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(54) Benævnelse: **FREMGANGSMÅDE TIL KVANTIFICERING OG KARAKTERISERING AF CARBON I JORD**

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FR-A1- 3 072 173
F. BEHAR ET AL: "Rock-Eval 6 Technology: Performances and Developments", OIL & GAS SCIENCE AND TECHNOLOGY &NDASH; REVUE DE L&RSQUO;INSTITUT FRANÇAIS DU PÉTROLE, vol. 56, no. 2, 1 March 2001 (2001-03-01), pages 111 - 134, XP055113461, ISSN: 1294-4475, DOI: 10.2516/ogst:2001013

Description

Field of the Invention

The present invention relates to the field of soil science and environmental geosciences, more particularly the characterization of carbon contained in superficial deposits (surface formations), and in particular in soils.

In order to meet ecological challenges or comply with certain environmental laws/directives, soil science and environmental geosciences protagonists (research laboratories, design offices, environmental agencies, agricultural operations) are increasingly being required to develop protocols for monitoring the impacts of human activities on carbon stocks in soils and in eco-agrosystems. These impact studies and monitoring operations require the ability to study large series of samples in relatively short time periods in respect of the methodologies which are conventionally employed. In addition, these methods are often accompanied by environmental and safety constraints which increase the time periods and the analytical costs and frequently necessitate calling in specialized service providers (analytical laboratories, for example).

The organic forms of carbon stored in superficial deposits, and in particular in soils, represent a major challenge to agriculture and to the climate. In fact, they play a key role in the structural quality and the fertilizing value of soils, but above all they are involved in the carbon cycle by representing the largest reservoir of organic carbon on the surface of the Earth. Ensuring food security for populations and promoting the sequestration of organic carbon in soils requires finding a compromise between keeping stocks of organic matter labile enough to release the nutrients which are necessary for plant growth while promoting the storage of forms of carbon which are resistant enough for the long-term mitigation of the anthropogenic emissions of greenhouse gases.

Inorganic forms of carbon are of variable mineralogy. Essentially represented by calcium (Ca) carbonates and oxalates in soils, they can sometimes involve other cations (Fe in siderite, Mg in dolomite, etc.), in particular in a tropical environment. Irrespective of their role in biogeochemical cycles (in particular as carbon sinks), mineral forms of carbon pose technical problems for the analysis of organic forms. In fact, no routine method exists which can be used to characterize the various forms of carbon with the aid of one single measurement, and the approaches which are conventionally employed are based on specific extractions and separations (acid fumigation, Walkley-Black method, Bernard calcimeter method), followed by targeted analyses using specialized scientific equipment (CHN elemental analysis, IR spectrometry, GC-MS, ^{13}C-NMR).

Methods for the thermal analysis of the organic matter of soils based on measurements of the amounts of hydrocarbon compounds (HC), carbon monoxide (CO) and/or carbon dioxide (CO_2) released over time by a sample exposed to a heating sequence in an inert atmosphere then/or to a heating sequence in an oxidizing atmosphere are also known. These methods were initially developed in the oil industry for the purposes of characterization of the organic fraction of sedimentary rocks. Thus, the ROCK-EVAL® device (IFP Energies nouvelles, France) developed by the Applicant and in particular described in patents FR 2 227 797 (US 3 953 171) and FR 2 472 754 (US 4 352 673), is known; it comprises a pyrolysis furnace which is distinct from an oxidation furnace, a flame ionization type detector (FID) for detecting hydrocarbon compounds (HC) and an infrared (IR) type detector for detecting carbon monoxide (CO) and/or carbon dioxide (CO_2). Methods developed for particular applications in the oil industry, each having their own sequence of heating temperatures for pyrolysis and/or heating in an oxidizing atmosphere, are also known. In particular, the "ROCK-EVAL® BULK ROCK" method, more particularly dedicated to conventional bedrock samples (Behar et al., 2001), is known. The heating sequence in an inert atmosphere of this method is characterized by an initial temperature T1 of the pyrolysis furnace generally of between 300°C and 350°C, a temperature which is maintained for a predetermined time period of a few minutes. It is during this phase that what are known as "free" hydrocarbons (actually corresponding to hydrocarbons with a low to high molecular weight) initially contained in the rock sample are released. Their amount is estimated by measuring the area of a first peak, denoted by S_1, of the curve (also referred to as thermogram) representing the amount of hydrocarbon compounds released during the heating sequence in an inert atmosphere. The pyrolysis temperature is then progressively increased up to a temperature T2, generally 650°C. During this phase, volatilization of very heavy hydrocarbon compounds as well as cracking of non-volatile organic matter (kerogen) takes place. The amount of hydrocarbon compounds released during this thermal cracking phase is estimated by measuring the area of a second peak, denoted by S_2. At the same time, the amounts of CO and CO_2 are measured and are also represented in the form of curves. These curves have two peaks, conventionally denoted by S3CO (respectively S3CO2), which is considered to correspond to CO (respectively CO_2) generated by cracking the organic matter of the sample during heating under **an inert atmosphere, and S3'CO (respectively S3'CO2),** which is considered to correspond to CO (respectively CO_2) generated by the thermal decomposition of the carbonate forms (in particular calcite) during heating under an inert atmosphere. The sample residue obtained from heating in an inert atmosphere then undergoes heating in an oxidizing atmosphere: from a temperature of between about 300°C and 400°C, and preferably equal to 300°C, the temperature of the sample residue under consideration is raised in accordance with a temperature gradient of between 20°C and 40°C/minute, up to a temperature at the end of oxidation of between 750 and 950°C, preferably equal to 850°C. During this heating sequence in an oxidizing atmosphere, the amounts of CO and of CO_2 released by the sample residue are measured and represented in the form of curves, leading to a peak conventionally denoted S4CO (respectively S4CO2), which is considered to correspond to the amount of CO (respectively CO_2) generated by the combustion of the organic matter during the oxidation cycle. From these measurements, this method defines a certain number of standard parameters, in particular the parameter denoted TOC (Total Organic Carbon), which corresponds to the carbon content of the sample, determined from the total amount of HC released by the sample and the amounts of CO and CO_2 released below threshold temperatures during the pyrolysis phase and the oxidation phase; and the parameter denoted by MinC (Mineral Carbon), which corresponds to the mineral carbon content of the sample, determined from the amounts of CO and CO_2 released by the sample above threshold temperatures during the pyrolysis phase and the oxidation phase.

Prior art

The following documents shall be mentioned in the description:

Behar F., Beaumont V., De B., Penteado H. L. (2001) Rock-Eval 6 Technology: Performances and Developments, Oil & Gas Science and Technology 56, 111-134.

Disnar, J. R., Guillet, B., Keravis, D., Di-Giovanni, C., Sebag, D., 2003. Soil organic matter (SOM) characterization by Rock-Eval pyrolysis: scope and limitations. Organic Geochemistry 34, 327-343.

Malou, O. P., Sebag, D., Moulin P., Chevallier, T., Badiane-Ndour, N. Y., Thiam, A., Chapuis-Lardy, L. 2020. The Rock-Eval® signature of soil organic carbon in arenosols of the Senegalese Groundnut Basin. How do agricultural practices matter? *Agriculture, Ecosystems & Environment* 301: 107030. https://doi.org/10.1016/j.agee.2020.107030.

Pillot, D., Deville, E., Prinzhofer, A., 2014. Identification and Quantification of Carbonate Species Using Rock-Eval Pyrolysis. Oil & Gas Science and Technology—Revue d'IFP Energies Nouvelles [IFP Energies Nouvelles review] 69, 341-349.

Sebag, D., Disnar, J. R., Guillet, B., Di Giovanni, C., Verrecchia, E. P., Durand, A., 2006. Monitoring organic matter dynamics in soil profiles by "Rock-Eval pyrolysis": bulk characterization and quantification of degradation. European Journal of Soil Science 57, 344-355.

Sebag, D., Verrecchia, E. P., Cécillon, L., Adatte, T., Albrecht, R., Aubert, M., Bureau, F., Cailleau, G., Copard, Y., Decaëns, T., Disnar, J.-R., Hetényi, M., Nyilas, T., Trombino, L., 2016. Dynamics of soil organic matter based on new Rock-Eval indices. Geoderma 284, 185-203.

Since the 2000s, this type of analysis has also been used and adapted in order to study the organic fraction of superficial deposits, and in particular of soils.

As an example, the method described in the document (Disnar et al., 2003) is known; it provides an adaptation of the pyrolysis heating sequence, consisting of an initial temperature of the heating sequence in an inert atmosphere of 200°C, instead of 300°C in the "ROCK-EVAL® BULK ROCK" method described above. This lower initial temperature enables the peak S2 defined above to be extended to the cracking temperatures of the most thermolabile organic components. In fact, these thermolabile constituents are much more abundant in superficial deposits than in sedimentary rocks. In order to estimate their contribution and therefore to evaluate the thermal stability of the organic matter, this method defines the parameter R400, which measures the relative proportion of peak S2 corresponding to temperatures below 400°C. Furthermore, that document highlights a negative difference between the parameter TOC as defined in the ROCK-EVAL® BULK ROCK method and the organic carbon contents measured with standardized methods (elemental analyses, for example), and recommends a statistical correction (i.e. the application of a correction coefficient established over a representative panel of soil samples) in order to correct the parameter TOC, defined for the oil industry, so that it is truly representative of the organic carbon content, in particular for samples which are rich in poorly decomposed organic matter with respect to their biogenic precursors (litter, compost, peat, etc.).

The document (Sebag et al., 2006) is also known; it uses this adapted heating sequence and in addition proposes a deconvolution of peak S2 in order to evaluate the degree of decomposition of the organic constituents. In fact, the thermograms for the superficial deposits, in particular organic samples, exhibit a multimodal distribution the principal modes of which are always in particular temperature ranges (300-320°C; 360-380°C; 420-440°C; 470-490°C and 540-560°C). The method described in that document breaks the peak S2 up into five elementary Gaussian distributions centred on these modes. This mathematical deconvolution amounts to estimating the relative contribution to peak S2 that each elementary distribution under consideration makes relative to a class of constituents defined by their single cracking temperature. These elementary contributions are then used to calculate new parameters which measure the overall thermal stability of the organic matter (R-index) and the degree of decomposition of the thermolabile fraction (I-index). However, the deconvolution method is based on an iterative approach for adjusting the position and the area of each elementary distribution as a function of arbitrarily set statistical parameters, which reduces the reproducibility of the decomposition.

The document (Sebag et al., 2016) is also known; it describes an alternative approach by demonstrating that an integration of the thermograms representative of the amount of HC contained in the sample by temperature bands (200-340°C; 340-400°C; 400-460°C; 460-520°C and 520-650°C) leads to results which are comparable to mathematical deconvolution, and are, moreover, completely reproducible. That approach has been used for many applications, but suffers from some intrinsic limits. Firstly, it is based on the definition of empirically defined threshold temperatures, so that the area of each temperature band best approximates the area of the corresponding elementary distribution obtained by deconvolution. Furthermore, those areas and the parameters resulting therefrom only provide qualitative information, insofar as they all correspond to relative proportions or to ratios of relative proportions. Finally, that approach is limited to the examination of the amounts of HC emitted during the pyrolysis phase, whereas the majority of the carbon is represented by the CO and the CO_2 emitted during the pyrolysis and oxidation phases. Another alternative approach using the ROCK-EVAL method is known from document FR 3 072 173.

Furthermore, despite these attempts at adaptation or improvement, the known methods do not provide values for the standard parameters TOC and MINC, which respectively represent the organic carbon and mineral carbon content of a sample in the case of superficial deposits. In fact, the parameter TOC (respectively MINC) of the "ROCK-EVAL® BULK ROCK" method measures the carbon content from the amounts of CO and CO_2 emitted below (respectively above) threshold temperatures considered to be thermal limits between the organic and mineral forms of carbon.

However, that definition is erroneous for both carbonate and non-carbonate formations. In fact, as shown in the document (Malou et al., 2020), that definition in particular involves the systematic calculation of a parameter MINC, even for samples with no forms of mineral carbon. However, more generally, as observed by the Applicant, this implies that, even in samples containing mineral forms of carbon, a portion of MINC originates from thermal cracking of the organic constituents above the threshold temperatures. Finally, as shown in the document (Pillot et al., 2014), certain mineral forms of carbon (such as siderite or oxalates) are likely to decompose at temperatures below the threshold temperatures used for calculating the standard parameters TOC and MINC.

The present invention aims to overcome the disadvantages linked to the use of a method initially developed for the oil industry for analysing the organic matter of superficial deposits, and especially of soils. In particular, the present invention aims to obtain thermograms presenting better-differentiated peaks which are common to each type of effluent (HC, CO and CO_2). This invention therefore enables better discrimination between the various classes of compound as a function of their thermal resistance. It also leads to determining the organic and/or mineral nature of the forms of carbon, and therefore to defining novel parameters, more representative of the organic and mineral carbon content of samples analysed by standardized methods.

More generally, the present invention enables rapid and reliable characterization of the forms of carbon present in a sample to determine whether they contain forms of a mineral nature or otherwise, in order to specify the degree of decomposition and/or the thermal stability of the most reactive portion of organic matter (bonded to the hydrogen atom), and to more precisely quantify the carbon contents (organic vs. mineral, thermolabile vs. thermostable).

Summary of the invention

The present invention concerns a method for characterizing and quantifying the carbon present in a superficial deposit, starting from a representative sample of said superficial deposit, in which at least the following stages are applied to said sample:

A. said sample is heated according to a first heating sequence under an inert atmosphere, and an amount of hydrocarbon compounds, an amount of CO and an amount of CO_2 which are released during said first heating sequence are continuously measured, said first heating sequence under an inert atmosphere comprising at least one sequence of at least six isothermal stationary phases of a predetermined duration, said sequence of said at least six isothermal stationary phases comprising a first isothermal stationary phase at a first temperature of between 80 and 200°C (T0), a second isothermal stationary phase at a second temperature of between 340 and 380°C (T1), a third isothermal stationary phase at a third temperature of between 400 and 440°C (T2), a fourth isothermal stationary phase at a fourth temperature of between 450 and 490°C (T3), a fifth isothermal stationary phase at a fifth temperature of between 500 and 540°C (T4), a sixth isothermal stationary phase at a sixth temperature of between 580 and 650°C (T5), said isothermal stationary phases being interconnected by a thermal gradient;

B. a residue of said sample resulting from said first heating sequence is heated according to a second heating sequence under an oxidizing atmosphere, and an amount of CO and an amount of CO_2 which are released during said second heating sequence are measured, said second heating sequence under an oxidizing atmosphere starting at a minimum temperature of between 150 and 300°C, ending at a maximum temperature of between 850 and 1200°C, and following a thermal gradient;

C. a value of a parameter SCmin representative of a proportion of mineral carbon with respect to the total carbon of said sample is determined from a ratio of said amount of CO_2 released by said residue of said sample beyond an intermediate temperature of said second heating sequence of between 620 and 680°C to said amount of CO_2 released by said residue during said second heating sequence;

D. an organic carbon content and/or a mineral carbon content of said sample is/are quantified in the following way:

i. if said value of said parameter SCmin is less than or equal to a predefined threshold value of said parameter SCmin, said mineral carbon content is zero and said organic carbon content is a function of the totality of said amounts of HC, of CO and of CO_2 which are released during said first heating sequence, and of said amounts of CO and of CO_2 which are released during said second heating sequence up to said intermediate temperature of said second heating sequence,

ii. if said value of said parameter SCmin is greater than said predefined threshold value of said parameter SCmin:

- an amount of CO_2 released by thermal cracking of the organic matter of said sample during said first heating sequence beyond said third temperature (T2) is estimated from said amount of CO_2 released during said first heating sequence up to said third temperature (T2) of said first heating sequence, multiplied by a predefined factor k; and/or
- said organic carbon content and/or said mineral carbon content

is/are determined as a function of said amounts of HC, of CO and of CO_2 which are released during said first heating sequence and of said amounts of CO and of CO_2 which are released during said second heating sequence up to said intermediate temperature of said second heating sequence, and while taking into account said estimated amount of CO_2 released by thermal cracking of the organic matter of said sample during said first heating sequence beyond said third temperature (T2).

In accordance with one implementation of the invention, if said value of said parameter SCmin is greater than said predefined threshold value of said parameter SCmin:

- said organic carbon content may be a function of the totality of said amount of HC released during said first heating sequence, of said amount of CO released during said first heating sequence up to said fifth temperature (T4), to which is added half of said amount of CO released during said first heating sequence beyond said fifth temperature (T4), of said amount of CO_2 released during said first heating sequence up to said third temperature (T2), to which is added said estimated amount of CO_2 released by thermal cracking of the organic matter of said sample during said first heating sequence beyond said third temperature (T2), and of said amounts of CO and of CO_2 released during said second heating sequence up to said intermediate temperature of said second heating sequence, and/or
- said mineral carbon content may be a function of said amount of CO_2 released during said first heating sequence beyond said third temperature (T2) of said first heating sequence at which said estimated amount of CO_2 released by thermal cracking of the organic matter of said sample during said first heating sequence beyond said third temperature (T2), said half of said amount of CO released during said first heating sequence beyond said fifth temperature (T4), and said amount of CO_2 released during said second heating sequence beyond said intermediate temperature of said second heating sequence.

In accordance with one implementation of the invention, said predefined factor k may be between 1.3 and 1.4, and preferably has the value 1.3724.

In accordance with one implementation of the invention, by means of a plurality of samples originating from non-carbonate superficial deposits, at least said first heating sequence may be applied to each of said samples of said plurality of samples, an amount of CO_2 released by each of said samples during said first heating sequence may be measured, and said factor k may be determined by means of a linear regression applied between said amounts of CO_2 which are released by said plurality of samples up to said third temperature (T2) of said first heating sequence and said amounts of CO_2 which are released by said plurality of samples beyond said third temperature (T2) of said first heating sequence.

In accordance with one implementation of the invention, said predefined threshold value of said parameter SCmin may be between 0.03 and 0.05, and preferably has the value 0.04.

In accordance with one implementation of the invention, said first temperature (T0) of said first heating sequence may be between 80°C and 150°C, and preferably has the value 150°C.

In accordance with one implementation of the invention, said minimum temperature of said second heating sequence may be equal to said first temperature (T0) of said first heating sequence.

In accordance with one implementation of the invention, said predetermined duration of one of said isothermal stationary phases of said first heating sequence may be between 3 and 5 minutes.

In accordance with one implementation of the invention, one of said thermal gradients of said first heating sequence may be between 1 and 50°C.min^{-1}, preferably between 20 and 25°C.min^{-1}.

In accordance with one implementation of the invention, said thermal gradient of said second heating sequence may be between

20 and 40°C.min^{-1}, preferably between 20 and 25°C.min^{-1}.

In accordance with one implementation of the invention, if said value of said parameter SCmin is less than or equal to said predefined threshold value of said parameter SCmin:

- said mineral carbon content may be defined by a parameter MinCfs such that MinCfs = 0; and/or
- said organic carbon content may be defined by a parameter TOCfs which is expressed according to a formula of the type:

$$TOC\mathrm{fs} = (S2_t\, x\, 0.083) + (S3CO2_t\, x \frac{12}{440}) + (S3CO_t\, x \frac{12}{280}) + (S4CO2_a x \frac{12}{440}) + (S4CO_a x \frac{12}{280})$$

in which $S2_t$, $S3CO2_t$, $S3CO_t$ represent said amounts of HC, of CO_2 and of CO respectively which are released during said first heating sequence, $S4CO2_a$ and $S4CO_a$ respectively represent said amounts of CO_2 and of CO which are released during said second heating sequence and up to said intermediate temperature of said second heating sequence.

In accordance with one implementation of the invention, if said value of said parameter SCmin is greater than said predefined threshold value of said parameter SCmin:

- said mineral carbon content may be defined by a parameter MinCfs which is expressed according to a formula of the type:

$$MinC\mathrm{fs} = ([S3CO2_b - S3CO2_c] x \frac{12}{440}) + (\tfrac{1}{2}\, S3CO_b x \frac{12}{280}) + (S4CO2_b\, x \frac{12}{440})$$

in which $S3CO2_b$ represents said amount of CO_2 released during said first heating sequence beyond said third temperature (T2), $S3CO2_c$ represents said estimated amount of CO_2 released by thermal cracking of the organic matter of said sample during said first heating sequence beyond said third temperature (T2), $S3CO_b$ represents said amount of CO released during said first heating sequence beyond said fifth temperature (T4), and $S4CO2_b$ represents said amount of CO_2 released during said second heating sequence beyond said intermediate temperature of said second heating sequence; and/or

- said organic carbon content is defined by a parameter TOCfs which is expressed according to a formula of the type:

$$TOC\mathrm{fs} = (S2_t x\, 0.083) + \left([S3CO2_a + S3CO2_c] x \frac{12}{440}\right) + \left([S3CO_a + \tfrac{1}{2}\, S3CO_b] x \frac{12}{280}\right) +$$
$$(S4CO2_a x \frac{12}{440}) + (S4CO_a x \frac{12}{280})$$

in which $S2_t$ represents said amount of HC released during said first heating sequence, $S3CO2_a$ represents said amount of CO_2 released during said first heating sequence up to said third temperature (T2), $S3CO2_c$ represents said estimated amount of CO_2 released by thermal cracking of the organic matter of said sample during said first heating sequence beyond said third temperature (T2), $S3CO_a$ and $S3CO_b$ represent said amounts of CO released during said first heating sequence respectively up to and beyond said fifth temperature (T4), $S4CO2_a$ and $S4CO_a$ respectively represent said amounts of CO_2 and of CO released during said second heating sequence and up to said intermediate temperature of said second heating sequence.

Other features and advantages of the method in accordance with the invention will become apparent from the description below of non-limiting exemplary embodiments, made with reference to the accompanying figures which are described below.

List of figures

Figure 1 diagrammatically illustrates the heating sequence under an inert atmosphere in accordance with the invention.

Figures 2A and 2B illustrate thermograms obtained by means of an implementation of the heating sequence under an inert atmosphere in accordance with the invention, respectively obtained for a non-carbonate soil sample and for a carbonate soil sample.

Figures 2C and 2D illustrate thermograms obtained by means of a heating sequence in accordance with the prior art, respectively obtained for the non-carbonate soil and carbonate soil samples of Figures 2A and 2B.

Figures 3A and 3B illustrate thermograms obtained by means of an implementation of the heating sequence under an oxidizing atmosphere in accordance with the invention, respectively obtained for the non-carbonate soil sample of Figures 2A and 2C and for the carbonate soil sample of Figures 2B and 2D.

Figures 4A and 4B show histograms respectively comparing the values for the organic carbon contents Corg and the mineral carbon contents Cmin determined by the method in accordance with the invention and in the prior art, for 9 soil samples.

Figures 5A and 5B show histograms respectively comparing the values for the organic carbon contents Corg and for the mineral carbon contents Cmin determined by the method in accordance with the invention and in the prior art, for 7 peat samples.

Description of embodiments

The invention concerns a method for characterizing and quantifying the carbon (or, in other words, the forms of carbon) present in a superficial deposit.

The term "superficial deposit" should be understood to mean a continental or coastal formation, unconsolidated or with secondary consolidation, resulting from the mechanical and/or chemical degradation of pre-existing rocks, and formed at the lithosphere/biosphere/atmosphere interface. A distinction is made between (i) **"allochthonous superficial deposits"** (such as colluvium, alluvium, loess, etc.), which have undergone or are still undergoing close or more remote displacements, and no **longer rest on their parent material, and "autochthonous superficial deposits"** (such as **grits, alterites, flint clays,** etc.), which have evolved locally from a parent material which is still their substrate.

The term "soil" should be understood to mean all of the outer layers of superficial deposits, the properties of which are directly controlled by the mutual actions of water, air and living and dead organisms, or even human activities for the most recent periods.

These terms have in particular been defined in the reference document (Dictionnaire encyclopédique de Science du Sol [Encylopaedic Dictionary of Soil Sciences], Mathieu & Lozet, Lavoisier, 2011).

The method in accordance with the invention requires the availability of at least one sample representative of the superficial deposit: this sample may have been taken manually from a pit or by core drilling using an auger bit. Advantageously, the sample as taken is sieved using a sieve with 2 mm diameter orifices, dried at a temperature below 40°C, then crushed until fragments with dimensions of less than 200 µm are obtained.

The method in accordance with the invention can advantageously, but not in a limiting manner, be implemented using the ROCK-EVAL® device (IFP Energies nouvelles, France) as described in patents FR 2 227 797 (US 3 953 171) and FR 2 472 754 (US 4 352 673). In fact, the ROCK-EVAL® device comprises at least:
- a furnace for pyrolysis in a non-oxidizing atmosphere,
- means for transferring the pyrolysis residues to an oxidation furnace,
- a furnace for oxidation in an oxidizing atmosphere,
- means for measuring the amount of hydrocarbon compounds (HC) released during pyrolysis,
- means for measuring carbon monoxide (CO) and carbon dioxide (CO_2).

The method may also be implemented using a single pyrolysis furnace which can operate both in a non-oxidizing atmosphere and in an oxidizing atmosphere, cooperating with a device for measuring the amount of hydrocarbon compounds released during pyrolysis, and a device for measuring carbon monoxide and carbon dioxide.

The method in accordance with the invention comprises at least the following steps:

1- Heating sequence under an inert atmosphere (pyrolysis)

2- Heating sequence under an oxidizing atmosphere (oxidation)
3- Characterization and quantification of carbon present in the sample.

The steps of the method in accordance with the invention are detailed below in a non-limiting manner for a soil sample. In fact, the steps of the method in accordance with the invention may also be applied to a sample originating from another layer of a superficial deposit.

1. Heating sequence under an inert atmosphere (pyrolysis)

During this step, a soil sample is heated under an inert atmosphere (such as in a stream of nitrogen, helium, for example) in accordance with a sequence of predefined temperatures which vary over time.

In accordance with the invention, the heating sequence under an inert atmosphere comprises at least one succession of isothermal stationary phases, each isothermal stationary phase having a predetermined duration, and two consecutive isothermal stationary phases in this succession of isothermal stationary phases being interconnected by a ramp in the form of a predetermined thermal gradient. In other words, the heating sequence under an inert atmosphere comprises a succession of isothermal stationary phases interconnected by a ramp, the duration of each isothermal stationary phase possibly being different from the duration of the other isothermal stationary phases, and the slope of one ramp possibly being different from the slope of the other thermal ramps.

In accordance with the invention, the succession of isothermal stationary phases comprises at least six isothermal stationary phases interconnected by five ramps. In accordance with the invention, the succession of isothermal stationary phases comprises a first isothermal stationary phase at a temperature (hereinafter denoted T0) of between 80 and 200°C, a second isothermal stationary phase at a temperature (hereinafter denoted T1) of between 340 and 380°C, a third isothermal stationary phase at a temperature (hereinafter denoted T2) of between 400 and 440°C, a fourth isothermal stationary phase at a temperature (hereinafter denoted T3) of between 450 and 490°C, a fifth isothermal stationary phase at a temperature (hereinafter denoted T4) of between 500 and 540°C, a sixth isothermal stationary phase at a temperature (hereinafter denoted T5) of between 580 and 650°C.

Figure 1 diagrammatically illustrates such a sequence of temperatures by showing the change in temperature T as a function of time t, the sequence of temperatures exhibiting six isothermal stationary phases at temperatures T0, T1, T2, T3, T4 and T5 as defined above.

In accordance with the invention, the predetermined duration of the isothermal stationary phases is non-zero (more than half a minute, for example), and it may preferably be between 3 and 5 minutes. Such durations allow it to be assumed that cracking of compounds having a cracking temperature close to the temperature of the isothermal stationary phase has been completed. In general, the duration of one isothermal stationary phase may be different from the duration of the other isothermal stationary phases in the heating sequence in an inert atmosphere.

Advantageously, the thermal gradient between two isothermal stationary phases may be between 1°C and 50°C.min^{-1}, preferably between 20°C and 25°C.min^{-1}. Such values constitute compromises, enabling thermal cracking of compounds associated with the isothermal stationary phase having the highest temperature among these two isothermal stationary phases to commence, while limiting the duration of the implementation of the method. In general, the value of a thermal gradient between two isothermal stationary phases may be different from the other thermal gradients in the heating sequence in an inert atmosphere.

In accordance with the invention, an amount of hydrocarbon compounds released during heating under an inert atmosphere, as well as the amount of CO_2 and CO contained in the effluent resulting from said heating, are also measured continuously. In other words, during this sequence, the amount of HC, CO and CO_2 released by the sample by thermal cracking of the organic matter and by the thermal decomposition of the carbonate minerals is measured continuously. Thus, a first curve which is representative of the amount of hydrocarbon compounds released over time during at least a portion of the pyrolysis phase, as well as two other curves which are representative of the amount of CO and CO_2 released over time during the pyrolysis phase, are obtained at the end of this step applied to a given sample. The amount of hydrocarbon compounds may be measured using a flame ionization type detector (FID). The amount of CO and CO_2 released may be measured using an infrared (IR) type detector. It should be noted that such detectors measure a stream of HC, CO and/or CO_2, and provide values measured in millivolt (mV). Conventionally, an amount of HC, CO and/or CO_2 may be determined by determining an area under the curve (possibly between predefined temperatures) measured by these detectors, and by dividing this area by the mass of the sample in mg. In a variation, other means for measuring the amount of HC, CO and/or CO_2 may be used.

In general, this particular heating sequence under an inert atmosphere enables thermal separation of the classes of compounds characterized by their specific cracking temperature. Thus, compounds cracking between T0 and T1 correspond to "highly thermally labile compounds", which are particularly abundant in fresh biological tissues; compounds cracking between T1 and T2 correspond to "thermally labile compounds", which predominate in organic samples such as litter or peat; compounds cracking between T2 and T3 correspond to "thermally resistant compounds" and predominate in organo-mineral samples (soils) or mineral samples (alluvium, colluvium); compounds cracking between T3 and T4 correspond to "thermally refractory compounds"; and compounds cracking between T4 and T5 correspond to "highly thermally refractory compounds" and are present in larger proportions in residues from decomposition or in exogenous fractions, such as pyrogenic or petrogenic organic matter.

In accordance with one implementation of the invention, the first isothermal stationary phase may preferably be at a temperature of between 80°C and 150°C, so as to enable recovery of the contributions from the most labile organic compounds present in a soil sample. Preferably, the first isothermal stationary phase is at a value of 150°C, which is a sufficient temperature for recovery of the contributions from the most labile organic compounds present in the majority of superficial deposits, in particular soils.

In accordance with one implementation of the invention, the maximum temperature T5 of the heating sequence under an inert atmosphere may preferably be 600°C. Such a temperature makes it possible to avoid obtaining CO and CO_2 curves with incomplete peaks at the end of pyrolysis, in particular when the maximum temperature reaches 650°C, in particular with vegetation samples (litter, peats, composts).

In accordance with one implementation of the invention, the succession of isothermal stationary phases in accordance with the invention as described above may be preceded by a pyrolysis furnace temperature ramp-up phase, which may be in the form of a thermal gradient of between 1 and 50°C.min^{-1}, for example, preferably between 20° and 25°C.min^{-1}, or of any other form of temperature ramp-up curve for the pyrolysis furnace. This preliminary phase of increasing the temperature of the pyrolysis furnace enables the pyrolysis furnace to be brought to the temperature of the first isothermal stationary phase of the heating sequence in an inert atmosphere in accordance with the invention. This preliminary phase may contribute to commencing thermal cracking of compounds with a cracking temperature which is lower than the temperature of the first isothermal stationary phase, in particular in the case of fresh biological tissues.

In accordance with one implementation of the invention, the succession of isothermal stationary phases in accordance with the invention as described above may be followed by a phase for reducing the temperature of the pyrolysis furnace, which may be in the form of a thermal gradient of **between** -1 **and** $-50°C.min^{-1}$, for example, **preferably between** $-20°$ **and** $-25°C.min^{-1}$, or any other shape of curve for decreasing the temperature of the pyrolysis furnace. This end phase for reducing the temperature of the pyrolysis furnace enables, if necessary, thermal cracking of compounds associated with the last isothermal stationary phase of the heating sequence under an inert atmosphere in accordance with the invention to be completed.

Thus, in general, this particular heating sequence under an inert atmosphere enables thermal separation of classes of compounds defined by their specific cracking temperature to be carried out. This thermal fractionation in particular makes it possible to obtain thermograms with dissociated peaks, and therefore to enable the streams of HC, CO and CO_2 released by each class of compound to be independently quantified and analysed. Figures 2A and 2B illustrate thermograms obtained by means of the heating sequence under an inert atmosphere in accordance with the invention, respectively for a non-carbonate soil sample and for a carbonate soil sample. Figures 2C and 2D illustrate thermograms obtained by using a heating sequence in accordance with the prior art, with no isothermal stationary phases, respectively obtained for the non-carbonate and carbonate soil samples of Figures 2A and 2B. More precisely, in these figures, curve T represents the change with time t of the temperature of the pyrolysis furnace during this step or, in other words, curve T represents the heating sequence in an inert atmosphere to which the samples are exposed. It should be noted in this figure that the heating sequence in an inert atmosphere implemented for these samples comprises a preliminary phase of raising the temperature of the pyrolysis furnace to a temperature of the first isothermal stationary phase equal to 200°C, as well as an end phase for reducing the temperature of the pyrolysis furnace at the end of the last isothermal stationary phase, which is at a temperature of 650°C. Furthermore, curve HC represents the change in the intensity Q (in mV) of the signal from a FID detector measuring the amount of hydrocarbon compounds released during the heating sequence in an inert atmosphere, and the curve CO_2 represents the change in intensity Q (in mV) of a signal from an IR detector measuring the amount of CO_2 released during the heating sequence in an inert atmosphere. It will be observed in Figures 2A and 2B that the curves HC and CO_2 have well-dissociated peaks, in contrast to the curves of Figures 2C and 2D, which demonstrates that the heating sequence with multiple stationary phases under an inert atmosphere enables correct thermal fractionation of the compounds contained in a sample into classes of compounds having their characteristic cracking temperature.

It should be noted that a sensitivity analysis carried out on a diverse panel of superficial deposits comprising recent soils and sediments demonstrates that the heating sequence under an inert atmosphere in accordance with the invention does not significantly modify the amounts of HC, CO and CO_2 released during pyrolysis. In other words, the total amount of HC, CO and CO_2 is conserved by the heating sequence under an inert atmosphere in accordance with the invention. On the other hand, the heating sequence with multiple stationary phases in accordance with the invention enables better dissociation of the peaks relative to distinct classes of compounds, as discussed above.

Subsequently, the parameters defined in Table 1 below are used. More precisely, parameters $S2_i$ ($S3CO2_i$ and $S3CO_i$ respectively), with i varying from 0 to 6, correspond to the amounts of HC (respectively CO_2 and CO) released in the temperature ranges DT_i defined as follows: $DT_0 = T0-$; $T0 < DT_1 \leq T1$; $T1 < DT_2 \leq T2$; $T2 < DT_3 \leq T3$; $T3 < DT_4 \leq T4$; $T4 < DT_5 \leq T5$; $DT_6 = T5+$; and in which **T0- corresponds to the first** isothermal stationary phase at temperature T0 of the heating sequence in an inert atmosphere, optionally preceded by a preliminary phase of temperature ramp-up of the pyrolysis furnace; and in which T5+ corresponds to the last isothermal stationary phase at temperature T5 of the heating sequence in an inert atmosphere, optionally followed by an end phase of reducing the temperature of the pyrolysis furnace.

[Table 1]

Temperature	HC measurement	CO_2 measurement	CO measurement
DT_0 = T0-	$S2_0$	$S3CO2_0$	$S3CO_0$
T0 < DT_1 ≤ T1	$S2_1$	$S3CO2_1$	$S3CO_1$
T1 < DT_2 ≤ T2	$S2_2$	$S3CO2_2$	$S3CO_2$
T2 < DT_3 ≤ T3	$S2_3$	$S3CO2_3$	$S3CO_3$
T3 < DT_4 ≤ T4	$S2_4$	$S3CO2_4$	$S3CO_4$
T4 < DT_5 ≤ T5	$S2_5$	$S3CO2_5$	$S3CO_5$
DT_6 = T5+	$S2_6$	$S3CO2_6$	$S3CO_6$

2) Heating sequence under an oxidizing atmosphere (oxidation)

During this second step, the solid residue of the sample obtained at the end of the heating sequence under an inert atmosphere as described in step 1 above undergoes oxidation in accordance with a predefined temperature programme which can vary with time.

The temperature programme for the heating sequence under an oxidizing atmosphere in accordance with the invention is as follows: starting **from a temperature** (T'min) of between 150°C and 300°C, preferably of between 150°C and 200°C, and preferably equal to 150°C or, more preferably, being equal to the temperature of the first isothermal stationary phase of the heating sequence in an inert atmosphere so as to be able to make comparisons, the temperature of the sample residue obtained from step 1) is increased in accordance with a temperature gradient of between 20 and 40°C.min^{-1}, preferably of between 20° and 25°C.min^{-1}**, up to an oxidation end temperature** (T'max) of between 850 and 1200°C, and preferably equal to 900°C, which is a temperature which is sufficient to deplete the mineral carbon stock for the majority of superficial deposit samples.

In accordance with the invention, a representative amount of CO and CO_2 released during this second heating sequence is measured continuously. In accordance with one implementation of the invention, this measurement may be carried out using an infrared (IR) type detector. It should be noted that such a detector measures a flow of CO and/or CO_2, and provides values measured in millivolt (mV). Conventionally, an amount of CO and/or CO_2 is determined by determining an area under the curve (optionally between predefined temperatures) measured by this detector, and this area is divided by the mass of the sample in mg. In a variation, other means for measuring the amount of CO and/or CO_2 may be used.

In general, the preferred temperature range for the initial temperature of the heating sequence in an oxidizing atmosphere, which is lower than the initial temperatures known from the prior art (300°C in general), makes it possible to avoid episodes of instantaneous combustion of the sample residue at the start of the oxidation cycle.

Figures 3A and 3B illustrate thermograms obtained by means of the heating sequence under an oxidizing atmosphere in accordance with the invention, respectively for the non-carbonate soil sample of Figures 2A and 2C and for the carbonate soil sample of Figures 2B and 2D. More precisely, in these figures, curve T represents the change as a function of time t of the temperature of the oxidation furnace during this step or, in other words, curve T represents the heating sequence in an oxidizing atmosphere to which the sample residues are exposed. In addition, curve CO_2 (respectively CO) represents the change in intensity QCO2 in mV (respectively QCO) of the signal from an IR detector measuring the amount of CO_2 (respectively CO) released over time by the residue obtained from step 1) and which is exposed to the heating sequence under an oxidizing atmosphere T. Streams of CO_2 above a temperature of approximately 650°C, which are specific to carbonate soils and testify to the presence of mineral forms of carbon, can be observed in these figures.

Subsequently, the parameters defined in Table 2 below are used. More precisely, the parameters $S4CO2_i$ and $S4CO_i$, with i varying from 0 to 4, correspond to the amounts of CO_2 and CO released in the temperature ranges DT'_i defined as follows: $DT'0 \leq T'min$; $T'min < DT'1 \leq T'int1$; $T'int1 < DT'2 \leq T'int2$; $T'int2 < DT'3 \leq T'int3$ and $T'int3 \leq DT'4 \leq T'max$, in which T'int1, T'int2 and T'int3 are intermediate temperatures between T'min and T'max and are such that T'int1 is between 420 and 480°C and is preferably equal to 450°C, T'int2 is between 520 and 580°C and is preferably equal to 550°C, and T'int3 is between 620 and 680°C and is preferably equal to 650°C. These intermediate temperatures correspond to relative minima observed by the Applicant on CO and CO_2 curves measured for a plurality of samples from superficial deposits, and in particular soils of various natures and origins. Assuming that, according to the literature, the combustion temperature is an approximation of thermal stability, the CO and CO_2 streams measured in the temperature ranges DT'1, DT'2 and DT'3 can be related to classes of organic constituents of increasing stability. Assuming that the thermal stability limit of calcite is close to T3, the CO_2 streams measured in the temperature range DT'4 can be related to mineral forms of carbon.
[Table 2]

$DT'_0 \leq T'min$	$S4CO2_0$	$S4CO_0$
$T'min < DT'_1 \leq T'int1$	$S4CO2_0$	$S4CO_1$
$T'int1 < DT'_2 \leq T'int2$	$S4CO2_2$	$S4CO_2$
$T'int2 < DT'_3 \leq T'int3$	$S4CO2_3$	$S4CO_3$
$T'int3 < DT'_4 \leq T'max$	$S4CO2_4$	$S4CO_4$

3) Characterization and quantification of carbon present in the sample

During this step, the carbon present in the soil sample is characterized and quantified, and in particular in order to determine an organic carbon content and/or a mineral carbon content. This step comprises at least the two sub-steps detailed below.

3.1) Determination of a parameter characterizing the proportion of mineral carbon in the sample

In accordance with the invention, the aim of this first sub-step is to determine a parameter characterizing the proportion of mineral carbon with respect to the total carbon present in the sample under consideration, starting from the amount of CO_2 measured in step 2 described above.

More precisely, in accordance with the invention, a parameter SCmin, which is representative of a proportion of mineral carbon with respect to the total carbon in said sample, is determined from a ratio between the amount of CO_2 released by the sample **residue above the intermediate temperature** T'int3 **of the heating** sequence under an oxidizing atmosphere of between 620 and 680°C (defined in step 2), and the total amount of CO_2 released by this residue during the heating sequence under an oxidizing atmosphere. Thus, the parameter SCmin is defined by the proportion of CO_2 released by thermal decomposition of the mineral carbon contained in the sample during the heating sequence in an oxidizing atmosphere with respect to the total amount of CO_2 emitted during this heating sequence in an atmosphere.

In accordance with one implementation of the invention, the parameter SCmin is determined in accordance with a formula of the type:
$SCmin = \frac{S4CO2_4}{S4CO2_t}$ in which $S4CO2_t = \sum_{i=0}^{i=4} S4CO2_i$

in which the terms $S4CO2_i$, with i from 1 to 4, are as defined in the preceding step. In general, the term $S4CO2_4$ highly predominantly corresponds to the CO_2 emitted by decomposition of the carbonate mineral species and $S4CO2_t$ corresponds to the total CO_2 stream during the oxidation phase.

In accordance with the invention, a threshold value is defined for parameter SCmin, below which it may be assumed that the soil sample is devoid of mineral forms (i.e. it is a non-carbonate sample), or in other words, below which it may be assumed that any form of carbon contained in this sample is organic in nature.

In accordance with one implementation of the invention, the threshold value of parameter SCmin, denoted *SCmin_threshold*, according to which the soil sample under consideration is devoid of mineral forms, may be between 0.03 and 0.05, and is preferably equal to 0.04. These values correspond to errors linked to the implementation of the method in accordance with the invention, due to the measuring apparatus itself and to the determination of the amounts of CO_2 **released in the temperature ranges** $\mathbf{DT'}_i$ defined in Table 2.

In accordance with one implementation of the invention, the carbon of a sample may also be characterized by defining four abundance classes for the mineral forms of carbon of a sample; the abundance classes can be defined as a function of the value of parameter SCmin in accordance with the invention in the following manner:

- if SCmin < 0.04, the sample comprises no mineral forms of carbon;
- if 0.04 < SCmin < 0.2: the sample comprises traces of mineral forms of carbon;
- if 0.2 < SCmin < 0.6: the sample comprises mineral forms of carbon;
- if SCmin > 0.6: the sample comprises mineral forms of carbon in abundance.

3.2) Determination of an organic carbon content and/or a mineral carbon content

During this step, an organic carbon content and/or a mineral carbon content is/are determined from the amounts of HC, CO and CO_2 measured during steps 1) and 2) described above, and as a function of the value of parameter SCmin described in the preceding sub-step 3.1).

In accordance with one implementation of the invention, new parameters are defined, hereinafter denoted TOCfs and MinCfs, which are specific to the heating sequences under an inert atmosphere and under an oxidizing atmosphere in accordance with the invention and dedicated to samples originating from a superficial deposit. The parameters TOCfs and MinCfs in accordance with the invention respectively represent the organic carbon content and the mineral carbon content of a sample from a superficial deposit, in contrast to the conventional parameters TOC and MinC defined in the prior art, which are not suitable for superficial deposit samples. In addition, in accordance with the invention, the formulae for determining the parameters TOCfs and MinCfs thus defined are a function of the value of parameter SCmin with respect to the threshold value *SCmin_threshold* defined in the preceding sub-step.

In accordance with the invention, two possible cases are defined, depending on the value of parameter SCmin:

a) First case: SCmin ≤ *SCmin_threshold*

In accordance with the invention, if the value of parameter SCmin is lower than the threshold value *SCmin_threshold* defined in the preceding sub-step (i.e. if the sample under consideration is a non-carbonate sample), the mineral carbon content is zero and the organic carbon content is a function of the total amounts of HC, CO and CO_2 released during the heating sequence under an inert atmosphere, and on the amounts of CO and CO_2 released during the heating sequence under an oxidizing atmosphere up to the intermediate temperature T'int3 defined above.

Thus, in contrast to the teaching of the prior art, which calculated a non-zero parameter MinC even in the case of an absence of mineral carbon in the sample, the present invention enables a mineral carbon content to be determined which is representative of the actual mineral carbon content of a sample from a superficial deposit with no mineral forms of carbon. In addition, in contrast to the prior art, the organic carbon content in accordance with the invention is determined by taking into account the total amounts of CO and CO_2 released during the heating sequences in an inert atmosphere and in an oxidizing atmosphere. In fact, the determination of the organic carbon content in accordance with the prior art only considered the amounts of CO and CO_2 released below the temperature T2 of the heating sequence under an inert atmosphere defined in step 1), half the amount of CO released above the temperature T2 of the heating sequence under an inert atmosphere defined in step 1, and the amounts of CO and CO_2 released below the intermediate **temperature T'int3 of the heating sequence** under an oxidizing atmosphere defined in step 2) of the heating sequence under an oxidizing atmosphere.

In accordance with one implementation of the invention, if the value of the parameter SCmin is less than threshold value *SCmin_threshold* defined in the preceding sub-step, parameters MinCfs and TOCfs, respectively representing the mineral carbon content and the organic carbon content of a sample from a superficial deposit, may also be defined in accordance with the following formulae:

- *MinC*fs=0;
- *TOC*fs = *PC*fs + *RC*fs, in which PCfs is a parameter which is representative of the pyrolyzed organic carbon content of a superficial deposit and RCfs is a parameter which is representative of the residual organic carbon content of a superficial deposit, these contents being defined by formulae specific to the heating sequences under an inert atmosphere and under an oxidizing atmosphere in accordance with the invention and which can be written as follows:

$$PC\mathrm{fs} = (S2_t\, x\, 0.083) + (S3CO2_t\, x \frac{12}{440}) + (S3CO_t\, x \frac{12}{280})) ;$$

$$RC\mathrm{fs} = (S4CO2_a x \frac{12}{440}) + (S4CO_a x \frac{12}{280}) ;$$

with:

$$S2_t = \sum_{i=0}^{i=6} S2_i \,; S3CO2_t = \sum_{i=0}^{i=6} S3CO2_i \,; S3CO_t = \sum_{i=0}^{i=6} S3CO_i \,;$$

$$S4CO2_a = \sum_{i=0}^{i=3} S4CO2_i \text{ and } S4CO_a = \sum_{i=0}^{i=3} S4CO_i \,.$$

b) Second case: SCmin > *SCmin_threshold*

In accordance with the invention, if the value of the parameter SCmin is greater than the threshold value *SCmin_threshold* defined in the preceding sub-step (i.e. if the sample under consideration is a carbonate), a preliminary estimation of an amount of CO_2 released by thermal cracking of the organic matter contained in the sample during the heating sequence under an inert atmosphere above temperature T2 defined in step 1) is carried out.

In accordance with the invention, this amount of CO_2 released by thermal cracking of the organic matter during the pyrolysis phase above temperature T2, hereinbelow denoted $S3CO2_c$, is estimated from the amount of CO_2 released during the heating sequence under an inert atmosphere up to temperature T2, hereinbelow denoted $S3CO2_a$, multiplied by a predefined factor k, which can be written in accordance with a formula of the type:

$$S3CO2_c = k \, x \, S3CO2_a$$

In accordance with a first implementation of the invention, the value of predefined factor k is between 1.3 and 1.4, and is preferably equal to 1.3724.

In accordance with a second implementation of the invention, the value of the predefined factor k may be determined experimentally, by means of a plurality (at least 10, preferably at least 50) samples originating from non-carbonate superficial deposits, and for which at least the heating sequence under an inert atmosphere in accordance with the invention is applied to each sample of the plurality of samples, an amount of CO_2 released by each of the samples during this heating sequence under an inert atmosphere is measured continuously, and the factor k is determined by means of a linear regression applied between the amounts of CO_2 released by the plurality of samples up to the temperature T2 of the heating sequence under an inert atmosphere defined in step 1) and the amounts of CO_2 released by the plurality of samples beyond this temperature T2. In fact, the samples from superficial deposits without forms of mineral carbon have a remarkable property: the amounts of CO_2 emitted

during the heating sequences in an inert atmosphere above and below the limiting temperature T2 are linearly correlated. In other words, the total amount of CO_2 emitted at a temperature above the limiting temperature T2 is equal to k times the total amount of CO_2 emitted at a temperature below the limiting temperature T3, which can be expressed in accordance with a formula of the type:
$\sum_{i=3}^{i=6} S3CO2_i = k \times \sum_{i=0}^{i=2} S3CO2_i$, in which k is established for samples for which SCmin ≤ *SCmin_threshold*. According to this implementation of the invention, the value of this factor k, predefined from a plurality of samples with no mineral forms, can be generalized to the case of samples with mineral forms of carbon (i.e. if SCmin is greater than the threshold value *SCmin_threshold*). In fact, considering that, to a first approximation, the source of organic carbon is comparable for non-carbonate soils and carbonate soils, it appears to be reasonable to assume that the distribution of labile compounds with respect to compounds which are thermally stable above the threshold temperatures is comparable for both types of samples.

In the case of a sample with mineral forms of carbon, the Applicant has demonstrated that the total amounts of CO_2 released above the temperature T2 of the pyrolysis phase (i.e. the parameter $S3CO_b$) combine the streams obtained from thermal cracking of the organic matter (i.e. the parameter $S3CO_c$) and those obtained from the thermal decomposition of these mineral forms. In addition, the higher the mineral carbon contents, the more negligible is the contribution from thermally stable organic forms.

In accordance with the invention, if the value of parameter SCmin is greater than the threshold value *SCmin_threshold* defined in the preceding sub-step, an organic carbon and/or mineral carbon content is determined by means of the amounts of HC, CO and CO_2 measured during the heating sequence in an inert atmosphere and the amounts of CO and CO_2 measured during the heating sequence in an oxidizing atmosphere, and by taking into account the amount $S3CO2_c$ of CO_2 released by thermal cracking of the organic matter of the sample during the heating sequence under an inert atmosphere beyond the temperature T2, previously estimated as described above.

In accordance with one implementation of the invention, if the value of parameter SCmin is greater than the threshold value *SCmin_threshold* defined in the preceding sub-step, the organic carbon content may be determined from the total amount of HC released during the heating sequence under an inert atmosphere, the amount of CO released during the heating sequence under an inert atmosphere up to temperature T4, to which is added half the amount of CO released during the heating sequence under an inert atmosphere above this temperature T4, the amount of CO_2 released during the heating sequence under an inert atmosphere up to the temperature T2, to which is added the estimated amount of CO_2 released by thermal cracking of the organic matter during the heating sequence under an inert atmosphere beyond the temperature T2, and the amounts of CO and CO_2 released during the heating sequence under an oxidizing atmosphere up to the **intermediate temperature T'int3 predefined in step 2).**

In accordance with one implementation of the invention, if the value of the parameter SCmin is greater than the threshold value *SCmin_threshold* defined in the preceding sub-step, a parameter TOCfs representing the organic carbon content of a superficial deposit sample may be defined in accordance with a formula of the type:

*TOC*fs = *PC*fs + *RC*fs, where PCfs is a parameter which is representative of the pyrolyzed organic carbon content of a sample from a superficial deposit and RCfs is a parameter which is representative of the residual organic carbon content of a superficial deposit, these contents being defined by formulae specific to the heating sequences under an inert atmosphere and under an oxidizing atmosphere in accordance with the invention, and which can be written as follows:

$$PC\text{fs} = (S2_t x\, 0.083) + \left([S3CO2_a + S3CO2_c] x \frac{12}{440}\right) + \left([S3CO_a + ½\, S3CO_b] x \frac{12}{280}\right)$$

$$RC\text{fs} = (S4CO2_a x \frac{12}{440}) + (S4CO_a x \frac{12}{280})$$

and in which $S2_t = \sum_{i=0}^{i=6} S2_i$;

$$S3CO2_a = \sum_{i=0}^{i=2} S3CO2_i \,; S3CO2_b = \sum_{i=3}^{i=6} S3CO2_i \,; S3CO2_c = k\ x\ S3CO2_a$$

$$S3CO_a = \sum_{i=0}^{i=4} S3CO_i \,; S3CO_b = \sum_{i=5}^{i=6} S3CO_i \,;$$

$$S4CO2_a = \sum_{i=0}^{i=3} S4CO2_i \,; S4CO_a = \sum_{i=0}^{i=3} S4CO_i$$

In accordance with one implementation of the invention, if the value of parameter SCmin is greater than the threshold value *SCmin_threshold* defined in the preceding sub-step, the mineral carbon content may be determined from the amount of CO_2 released during the heating sequence under an inert atmosphere beyond the temperature T2 at which the estimated amount of CO_2 released by thermal cracking of the organic matter during the heating sequence under an inert atmosphere beyond the temperature T2 is withdrawn, half the amount of CO released during the heating sequence under an inert atmosphere beyond the temperature T4, and the amount of CO_2 released during the heating sequence under an oxidizing atmosphere above the intermediate temperature T'int3.

In accordance with one implementation of the invention, if the value of the parameter SCmin is greater than the threshold value *SCmin_threshold* defined in the preceding sub-step, the parameter MinCfs representing the mineral carbon content of a sample from a superficial deposit can be defined in accordance with a formula of the type:

$$MinCfs = \left([S3CO2_b - S3CO2_c]x\frac{12}{440}\right) + \left(\tfrac{1}{2}\, S3CO_b x\frac{12}{280}\right) + \left(S4CO2_b\ x\frac{12}{440}\right)$$

in which $S3CO2_b = \sum_{i=3}^{i=6} S3CO2_i \,; S3CO2_c = k\ x\ S3CO2_a \,;$ $S3CO_b = \sum_{i=5}^{i=6} S3CO_i \,; S4CO2_b = \sum_{i=3}^{i=4} S4CO2_i$.

Thus, the definitions of the mineral carbon and organic carbon contents in accordance with the invention account for the forms of carbon present as follows: (i) all the forms of carbon are organic in the samples for which SCmin ≤ *SCmin_threshold*, and (ii) the other classes of mineral carbon abundance comprise a thermally stable organic carbon portion to which a mineral carbon portion, which is variable in nature as well as in proportion, is added.

Thus, at the end of these two sub-steps, a reliable characterization and quantification of the carbon present in a sample from a superficial deposit is obtained via the determination of a parameter SCmin representing a proportion of mineral carbon in the sample and the determination of the organic carbon and/or mineral carbon content of the sample, for example by means of parameters TOCfs and MinCfs specifically defined for carbonate and non-carbonate superficial deposits.

3.3) Determination of the thermal status of the organic forms of carbon

During this sub-step, which is optional, the thermal status of the organic forms of carbon present in the sample is determined. The term "thermal status of the organic forms of carbon present in the sample" should be understood to mean an indicator of the distribution of the various classes of compounds present in the sample and each defined by their cracking temperature.

The organic matter of a soil is a complex heterogeneous mixture comprising constituents of various natures and origins: residues from the gradual decomposition of the most labile biogenic constituents, free particles and constituents involved in organo-mineral complexes, and pyrogenic or petrogenic constituents. The thermal fractionation method in accordance with the invention does not enable these specific constituents to be separated. However, it can be used to measure the contributions of classes of compounds, each defined by their cracking temperature. Since thermal stability is considered to be a variable linked to biogeochemical stability (i.e. the resistance to decomposition by micro-organisms), the contributions of the classes of compound, defined thereby may be used to describe the heterogeneity of the organic matter of the soils.

In accordance with a first embodiment of this variation of the invention comprising a sub-step for determining the thermal status of the forms of carbon of the sample, a decomposition index ID and a stability index IS can be defined from the contributions of the classes of compounds defined in the preceding steps 1 and 2 in accordance with formulae of the type:

- decomposition index $ID = \log [S2_1 + S2_2] / S2_3$
- stability index $IS = [S2_3 + S2_4 + S2_5 + S2_6] / 100$

Thus, these two indices are directly linked to the most reactive fraction of the organic carbon (i.e. the pyrolyzed carbon portion in the form of hydrocarbon compounds).

The stability index IS measures the relative contributions of the thermally stable classes of compounds ($S2_3$, $S2_4$, $S2_5$ and $S2_6$) which are particularly abundant in superficial deposits and in the deep layers of the soils, in contrast to the more labile and more abundant classes of compounds ($S2_1$ and $S2_2$) in the poorly decomposed plant tissues present in the organic layers and the superficial layers of the soils. The decomposition index ID measures the ratio between these most labile classes of compounds ($S2_1$ and $S2_2$) and the intermediate class of compounds ($S2_3$), which is particularly abundant in the organic and organo-mineral layers of the soils. In general, the decomposition index ID measures the degree of transformation of the organic matter as the compounds of the most labile classes of compounds are decomposed and the compounds of the most stable classes of compounds accumulate.

In accordance with a second embodiment of this variation of the invention comprising a sub-step for determining the thermal status of the forms of carbon of the sample, the thermal status of the forms of carbon of a sample may be determined from the relative contributions of the various classes of compounds of a sample in order to calculate a thermally labile organic carbon content (i.e. resulting from thermal cracking and combustion below T3) and a thermally stable organic carbon content (i.e. resulting from thermal cracking and combustion below T3).

In accordance with one implementation of the invention, at least one of the following parameters characterizing the thermal status of the sample may be determined:

- a thermally labile pyrolyzed organic carbon content, denoted COPL, defined in accordance with a formula of the type:

$$COPL\,(\%C) = (S2_L\,x\,0.083) + ([KCOPL * S3CO2_L]\,x\,\frac{12}{440}) + (S3CO_L\,x\,\frac{12}{280})$$

in which KCOPL is between 1 and 2, preferably equal to 1.3359.

- a thermally stable pyrolyzed organic carbon content, denoted COPS, defined in accordance with a formula of the type:

$$COPS\,(\%C) = (S2_S x\,0.083) + ([KCOPS * S3CO2_L] x \frac{12}{440}) + ([½\,S3CO_S] x \frac{12}{280})$$

in which KCOPS is between 0.1 and 1 and is preferably equal to 0.6274.

- a thermally labile residual organic carbon content, denoted CORL, defined in accordance with a formula of the type:

$$CORL\,(\%C) = (S4CO2_L\,x\,\frac{12}{440}) + (S4CO_L\,x\,\frac{12}{280})$$

- a thermally stable residual organic carbon content, denoted CORS, defined in accordance with a formula of the type:

$$CORS\,(\%C) = (S4CO2_S\,x\,\frac{12}{440})$$

in which $S2_L = \sum_{i=0}^{i=3} S2_i$; $S2_S = \sum_{i=4}^{i=6} S2_i$

$S3CO2_L = \sum_{i=0}^{i=3} S3CO2_i$; $S3CO2_S = \sum_{i=4}^{i=6} S3CO2_i$;

$S3CO_L = \sum_{i=0}^{i=4} S3CO_i$; $S3CO_S = \sum_{i=5}^{i=6} S3CO_i$;

$S4CO2_L = \sum_{i=0}^{i=1} S4CO2_i$; $S4CO2_S = \sum_{i=2}^{i=3} S4CO\,2_i$;

$S4CO_L = \sum_{i=0}^{i=1} S4CO_i$; $S4CO_S = \sum_{i=2}^{i=3} S4CO_i$.

These partial contents are particularly useful in understanding the dynamics of the organic matter in soils, because they enable the total organic carbon stocks to be compared with the contributions of the various forms of carbon, and enable monitoring of the change in these stocks over time to be carried out. In particular, they enable the relationships between stocks of thermally labile organic carbon and thermally stable organic carbon, which are directly correlated in soils, to be explored, which indicates that transfer from one stock to the other operates effectively in the soils.

Examples

The features and advantages of the method in accordance with the invention will become more apparent from the application example described below.

The method in accordance with the invention was applied to a series of 9 distinct soil samples, hereinbelow denoted ECHSi, with i varying from 1 to 9, samples ECHS2, ECHS3, ECHS8, ECHS9 originating from carbonate soils, and samples ECHS1, ECHS4, ECHS5, ECHS6, ECHS7 originating from non-carbonate soils.

The method in accordance with the invention was also applied to a series of 7 distinct peat samples, hereinbelow denoted ECHTi, with i=1 to 7, originating from the same peat sequence and dated at 340, 2850, 4540, 5220, 6050, 8850 and 9640 years.

Figure 4A (respectively Figure 4B) presents a histogram comparing the values for the organic carbon contents Corg (respectively the mineral carbon content Cmin) determined by the method in accordance with the invention and by the prior art for each of the 9 soil samples ECHS1 to ECHS9. More precisely, Figure 4A (respectively Figure 4B) presents the values (pale grey bars on the right) for the parameter TOCfs (respectively MinCf) in accordance with the invention and the values (dark grey bars on the left) for the parameter TOC (respectively MinC) of the prior art for each of these 9 samples. In general, the values for the TOCfs are all higher (by about 8%) than the values for the TOC of the prior art, which corresponds to the proportion of organic carbon wrongly considered to be mineral in the prior art. It will also be noted that the values for MinCfs are significantly lower than the MinC values for the non-carbonate soil samples for which the value for MinC of the prior art corresponds to the streams of CO and CO_2 emitted during pyrolysis and oxidation of organic forms of carbon. It will also be observed that the values for MinCfs are closer or even identical to that for MinC for the carbonate soil samples for which the proportion of organic carbon, wrongly placed in MinC in the prior art, is lower than in the non-carbonate soils, or even negligible if the organic forms of carbon are completely pyrolyzed and oxidized below the threshold temperatures used to calculate the MINC of the prior art.

Figure 5A (respectively Figure 5B) presents a histogram comparing the values for the organic carbon contents Corg (respectively the mineral carbon contents Cmin) determined by the method in accordance with the invention and by the prior art for each of the 7 peat samples ECHT1 to ECHT7. More precisely, Figure 5A (respectively Figure 5B) presents the values (pale grey bars on the right) for the parameter TOCfs (respectively MinCf) in accordance with the invention and the values (dark grey bars on the left) for the parameter TOC (respectively MinC) of the prior art for each of these 7 samples. It will be observed in this figure that the values for TOC (respectively MinC) and for TOCfs (respectively MinCfs) are significantly higher (respectively lower) since for these organic samples, nearly all of the carbon taken into account for the calculation of MINC of the prior art in fact originates from the pyrolysis and oxidation of organic compounds.

Thus, the present invention enables the forms of carbon present in a sample from a superficial deposit to be reliably characterized and quantified, whether the superficial deposit is a carbonate deposit or not. In particular, the present invention defines heating sequences in an inert atmosphere and in an oxidizing atmosphere which are appropriate for superficial deposits, as well as organic carbon contents and/or mineral carbon contents taking into account an estimated amount of CO_2 released by thermal cracking of the organic matter of the sample during the heating sequence in an inert atmosphere above temperature T2.

Patentkrav

1. Fremgangsmåde til karakterisering og kvantificering af carbon, der forefindes i en overfladeformation, ud fra en repræsentativ prøve af overfladeformationen, kendetegnet ved, at mindst følgende trin anvendes på prøven:

A. prøven opvarmes ifølge en første opvarmningssekvens under en inert atmosfære, og der måles kontinuerligt en mængde carbonhydridforbindelser, en mængde CO og en mængde CO_2, der frigives under den første opvarmningssekvens, idet den første opvarmningssekvens under en inert atmosfære omfatter en rækkefølge af mindst seks isotermiske trin af en forud fastlagt varighed, idet rækkefølgen af de mindst seks isotermiske trin omfatter et første isotermisk trin ved en første temperatur på mellem 80 og 200 °C (T0), et andet isotermisk trin ved en anden temperatur på mellem 340 og 380 °C (T1), et tredje isotermisk trin ved en tredje temperatur på mellem 400 og 440 °C (T2), et fjerde isotermisk trin ved en fjerde temperatur på mellem 450 og 490 °C (T3), et femte isotermisk trin ved en femte temperatur på mellem 500 og 540°C (T4), et sjette isotermisk trin ved en sjette temperatur på mellem 580 og 650 °C (T5), idet de isotermiske trin er forbundet med hinanden af en termisk gradient,

B. der opvarmes en rest af prøven fra den første opvarmningssekvens ifølge en anden opvarmningssekvens under en oxiderende atmosfære, og der måles en mængde CO og en mængde CO_2, der frigives under den anden opvarmningssekvens, idet den anden opvarmningssekvens under en oxiderende atmosfære starter ved en minimumstemperatur på mellem 150 og 300 °C, slutter ved en maksimumstemperatur på mellem 850 og 1200°C, og følger en termisk gradient,

C. der bestemmes en værdi af en parameter SCmin, som er repræsentativ for en andel af mineralsk carbon i forhold til det samlede carbon i prøven, ud fra et forhold mellem den mængde CO_2, der frigives af resten af prøven over en mellemtemperatur for den anden opvarmningssekvens på mellem 620 og 680 °C, og den mængde CO_2, der frigives af resten under den anden opvarmningssekvens,

D. et indhold af organisk carbon og/eller et indhold af mineralsk carbon i prøven kvantificeres på følgende måde:

i. hvis værdien af parameteren SCmin er mindre end eller lig med en forud fastlagt tærskelværdi for parameteren SCmin, er indholdet af mineralsk carbon nul, og indholdet af organisk carbon er en funktion af helheden af de mængder af HC, CO og CO_2, der frigives under den første opvarmningssekvens, og de mængder af CO og CO_2, der frigives under den anden opvarmningssekvens op til mellemtemperaturen for den anden opvarmningssekvens.

ii. hvis værdien af parameteren SCmin er større end den forud fastlagte tærskelværdi for parameteren SCmin:

- der estimeres en mængde CO_2, som frigives ved termisk krakning af det organiske stof i prøven under den første opvarmningssekvens over den tredje temperatur (T2) ud fra den mængde CO_2, der frigives under den første opvarmningssekvens op til den tredje temperatur (T2) for den første opvarmningssekvens, multipliceret med en forud fastlagt faktor k, og/eller
- indholdet af organisk carbon og/eller indholdet af mineralsk carbon bestemmes som en funktion af de mængder af HC, CO og CO_2, der frigives under den første opvarmningssekvens, og de mængder af CO og CO_2, der frigives under den anden opvarmningssekvens op til mellemtemperaturen for den anden opvarmningssekvens, og under hensyntagen til den estimerede mængde CO_2, der frigives ved termisk krakning af det organiske stof i prøven under den første organiske opvarmningssekvens over den tredje temperatur (T2).

2. Fremgangsmåde ifølge krav 1, hvorved det følgende gælder, hvis værdien af parameteren SCmin er større end den forud fastlagte tærskelværdi for parameteren SCmin:

- indholdet af organisk carbon er en funktion af helheden af den mængde HC, der frigives under den første opvarmningssekvens, den mængde CO, der frigives under den første opvarmningssekvens op til den femte temperatur (T4), hvortil halvdelen af den mængde CO, der frigives under den første opvarmningssekvens over den femte temperatur (T4), tilføjes, den mængde CO_2, der frigives under den første opvarmningssekvens op til den tredje temperatur (T2), hvortil den estimerede mængde CO_2, der frigives ved termisk krakning af det organiske stof i prøven under den første opvarmningssekvens over den tredje temperatur (T2), tilføjes, og de mængder af CO og CO_2, der frigives under den anden opvarmningssekvens op til mellemtemperaturen for den anden opvarmningssekvens, og/eller

- indholdet af mineralsk carbon er en funktion af den mængde CO_2, der frigives under den første opvarmningssekvens over den tredje temperatur (T2) for den første opvarmningssekvens, hvorfra den estimerede mængde CO_2, der frigives ved termisk krakning af det organiske stof i prøven under den første opvarmningssekvens over den tredje temperatur (T2), fjernes, halvdelen af den mængde CO, der frigives under den første opvarmningssekvens over den femte temperatur (T4), og den mængde CO_2, der frigives under den anden opvarmningssekvens over mellemtemperaturen for den anden opvarmningssekvens.

3. Fremgangsmåde ifølge et af kravene 1 eller 2, hvorved den forud fastlagte faktor k ligger mellem 1,3 og 1,4, og fortrinsvis har værdien 1,3724.

4. Fremgangsmåde ifølge et af kravene 1 eller 2, hvorved hver af prøverne i flerheden af prøver påføres i det mindste den første opvarmningssekvens ved hjælp af en flerhed af prøver, som stammer fra ikke-carbonaterede overfladeformationer, der måles en mængde CO_2, der frigives af hver af prøverne under den første opvarmningssekvens, og faktoren k bestemmes ved hjælp af en lineær regression, der anvendes mellem de mængder CO_2, der frigives af flerheden af prøver op til den tredje temperatur (T2) for den første opvarmningssekvens, og de mængder CO_2, der frigives af flerheden af prøver over den tredje temperatur (T2) for den første opvarmningssekvens.

5. Fremgangsmåde ifølge et af de foregående krav, hvorved den forud fastlagte tærskelværdi for parameteren SCmin ligger mellem 0,03 og 0,05, og fortrinsvis har værdien 0,04.

6. Fremgangsmåde ifølge et af de foregående krav, hvorved den første temperatur (T0) for den første opvarmningssekvens ligger mellem 80 °C og 150 °C, og fortrinsvis har værdien 150 °C.

7. Fremgangsmåde ifølge et af de foregående krav, hvorved minimumstemperaturen for den anden opvarmningssekvens er lig med den første temperatur (T0) for den første opvarmningssekvens.

8. Fremgangsmåde ifølge et af de foregående krav, hvorved den forud fastlagte varighed af et af de isotermiske trin i den første opvarmningssekvens ligger mellem 3 og 5 minutter.

9. Fremgangsmåde ifølge et af de foregående krav, hvorved en af de termiske gradienter i den første opvarmningssekvens ligger mellem 1 og 50 $°C.min^{-1}$, fortrinsvis mellem 20 og 25 $°C.min^{-1}$.

10. Fremgangsmåde ifølge et af de foregående krav, hvorved den termiske gradient i den anden opvarmningssekvens ligger mellem 20 og 40 $°C.min^{-1}$, fortrinsvis mellem 20 og 25 $°C.min^{-1}$.

11. Fremgangsmåde ifølge et af de foregående krav, hvorved det følgende gælder, hvis værdien af parameteren SCmin er mindre end eller lig med den forud fastlagte værdi af parameteren SCmin:
- indholdet af mineralsk carbon defineres af en parameter MinCfs således, at MinCfs = 0, og/eller
- indholdet af organisk carbon defineres af en parameter TOCfs, der udtrykkes med en formel af typen:

$$TOCfs = (S2_t \, x \, 0.083) + \left(S3CO2_t \, x \, \frac{12}{440}\right) + \left(S3CO_t \, x \, \frac{12}{280}\right) + \left(S4CO2_a \, x \, \frac{12}{440}\right) + \left(S4CO_a \, x \, \frac{12}{280}\right)$$

hvor S2t, S3CO2t, S3COt betegner de mængder af henholdsvis HC, CO_2 og CO, der frigives under den første opvarmningssekvens, S4CO2a og S4COa henholdsvis betegner de mængder af CO_2 og CO, der frigives under den anden opvarmningssekvens op til mellemtemperaturen for den anden opvarmningssekvens.

12. Fremgangsmåde ifølge et af de foregående krav, hvorved det følgende gælder, hvis værdien af parameteren SCmin er større end den forud fastlagte værdi af parameteren SCmin:

- indholdet af mineralsk carbon defineres af en parameter MinCfs, der udtrykkes med en formel af typen:

$$MinCfs = ([S3CO2_b - S3CO2_c] x \frac{12}{440}) + (½ S3CO_b x \frac{12}{280}) \\ + (S4CO2_b x \frac{12}{440})$$

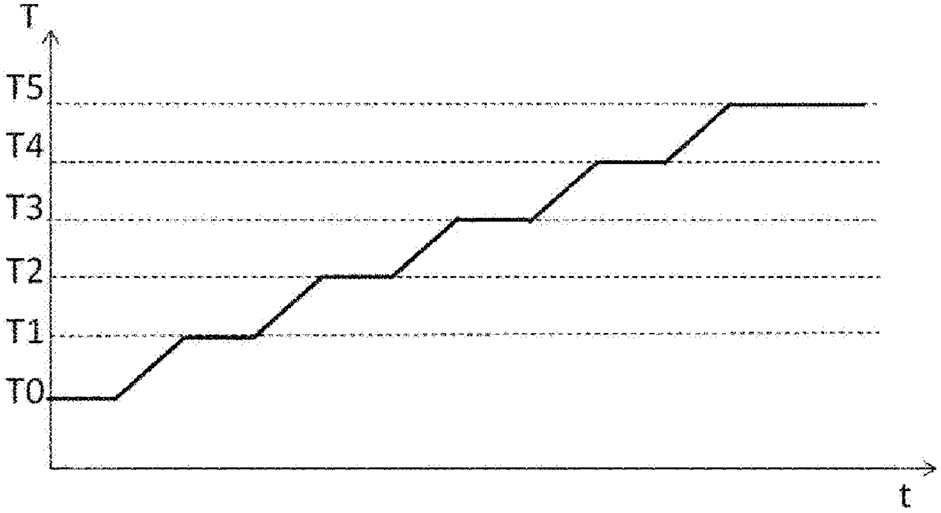
hvor S3CO2b betegner den mængde CO$_2$, der frigives under den første opvarmningssekvens over den tredje temperatur (T2), S3CO2b betegner den estimerede mængde CO$_2$, der frigives ved termisk krakning af det organiske stof i prøven under den første opvarmningssekvens over den tredje temperatur (T2), S3COb betegner den mængde CO, der frigives under den første opvarmningssekvens over den femte temperatur (T4), og S4CO2b betegner den mængde CO$_2$, der frigives under den anden opvarmningssekvens over mellemtemperaturen for den anden opvarmningssekvens, og/eller

- indholdet af organisk carbon defineres af en parameter TOCfs, der udtrykkes med en formel af typen:

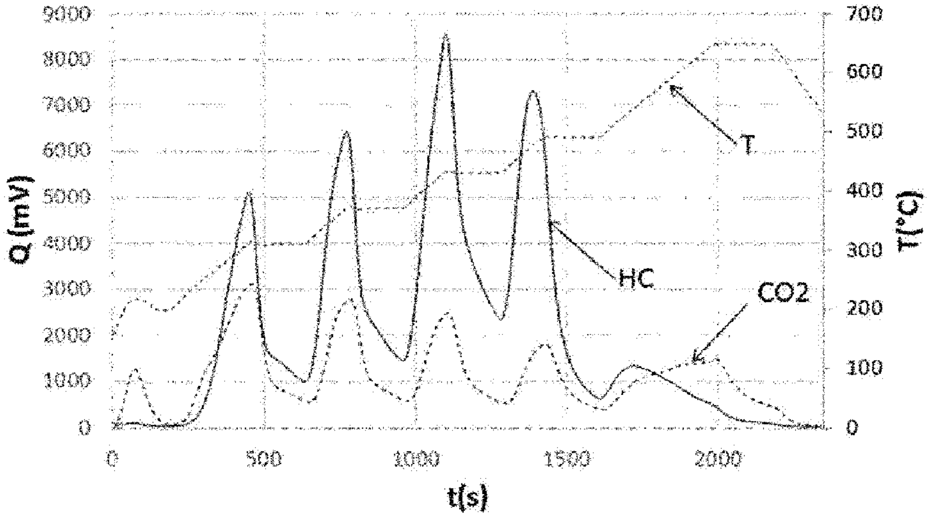
$$TOCfs = (S2_t x 0{,}083) + ([S3CO2_a + S3CO2_c] x \frac{12}{440}) + ([S3CO_a \\ + ½S3CO_b] x \frac{12}{280}) + (S4CO2_a x \frac{12}{440}) + (S4CO_a x \frac{12}{280})$$

hvor S2t betegner den mængde HC, der frigives under den første opvarmningssekvens, S3CO2a betegner den mængde CO$_2$, der frigives i den første opvarmningssekvenser op til den tredje temperatur (T2), S3CO2b betegner den estimerede mængde CO$_2$, der frigives ved termisk krakning af det organiske stof i prøven under den første opvarmningssekvens over den tredje temperatur (T2), S3COa og S3COb betegner de mængder CO, der frigives under den første opvarmningssekvens henholdsvis op til og over den femte temperatur (T4), S4CO2a og S4COa henholdsvis betegner de mængder af CO$_2$ og CO, der frigives under den anden opvarmningssekvens og op til mellemtemperaturen for den anden opvarmningssekvens.

[Fig. 1]


T
T5
T4
T3
T2
T1
T0
t

[Fig. 2A]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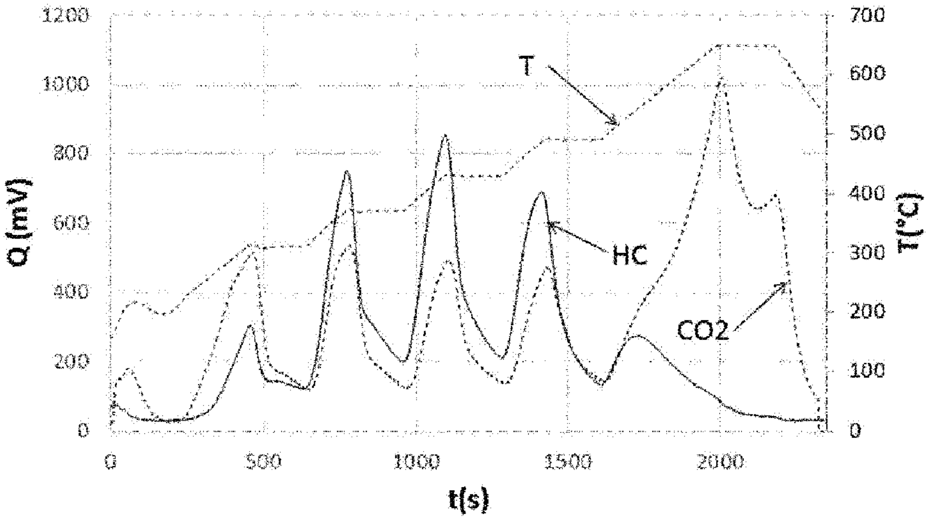
8000
7000
6000
5000
4000
3000
2000
1000
0
Q (mV)
700
600
500
400
300
200
100
0
T(°C)
T
HC
CO2
0
500
1000
1500
2000
t(s)

[Fig. 2B]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800
600
400
200
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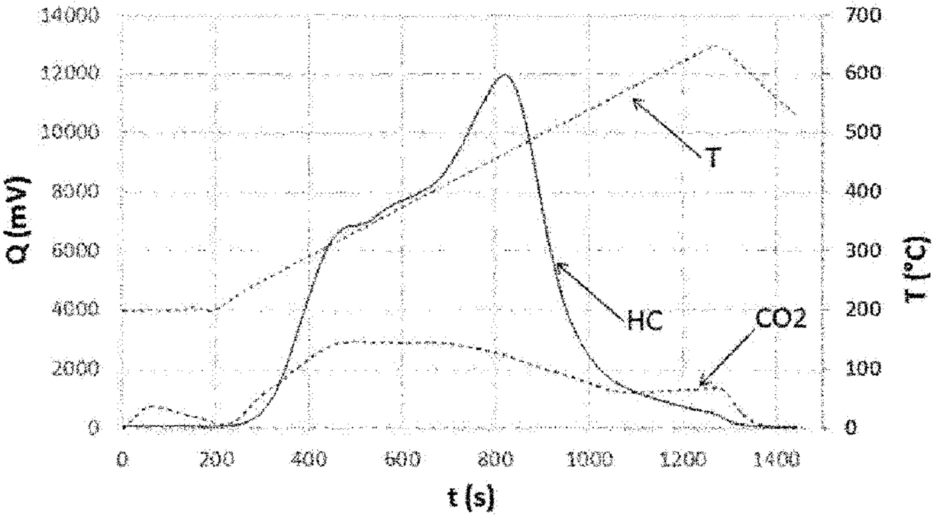
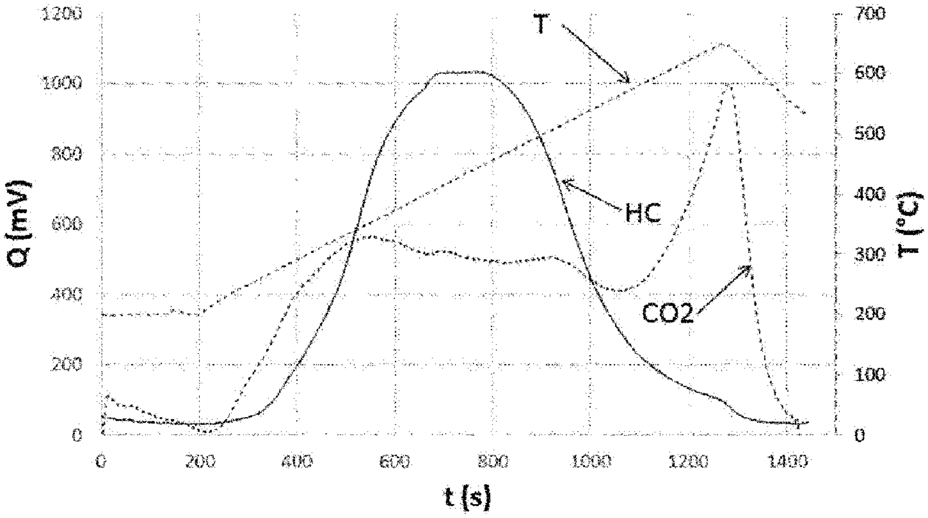
Q (mV)
0
500
1000
1500
2000
t(s)
700
600
500
400
300
200
100
0
T(°C)
T
HC
CO2

[Fig. 2C]


14000
12000
10000
8000
6000
4000
2000
0
Q (mV)
0
200
400
600
800
1000
1200
1400
t (s)
700
600
500
400
300
200
100
0
T (°C)
T
HC
CO2

[Fig. 2D]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800
600
400
200
0
Q (mV)
0
200
400
600
800
1000
1200
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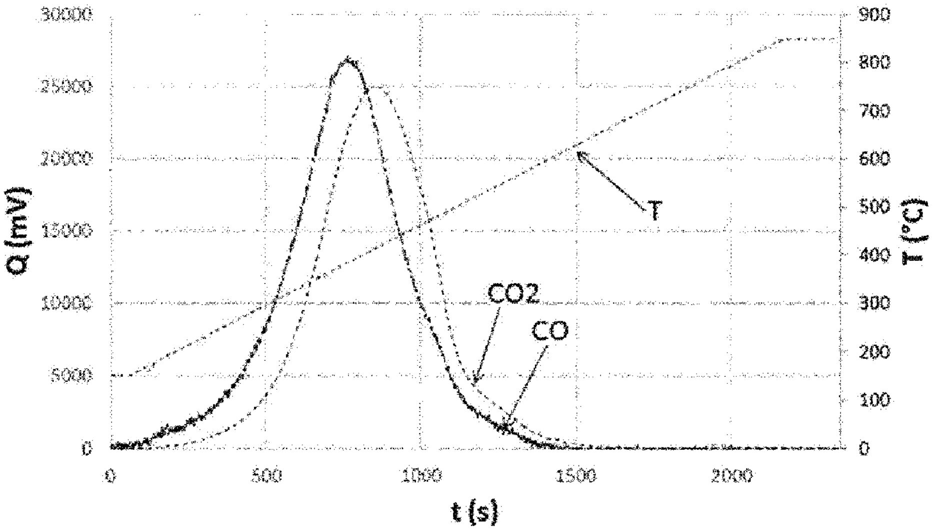
t (s)
700
600
500
400
300
200
100
0
T (°C)
T
HC
CO2

[Fig. 3A]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25000
20000
15000
10000
5000
0
Q (mV)
0
500
1000
1500
2000
t (s)
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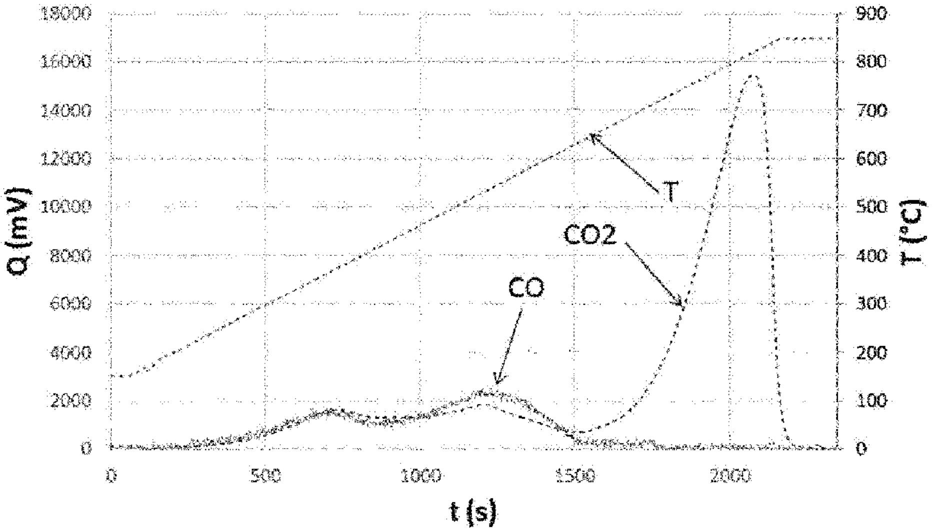
800
700
600
500
400
300
200
100
0
T (°C)
T
CO2
CO

[Fig. 3B]


Q (mV)
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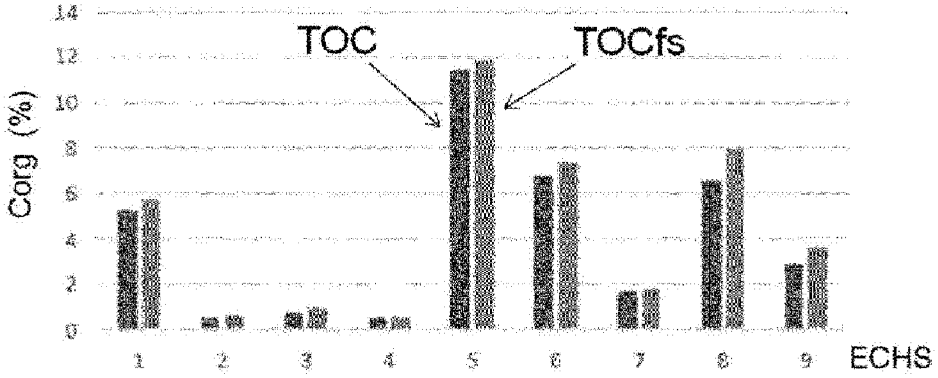
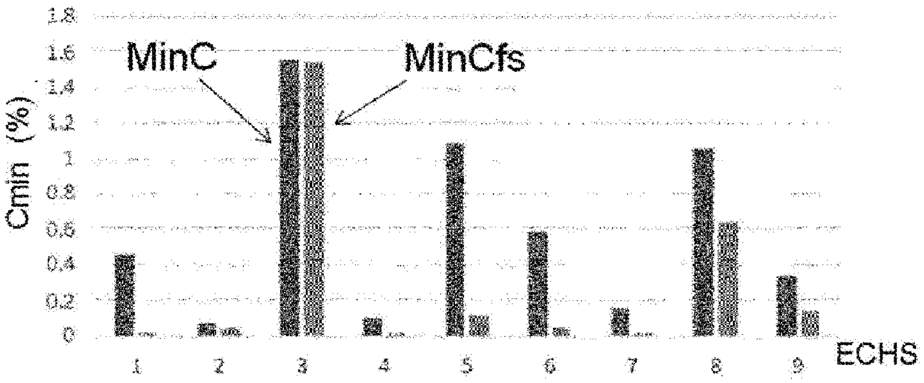
16000
14000
12000
10000
8000
6000
4000
2000
0
T (°C)
900
800
700
600
500
400
300
200
100
0
T
CO2
CO
0
500
1000
1500
2000
t (s)

[Fig. 4A]


Corg (%)
14
12
10
8
6
4
2
0
TOC
TOCfs
1
2
3
4
5
6
7
8
9
ECHS

[Fig. 4B]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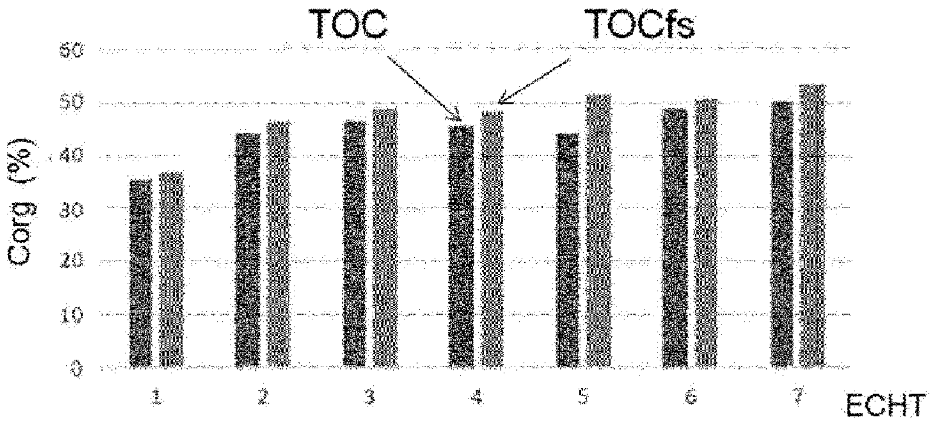
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Cmin (%)
MinC
MinCfs
1
2
3
4
5
6
7
8
9
ECHS

[Fig. 5A]


TOC
TOCfs
60
50
40
30
20
10
0
Corg (%)
1
2
3
4
5
6
7
ECHT

[Fig. 5B]