



Review

Application of thermal analysis techniques in soil science

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ABSTRACT

Thermal analysis techniques have long been used in the study of soils, particularly in clay mineralogy. While there exists a large volume of literature (including several books) on the theoretical underpinnings of thermal analysis and its application to the analysis of minerals, the exothermic reactions associated with the thermal oxidation of soil organic matter have received much less attention. The proposition that soil thermograms represent characteristic properties and can be used to characterize soil organic matter quality has existed for decades. However, only recently has the number of tested soils and fractions been large enough to test this proposition and the potential link between thermal and biological soil organic matter stability. Due to the increasing demands for rapid and quantitative assessments of soil organic matter quality, thermal analysis techniques are a unique means to characterize the complete continuum that comprises soil organic matter. The interpretation of thermal analysis results must, however, go beyond the qualitative and therefore requires careful attention to analytical parameters and post-analysis data manipulations. The objectives of this review are to summarize the historical development of the application of thermal analysis techniques in soil science, and to present the emerging application of thermal analysis for the characterization of soil organic matter.

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1. Introduction

The International Confederation for Thermal Analysis and Calorimetry (ICTAC) defines “thermal analysis” as a group of techniques in which a

physical or chemical property of a sample is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed (Langier-Kuźniarowa, 2002). Observations of the response of many materials to heating have been made since ancient times, but serious investigations could not be made until the temperature of the material could be measured accurately. Two events at the end of the 19th century mark the beginning of serious thermal analysis investigations: the invention of the thermocouple and the joining

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of two thermocouples so that the total voltage produced reflected the difference in temperature between them (Mackenzie, 1984).

Thermal techniques have a long history of use in the geosciences. In his original thermal analysis experiments, Le Chatelier (1887) heated samples of clay and measured the point of dehydration to differentiate them. During this time, however, thermal analysis was primarily a metallurgical method used to study phase changes (Roberts-Austen, 1899). It was during the late 1930s that thermal analysis found its greatest and most intense application in mineralogy (Mackenzie, 1957; Mackenzie and Mitchell, 1962). At the time, X-ray diffraction (XRD) was too expensive to be found in many laboratories and many mineralogists (somewhat erroneously) saw thermal analysis as a simple and inexpensive alternative to XRD.

The first commercial thermal analysis units were produced in the 1950s, and in 1964, a new approach to thermal analysis was devised. Rather than measuring temperature differences between a sample and a reference, the new method was based on measuring the electrical power required to keep the sample and reference at the same temperature during a heating experiment (Watson et al., 1964). The most recent major advances in thermal analysis techniques were the application of computers to control the experimental conditions and collect the resulting data (Giese, 1990), and the coupling of thermal analysis with other analytical techniques. At each step, work performed on clays has been instrumental to the development of thermal analysis (Mackenzie, 1991).

For much of the time that thermal analysis techniques have been applied to the study of soils, the focus has been on the mineral components. Similar to many other analytical approaches in soil science, it was customary to separate the mineral and organic components of soil before examination. The rationale is that the thermal reactions of one component can mask those of the other. The first use of thermal analysis in soil science is reported to have been in 1935, when Agafonoff applied the technique to soil clays rather than the clean (geological) clay samples that had previously been analyzed (Mackenzie and Mitchell, 1972). However, the application of thermal analysis to the study of soil organic components has continued to be less common in spite of the fact that organic compounds can influence thermal behavior to a much greater degree than mineral components (Langier-Kuźniarowa, 2002). Interestingly, the relevant chapter on the methodology of thermal analysis techniques published in the *Methods of Soil Analysis* book series (Tan et al., 1986) makes only passing reference to the soil organic component. Recent studies (e.g., Lopez-Capel et al., 2005; Plante et al., 2005) have demonstrated differences in the thermal pattern of different soil fractions that might be indicative of systematic burning patterns of particular fractions. The thermal stability of any material is related to its chemistry and surface properties, and it thus seems obvious to test if thermal stability of soil organic matter may serve as a proxy for biogeochemical stability. Differences in the thermal behavior of organo-mineral complexes compared to individual organic compounds and minerals may also provide insight about the energy of interaction between soil organic matter and soil minerals.

The objectives of this review are to: 1) provide an overview of the historical development of the application of thermal analysis techniques in soil science, 2) briefly describe each thermal analysis technique and how it is used in the study of soil, and 3) present the emerging application of thermal analysis for the characterization of soil organic matter to demonstrate its potentiality for future research. While thermal analysis techniques have been used to study both mineral and organic soil components, our emphasis will be on the organic component.

2. Thermal analysis techniques

2.1. Thermogravimetry

Thermogravimetry (TG) is a technique in which sample weight is measured as a function of temperature. The sample is loaded on a high-

precision thermobalance within the furnace and weighed continuously during the course of the heating program. The mass loss associated with a thermal reaction is measured between the inflection points of the TG curve (Karathanasis and Harris, 1994). It is often simpler to interpret and resolve thermal events by plotting the derivative of the TG curve. Derivative TG (DTG, units of % mass loss °C⁻¹) is thus the preferred method to resolve the position of inflection points against a background of continuous mass loss. The temperature at which mass loss reactions occur in TG instruments is calibrated by measurement of the melting transition temperature of standard reference materials, typically pure metals (e.g., indium (156.6 °C), zinc (419.6 °C) or gold (1064.2 °C)) or salts (e.g., RbNO₃ (164.2 °C), KClO₄ (300.8 °C) or Ag₂SO₄ (426.4 °C)). Deviations from the reference temperatures can be corrected in subsequent measurements. Weight calibration is readily achieved using standard weights, and the balance may be calibrated for buoyancy effects if necessary. Buoyancy is an apparent mass gain during the initial stage of thermogravimetric analysis caused by the aerodynamic drag of gas flow through the furnace (Crewe et al., 2007). Principal uses of TG include measurement of a material's thermal stability and composition.

2.2. Differential thermal analysis

Differential thermal analysis (DTA) is a technique for recording the difference in temperature using a set of thermocouples between a substance and a reference (often inert) material against either time or temperature as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate. The temperature difference (ΔT) is then plotted against time or temperature, and the instrument must be calibrated for temperature using standards with known temperatures of phase transition. DTA allows for detecting exothermic (sample temperature increases relative to reference) and endothermic (sample temperature decreases relative to reference) reactions as a function of temperature and is often applied for the determination of phase diagrams and decomposition studies. The portion of the curve for which ΔT is approximately zero is considered to be the baseline. Points on the DTA curve with maximum ΔT are called peak temperatures and in any thermal technique the entire curve is often called a thermogram. But, if endothermic and exothermic reactions occur simultaneously and are of similar magnitude, they cannot be distinguished by DTA and the curve appears as a baseline without reaction. Using DTA, one can measure all reactions and processes that involve a change in energy during heating or cooling of a sample (Smykatz-Kloss, 1982), including endothermic reactions due to dehydration, dehydroxylation, structural decomposition and transformation, magnetic changes, sintering and melting, or evaporation and sublimation, as well as exothermic reactions due to oxidation/burning of organic matter, iron oxidation, or crystallization of amorphous material.

2.3. Differential scanning calorimetry

Differential scanning calorimetry (DSC) is a technique for measuring the energy added to a sample and reference as a function of temperature. Two classes of DSC instruments can be distinguished by their principles of operation: power compensation DSC and heat flux DSC. In a heat flux DSC, both sample and reference are heated or cooled by the same single heat source. As the temperature of the furnace is changed according to the applied temperature program, heat is transferred to the sample and reference through the thermoelectric disk. Like DTA, heat flux DSC measures a temperature difference between sample and reference, and the corresponding voltage signal is converted to a heat flow rate (usually in units J s⁻¹). The advantage of heat flux DSC over DTA is that the signal is independent of the thermal properties of the sample. In power compensation DSC, the objective is to establish a near-zero temperature difference between the sample and reference materials as the two specimens are subjected to identical temperature regimes. The

sample and reference are situated in two separate, identical furnaces and the same temperature is maintained for both. The differential power input required to compensate for temperature deviations between the two cells is recorded, and the energy required to do this is a measure of the enthalpy or heat capacity changes in the sample relative to the reference. DSC measures not only endothermic and exothermic effects, but also changes in sample heat capacity as a function of temperature, but for reliable measurements of heat fluxes, each calorimeter must be calibrated for its thermal resistance, heat capacity, and temperature. A detailed description of calibration procedures can be found in Danley (2003) and Höhne et al. (2003).

All reactions that absorb or release heat are detectable by DSC or DTA, while not all of them are associated with a change in mass and thus detectable by TG. Although DTA can yield an approximation of the enthalpy of a particular reaction, this is directly quantifiable only by DSC. The latter technique is also the only one suitable for measuring sample heat capacity. It is thus the combination of various thermal techniques and their different sensitivities that makes them a useful tool in environmental and soil research (Dell'Abate et al., 2003). While previous generations of instruments were capable of only a single measurement technique, many modern instruments are capable of simultaneous measurements (e.g., TG–DSC).

Results of TG/DTG, DTA and DSC analyses are typically reported in graphical form. As an illustrative example (Fig. 1), 10 mg of calcium oxalate monohydrate ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) was analyzed using a Netzsch STA 409PC Luxx (Netzsch-Gerätebau GmbH, Selb, Germany) equipped with a type-S TG–DSC sample carrier, heated in a Pt crucible from ambient ($\sim 25^\circ\text{C}$) to 900°C at $10^\circ\text{C min}^{-1}$ in a flowing air atmosphere. Thermogram abscissa may be expressed in terms of time if the heating program is illustrated, but are most frequently expressed in terms of temperature. The ordinate axis for TG is mass loss and is typically expressed in percent (%) or g kg^{-1} to normalize for the initial sample mass. High rates of mass loss are illustrated in DTG thermograms as negative peaks. In the case of Ca-oxalate (Fig. 1), the first thermal reaction (DTG peak near 170°C) resulted in a mass loss of 11%, and is associated with the dehydration of Ca-oxalate monohydrate. An analogous reaction is typically observed in soil samples due to the removal of pore and hygroscopic water. The second thermal reaction (DTG peak near 476°C) resulted in a mass loss of 17%, and is associated with the oxidation of Ca-oxalate to calcium carbonate and the evolution of CO_2 . In soil samples, mass losses in this region are associated with the oxidation of organic matter. The third thermal reaction (DTG peak near 703°C) resulted in a mass loss of 33%, and is associated with the decomposition of the calcium carbonate. This reaction can be used for the detection of carbonates in soil samples. The ordinate axis of DSC data are typically reported in units of microvolts per milligram of sample ($\mu\text{V mg}^{-1}$) when reported as raw, uncalibrated signal, or in units of milliWatts per milligram (mW mg^{-1}) when the instrument has undergone sensitivity or enthalpy calibration. DSC peaks in Fig. 1 are

plotted with exothermic behavior in the upward direction, and thus the Ca-oxalate reactions are endothermic, exothermic and endothermic, respectively. The convention for the direction of DSC and DTA peaks differs among regions and scientific communities. Applications in soil science have typically reported exothermic reactions as upward peaks. Integration of the DSC peaks provides a measure of the total amount of energy consumed or released during the reaction, in this case, -518 J g^{-1} , $+1308 \text{ J g}^{-1}$ and -1730 J g^{-1} respectively using the mass of the sample just before each reaction.

2.4. Evolved gas analysis

A milestone for thermal analysis has been the development of coupling techniques where the thermal reaction products are subsequently measured by other detectors. Such a coupling allows a better distinction of the underlying processes and reactions observed during the temperature program. Evolved gas analysis (EGA) by Fourier-transformed infrared (FTIR) spectrometry, gas chromatography (GC), mass spectrometry (MS), isotope-ratio mass spectrometry (IRMS) and elemental analysis will be discussed here. The most frequently applied thermal degradation technique that is coupled to EGA is analytical pyrolysis. Analytical pyrolysis is distinguished from other thermal degradation techniques (e.g., TG/DTG, DTA, DSC) by its exclusive use of an inert atmosphere, rapid heating rates ($>1^\circ\text{C ms}^{-1}$ in Curie-point pyrolysis) and most importantly by the fact that pyrolysis characterizes the volatile component rather than properties of the bulk sample. An extensive review of analytical pyrolysis is beyond the scope of this study, but readers are directed to several good reviews of this technique (e.g., Schnitzer and Schulten, 1995; Schulten, 1996; Leinweber and Schulten, 1999) and a study comparing results from several thermal degradation techniques (Leinweber and Schulten, 1992).

Evolved gas analysis is a technique to determine the nature and amount of volatile products formed during thermal degradation of materials. Recently, Hsieh (2007; Hsieh and Bugna, 2008) introduced a prototype for the detection of the elemental composition (C, N, S) of reaction products where volatilized sample components are subsequently fully oxidized in an O_2 -atmosphere and detected by IR (CO_2) or chemiluminescence (NO_2 , SO_2). Commercially available combinations often comprise a TG or TG–DSC system coupled to detection of gases either by FTIR or by MS and thus allow for some structural identification of volatiles.

Compound detection by FTIR is hampered by overlapping of peaks, making unique assignment difficult when several products occur simultaneously. Also, FTIR has a slower response time and is less sensitive than MS. Low sensitivity is however not problematic for detecting major compounds such as CO_2 , CO , or H_2O , which are the primary products of thermal analysis in an oxidizing atmosphere. Structural identification of evolved compounds is more conclusive with MS systems but also limited when isomers are formed or

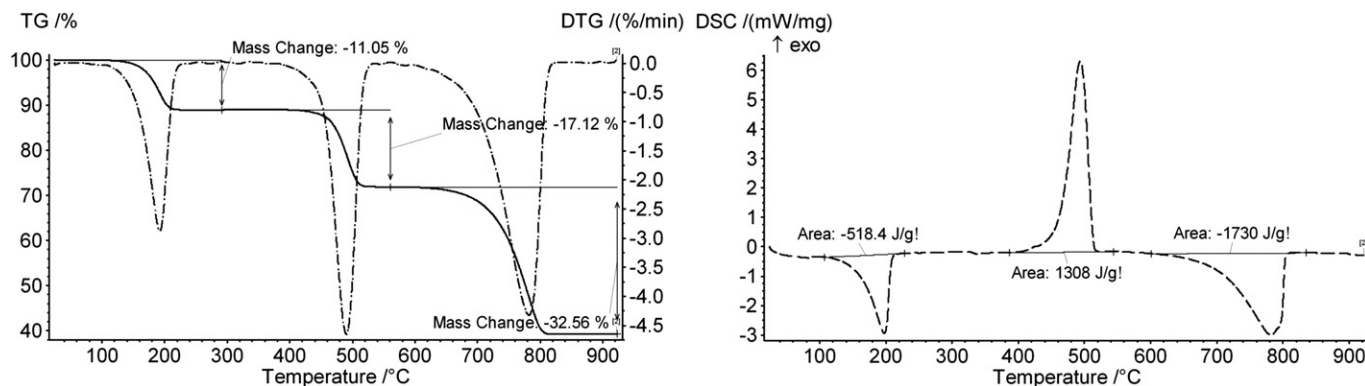


Fig. 1. (a) Thermogravimetry (TG, solid line) and derivative thermogravimetry (DTG, dashed line) and (b) differential scanning calorimetry (DSC, dashed line) thermograms of calcium oxalate analyzed in an air atmosphere, as an example of the mass loss and endo- and exothermic thermal regions observable during soil analysis.

released. Pitkänen et al. (1999) used TG–FTIR for identification of gaseous reaction products from the combustion (in synthetic air) of coal, peat, and plant tissue. In addition to CO₂, CO, and H₂O, they identified trace amounts of several low-molecular organic compounds. The latter may stem from volatilization of native compounds present in the sample but may equally indicate their formation during heating. Formation of some low-molecular organic compounds and CO seems a likely mechanism since many of them vaporize at ambient temperature and would therefore not form a large proportion of organic materials in situ. This example highlights the usefulness of EGA for detecting possible reaction mechanisms in a solid sample upon heating and testing the assumption of fully oxic conditions in the whole sample volume even in an atmosphere containing 20% O₂.

Dell'Abate et al. (2003) used DSC–TG–MS to follow the evolution of pyrolysis products of humic substances in an inert atmosphere (He). Similar to Pitkänen et al. (1999), they reported H₂O, CO, and CO₂ as the principal gases evolved plus $m/z = 32$ (possibly methanol). Lopez-Capel et al. (2006a) heated degraded wheat straw in a TG–DSC system (synthetic air) and recorded evolved gases using MS (temporal resolution 10 s or 3 °C) and IRMS (six selected intervals over the whole combustion process each accumulating sample over 50–100 s). Compared to Dell'Abate et al. (2003), they also reported H₂O and CO₂ as the principal gases but not CO, probably due to oxic conditions or different source materials. Other masses included reduced C and CN species. Detection of $\delta^{13}\text{C}_{\text{CO}_2}$ at six points in time revealed differences in the isotopic composition during fungal degradation of straw and showed a dependence of the isotopic signal on the heating temperature. The approach of combined MS and IRMS offers great potential in particular for future studies with labeled material (Lopez-Capel et al., 2006a). Recently, Lopez-Capel et al. (2008) used $\delta^{13}\text{C}_{\text{CO}_2}$ to infer the effect of a C₄–C₃ vegetation change on the isotopic signal of thermally labile versus thermally stable compounds. Their data indicate a reasonable correspondence between the isotopic signature (which in their study roughly corresponds to age) and thermal stability.

Compared to online detection systems for reaction products above, determination of the radiocarbon content during heating is still in an early stage of development. Such a technique may prove useful for soils, in particular since it relates thermal stability to age. Szidat et al. (2004) reported on radiocarbon measurements of the NIST standard SRM 1649a (urban dust) and identified two discrete radiocarbon ages of the material, depending on the applied heating temperature. A higher time or temperature resolution of the evolved $^{14}\text{CO}_2/^{12}\text{CO}_2$ signal would be necessary, and the current work is limited by the detection limit of the accelerator mass spectrometer for measuring ^{14}C .

Finally, none of the studies above provided an approach for calculating the mass balance of the thermal reactions. Such a computation is, however, necessary for a reliable evaluation and quantification of reaction products. The same holds true for a rough energy budget during DSC experiments that is not usually conducted.

3. Thermal analysis of the mineral soil fraction

The application of thermal analysis to earth science materials has an extensive history of use, particularly in mineralogy. There are thousands of minerals in nature, and a large majority of them exhibit at least one thermal effect. In 1887, Le Chatelier performed the first thermal analysis of a soil mineral fraction, heating a small quantity of clay and controlling its temperature. Some years after, Nernst and Riesenfel (1903) studied the change in mass of various minerals as a function of temperature. These experiments were followed by studies of thermal reactions of a wide variety of clay minerals and subsequently a variety of non-clay minerals including very reactive mineral such as sulfides and borates (Giese, 1990).

In fact, the evolution of thermal analysis as a set of analytical methods occurred largely through its application to clay mineralogy. The “golden age” of thermal analysis in mineralogy reached its peak in

the 1950s. Despite some success, it was apparent to many at the time that mineral identification was not the strong point of DTA because of experimental and mineral variations such as exchangeable cations. XRD became a much more popular technique, partially because of the lack of cheap and readily available commercial thermo-analytical instrumentation (Mackenzie, 1987). The development of DSC, EGA and the incorporation of computers into the control of the experiment and data collection increased the sensitivity and versatility of thermal techniques, prompting renewed interest from the mineralogy community (Giese, 1990; Yariv, 1989).

In spite of their limitations, all four major thermal analysis techniques (TG/DTG, DTA and DSC) are currently used for quantitative determination of the mineralogical composition of soil materials, typically in combination or association with other techniques such as XRD or chemical analysis (Karathanasis and Harris, 1994). Quantitative estimation of soil minerals is based on the measurement of characteristic weight loss or gain (by TG) associated with dehydration, dehydroxylation, oxidation, decomposition or evaporation of a particular mineral, or based on characteristic energy changes (by DTA or DSC) associated with these reactions (Table 1). Karathanasis and Hajek (1982) used a combination of TG, DSC and XRD to quantitatively determine the mineralogical composition of clay fractions from several soils, and found smectite, vermiculite, kaolinite, gibbsite and calcite contents to be consistent with previous measures using more elaborate methods.

Thermal analyses of minerals in bulk soil samples are uncommon, mainly because soil is a mixture of mineral and organic material, and the organic component can obscure characteristic mineral endothermic peaks with strong exothermic reactions at 300–500 °C. For instance, many of the major clay minerals feature endothermic peaks at temperatures below 200 °C due to the loss of adsorbed water and at higher temperatures due to dehydroxylation (Fig. 2). For this reason, organic matter is usually removed from soil with H₂O₂ prior to analysis, or thermal analysis is performed in an inert N₂ atmosphere (Tan et al., 1986).

The thermal analysis of mineral soil components has already been the subject of extensive study with a number of excellent reviews, including books, that have previously been published (e.g., Mackenzie, 1957; Todor, 1976; Stucki and Bish, 1990; Smykatz-Kloss and

Table 1

Thermogravimetric (TG) weight loss, differential thermal analysis (DTA) or differential scanning calorimetry (DSC) temperature regions, and heats of reaction (ΔH) used for quantitative soil mineral analysis (from Karathanasis and Harris, 1994).

Mineral	Reaction	Temperature region (°C)	Weight loss (g kg ⁻¹)	ΔH (J g ⁻¹)	Reference
Gibbsite	–OH → H ₂ O ↑	250–250	312	1075.3	Karathanasis and Hajek (1982)
Quartz	$\alpha \rightarrow \beta$ inversion	~573	–	5.4	Bartenfelder and Karathanasis (1989)
Calcite	–CO ₃ → CO ₂ ↑	750–990	440	1787	Todor (1976)
Kaolinite	–OH → H ₂ O ↑	400–600	140	656.9	Jackson (1975)
Mg-smectite	H–OH → H ₂ O ↑	25–250	228	592.5	Karathanasis and Hajek (1982)
	–OH → H ₂ O ↑	600–900	50		Jackson (1975)
Mg-vermiculite	H–OH → H ₂ O ↑	220–250	24	159.0	Barshad (1952), Karathanasis and Hajek (1982)

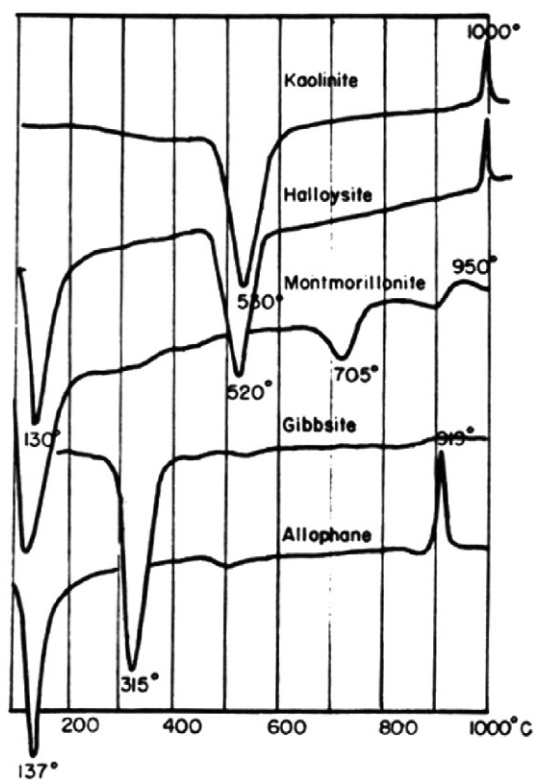


Fig. 2. Differential thermal analysis (DTA) thermograms of selected major clay minerals: kaolinite (Macon, GA); halloysite (Bedford, Indiana); montmorillonite (Oklahoma Geol. Survey); gibbsite (Brazil); allophane (<2 μm fraction of soil extracted from a tropical Andept) (from Tan et al., 1986).

Warne, 1991; Langier-Kuźniarowa, 2002). The reader is directed to these sources for further details.

4. Thermal analysis of the organic soil fraction

While thermal analysis had previously been used to study soil minerals, it was not until the development of a controlled-atmosphere apparatus, in the early 1950s, that valid results on organic samples could be obtained (Mackenzie and Mitchell, 1962). A controlled-atmosphere apparatus permits the analysis of a sample in an oxidizing atmosphere to assess the burning characteristics of the organic material, and in an inert atmosphere that suppresses combustion but allows observation of other thermal reactions such as dehydration or melting and boiling points, phase transitions, auto/oxidation reactions and fragmentation during pyrolysis.

Several organic compounds were analyzed during the 1950s and 60s. The earliest thermal analysis studies on organic materials were related to substances of industrial value such as fuels (e.g., peat, wood, coal). Perkins and Mitchell (1957) obtained thermograms for a number of sugars, starches, amino acids, and proteins, and Mitchell and Knight (1965) applied DTA to a number of plant materials. Finally, Mackenzie and Mitchell (1962) stated that the curve obtained for a specific compound is reasonably characteristic of that compound and that peak area is related to the amount of reacting material. They suggested that this method could be applied to indicate the degree of decomposition of soil organic matter and aid in identifying soil type. In addition, Mitchell and Birnie (1970) also proposed that the maximum peak temperatures and the curve recorded are characteristic parameters that could be used as a fingerprint of the sample, thus offering new and interesting possibilities for soil organic matter analyses.

Up to now, no single analytical method can adequately describe the complete continuum of materials that comprise soil organic matter. One response has been the development of a large number of

physical, chemical and biological fractionation schemes to separate SOM into more homogeneous pools for subsequent characterization. However, thermal stability may have the potential to serve as an indicator of the distribution of SOM between biogeochemically labile and stable fractions, with the added value that data are obtained relatively rapidly and their measurement requires little sample preparation. Two important milestones have marked the development of thermal techniques as a method for characterizing soil organic matter: the identification of typical patterns in the thermal curves together with their chemical interpretation, and the development of indices to describe the degree of organic matter stability in relation with its thermal stability.

4.1. Typical patterns of thermal curves and their interpretation

During the 1960s, Turner and Schnitzer (1962), Schnitzer et al. (1964) and Schnitzer and Hoffman (1965) pioneered the use of TG, in combination with other techniques such as infrared spectroscopy and elemental analysis, for studying podzolic soil humic substances. They detected two exothermic peaks between 200 and 500 $^{\circ}\text{C}$ for all samples. The authors hypothesized that the two peaks were the result of the decomposition and combustion reactions of two organic fractions with different thermal stabilities. The first peak was associated with less humified components, while the second peak increased with greater humification. Schnitzer and Hoffman (1966) associated the first exothermic peak with volatilization of $-\text{OH}$ and $-\text{COOH}$ groups and the second peak with carbon oxidation. These studies also reported differences between the humic substances extracted from the A_0 and B_h horizons.

In further studies, other researchers such as Orlov (1968), Jambu et al. (1975) and Shurygina et al. (1971) inferred considerable differences in the relative aromatic and aliphatic composition of humic and fulvic acids of different soils using DTA and infrared spectroscopy. Gonet and Cieslewicz (1998) found significantly negative correlations between the H/C and N/C ratio of HA and their thermal stability. Provenzano and Senesi (1999) studied humic substances with DSC in combination with FTIR spectroscopy by placing samples in hermetically sealed capsules and analyzing under 20 mL min^{-1} air flow. They ascribed low-temperature endotherms at 250 $^{\circ}\text{C}$ to decarboxylation of surface carboxyl groups and high temperature exotherms at around 500 $^{\circ}\text{C}$ to the thermal reaction of the aromatic nuclei of humic substances. In addition to these studies with humic substances, DTA-screening of 62 Na-saturated soil samples led Satoh (1984) to suggest that exotherms at higher temperatures (400–450 $^{\circ}\text{C}$; $10\text{ }^{\circ}\text{C min}^{-1}$) are attributable to plant debris while lower temperature exotherms (at around 300 $^{\circ}\text{C}$) are derived from soluble humic substances. Leinweber et al. (1992) also observed differences in soil organic matter thermal behavior due to management, in particular the enrichment of more thermolabile organic compounds in samples where farmyard manure was spread annually. Grisi et al. (1998) proposed that soil organic matter consists of two main fractions with different thermal stabilities, and defined two different sections of the thermogram that they called exotherms 1 and 2. They compared thermogravimetric weight losses in these temperature regions to other techniques for measuring the extent of humification of organic matter in tropical soils. Escudéy et al. (1999) provided a summary table of the reactions and transformations occurring in the exothermic region during the thermal analysis of volcanic-derived soil material. They suggested that heating of SOM resulted in dehydration (105–220 $^{\circ}\text{C}$), further dehydration of SOM and dehydroxylation of allophane (220–280 $^{\circ}\text{C}$), dehydrogenation and decarboxylation of organic matter, and further dehydroxylation of allophane (280–370 $^{\circ}\text{C}$), decarboxylation of organic matter (370–420 $^{\circ}\text{C}$), and finally, the oxidation of organic matter (420–500 $^{\circ}\text{C}$).

Many different samples have been analyzed by TG, DTA and DSC in recent decades, including organic matter of soils, peat, compost, marine sediments and black carbon (Mitchell and Birnie, 1970; Leinweber et al., 1992; Blanco and Almendros, 1994; Dell'Abate et al., 2003; Lopez-Capel

et al., 2006b; De la Rosa et al., 2008). In general, the exotherm in a combustion thermogram of a mineral soil containing a few percent of organic matter is often a weakly shaped curve with some identifiable peaks related with the presence of different labile and recalcitrant organic matter compounds (Fig. 3c). By comparison, highly organic samples such as peat consist of intense peaks and shoulders in the region above 300 °C (Fig. 3b), depending on the degree of humification of the organic matter. Soil organic matter precursors such as plant leaves (Fig. 3a) consist of two or more well separated peaks, usually with a characteristic one present at temperatures between 460 and 480 °C. Thermograms of coal or black carbon (Fig. 3d) show a distinct peak at high temperatures attributable to highly recalcitrant forms of organic matter such as polycondensed aromatic carbon (Almendros et al., 1982; Lopez-Capel et al., 2005; De la Rosa et al., 2008). These patterns have been observed frequently and seem typical for those materials, though systematic differences can be seen depending on the origin of the soil and how it is managed. Commonly, the low-temperature part of the exothermic region around 300–350 °C (at a heating rate of 20 °C min⁻¹) has been ascribed to the burning of carbohydrates and other aliphatic compounds, while peaks with a maximum at approximately 400–450 °C are thought to result from the loss of aromatic compounds such as lignin or other polyphenols (Ranalli et al., 2001; Dell'Abate et al., 2002; Strezov et al., 2004).

While there are distinct patterns in the thermal curves of organic samples, the thermal behavior of soil samples is also affected by a number of experimental parameters (Cebulak and Langier-Kuzniarowa, 1997). Nevertheless, under identical experimental conditions, thermal stability of SOM is essentially a function of the chemical composition and degree of humification of the organic matter and the

degree of mineral association. The frequency and type of chemical bonds between the major constituent elements (C, H, O and N) determine the binding energy within a molecule. Single bonds between C–O, C–N and C–C are relatively weak (350–412 kJ mol⁻¹), while unsaturated bonds between carbon atoms reach energies between 610 and 840 kJ mol⁻¹. Aromatic bonds are situated midway (≈ 520 kJ mol⁻¹). Consequently, the higher binding energy between carbon atoms of aromatic molecules compared to saturated bonds results in a higher thermal stability (Leinweber and Schulten, 1992). Soil mineralogy also profoundly affects SOM stability through the formation of organo-mineral complexes (Kleber et al., 2007). Typically, organic compounds sorbed to mineral phases are decomposed more slowly and to a lesser extent than OM either dissolved or uncomplexed with minerals (Kaiser and Guggenberger, 2003). Although the processes operating at the organo-mineral interface are not fully understood, they clearly affect SOM stability and must be considered when bulk soil samples are analyzed. Using pyrolysis with field ionization mass spectrometry, Schulten and Leinweber (1999) measured higher thermal stability of heavy, mineral-associated organic matter as compared to lighter OM for similar compound classes. This may be ascribed to an amplification of thermal stability by organo-mineral association, but a study that directly compares the thermal stability of well characterized organic molecules either free or sorbed remains to be accomplished. Lastly, in contrast to spectroscopy where the physical arrangement of molecules and macro-structures has only a modest influence on the measured sample attributes, the thermal stability of a sample is strongly affected by its physical structure. This is because thermal analysis does not provide information at the atomic or molecular level, but rather registers irreversible

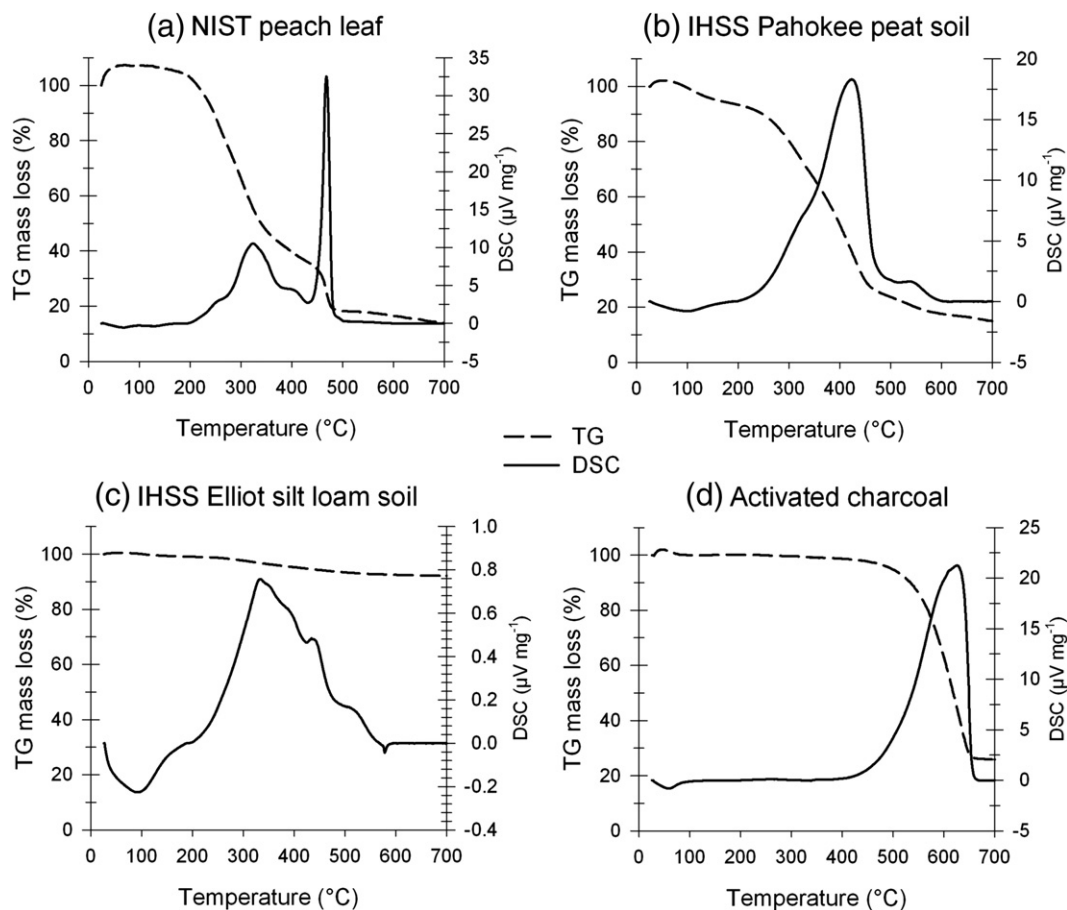


Fig. 3. Weight loss (TG, dashed line) and differential scanning calorimetry (DSC, solid line) thermograms of samples: a) peach leaf (National Institute of Standards and Testing (NIST) standard), b) Pahokee peat soil (International Humic Substances Society (IHSS) standard), c) Elliot silt loam soil (IHSS standard), and d) activated charcoal within the range from 25 °C to 725 °C.

thermal reactions that occur at the whole-matrix level. In calorimetry, the heat flux through the sample is determined by the thermal conductivity of the material which typically changes over time as the sample oxidizes. Grain size and packing density regulate the flow of air into and reaction products out of the sample, and a high bulk density may impede sufficient oxygen delivery. Available surface of the sample is also important, as it increases the theoretical reaction rate. For example, the reactivity of soot and coal char toward thermal oxidation depends on the size, orientation, and organization of the graphene layer (Vander Wal and Tomasek, 2003).

It is tempting to assign chemical structures to individual components of thermal patterns of organic materials, but it would be misguided trying to obtain accurate information about chemical structures with thermal techniques in the same way that we use other techniques such as NMR or XRD. The analysis of thermograms from cellulose, for example, sometimes reveals a two-peak structure with the second peak positioned in the temperature region $>400^{\circ}\text{C}$ (Dahiya and Rana, 2004; Vicini et al., 2004), a region of higher thermal stability that has been attributed to the formation of char from cellulose (e.g., Le Van, 1984). In that temperature region, lignin or tannin oxidize, though typically at temperatures above the second cellulose exotherm. Furthermore, there are still unresolved issues related to differences in the thermal stability of single components compared to their mixtures. Rovira and Vallejo (2000) reported on DSC measurements of plant litter and mineral soil alone or as composite samples. They observed pronounced differences between the calculated thermogram of mixtures based on the thermal behavior of single components and the actual measurement. In particular, the second exotherm of plant litter was greatly reduced after mixing with soil. Leifeld (2007) found systematic, albeit not significant, differences between thermograms of mixtures of mineral soil and a lignin standard prepared dry or in water. Sample preparation under moist or wet conditions facilitates sorption reactions which may systematically alter the thermal stability of a sample, but more research is needed.

Together, the above findings indicate that peak positions in thermograms cannot necessarily replace chemical analysis because they do not provide equivalent information, but thermal analysis is highly suitable for providing sufficient data for developing valuable indices of SOM decomposability through the analysis of bulk soil samples or isolated fractions.

4.2. Thermal stability indices

Typical thermal stability patterns are observed during organic matter thermal degradation and can provide us valuable information about the sample being analyzed. Kristensen (1990) advanced the use of thermal techniques for organic matter characterization by proposing an index called R_p in an attempt to shift to quantitative analysis. This index corresponds to the ratio of sample weight loss in the temperature range of $280\text{--}520^{\circ}\text{C}$ to total weight loss from 130 to 520°C . Therefore, R_p

represents the fraction of total combustible organic matter which was lost at the high temperature range. In combination with the C/N ratio, thermal analysis proved to be a promising tool for characterization of organic matter, although it was mainly restricted to the study of early decomposition of organic materials and it was performed in a stepwise manner rather than continuously.

Seeking a method to evaluate the degree of maturation and stabilization of compost without extraction and fragmentation procedures to isolate humic-like materials, Dell'Abate et al. (1998), studied the sensitivity of some parameters deduced from TG and DSC measurements during the composting process of agroindustrial wastes. They defined a new index called R_1 , which corresponds to the ratio between the mass loss associated with the second and first exothermic reactions, which in their case were identified by peaks at approximately 300 and 440°C . R_1 indicates the relative amount of the thermally stable fraction of organic matter with respect to the less stable fraction. Results obtained were well correlated with different humification parameters previously reported by other authors (e.g., Ciavatta et al., 1990). Consequently, R_1 was defined as a reliable parameter for evaluating the degree of maturation of organic matter in composts and also to monitor composting processes (Dell'Abate et al., 2000).

In subsequent studies, other indices were tested to develop one that allows a quantitative interpretation of the thermal stability of different kinds of organic matter or its components. Dell'Abate et al. (2002) proposed the analysis of humic substances using $\%Exo_1$. This index was the weight loss in the first exotherm interval as a proportion of total weight loss associated with the whole temperature range, which in this case included a third interval at temperatures between 507 and 570°C corresponding to the most thermally resistant organic components. Dell'Abate et al. (2003) also combined thermal analysis of soil humic substances under oxidizing and inert atmospheres with other techniques such as EGA to obtain other indices: the index of thermal decomposability ($ID = \text{total TG weight loss in He} \times 100 / \text{total TG weight loss in air}$), and the index of thermal recalcitrance ($IR = (\text{total weight loss in Air} - \text{total weight loss in He}) \times 100 / \text{total weight loss in air}$). Both indices showed values in agreement with previous results obtained in studies on the microbial dynamics and organic matter turnover of the respective soils analyzed.

In recent years, it has become more common to use the terms Exo_1 , Exo_2 and Exo_3 , as introduced by Lopez-Capel et al. (2005) based on the work of Dell'Abate et al. (2000, 2002). These indices correspond to the relative weight loss (%) in relation with the total percentage of weight loss (Exo_{tot}) in several temperature ranges. These values indicate the relative abundance of organic materials with different thermal stabilities. It should be noted that each of these indices were developed on the basis of the weight loss associated with the main exothermic peaks. However temperature limits for Exo_1 , Exo_2 and Exo_3 regions have not been rigorously defined, and vary significantly. Table 2 summarizes the different temperature ranges used in studies

Table 2
Exothermic mass loss regions used for calculating indices of thermal stability.

Authors	Exotherm 1	Exotherm 2	Exotherm 3	Index proposed
Kristensen (1990)	130–280 °C	280–520 °C	–	$R_p = Exo_2 / (Exo_1 + Exo_2)$
Grisi et al. (1998)	Peak at 380 °C	Peak at 480 °C	–	None
Dell'Abate et al. (2000)	295–307 °C	436–469 °C	–	$R_1 = Exo_2 / Exo_1$
Dell'Abate et al. (2002)	301–388 °C	424–448 °C	507–570 °C	$\%Exo_1 = Exo_1 / Exo_{tot}$
Dell'Abate et al. (2003)	200–350 °C	350–500 °C	–	$ID (\%) = \text{total weight loss in He} \times 100 / \text{total weight loss in air}$
	180–325 °C	325–540 °C	–	$IR (\%) = (\text{total weight loss in air} - \text{total weight loss in He}) \times 100 / \text{total weight loss in air}$
Lopez-Capel et al. (2005)	295–344 °C	414–473 °C	–	Exo_1 / Exo_2 , $\%Exo_1$, $\%Exo_2$
Plante et al. (2005)	180–310 °C	310–450 °C	–	Exo_1 / Exo_2
Leifeld et al. (2007)	Peak at 354 °C	Peak at 430 °C	Peak at 520 °C	Exo_1 / Exo_2
Lopez-Capel et al. (2006a)	230–330 °C	330–430 °C	430–530 °C	$\%Exo_1$, $\%Exo_2$, $\%Exo_3$, $Exo_1 / (Exo_2 + Exo_3)$
Lopez-Capel et al. (2006b)	200–400 °C	400–550 °C	550–600 °C	$\%Exo_1$, $\%Exo_2$, $\%Exo_3$
Baffi et al. (2007)	180–410 °C	410–600 °C	–	Exo_2 / Exo_1
De la Rosa et al. (2008)	200–380 °C	380–475 °C	475–650 °C	$\%Exo_1$, $\%Exo_2$, $\%Exo_3$
Fernandez et al. (2008)	338–341 °C	439–456 °C	539–560 °C	None

published during the last decade. This summary illustrates the variability in temperature cutoffs selected by their authors, which in many cases are not explicitly justified. It may be advantageous to develop a consistent basis for selecting these temperature limits, though this has only recently become possible due to the increasing number of thermal analyses of SOM reported in recent years.

4.3. Thermal analyses for other SOM properties

Aside from its applications in elucidating SOM decomposability, thermal analysis techniques have been applied to study several other properties of the organic component of soils. [Dlapa et al. \(2008\)](#) used TG and DTA to assess the effects of thermal energy input on water repellency of sandy soil. They found that repellency increased during heating up to 200 °C, but was eliminated at temperatures >200 °C due to the destruction of SOM. Several studies have also used thermal analysis to identify specific domains within soils that are responsible for nonlinear and linear sorption behaviors important to contaminant transport in the environment ([DeLapp and LeBoeuf, 2004](#)). Conceptual models suggest that nonlinear sorption behavior is attributable to rigid, glass-like regions in SOM, while linear sorption is attributable to more fluid, gel-like regions. The glass transition temperature (T_g) marks the transition between these two regions. [Schaumann and Antelmann \(2000\)](#) detected a glass transition at 79 °C for air-dried samples and 77 °C for pre-moistened samples by DSC analysis of a sample of a sandy forest soil. Further study by [Hurrass and Schaumann \(2005\)](#) found that glassiness “has to be considered a common characteristic of soil organic matter (SOM)”.

5. Future challenges to thermal analysis in soil science

Thermal analysis of the organic soil component has recently gained increasing interest, and is applied more frequently to the analysis of bulk soils as well as physical and chemical soil fractions. There are three reasons to add thermal methods to the complement of analytical methods currently used to characterize soils and soil organic matter. First, thermal methods are quite inexpensive, require little sample preparation, are rapid, give reproducible results, and are information rich. Results of thermal analyses have been shown to be strongly correlated to a number of fundamental soil properties ([Siewert, 2004](#)) in much the same way that mid- and near-infrared analyses are currently being applied ([Rosset et al., 2006](#)). Without being a panacea, thermal analysis may potentially replace or supplement more expensive, sophisticated and elaborate techniques of soil analysis. Secondly, thermal methods may aid to unravel the basis of organic matter stability in soil and thus be used as a tool for detecting patterns in SOM decomposability, particularly in conjunction with multivariate statistics ([Persson et al., 1986](#)). The thermal stability of any material is strongly related to the activation energy needed for its pyrolysis or combustion. Soil organic matter stabilization is thought to derive from a combination of primary recalcitrance of precursors and secondary recalcitrance of metabolites, effects of spatial inaccessibility due to aggregation, and interaction with soil surfaces (e.g., [von Lützow et al., 2006](#)). Biochemical recalcitrance may be considered as a high barrier of activation energy to the enzymes involved in the depolymerisation and decomposition of organic molecules, and this concept is discussed in the context of SOM decomposition and global warming ([Davidson and Janssens, 2006](#)). A rigorous analysis of the relationship between biochemical and thermal stability would likely lead to a better understanding of the nature of recalcitrant SOM. Thirdly, many terrestrial ecosystems are prone to periodic fires, and thus to temperatures beyond the physiological range. Fire profoundly changes the composition of SOM by selectively removing or transforming thermally labile materials while thermally stable ones are less altered ([Baldock and Smernik, 2002](#); [González-Pérez et al., 2004](#)). Thermal methods offer

the unique opportunity to directly measure changes in thermal stability of SOM or litter as a function of fire and thus complement structural–chemical investigations. Furthermore, non-biogenic soil carbon with characteristically high thermal stability can originate from geogenic or atmospheric input of coal, lignite, or soot ([Helfrich et al., 2007](#); [Jenkinson et al., 2008](#)). This material, abundant in many ecosystems, differs in structure and isotopic composition from SOM and thereby confounds the interpretation of data on SOM chemistry unless it is quantified or separated. It is known that such carbonaceous materials are thermally more stable than carbon from native organic inputs and often show distinct burning patterns ([Leifeld, 2007](#)). Thermal methods may thus be suitable for their quantification in soil, for example in relation to organic matter accumulation in reclaimed mine soils ([Maharaj et al., 2007](#)).

In recent years, most TG, DSC and DTA analyses were focused on humic substances, composts or soil fractions, and few of them reported analyses of whole soil samples. Previous studies show promising results, but there are other authors that point out several problems in the analysis of bulk soils or in obtaining quantitative information. [Yariv \(1991\)](#) and [Rovira and Vallejo \(2000\)](#) have highlighted the problems of quantifying the effects of organo-mineral complexes, and [Baffi et al. \(2007\)](#) indicated the lack of suitable quantitative indices for relating thermal and biology stability for composts. However, other studies are pointing to new and interesting approaches that need to be explored. [Plante et al. \(2005\)](#) proposed the analysis of thermal data using a peak deconvolution approach. They analyzed clay-associated organic matter, and the DSC traces obtained were fitted using the residuals method with Gaussian–Lorentzian sum on area peak types. Results revealed that these thermograms consisted of several hidden peaks, although their interpretation is still problematic mainly due to the lack of studies performed using this technique and the absence of matching results with complementary techniques such as EGA. [Rovira et al. \(2008\)](#) have proposed the quantification of the energy stored in SOM by thermal methods to determine the energetic benefit/cost ratio to release this energy and use that as a measure of SOM quality.

While thermal analysis can be implemented as routine analysis, the number of thermal runs per day is limited by the temperature range and heating rate of the experiments. The resolution of the exothermic region is also limited in high clay soils poor in organic matter content by the overlapping of dehydroxylation reactions of many clay minerals with organic matter oxidation. Another significant challenge to quantitative thermal analysis of soil materials is the large number of operational parameters and their inconsistent use across studies. Operational parameters that can affect the results of thermal analyses include: arrangement and type of sample holder, packing density and grain size of sample, heating rate, initial sample mass, crucible material, and furnace atmosphere. While [Smykatz-Kloss \(1974\)](#) proposed a set of standard conditions for the DTA of minerals, the conditions were specific to the use of a reference material (e.g., annealed alumina) and were designed specifically for the study of the mineral component rather than the organic component of soil. Therefore, it is imperative to determine the effect of operational parameters on the exothermic region of thermal analysis results and standardize protocols for soil organic matter thermal analysis.

6. Conclusions

Originally developed as a metallurgical method, thermal analysis found its most intense application in clay mineralogy during the first half of the 20th century. Since then, it has been used in a wide range of applications, ranging from materials science to pharmaceuticals. Thermal analysis continues to be applied in soil science, though more sporadically. Recent interest in the quick and inexpensive means of assessing soil organic matter quality in reference to decomposability and turnover, has spurred a re-examination of

thermal analysis techniques to study the soil organic component. It is important to explore prospects and limits of thermal techniques for providing a quantitative assessment of the thermal stability of SOM, which could well be the best representation of the complete continuum that comprises SOM quality. The development of standardized protocols for thermal analysis of soil samples that can be linked to SOM quality as determined by conventional means would be a significant advance in our fundamental understanding of the nature, dynamics and vulnerability of SOM to perturbations, as well as a state-of-the-art tool with potential widespread applicability to soil quality assessments.

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References

- Almendros, G., Polo, A., Vizcayno, C., 1982. Application of thermal analysis to the study of several Spanish peats. *Journal of Thermal Analysis* 24 (2), 175–182.
- Baffi, C., Dell'Abate, M.T., Nassisi, A., Silva, S., Benedetti, A., Genevini, P.L., Adani, F., 2007. Determination of biological stability in compost: a comparison of methodologies. *Soil Biology & Biochemistry* 39 (6), 1284–1293.
- Baldock, J.A., Smernik, R.J., 2002. Chemical composition and bioavailability of thermally altered *Pinus resinosa* (Red Pine) wood. *Organic Geochemistry* 33 (9), 1093–1109.
- Barshad, I., 1952. Temperature and heat of reaction calibration of the differential thermal analysis apparatus. *American Mineralogist* 37 (7–8), 667–694.
- Bartenfelder, D.C., Karathanasis, A.D., 1989. A differential scanning calorimetry evaluation of quartz status in geogenic and pedogenic environments. *Soil Science Society of America Journal* 53 (3), 961–967.
- Blanco, M.J., Almendros, G., 1994. Maturity assessment of wheat straw composts by thermogravimetric analysis. *Journal of Agricultural and Food Chemistry* 42 (11), 2454–2459.
- Cebulak, S., Langier-Kuzniarowa, A., 1997. Application of oxyreactive thermal analysis to the examination of organic matter associated with rocks. *Journal of Thermal Analysis and Calorimetry* 50 (1–2), 175–190.
- Ciavatta, C., Gavi, M., Antisari, L.V., Sequi, P., 1990. Characterization of humified compounds by extraction and fractionation on solid ployvinylpyrrolidone. *Journal of Chromatography A* 509 (1), 141–146.
- Crewe, R.J., Staggs, J.E.J., Williams, P.T., 2007. Drag-induced apparent mass gain in thermogravimetry. *Polymer Degradation and Stability* 92 (11), 2070–2075.
- Dahiya, J.B., Rana, S., 2004. Thermal degradation and morphological studies on cotton cellulose modified with various arylphosphorodichloridites. *Polymer International* 53 (7), 995–1002.
- Danley, R.L., 2003. New heat flux DSC measurement technique. *Thermochimica Acta* 395 (1–2), 201–208.
- Davidson, E.A., Janssens, I.A., 2006. Temperature sensitivity of soil carbon decomposition and feedbacks to climate change. *Nature* 440 (7081), 165–173.
- De la Rosa, J.M., Knicker, H., Lopez-Capel, E., Manning, D.A.C., Gonzalez-Perez, J.A., Gonzalez-Vila, F.J., 2008. Direct detection of black carbon in soils by Py-GC/MS, carbon-13 NMR spectroscopy and thermogravimetric techniques. *Soil Science Society of America Journal* 72 (1), 258–267.
- DeLapp, R.C., LeBoeuf, E.J., 2004. Thermal analysis of whole soils and sediment. *Journal of Environmental Quality* 33 (1), 330–337.
- Dell'Abate, M.T., Canali, S., Trinchera, A., Benedetti, A., Sequi, P., 1998. Thermal analysis in the evaluation of compost stability: a comparison with humification parameters. *Nutrient Cycling in Agroecosystems* 51 (3), 217–224.
- Dell'Abate, M.T., Benedetti, A., Sequi, P., 2000. Thermal methods of organic matter maturation monitoring during a composting process. *Journal of Thermal Analysis and Calorimetry* 61 (2), 389–396.
- Dell'Abate, M.T., Benedetti, A., Trinchera, A., Dazzi, C., 2002. Humic substances along the profile of two Typic Haploxerit. *Geoderma* 107 (3–4), 281–296.
- Dell'Abate, M.T., Benedetti, A., Brookes, P.C., 2003. Hyphenated techniques of thermal analysis for characterisation of soil humic substances. *Journal of Separation Science* 26 (5), 433–440.
- Diapla, P., Simkovic, I., Doerr, S.H., Simkovic, I., Kanka, R., Mataix-Solera, J., 2008. Application of thermal analysis to elucidate water-repellency changes in heated soils. *Soil Science Society of America Journal* 72 (1), 1–10.
- Escudéy, M., Diaz, P., Galindo, G., Chang, A.C., 1999. Differential thermogravimetric analysis of oxalate in hydrogen peroxide-treated allophanic soils. *Communications in Soil Science & Plant Analysis* 30 (7/8), 937–946.
- Fernandez, J.M., Hockaday, W.C., Plaza, C., Polo, A., Hatcher, P.G., 2008. Effects of long-term soil amendment with sewage sludges on soil humic acid thermal and molecular properties. *Chemosphere* 73 (11), 1838–1844.
- Giese, R.F., 1990. Thermal analysis in clay science. In: Stucki, J.W., Bish, D.L., Mumpton, F.A. (Eds.), *CMS Workshop Lectures. The Clay Minerals Society*, Boulder CO, pp. 1–9.
- Gonet, S.S., Cieslewicz, J., 1998. Differential thermal analysis of sedimentary humic acids in the light of their origin. *Environment International* 24 (5–6), 629–636.
- González-Pérez, J.A., González-Vila, F.J., Almendros, G., Knicker, H., 2004. The effect of fire on soil organic matter – a review. *Environment International* 30 (6), 855–870.
- Grisi, B., Grace, C., Brookes, P.C., Benedetti, A., Dell'Abate, M.T., 1998. Temperature effects on organic matter and microbial biomass dynamics in temperate and tropical soils. *Soil Biology & Biochemistry* 30 (10/11), 1309–1315.
- Helfrich, M., Flessa, H., Mikutta, R., Dreves, A., Ludwig, B., 2007. Comparison of chemical fractionation methods for isolating stable soil organic matter pools. *European Journal of Soil Science* 58 (6), 1316–1329.
- Höhne, G.W.H., Hemminger, W.F., Flammersheim, H.J., 2003. *Differential Scanning Calorimetry: an Introduction for Practitioners*. Springer, Berlin.
- Hsieh, Y.P., 2007. A novel multielemental scanning thermal analysis (MESTA) method for the identification and characterization of solid substances. *Journal of AOAC International* 90 (1), 54–59.
- Hsieh, Y.P., Bugna, G.C., 2008. Analysis of black carbon in sediments and soils using multi-element scanning thermal analysis (MESTA). *Organic Geochemistry* 39 (11), 1562–1571.
- Hurrass, J., Schaumann, G.E., 2005. Is glassiness a common characteristic of soil organic matter? *Environmental Science & Technology* 39 (24), 9534–9540.
- Jackson, M.L. (Ed.), 1975. *Soil Chemical Analysis – Advanced Course*, 2nd ed. Madison, WI.
- Jambu, P., Dupuis, T., Garais, M., 1975. Use of differential thermal analysis to characterize fulvic acid metal complexes and humic acid metal complexes. 2. Application to natural organometallic complexes. *Journal of Thermal Analysis* 8 (2), 231–237.
- Jenkinson, D.S., Poulton, P.R., Bryant, C., 2008. The turnover of organic carbon in subsoils. Part 1. Natural and bomb radiocarbon in soil profiles from the Rothamsted long-term field experiments. *European Journal of Soil Science* 59 (2), 91–113.
- Kaiser, K., Guggenberger, G., 2003. Mineral surfaces and soil organic matter. *European Journal of Soil Science* 54 (2), 219–236.
- Karathanasis, A.D., Hajek, B.F., 1982. Revised methods for rapid quantitative determination of minerals in soil clays. *Soil Science Society of America Journal* 46 (2), 419–425.
- Karathanasis, A.D., Harris, W.G., 1994. Quantitative thermal analysis of soil materials. In: Amonette, J.E., Zelazny, L.W. (Eds.), *Quantitative Methods in Soil Mineralogy*. Soil Science Society of America, Madison WI, pp. 360–411.
- Kleber, M., Sollins, P., Sutton, R., 2007. A conceptual model of organo-mineral interactions in soils: self-assembly of organic molecular fragments into zonal structures on mineral surfaces. *Biogeochemistry* 85 (1), 9–24.
- Kristensen, E., 1990. Characterization of biogenic organic matter by stepwise thermogravimetry (STG). *Biogeochemistry* 9 (2), 135–159.
- Langier-Kuzniarowa, A., 2002. Thermal analysis of organo-clay complexes. In: Yavir, S., Cross, H. (Eds.), *Organo-Clay Complexes and Interactions*. Marcel-Dekker, New York, pp. 273–344.
- Le Chatelier, H., 1887. De l'action de la chaleur sur des argiles. *Bulletin de la Société Française de Minéralogie* 10, 204–210.
- Le Van, S.L., 1984. Chemistry of fire retardancy. In: Rowell, R.E. (Ed.), *The Chemistry of Solid Wood*. American Chemical Society, Washington DC, pp. 531–574.
- Leifeld, J., 2007. Thermal stability of black carbon characterised by oxidative differential scanning calorimetry. *Organic Geochemistry* 38 (1), 112–127.
- Leifeld, J., Fenner, S., Muller, M., 2007. Mobility of black carbon in drained peatland soils. *Biogeochemistry* 4 (3), 425–432.
- Leinweber, P., Schulten, H.-R., 1992. Differential thermal analysis, thermogravimetry and in-source pyrolysis-mass spectrometry studies on the formation of soil organic matter. *Thermochimica Acta* 200, 151–167.
- Leinweber, P., Schulten, H.R., 1999. Advances in analytical pyrolysis of soil organic matter. *Journal of Analytical and Applied Pyrolysis* 49 (1–2), 359–383.
- Leinweber, P., Schulten, H.-R., Horte, C., 1992. Differential thermal analysis, thermogravimetry and pyrolysis-field ionisation mass spectrometry of soil organic matter in particle-size fractions and bulk soil samples. *Thermochimica Acta* 194, 175–187.
- Lopez-Capel, E., Sohi, S.P., Gaunt, J.L., Manning, D.A.C., 2005. Use of thermogravimetry-differential scanning calorimetry to characterize modelable soil organic matter fractions. *Soil Science Society of America Journal* 69 (1), 136–140.
- Lopez-Capel, E., Abbott, G.D., Thomas, K.M., Manning, D.A.C., 2006a. Coupling of thermal analysis with quadrupole mass spectrometry and isotope ratio mass spectrometry for simultaneous determination of evolved gases and their carbon isotopic composition. *Journal of Analytical and Applied Pyrolysis* 75 (2), 82–89.
- Lopez-Capel, E.L., Arranz, J., Gonzalez-Vila, F.J., Gonzalez-Perez, J.A., Manning, D.A.C., 2006b. Elucidation of different forms of organic carbon in marine sediments from the Atlantic coast of Spain using thermal analysis coupled to isotope ratio and quadrupole mass spectrometry. *Organic Geochemistry* 37 (12), 1983–1994.
- Lopez-Capel, E., Krull, E.S., Bol, R., Manning, D.A.C., 2008. Influence of recent vegetation on labile and recalcitrant carbon soil pools in central Queensland, Australia: evidence from thermal analysis-quadrupole mass spectrometry-isotope ratio mass spectrometry. *Rapid Communications in Mass Spectrometry* 22 (11), 1751–1758.
- Mackenzie, R.C., 1957. *The Differential Thermal Investigation of Clays*. Mineralogical Society (Clay Minerals Group), London, UK. 456 pp.
- Mackenzie, R.C., 1984. Origin and development of differential thermal analysis. *Thermochimica Acta* 73 (3), 307–367.
- Mackenzie, R.C., 1987. Some reflections on thermal analysis. *Thermochimica Acta* 110, 1–10.
- Mackenzie, R.C., 1991. *Geosciences in thermal analysis development. Lecture Notes in Earth Sciences*. Springer-Verlag, Berlin, pp. 328–351.
- Mackenzie, R.C., Mitchell, B.D., 1962. Differential thermal analysis: a review. *Analyst* 87 (1035), 420–434.
- Mackenzie, R.C., Mitchell, B.D., 1972. Soil. In: Mackenzie, R.C. (Ed.), *Differential Thermal Analysis*. Academic Press, New York, pp. 267–297.
- Maharaj, S., Barton, C.D., Karathanasis, T.A.D., Rowe, H.D., Rimmer, S.M., 2007. Distinguishing “new” from “old” organic carbon in reclaimed coal mine sites using thermogravimetry: II. Field validation. *Soil Science* 172 (4), 302–312.

- Mitchell, B.D., Birnie, A.C., 1970. Biological materials. In: Mackenzie, R.C. (Ed.), *Differential Thermal Analysis*. Academic Press, London UK, pp. 611–637.
- Mitchell, B.D., Knight, A.H., 1965. Application of differential thermal analysis to plant materials. *Journal of Experimental Botany* 16 (46), 1–15.
- Nernst, W., Riesenfel, E.H., 1903. Über quantitative gewichtanalyse mit sehr kleinen substanzmengen. *Chemische Berichte* 36, 2086–2093.
- Orlov, D.S., 1968. Adsorption and distribution of spectra of P-type humic acids in USSR soils. *Soviet Soil Science* 10, 1384–1393.
- Perkins, A.T., Mitchell, H.L., 1957. Differential thermal analysis of organic compounds. *Transactions of the Kansas Academy of Science* 60 (4), 437–440.
- Persson, J.A., Johansson, E., Albano, C., 1986. Quantitative thermogravimetry on peat: a multivariate approach. *Analytical Chemistry* 58 (6), 1173–1178.
- Pitkänen, A., Turunen, J., Tolonen, K., 1999. The role of fire in the carbon dynamics of a mire, eastern Finland. *Holocene* 9 (4), 453–462.
- Plante, A.F., Pernes, M., Chenu, C., 2005. Changes in clay-associated organic matter quality in a C depletion sequence as measured by differential thermal analyses. *Geoderma* 129 (3–4), 186–199.
- Provenzano, M.R., Senesi, N., 1999. Thermal properties of standard and reference humic substances by differential scanning calorimetry. *Journal of Thermal Analysis and Calorimetry* 57 (2), 517–526.
- Ranalli, G., Bottura, G., Taddei, P., Marchetti, R., Sorlini, C., 2001. Composting of solid and sludge residues from agricultural and food industries. Bioindicators of monitoring and compost maturity. *Journal of Environmental Science and Health. Part A Toxic/Hazardous Substances & Environmental Engineering* 36 (4), 415–436.
- Roberts-Austen, W.C., 1899. Fourth report to alloys research committee. *Proceedings of the Institute of Mechanical Engineers*, pp. 31–100.
- Rossel, R.A.V., Walvoort, D.J.J., McBratney, A.B., Janik, L.J., Skjemstad, J.O., 2006. Visible, near infrared, mid infrared or combined diffuse reflectance spectroscopy for simultaneous assessment of various soil properties. *Geoderma* 131 (1–2), 59–75.
- Rovira, P., Vallejo, V.R., 2000. Examination of thermal and acid hydrolysis procedures in characterization of soil organic matter. *Communications in Soil Science and Plant Analysis* 31 (1–2), 81–100.
- Rovira, P., Kurz-Besson, C., Couteaux, M.M., Vallejo, V.R., 2008. Changes in litter properties during decomposition: a study by differential thermogravimetry and scanning calorimetry. *Soil Biology & Biochemistry* 40 (1), 172–185.
- Satoh, T., 1984. Organo-mineral complex status in soils. II. Thermal nature of organo-mineral complex particles and their humic substances. *Soil Science and Plant Nutrition* 30 (1), 95–104.
- Schaumann, G.E., Antelmann, O., 2000. Thermal characteristics of soil organic matter measured by DSC: a hint on a glass transition. *Journal of Plant Nutrition and Soil Science-Zeitschrift Für Pflanzenernährung Und Bodenkunde* 163 (2), 179–181.
- Schnitzer, M., Hoffman, I., 1965. Thermogravimetry of soil humic compounds. *Geochimica et Cosmochimica Acta* 29 (8), 859–870.
- Schnitzer, M., Hoffman, I., 1966. A thermogravimetric approach to the classification of organic soils. *Soil Science Society of America Proceedings* 30, 63–66.
- Schnitzer, M., Schulten, H.R., 1995. Analysis of organic matter in soil, extracts and whole soils by pyrolysis mass spectrometry. In: Sparks, D.L. (Ed.), *Advances in Agronomy*, Vol 55. *Advances in Agronomy*. Academic Press, San Diego CA, pp. 167–217.
- Schnitzer, M., Turner, R.C., Hoffman, I., 1964. A thermogravimetric study of organic matter of representative Canadian Podzol soils. *Canadian Journal of Soil Science* 44, 7–13.
- Schulten, H.R., 1996. Direct pyrolysis-mass spectrometry of soils: a novel tool in agriculture, ecology, forestry and soil science. In: Bouton, T.W., Yamasaki, S. (Eds.), *Mass Spectrometry of Soils*. Marcel-Dekker, New York, NY, pp. 373–436.
- Schulten, H.R., Leinweber, P., 1999. Thermal stability and composition of mineral-bound organic matter in density fractions of soil. *European Journal of Soil Science* 50 (2), 237–248.
- Shurygina, E.A., Larina, N.K., Chubarov, M.A., Kononova, M.M., 1971. Differential thermal analysis (DTA) and thermogravimetry (TG) of soil humus substances. *Geoderma* 6 (3), 169–177.
- Siewert, C., 2004. Rapid screening of soil properties using thermogravimetry. *Soil Science Society of America Journal* 68 (5), 1656–1661.
- Smykatz-Kloss, W., 1974. *Differential thermal analysis: application and results in mineralogy*. Springer-Verlag, Berlin, 185 pp.
- Smykatz-Kloss, W., 1982. Application of differential thermal analysis in mineralogy. *Journal of Thermal Analysis* 23 (1–2), 15–44.
- Smykatz-Kloss, W., Warne, S.S., 1991. *Thermal Analysis in the Geosciences*. Springer-Verlag, Secaucus NJ, 379 pp.
- Strezov, V., Moghtaderi, B., Lucas, J.A., 2004. Computational calorimetric investigation of the reactions during thermal conversion of wood biomass. *Biomass & Bioenergy* 27 (5), 459–465.
- Thermal analysis in clay science. In: Stucki, J.W., Bish, D.L. (Eds.), *CMS Workshop Lectures*, vol. 3. The Clay Minerals Society, Boulder CO, 192 pp.
- Szidat, S., Jenk, T.M., Gaggeler, H.W., Synal, H.A., Hajdas, I., Bonani, G., Saurer, M., 2004. THEODORE, a two-step heating system for the EC/OC determination of radiocarbon (C-14) in the environment. *Nuclear Instruments & Methods in Physics Research. Section B, Beam Interactions with Materials and Atoms* 223, 829–836.
- Tan, K.H., Hajek, B.F., Barshad, I., 1986. Thermal analysis techniques. In: Klute, A. (Ed.), *Methods of Soil Analysis, Part I. Physical and Mineralogical Methods*. Agronomy Monograph, vol. 9. American Society of Agronomy, Madison, WI, pp. 151–183.
- Todor, D.N., 1976. *Thermal analysis of minerals*. Abacus Press, Kent, England, 256 pp.
- Turner, R.C., Schnitzer, M., 1962. Thermogravimetry of the organic matter of a Podzol. *Soil Science* 93 (4), 225–232.
- Vander Wal, R.L., Tomasek, A.J., 2003. Soot oxidation: dependence upon initial nanostructure. *Combustion and Flame* 134 (1–2), 1–9.
- Vicini, S., Princi, E., Luciano, G., Franceschi, E., Pedemonte, E., Oldak, D., Kaczmarek, H., Sionkowska, A., 2004. Thermal analysis and characterisation of cellulose oxidised with sodium methaperiodate. *Thermochimica Acta* 418 (1–2), 123–130.
- von Lütow, M., Kögel-Knabner, I., Ekschmitt, K., Matzner, E., Guggenberger, G., Marschner, B., Flessa, H., 2006. Stabilization of organic matter in temperate soils: mechanisms and their relevance under different soil conditions – a review. *European Journal of Soil Science* 57 (4), 426–445.
- Watson, E.S., Justin, J., Brenner, N., O'Neill, M.J., 1964. Differential scanning calorimeter for quantitative differential thermal analysis. *Analytical Chemistry* 36 (7), 1233–1238.
- Yariv, S., 1989. Thermal analysis of minerals. *Thermochimica Acta* 148, 421–430.
- Yariv, S., 1991. Differential thermal analysis (DTA) of organo-clay complexes. *Lecture Notes in Earth Sciences*. Springer-Verlag, Berlin, pp. 328–351.