatibilities that must be avoided such as fusion of melting products with the crucible, corrosion, or even crucible melting (e.g., Al crucibles can melt at temperatures above 600 °C). These incompatibilities are well documented, making crucible material selection straightforward. For soil analysis, the use of Pt–Rh crucibles are recommended because they provide better peak resolution than Al_2O_3 crucibles, do not present incompatibilities with soil components, and can be heated to higher temperatures than Al crucibles for black C and carbonate analyses.

Heating rate

Changes in the heating rates strongly affected the width and height of the DSC exothermic region, as well as the shape of the TG curves of the clay (30 mg) and LF

(10 mg) samples analyzed using Pt–Rh crucibles (Fig. 3). For both samples, DSC curves obtained with the slowest heating rate (2 °C min^{-1}) featured only weak exothermic signals in terms of peak height when plotted against temperature. Meanwhile, faster heating rates (20 °C min^{-1} and especially 40 °C min^{-1}) showed peak overlaps (Fig. 3), higher exothermic signals, and shifts in peak temperature (Table 3). Temperature shift of peaks obtained at different heating rates is a well-documented phenomenon that has been suggested by the ASTM as a way to measure activation energies [33]. Peaks shifting with increasing heating rates generally shows a strong logarithmic relationship [34], and in the current study fitting peak temperature to a logarithmic function yielded $r^2 = 0.95$ for clay samples and 0.99 for LF samples.

Rapid heating rates can induce significant thermal disequilibrium. Instrumental heating rates can vary from 0.1 to 200 °C min^{-1}, but a heating rate of 10 °C min^{-1} is usually considered optimal for clay mineralogical analysis [35], and heating rates are typically 5–20 °C min^{-1} for soil analysis [25]. At faster heating rates, the temperature gradient inside the sample will be larger, such that neighboring peaks tend to overlap and get broader (Fig. 3). As a result, slower heating rates are preferred when two or more reactions might overlap in a relatively small temperature interval, such as in the case of SOM quality characterization. However, thermal effects are less pronounced and without well-defined start and end points when heating rates are too slow [32]. While using the slowest heating rate appears to be the best option for TG analyses, researchers must balance this with the loss of resolution in DSC analyses. We recommend using a 10 °C min^{-1} heating rate as a good compromise between peak resolution, overlapping problems and total time required for analysis, which is consistent with the frequency of use by other researchers (Table 1).

Sample quantity

When different quantities of clay or LF were analyzed using Pt–Rh crucibles with a 10 °C min^{-1} heating rate, patterns of TG curves varied significantly only for the smallest sample quantities (1 and 2 mg) (Fig. 4). Meanwhile, DSC curve peaks become less defined as the quantity of the sample increases. Differences in results between larger sample quantities (≥10 mg) were smaller for those samples with lower carbon content (i.e., clay) than for LF samples, which exhibited shifts in peak temperature and decreases in peak height with increasing sample weight (Table 4).

Thermal transformations rarely occur simultaneously throughout the sample volume because of differences between the temperature of the walls of the crucible and the center of the sample. This temperature gradient depends directly on the amount of the sample. If the sample is too large, then the gradient will adversely affect the results of analyses because of a delay of thermal effects [12]. In addition, large sample mass may hinder oxygen diffusion into the sample if consumption rates are high during combustion [36]. This is especially important in samples with high SOM content. If the sample is too small, then sample homogeneity and representativeness can be compromised. Generating a uniform flux of energy also becomes more problematic, producing an overestimation of evolved energy and errors in mass loss such as those observed for the 1 and 2 mg samples. In the case of bulk soils, isolated soil fractions, litters, or composts, a standardized quantity of sample cannot be recommend because the exothermic signal and mass loss during the heating process are strongly correlated to sample SOM content. In these kinds of samples, carbon content can vary widely and consequently, comparisons between samples may be improved when equivalent quantities of SOM rather than bulk sample are used, for example, by diluting C-rich materials. On the other hand, the quantity of the sample in the crucible must be sufficient to ensure a uniform flux of energy. Resulting data may also be normalized by initial organic C mass rather than initial sample mass for further comparisons.

Baseline correction

Baselines for DSC curves from soils samples can differ strongly from other materials commonly analyzed by

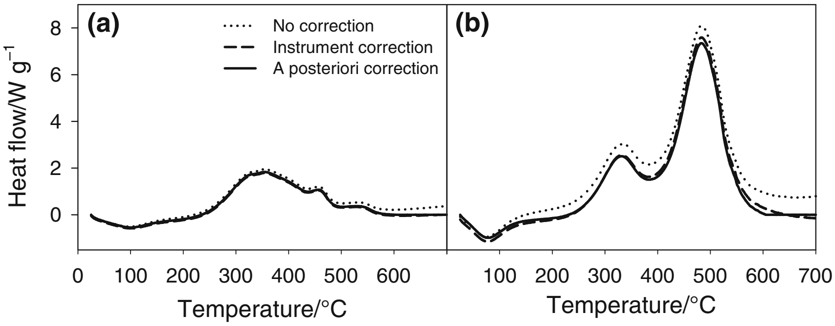

Fig. 5 Comparisons of baseline correction techniques for differential scanning calorimetry (Exo up) of **a** dispersable clay and **b** light fractions

thermal techniques because the heat capacity of the mineral matrix of the soil can increase upon heating and can cause a slope in heat flow [34]. The application of no baseline correction, instrumental baseline correction, or a posteriori baseline correction to DSC curves did not show significant differences in peak positions or areas (Fig. 5). However, the lack of large differences is likely due to high SOM concentrations in the samples analyzed, which resulted in large exothermic regions. In our experience, supplemental baseline correction is essential for samples with low SOM concentration where changes in heat capacity or transfer rate may cause the baseline to drift and generate more significant errors. In these cases, subtracting a second measurement of the already oxidized sample can reduce the effects of changes in heat capacity of the mineral compounds [34].

Conclusions

Cebuliak and Langier-Kuzniarowa [36] suggested that one of the reasons for the decline in use of thermal analysis in recent decades can be attributed to the lack of comparability of analytical results between laboratories. We have demonstrated that thermal analysis of soils for the characterization of SOM quality is highly repeatable (Fig. 1), but those results are strongly influenced by a number of experimental conditions such as crucible material, heating rate, and sample quantity. It is indispensable to consider that these conditions can affect the results obtained, and whether it is possible to make reliable comparisons among DSC and TG curves obtained under different conditions or in different laboratories.

Thermal methods are a promising approach for characterizing SOM quality. While a single optimal set of experimental conditions may be impractical due to the large inherent variability of environmental samples, the thermal analysis of SOM will be most widely applicable when individual researchers balance the need to standardize experimental conditions with the needs of specific scientific objectives. The results reported here together with our experience in running hundreds of samples and the experience collected from other researchers lead us to provide the following recommendations: 1) the use of an empty crucible as a reference once this is verified as adequate for the given instrument; 2) the use of Pt–Rh crucibles, which will favor good peak resolution and permit heating samples to high temperatures; 3) the use of a 10 °C min^{-1} heating rate as an efficient option to avoid peak overlapping and low resolution problems; 4) the quantity of sample analyzed should be based on the characteristics of the sample itself, especially its carbon content, but the final quantity analyzed should always ensure good representativeness and an uniform energy flux.

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References

1. Amundson R. The carbon budget in soils. Annu Rev Earth Planet Sci. 2001;29:535–62.
2. Lal R. Global potential of soil carbon sequestration to mitigate the greenhouse effect. Crit Rev Plant Sci. 2003;22(2):151–84.
3. Bosatta E, Ågren GI. Soil organic matter quality interpreted thermodynamically. Soil Biol Biochem. 1999;31(13):1889–91.
4. Smith P, Fang CM, Dawson JJC, Moncrieff JB. Impact of global warming on soil organic carbon. Advances in Agronomy, vol 97. Advances in Agronomy. San Diego: Elsevier Academic Press Inc; 2008. p. 1–43.
5. Gruber N, Friedlingstein P, Field CB, Valentini R, Heimann M, Richey JE, et al. The vulnerability of the carbon cycle in the 21st century: an assessment of carbon-climate-human interactions. In: Field CB, Raupach MR, editors. The global carbon cycle: integrating humans, climate, and the natural world. Washington, DC: Island Press; 2004. p. 45–76.
6. Smith P. An overview of the permanence of soil organic carbon stocks: influence of direct human-induced, indirect and natural effects. Eur J Soil Sci. 2005;56(5):673–80.
7. Denef K, Plante AF, Six J. Characterization of soil organic matter. In: Kutsch W, Bahn M, Heinemeyer A, editors. Soil carbon dynamics: an integrated methodology. London, UK: Cambridge University Press; 2009. p. 91–126.
8. Smykatz-Kloss W. Application of differential thermal analysis in mineralogy. J Therm Anal. 1982;23(1–2):15–44.
9. Mackenzie RC, Mitchell BD. Soil. In: Mackenzie RC, editor. Differential thermal analysis. New York: Academic Press; 1972. p. 267–97.
10. Langier-Kuzniarowa A. Evolution of the approach to thermal studies of clays. J Therm Anal. 1993;39(1993):1169–79.
11. Plante AF, Fernández JM, Leifeld J. Application of thermal analysis techniques in soil science. Geoderma. 2009;153(1–2): 1–10.
12. Smykatz-Kloss W. Differential thermal analysis: application and results in mineralogy. Berlin: Springer; 1974.
13. Group SCW. The Canadian system of soil classification. Ottawa: NRC Research Press; 1998.
14. Staff SS. Keys to soil taxonomy. Washington, DC: U.S. Department of Agriculture, Natural Resources Conservation Service; 2003.
15. Six J, Elliot ET, Paustian K. Soil macroaggregate turnover and microaggregate formation: a mechanism for C sequestration under notillage agriculture. Soil Biol Biochem. 2000;32:2099–103.
16. Six J, Elliot ET, Paustian K, Doran JW. Aggregation and soil organic matter accumulation in cultivated and native grassland soils. Soil Sci Soc Am J. 1998;62:1367–77.
17. Plante AF, Stewart CE, Conant R, Paustian K, Six J. Soil management effects on organic carbon storage in fractions physically isolated from a Gray Luvisol soil. Can J Soil Sci. 2006;86(1):141–51.
18. Stewart CE, Plante AF, Paustian K, Conant RT, Six J. Soil carbon saturation: linking concept and measurable carbon pools. Soil Sci Soc Am J. 2008;72(2):379–92.
19. Stevenson FJ. Humus chemistry: genesis, composition, reactions. 2nd ed. New York: Wiley; 1994.
20. Lopez-Capel E, Sohi SP, Gaunt JL, Manning DAC. Use of thermogravimetry-differential scanning calorimetry to characterize modelable soil organic matter fractions. Soil Sci Soc Am J. 2005;69(1):136–40.

21. Rovira P, Kurz-Besson C, Coûteaux M, Vallejo VR. Changes in litter properties during decomposition: a study by differential thermogravimetry and scanning calorimetry. Soil Biol Biochem. 2008;40(1):172–85.
22. Chatterjee A, Lal R, Wielopolski L, Martin MZ, Ebinger MH. Evaluation of different soil carbon determination methods. Crit Rev Plant Sci. 2009;28:164–78.
23. Schulte EE, Hopkins BG. Estimation of soil organic matter by weightloss-on-ignition. In: Magdoff FR, editor. Soil organic matter: analysis and interpretation, SSSA special publication no. 46. Madison: Soil Science Society of America, Inc; 1996. p. 21–31.
24. Atanasov O, Rustschev D. Thermal analysis of peat and peat soils. Thermochim Acta. 1985;90:373–7.
25. Tan KH, Hajek BF, Barshad I. Thermal analysis techniques. In: Klute A, editor. Methods of soil analysis, part I. Physical and mineralogical methods. 2nd ed. Madison: Agronomy Monograph No 9, American Society of Agronomy; 1986. p. 151–83.
26. Howard PJA, Howard DM. Use of organic carbon and loss-on-ignition to estimate soil organic matter in different soil types and horizons. Biol Fertil Soils. 1990;9:306–10.
27. De Vos B, Vandecasteele B, Deckers J, Muys B. Capability of loss-on-ignition as a predictor of total organic carbon in non-calcareous forest soils. Commun Soil Sci Plan. 2005;36:2899–921.
28. Hsieh YP, Bugna GC. Analysis of black carbon in sediments and soils using multi-element scanning thermal analysis (MESTA). Org Geochem. 2008;39:1562–71.
29. Dell'abate MT, Benedetti A, Trinchera A, Dazzi C. Humic substance along the profile of two Typic Haploxerert. Geoderma. 2002;107:281–96.
30. Strezov V, Moghtaderi B, Lucas JA. Computational calorimetric investigation of the reactions during thermal conversion of wood biomass. Biomass Bioenergy. 2004;27(5):459–65.
31. Langier-Kuźniarowa A. Thermal analysis of organo-clay complexes. In: Yariv S, Cross H, editors. Organo-clay complexes and interactions. New York: Marcel-Dekker; 2002. p. 273–344.
32. Todor DN. Thermal analysis of minerals. Tunbridge Wells: Abacus Press; 1976.
33. ASTM. Standard test method for Arrhenius kinetic constants for thermally unstable materials using DSC. E-698-04. American Society for Testing and Materials; 2005.
34. Leifeld J. Thermal stability of black carbon characterised by oxidative differential scanning calorimetry. Org Geochem. 2007;38(1):112–27.
35. Mackenzie RC. The differential thermal investigation of Clays. London: Mineralogical Society (Clay Minerals Group); 1957.
36. Cebulak S, Langier-Kùzniarowa A. Application of oxyreactive thermal analysis to the examination of organic matter associated with rocks. J Therm Anal Calorim. 1997;50(1–2):175–90.
37. Dell'abate MT, Benedetti A, Brookes PC. Hyphenated techniques of thermal analysis for characterisation of soil humic substances. J Sep Sci. 2003;26:433–40.
38. Francioso O, Montecchio D, Gioacchini P, Ciavatta C. Thermal analysis (TG-DTA) and isotopic characterization (^{13}C-^{15}N) of humic acids from different origins. Appl Geochem 2005;20:537–44.
39. Plante AF, Pernes M, Chenu C. Changes in clay-associated organic matter quality in a C depletion sequence as measured by differential thermal analyses, Geoderma. 2005;129:186–99.
40. Baffi C, Dell'abate MT, Nassisi A, Silva S, Benedetti A, Genevini PL, Adani F. Determination of biological stability in compost: a comparison of methodologies. Soil Biol Biochem. 2007;39: 1284–93.
41. Dorodnikov M, Fangmeier A, Kuzyakov Y. Thermal stability of soil organic matter pools and their δ^{13}C values after C_3-C_4 vegetation change. Soil Biol Biochem. 2007;39:1173–80.
42. De la Rosa JM, González-Perez JA, González-Vázquez R, Knicker H, Lopez-Capel E, Manning DAC, González-Vila FJ. Use of pyrolisis/GC-MS combined with thermal analysis to monitor C and N changes in soil organic matter from a Mediterranean fire affected forest. Catena. 2008;74:296–303.
43. Lopez-Capel E, Krull ES, Bol R, Manning DAC. Influence of recent vegetation on labile and recalciltrant carbon soil pools in central Queensland, Australia: evidence from thermal analysis-quadrupole mass spectrometry-isotope ratio mass spectrometry. Rapid Commun Mass Spectrom. 2008;22:1751–8.
44. Rasmussen C, White DA. Vegetation effects on soil organic carbon quality in an arid hyperthermic ecosystem. Soil Sci. 2010; 175:438–46.