

(19) **DANMARK**

(10) **DK/EP 3454061 T3**



Patent- og
Varemærkestyrelsen

(12) Oversættelse af
europæisk patentskrift

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- (51) Int.Cl.: **G 01 N 33/24 (2006.01)** **G 01 N 31/12 (2006.01)**
- (45) Oversættelsen bekendtgjort den: **2020-05-25**
- (80) Dato for Den Europæiske Patentmyndigheds bekendtgørelse om meddelelse af patentet: **2020-03-11**
- (86) Europæisk ansøgning nr.: **18191048.0**
- (86) Europæisk indleveringsdag: **2018-08-28**
- (87) Den europæiske ansøgnings publiceringsdag: **2019-03-13**
- (30) Prioritet: **2017-09-12 FR 1758413**
- (84) Designerede stater: **AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR**
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- (54) Benævnelse: **FREMGANGSMÅDE TIL KVANTIFICERING AF PYRITSVOVL OG ORGANISK SVOVL I EN BJERGARTSPRØVE**
- (56) Fremdragne publikationer:
EP-A1- 2 342 557
US-A- 4 845 040
US-B1- 6 319 717

Description

The present invention relates to the technical field of the petroleum industry and more particularly to the field of the exploration and exploitation of a geological formation in which hydrocarbons are trapped.

More specifically, the present invention relates to the characterization and the quantification of the sulfur present within a sedimentary rock, such as a marine clay rich in organic matter.

In order to meet the growing demand for energy, the petroleum industry is increasingly turning to the production of unconventional crude oils, which are richer in sulfur than conventional oils. In point of fact, the sulfur content of an unconventional crude oil, and also the type of organosulfur compounds which it contains, are key parameters of the quality of this oil and of the refinery products which result therefrom. Furthermore, regulations are imposing increasingly low sulfur contents for the products resulting from refining. For these reasons, it is important to know how to precisely characterize and quantify the sulfur present in the rocks that these sulfur-containing crude oils originate from.

In the case of petroleum source rocks, the two main sulfur compounds are organic sulfur and pyritic sulfur. The quantification of the organic sulfur, independently of the pyritic sulfur, is of great importance in oil exploration because it makes it possible to know exactly the amount of sulfur associated with the organic matter of the source rocks, which is the source of the sulfur present in the oil generated by these source rocks. In particular, the separate quantification of the pyritic sulfur and of the organic sulfur makes it possible:

- to characterize the type of organic matter of the source rock and to predict the quality of the oil generated by the

source rock as regards its sulfur content: in point of fact, the characterization of the type of organic matter of the source rocks is conventionally carried out as a function of the elemental content of this organic matter in Carbon (C), in Hydrogen (H) and in Oxygen (O). This conventional characterization of the type of organic matter is carried out using the conventional Van Krevelen diagram, which represents the Hydrogen/Carbon (H/C) atomic ratio as a function of the Oxygen/Carbon (O/C) atomic ratio. As the potential of an organic matter to generate oil depends on its composition of H, C and O, this diagram makes it possible to distinguish three types of organic matter according to their oil potential. In point of fact, this diagram can be correlated with the source and with the deposition environment of the organic matter. Conventionally, organic matter of lacustrine type (type I), of marine type (type II) and of terrestrial type (type III) are distinguished. The quantification of the sulfur of the organic matter independently of the sulfur of the pyrite (or pyritic sulfur) provides an additional parameter which makes possible a finer characterization of the type of organic matter and thus a finer characterization of its deposition environment and of the type of oil which it can generate. This finer characterization is carried out with the Van Krevelen diagram extended to three dimensions: H/C as a function of O/C and of S^{org}/C , where S^{org} is the content of organic sulfur. This extended diagram makes it possible to distinguish with greater sensitivity the various types of organic matter, in particular to identify organic matters of type IS and IIS, which have the same sources as the types I and II but which contain sulfur and which were probably deposited in an anoxic or euxinic environment. This presence of sulfur also indicates that the oil resulting from cracking of this organic matter will contain more sulfur. Generally, the data on the type of organic matter of the source rock gives information on the potential of the source rock to generate oil and on the expected quality of this oil, in particular as regards its sulfur content;

- to contribute an additional parameter to the oil/source

rock correlation: this is because the oil/source rock correlation is a very important analysis which a person skilled in the art has to carry out in order to evaluate the petroleum system. It consists in making the connection between the oils
5 contained in a reservoir and the source rock(s) which have generated these oils. As it is known that the cracking of source rocks containing organic matter rich in sulfur results in the formation of oils and of gases which are rich in sulfur, a method for the quantification of the sulfur of the organic matter,
10 independently of the sulfur of the pyrite, thus provides a key parameter for the oil/source rock correlation.

State of the art

15 Patent EP 2 342 557 (US 8 796 035), which relates to a device and a method for the characterization and the quantification of the sulfur in a sample of sedimentary rocks or of petroleum products, is known in particular. More specifically, the method described in this patent comprises the following stages:

20

- the sample under consideration is heated in a pyrolysis oven in a non-oxidizing atmosphere,

- a part of the pyrolysis effluents is oxidized, and the
25 amount of SO₂ contained in this part of the effluents which have been oxidized is continuously measured,

- the pyrolysis residues are transferred into an oxidation oven, and the amount of SO₂ contained in the effluents resulting
30 from the oxidizing heating of the pyrolysis residue is continuously measured,

- and the sulfur content in the sample is deduced therefrom.

35

However, this method makes it possible to determine the content of total sulfur present in the sample studied but does not make it possible to separately quantify the pyritic sulfur from the

organic sulfur. This is because this method makes it possible to quantify the content of total sulfur of a rock sample, via the measurement of the sulfur effluents released by this sample during a pyrolysis followed by an oxidation. Two profiles
5 corresponding to the sulfur are thus obtained: the first during the pyrolysis phase and the second during the oxidation phase. As regards the pyrolysis sulfur signal, it is possible to distinguish the organic sulfur from the inorganic sulfur due to pyrite as they systematically form two sufficiently distinct
10 peaks. However, in oxidation, the signals of these two sulfur compounds merge, which prevents speciation of the organic and pyritic sulfur. Furthermore, many chemical reactions take place in the rock during the actual analysis. If some involve the organic sulfur and/or the pyritic sulfur, then they are likely
15 to modify their signals, which adds a level of difficulty to the quantification of the organic sulfur and of the pyritic sulfur by means of the method as described in the aforementioned patent.

The following documents will be cited in the continuation of the
20 description:

Acholla, F.V., Orr, W.L., 1993. Pyrite removal from kerogen without altering organic matter: The chromous chloride method. Energy Fuels, 7, 406-410.

25 Bolin, T.B., 2010. Direct determination of pyrite content in Argonne premium coals by the use of sulfur X-ray near edge absorption spectroscopy (S-XANES). Energy and Fuels, 24, 5479-5482.

30 Canfield, D.E., Raiswell, R., Westrich, J.T., Reaves, C.M., Berner, R.A., 1986. The use of chromium reduction in the analysis of reduced inorganic sulfur in sediments and shales. Chemical Geology, 54, 149-155.

35 Orr W., 1986, "Kerogen/asphaltene/sulfur relationships in sulfur-rich Monterey oils", Org. Geochem., Vol. 10, pp. 499-516, 1986.

Vairavamurthy, M.A., Maletic, D., Wang, S., Manowitz, B., Eglinton, T., Lyons, T., 1997. Characterization of sulfur-containing functional groups in sedimentary humic substances by X-ray absorption near-edge structure spectroscopy. *Energy and Fuels*, 11, 546-553.

Vandenbroucke, M., Largeau, C., 2007. Kerogen origin, evolution and structure. *Organic Geochemistry*, 38, 719-833.

Laboratory methods which make it possible to separately quantify pyritic sulfur from organic sulfur are known, such as the following techniques:

- Elemental analysis of the kerogens, as described in the document (Vandenbroucke and Largeau, 2007). It is one of the commonest methods routinely used in laboratories. It takes place in 2 stages:

- Isolation of the kerogen (or also isolation of the organic matter): the kerogen is isolated from the crude rock by a series of chemical attacks with hydrochloric acid and hydrofluoric acid targeted at destroying the mineral matrix, the carbonates and the silicates. As pyrite (FeS_2), other metal sulfides, and also some minor oxides, including iron oxides, are resistant to these different chemical attacks, they remain preserved in the organic residue obtained. Thus, a kerogen is obtained which has been freed from the mineral matrix but which still contains pyrite.

- Elemental analysis of the iron (by Inductively Coupled Plasma-Atomic Emission Spectrometry, ICP-AES) and of the sulfur (by infrared analysis): it is assumed here that the iron present in the kerogen obtained is only in the pyrite (FeS_2) form. Consequently, from the measurement of the iron content (ICP-AES) of the kerogen, the pyrite content can be stoichiometrically calculated, making it possible to thus determine the content of pyritic sulfur. Then, from the measurement of the sulfur content (IR) of the kerogen, the content of organic sulfur is deduced

therefrom by the difference between the total sulfur (measured by infrared spectroscopy) and the pyritic sulfur.

5 This first laboratory method according to the prior art exhibits the following disadvantages:

- the length of the analysis time: approximately one week;
 - it requires stages of preparation and of chemical
10 separation, which are extensive and dangerous as they use strong acids;
 - it does not make it possible for the measurements to be automated;
 - 15 - it is based on the assumption that all the iron contained in the organic matter is pyritic. In point of fact, if the iron contained in the organic matter is also in other forms, such as oxides or sulfides other than FeS_2 , then the content of pyritic
20 sulfur is overestimated and the content of organic sulfur is underestimated.
- Extraction of the pyrite by chromium(II) chloride and by the elemental analysis of the starting rock, as described in the
25 documents (Canfield et al., 1986; Acholla and Orr, 1993). According to this approach, a chemical attack with hot hydrochloric acid (HCl) is carried out in a first step in order to extract all of the volatile sulfur contained in rock samples. Once this stage has been carried out, the samples are
30 subsequently treated, under hot conditions, with a solution formed of hydrochloric acid (HCl) and of chromium(II) chloride (CrCl_2) which makes it possible to extract the pyrite (FeS_2). The sulfur effluent (H_2S), released by the reduction of the
35 pyrite by this solution, passes into a trap composed of a silver nitrate (AgNO_3) solution, where it precipitates in the form of silver sulfide (Ag_2S). The Ag_2S precipitate obtained is weighed, which makes it possible to stoichiometrically quantify the content of pyritic sulfur, it being assumed that the pyrite has

been completely converted into silver sulfide. The content of organic sulfur is then deduced by the difference between the content of total sulfur, obtained by the elemental analysis of the starting rock, and the content of pyritic sulfur. This method is based on the assumption that all the pyrite is reduced to give H_2S .

This second laboratory method according to the prior art exhibits the following disadvantages:

- it requires preparation and chemical separation steps that are extensive and dangerous since they use strong acids;

- it does not make it possible for the measurements to be automated;

- it is based on the assumption that all the pyrite is reduced to give H_2S . If a part of the pyrite is not reduced, then the content of pyritic sulfur is underestimated and the content of organic sulfur is overestimated. In particular, this may be the case for the pyrite-rich samples.

- Sulfur X-ray Absorption Near Edge Structure Spectroscopy (S-XANES), as described in the documents (Vairavumurthy et al., 1997; Bolin, 2010): according to this approach, S-XANES gives information on the oxidation state of the sulfur compounds. In a typical analysis, the spectrum of a sample is deconvoluted with various linear combinations of the spectra of different sulfur standards. The best adjustment is chosen in order to indicate the true composition of the different sulfur compounds of this sample. This technique thus makes it possible to quantitatively determine the pyritic sulfur, the organic sulfur and the sulfates. In the case of analysis of rocks, it should be noted that a very fine milling of the sample is often necessary in order to achieve a better quantification of the pyritic sulfur, the peak of which is attenuated in the samples which are not finely milled.

This third laboratory method according to the prior art exhibits the following disadvantages:

- it requires a very fine milling of the samples;
- it requires access to a synchrotron, which is a very bulky and very expensive piece of equipment.

The present invention is targeted at overcoming these disadvantages. Thus, the present invention relates to a method for characterizing the sulfur present in a rock sample, by separately quantifying the pyritic sulfur and the organic sulfur, this being achieved in a rapid, simple and accurate way.

The method according to the invention

The invention relates to a method for the quantification of the pyritic sulfur in a sedimentary rock sample, in which at least the following stages are applied:

A. the said sample is heated in an inert atmosphere, between a first temperature of between 100°C and 320°C and a second temperature of between 600°C and 700°C, a first temperature gradient of between 1°C/min and 30°C/min being followed;

B. at least a part of the effluents resulting from the said heating of the said sample in an inert atmosphere is continuously oxidized, a first amount of SO₂ released is measured continuously as a function of the time of the said heating in an inert atmosphere, and at least a content of pyrolysis sulfur S_{Pyrol} and a content of pyrolysis pyritic sulfur S_{Pyrol}^{Pyrit} are determined from the said first amount of SO₂;

C. the residue of the said sample resulting from the said heating in an inert atmosphere is heated in an oxidizing atmosphere between a third temperature of between 280°C and 320°C and a fourth temperature of greater than or equal to 800°C, a second temperature gradient of between 1°C/min and 30°C/min

being followed;

D. a second amount of SO₂ released is continuously measured as a function of the time of the said heating in an oxidizing atmosphere, at least a content of oxidation sulfur S_{oxy} is determined from the said second amount of SO₂, and at least a content of total sulfur S_{Total} is determined by the sum of the said content of pyrolysis sulfur S_{pyrol} and of the said content of oxidation sulfur S_{oxy} .

According to the invention, at least a content of pyritic sulfur S^{Pyrit} contained in the said sample is determined from a formula of the type:

$$S^{Pyrit} = p(\alpha, \beta, \gamma) \cdot S_{Pyrol}^{Pyrit} ,$$

where $p(\alpha, \beta, \gamma)$ is a weighting function depending on a parameter α representing a proportion of the said pyrolysis pyritic sulfur with respect to the said total sulfur, on a parameter β representing an effect of the mineral matrix on the said proportion and on a parameter γ representing an effect of the organic matrix on the said proportion, the values of the said parameters being predetermined.

The said weighting function $p(\alpha, \beta, \gamma)$ is written in the form:

$$p(\alpha, \beta, \gamma) = \frac{(1 + \beta + \gamma)}{\alpha}$$

According to one embodiment of the invention, the said sample is of reservoir rock type and the said first temperature can be between 100°C and 200°C.

According to another embodiment of the invention, the said sample is of source rock type and the said first temperature can be between 280°C and 320°C.

According to the invention, the parameter α is between 0.40 and 0.46 and preferentially has a value of 0.43.

According to an implementational variant of the invention, the said rock sample is of clay type and the parameter β can be between 0.04 and 0.7 and preferentially has a value of 0.38.

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According to another implementational variant of the invention, the said rock sample is of marl type and the parameter β can be between 0.7 and 0.9 and preferentially has a value of 0.78.

10 According to an alternative implementational variant of the invention, the said rock sample is of limestone type and the parameter β can be between 0.85 and 0.97 and preferentially has a value of 0.9.

15 According to the invention, the said rock sample contains an organic matter of lacustrine and/or marine origin and which the parameter γ has a value of 0, or the said rock sample contains an organic material of terrestrial origin and the parameter γ can be between 0.23 and 0.29 and preferentially has a value of
20 0.26.

According to an implementational variant of the invention, the said fourth temperature is between 800°C and 900°C and a content of organic sulfur S^{Org} can be determined according to the
25 formula:

$$S^{Org} = S_{Total} - S^{Pyrit}.$$

According to another implementational variant of the invention,
30 the said fourth temperature is greater than 1150°C and preferentially less than 1250°C, and in addition a content of sulfate sulfurs S_{Oxy}^{Sulfa} can be determined from the said second amount of SO₂, and a content of organic sulfur can be deduced therefrom according to the formula:

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$$S^{Org} = S_{Total} - S^{Pyrit} - S_{Oxy}^{Sulfa}.$$

According to one implementation of the invention, the said

content of pyrolysis sulfur and/or the said content of pyrolysis pyritic sulfur can be determined from the said first amount of SO₂ and from a calibration coefficient of the pyrolysis sulfur established on a reference sample, the sulfur content of which is known, the said reference sample preferably being native sulfur.

According to one implementation of the invention, the said content of oxidation sulfur can be determined from the said second amount of SO₂ and from a calibration coefficient of the oxidation sulfur established on a reference sample, the sulfur content of which is known, the said reference sample preferably being a coal.

Advantageously, it is additionally possible to measure:

- the amounts of hydrocarbon products, of CO and of CO₂ contained in the said effluents resulting from the said heating of the said sample in an inert atmosphere,

- the amounts of CO and of CO₂ contained in the effluents resulting from the said heating in the effluents resulting from the said heating in an oxidizing atmosphere.

Other characteristics and advantages of the method according to the invention will become apparent on reading the description below of nonlimiting implementational examples, with reference to the appended figures described below.

Brief presentation of the figures

- Figure 1a presents an example of a measurement carried out by an SO₂ detector during a heating sequence under an inert atmosphere to which a rock sample is subjected.

- Figure 1b presents an example of a measurement carried out by an SO₂ detector during a heating sequence under an oxidizing atmosphere to which a rock sample is subjected.

- Figure 2 presents curves representative of the amount of SO₂ released by four samples of pure igneous pyrite having distinct weights during a heating sequence under an inert atmosphere.

- Figure 3a presents a histogram representative of the effect of the mineral matrix, as a function of the category of mixtures of minerals which is under consideration.

- Figure 3b presents a histogram representative of the mean effect of clays, carbonates and intermediate formations on the proportion of sulfur of the pyrite released during the pyrolysis as a function of the category of mixtures of minerals which is under consideration.

- Figure 3c presents the change in the effect of the mineral matrix as a function of the mineral carbon.

- Figure 4a presents an assessment of the effect of the organic matrix on the amount of sulfur released by the pyrite during the pyrolysis phase as a function of a first series of categories of pyrite/organic matter mixtures.

- Figure 4b presents an assessment of the effect of the organic matrix on the amount of sulfur released by the pyrite during the pyrolysis phase as a function of a second series of categories of pyrite/organic matter mixtures.

- Figures 5a, 5b and 5c respectively present the change in the content of total sulfur, of pyritic sulfur and of organic sulfur obtained for different rock samples by the method according to the invention as a function of the content of total sulfur obtained for these same samples by a method according to the prior art.

Detailed description of the method

Generally, one of the objects of the invention relates to a method for separately quantifying the pyritic sulfur from the organic sulfur present in a rock sample.

5 The present invention can be applied to any type of sedimentary rock, such as, for example, to a source rock, to a reservoir rock or else to an unconventional source rock. In particular, the present invention is suited to rock samples originating from marine source rocks.

10

Generally, the rock sample can, for example, have been removed by core drilling within an underground formation of interest or else can result from cuttings resulting from a drilling. Advantageously, the sample as withdrawn is prepared (by a washing, a sieving, a sorting, and the like), in order to remove the impurities (drilling sludge, for example, contaminants, and the like) therefrom, and is then milled by hand or with a mechanical grinder.

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20 The method according to the invention is based on the measurement of the sulfur dioxide (SO₂) released by a sample of a rock subjected, in a first step, to a pyrolysis (that is to say, to a heating under an inert atmosphere) and then to an oxidation (that is to say, to a heating under an oxidizing atmosphere).

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The method according to the invention can advantageously but nonlimitingly be carried out by means of the Rock-Eval® device (IFP Energies nouvelles, France), such as described in Patent EP 2 342 557 (US 8 796 035).

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The method according to the invention comprises at least the following stages:

1. Heating sequence under an inert atmosphere (pyrolysis)

35

2. Heating sequence under an oxidizing atmosphere (oxidation)

3. Quantification of the pyritic sulfur.

1. Heating sequence under an inert atmosphere (pyrolysis)

During this stage, the sample under consideration is heated under an inert atmosphere (such as, for example, under a stream of nitrogen or helium) according to a programme of predefined temperatures which can vary over time.

According to one implementation of the invention, this stage is carried out by means of a pyrolysis oven, the sample of interest placed in this oven being flushed with a stream of nonoxidizing gas.

According to the invention, the sample is heated by pyrolysis between a temperature T1 of between 100°C and 320°C and a temperature T2 of between 600°C and 700°C, preferentially 650°C, the rise in temperature following a temperature gradient (or heating rate) of between 1°C/min and 30°C/min, preferentially between 20°C/min and 30°C/min, and very preferentially has a value of 25°C/min. According to one implementation of the invention, according to which the sample analysed is a reservoir rock, the temperature T1 is between 100°C and 200°C and is preferentially 180°C. According to one implementation of the invention according to which the sample analysed is a source rock, the temperature T1 is between 280°C and 320°C and is preferentially 300°C.

According to the invention, at least a part of the pyrolysis effluents are oxidized as they are released. The sulfur gases present in the pyrolysis effluents are thus oxidized to give SO₂. According to one implementation of the invention, this oxidation of the pyrolysis effluents is carried out by means of a combustion chamber, such as an oxidation oven, in the presence of an oxygen-comprising gas and optionally of a catalyst.

According to the invention, the SO₂ thus generated is continuously measured, as the pyrolysis proceeds, by means of an SO₂ detector, such as an ultraviolet (UV) or infrared (IR)

spectrophotometer. A measurement of the SO₂ released during the pyrolysis, as a function of the pyrolysis time and/or temperature, is thus obtained.

5 **2. Heating sequence in an oxidizing atmosphere (oxidation)**

During this second stage, the solid residue of the sample obtained after conclusion of the pyrolysis sequence as described in stage 1 above is subjected to an oxidation according to a
10 program of predefined temperatures which can vary over time.

According to the invention, the sample is heated under an oxidizing atmosphere between a temperature T3 of between 280°C and 320°C, preferentially 300°C, and a temperature T4 of greater
15 than or equal to 800°C, the rise in temperature following a temperature gradient (or heating rate) of between 1°C/min and 30°C/min, preferentially between 20°C/min and 30°C/min, and very preferentially has a value of 20°C/min.

20 According to one implementation of the invention, this stage is carried out by means of an oxidation oven, the pyrolysis residue being flushed with a stream of air.

According to the invention, the SO₂ generated by the oxidation
25 of the pyrolysis residue and contained in the oxidation effluents is continuously measured, that is to say during the heating sequence under an oxidizing atmosphere. The SO₂ measurement is, for example, carried out by means of a UV or IR spectrophotometer. A measurement of the SO₂ released during the
30 oxidation, for example as a function of the oxidation time and/or temperature, is thus obtained.

3. Quantification of the pyritic sulfur

35 On conclusion of the two preceding stages, two curves representative of the SO₂ measurements carried out during stages 1 and 2 as described above are available.

Figure 1a presents an example of a curve (denoted C1) of measurement of the amount of SO₂ (more specifically the amplitude A measured by an SO₂ detector, such as an ultraviolet spectrophotometer) as a function of the pyrolysis time (denoted t), and also presents the change in the pyrolysis temperature (denoted T) as a function of the pyrolysis time. Figure 1b presents an example of a curve (denoted C2) of measurement of the amount of SO₂ (more precisely, the amplitude A measured by an SO₂ detector, such as an ultraviolet spectrophotometer) as a function of the oxidation time (denoted t), and also presents the change in the oxidation temperature (denoted T) as a function of the oxidation time. For this example and for illustrative purposes, the temperature T1 has been chosen equal to 300°C, the temperature T2 has been chosen equal to 650°C, the temperature T3 has been chosen equal to 300°C and the temperature T4 has been chosen equal to 1200°C.

It may be observed that each one of these curves comprises different peaks and is identifiable by the number of these peaks, their peak summit temperature, their shape and their area. In particular, there may be observed, in curve C1, the peak C, which corresponds to the release during the pyrolysis of part of the sulfur contained in the pyrite (subsequently called "pyrolysis pyritic sulfur" and denoted S_{Pyrol}^{Pyrit}). There may be observed, in the curve C2, the peak F, which corresponds to the release of the sulfur contained in the sulfates (subsequently called "sulfate sulfur" and denoted S_{Oxy}^{Sulfa}) during the oxidation. Furthermore, the first two peaks A and B of the curve C1 correspond to the sulfur contained in the thermally labile organic compounds, which are respectively vaporizable and thermally crackable. Also, it may be observed that the curve C2 presents two first peaks D and E which have virtually merged, which respectively correspond to organic sulfur contained in organic compounds, which are thermally refractory or else which have been generated during the pyrolysis phase, and to pyritic sulfur. It is thus found that the recording of the SO₂ released during the oxidation phase does not make it possible to distinguish between these two peaks and thus between the organic

sulfur and the pyritic sulfur.

During this stage, according to the invention, the content of
pyrolysis sulfur S_{Pyrol} released during the pyrolysis, the content
5 of oxidation sulfur S_{Oxy} released during the oxidation of the
pyrolysis residue and the content of pyrolysis pyritic sulfur
 S_{Pyrol}^{Pyrit} released during the pyrolysis are quantified from the
measurements carried out during the heating sequence in an inert
atmosphere and the heating sequence in an oxidizing atmosphere.

10 According to one implementation of the invention, the content
of pyrolysis sulfur S_{Pyrol} (respectively the content of oxidation
sulfur S_{Oxy}) of the sample analysed can be determined from the
area under the curve of measurement of the SO_2 recorded during
15 the pyrolysis-heating sequence (respectively during the
oxidizing heating sequence), divided by the weight of the sample
analysed, weighted by a calibration coefficient for the
pyrolysis sulfur (respectively a calibration coefficient for the
oxidation sulfur). These contents are expressed as percentage
20 by weight, i.e. as weight of pyrolysis sulfur (respectively
oxidation sulfur), divided by the weight of the sample and
multiplied by 100.

25 According to one implementation of the invention, it is possible
to determine the content of pyrolysis pyritic sulfur S_{Pyrol}^{Pyrit} from
the area under the peak representative of the pyrolysis pyritic
sulfur in the curve of measurement of the SO_2 recorded during
the pyrolysis phase (cf. peak C in Figure 1a), divided by the
weight of the sample analysed, weighted by a calibration
30 coefficient for the pyrolysis sulfur. The content of pyrolysis
pyritic sulfur is expressed as percentage by weight, i.e. as
weight of pyrolysis pyritic sulfur, divided by the weight of the
sample and multiplied by 100.

35 According to one implementation of the invention, it is possible
to determine a calibration coefficient for the pyrolysis sulfur
(respectively a calibration coefficient for the oxidation
sulfur) from at least one reference sample, the sulfur content

of which is known, which sample is subjected to a pyrolysis-heating sequence (respectively an oxidizing heating sequence). The calibration coefficient for the pyrolysis sulfur is then determined from the area under the curve of measurement of the SO₂ released by this reference sample during a pyrolysis-heating sequence (respectively during an oxidizing heating sequence), itself divided by the weight of the reference sample. According to one implementation of the invention, the reference sample can be native sulfur for the determination of the calibration coefficient for the pyrolysis sulfur. According to one implementation of the invention, the reference sample can be a coal for the determination of the calibration coefficient for the oxidation sulfur.

According to the invention, the content of total sulfur S_{Total} is additionally determined as the sum of the two contents S_{Pyrol} and S_{Oxy} , i.e.:

$$S_{Total} = S_{Pyrol} + S_{Oxy} ,$$

expressed as percentage by weight (wt.%), i.e. as weight of total sulfur divided by the weight of the sample and multiplied by 100.

According to the invention, the content of pyritic sulfur S^{Pyrit} is determined according to a formula of the type:

$$S^{Pyrit} = p(\alpha, \beta, \gamma) \cdot S_{Pyrol}^{Pyrit}$$

expressed as percentage by weight, i.e. as weight of pyritic sulfur divided by the weight of the sample and multiplied by 100, $p(\alpha, \beta, \gamma)$ being a weighting function dependent on the parameters α , β and γ , these parameters having been determined beforehand, with:

- the parameter α , which represents the proportion of the pyritic sulfur released during the pyrolysis phase with respect to its total sulfur and can be viewed as a degree of thermal

degradation of the pyrite. According to one implementation of the invention, the parameter α is between 0.40 and 0.46 and preferentially has a value of 0.43;

5 - the parameter β , which represents the impact of the mineral matrix on the proportion of the pyritic sulfur released during the pyrolysis phase. This is because the mineral matrix reduces the amount of sulfur of the pyrite released during the pyrolysis phase. According to one aspect of the invention, the parameter
10 β can be between 0.04 and 0.97, as a function of the type of rock from which the sample studied originates. According to one implementation of the invention in which the rock sample studied is of clay type, the parameter β can be between 0.04 and 0.7 and preferentially has a value of 0.38. According to one
15 implementation of the invention in which the rock sample studied is of marl type, the parameter β can be between 0.7 and 0.9 and preferentially has a value of 0.78. According to one implementation of the invention in which the rock sample studied is of limestone type, the parameter β can be between 0.85 and
20 0.97 and preferentially has a value of 0.90;

- the parameter γ , which represents the impact of the organic matrix on the proportion of the pyritic sulfur released during the pyrolysis phase. According to one implementation of the
25 invention, the parameter γ can be between 0 and 0.29, as a function of the type of organic matter. According to one implementation of the invention in which the organic matter present in the rock sample studied is of marine or lacustrine type, the parameter γ has a value of 0 (no significant effect
30 on the degradation of the pyrite during the pyrolysis phase). According to one implementation of the invention in which the organic matter present in the rock sample studied is of terrestrial type, the parameter γ can be between 0.23 and 0.29, and preferentially has a value of 0.26.

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According to one implementation of the invention, the weighting function $p(\alpha, \beta, \gamma)$ can be written in the form:

$$p(\alpha, \beta, \gamma) = \frac{(1+\beta+\gamma)}{\alpha}.$$

4. Quantification of the organic sulfur

- 5 During this stage, which is optional, the content of organic sulfur S^{Org} contained in the rock sample under consideration can be determined from at least the difference between the content of total sulfur S_{Total} and the content of pyritic sulfur S^{Pyrit} .
- 10 According to a first implementational variant of the invention according to which the temperature of the end of oxidation T4 is between 800°C and 900°C, the content of organic sulfur S^{Org} contained in the said sample can be determined according to a formula of the type:
- 15 $S^{Org} = S_{Total} - S^{Pyrit}$

According to a second implementational variant of the invention according to which the temperature of the end of oxidation T4 is between 1150°C and 1250°C, preferentially 1200°C, the content of organic sulfur S^{Org} contained in the sample can be determined in the following way:

- a content of sulfate sulfurs S_{Oxy}^{Sulfa} is quantified from the area under the peak representative of the sulfates sulfur of the curve of measurement of the SO₂ recorded during the oxidation phase, divided by the weight of the sample analysed and weighted by a calibration coefficient for the oxidation sulfur (cf. stage 3 above for the determination of this calibration coefficient);
- 25 - the content of organic sulfur S^{Org} is determined according to a formula of the type:

$$S^{Org} = S_{Total} - S^{Pyrit} - S_{Oxy}^{Sulfa}.$$

- 35 This is because, for this implementational variant, it is possible to distinguish the S_{Oxy}^{Sulfa} peak (cf. peak F in Figure 1a) which corresponds to the release during the oxidation of the sulfur contained in the sulfates, occurring for the high

temperatures. The determination of the content of organic sulfur is more accurate according to this second implementation of the invention.

5 **5. Calibration of the parameters α , β and γ**

According to one implementation of the invention, the parameters α and/or β and/or γ as defined above can be calibrated prior to the implementation of the method according to the invention or
10 else during the implementation of a method according to the invention, for example prior to stage 1, to stage 2 or to stage 3 described above.

- **calibration of the parameter α**

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According to one implementation of the invention, the parameter α can be calibrated by estimating the proportion of the pyritic sulfur released during the pyrolysis phase with respect to the total sulfur from at least one sample of pure igneous pyrite.

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According to one implementation of the invention, a "pure" pyrite can be obtained by cleaning a natural pyrite of its impurities by chemical attacks.

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An example of the calibration of the parameter α is described below. Four samples resulting from a single sample of pure igneous pyrite (respectively denoted E1, E2, E3 and E4), with different weights (respectively 2 mg, 3 mg, 4 mg and 8 mg), are each subjected to a pyrolysis by means of the Rock-Eval® device (IFP Energies nouvelles, France). In particular, for this
30 example of the calibration of the parameter α , each sample was placed in the pyrolysis oven of the Rock-Eval® device and then the sample was heated between 300°C and 650°C, with a temperature gradient of 25°C/min and under a stream of nitrogen at 150 ml/min. The sulfur effluents released by each sample of pure
35 igneous pyrite under consideration were then entrained by the stream of nitrogen to the combustion chamber (oxidation oven) of the Rock-Eval® device, where they were converted into SO₂ in a continuous stream, and then the SO₂ was entrained up to an SO₂

detector, where it was continuously quantified by means of the SO₂ detector of the Rock-Eval® device. The solid residue of each sample of igneous pyrite, obtained on conclusion of the pyrolysis sequence, was subsequently placed in the oxidation oven of the Rock-Eval® device and then the sample was heated between 300°C and 850°C, with a temperature gradient of 20°C/min and under a stream of air at 100 ml/min. The SO₂ effluents released were entrained up to an SO₂ detector, where they were continuously quantified by means of the SO₂ detector of the Rock-Eval® device.

Figure 2 presents the recording, in the time t , of the amount of SO₂ (more precisely the amplitude) released by the samples E1, E2, E3 and E4 during the pyrolysis phase as described above. The curve T, also presented in this Figure 2, corresponds to the change of the temperature to which each of the samples under consideration is subjected during this same pyrolysis phase. It is possible in particular to observe, in this figure, the presence of the peaks representative of the thermal degradation of the pyrite at the different weights analysed during the pyrolysis phase. The content of pyrolysis sulfur of the igneous pyrite sample (content of pyrolysis pyritic sulfur) was calculated by multiplying, by the sulfur content of the reference sample, the area under each of the curves E1, E2, E3 and E4, divided by the weight of the sample, and related back to the area under the curve of measurement of the SO₂ released by a reference sample (such as native sulfur) during the pyrolysis-heating sequence, itself divided by the weight of the reference sample. The ratio of this content of pyrolysis pyritic sulfur to the content of total sulfur of the pyrite (described in stage 3 above) is calculated. The results show that, whatever the mass analysed, the proportion by weight of the pyritic sulfur which is released during the pyrolysis is 0.43 ± 0.03 wt%. The remaining proportion of pyritic sulfur on conclusion of the pyrolysis (0.57 ± 0.03 wt%) is subsequently released during the oxidation phase (stage 2 described above).

Thus, the calibration as described above makes it possible to

determine that the parameter α is between 0.40 and 0.46 and has a value of 0.43 on average.

- **calibration of the parameter β**

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According to one implementation of the invention, the parameter β , which represents the impact of the mineral matrix on the amount of sulfur of the pyrite released during the pyrolysis phase, is calibrated from at least a mixture of pyrite and of
10 at least one type of mineral, this mixture being representative of the rock sample to be studied by the method according to the invention.

An example of the calibration of the parameter β for different
15 types of minerals is described below. For this example of the calibration of the parameter β , mixtures were prepared from the following two main groups of minerals:

- clay/silicate minerals, such as:

20

- silica (Fontainebleau sand, France): the mixture produced with silica is the reference mixture as silica is known to be nonreactive;

- 25 ▪ kaolinite (reference: CMS Kga 1b);

- smectite (reference: Mx80);

- illite (clay from Velay, France): as this sample naturally
30 contains carbonates, it was decarbonated with hydrochloric acid;

- carbonate minerals, such as:

- calcite (France);

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- dolomite (Euguy, Spain);

- siderite (Peru).

The following mixtures are then produced:

- 2 mg of pyrite + 98 mg of each clay/silicate mineral;
- 2 mg of pyrite + 58 mg of each carbonate mineral;
- 2 mg of pyrite + 98 mg of clays (all the clay/silicate minerals in equal parts $\frac{1}{4}$; $\frac{1}{4}$; $\frac{1}{4}$; $\frac{1}{4}$);
- 2 mg of pyrite + 58 mg of carbonates (all the carbonate minerals in equal parts $\frac{1}{3}$; $\frac{1}{3}$; $\frac{1}{3}$);
- 2 mg of pyrite + 58 mg of clays and of carbonates in different proportions, i.e.:
 - 93% of clays and 7% of carbonates;
 - 69% of clays and 31% of carbonates;
 - 51% of clays and 49% of carbonates;
 - 26% of clays and 74% of carbonates.

These different samples are then subjected to stages 1 and 2 as described above by means of the Rock-Eval® device (IFP Energies nouvelles, France). More precisely, each sample is placed in the pyrolysis oven of the Rock-Eval® device and then the sample is heated between 300°C and 650°C, with a temperature gradient of 25°C/min and under a stream of nitrogen at 150 ml/min. According to one implementation of the invention, the sulfur effluents released by each sample are entrained by a stream of nitrogen to the combustion chamber (oxidation oven) of the Rock-Eval® device, where they are converted into SO₂ in a continuous stream, and then the SO₂ is entrained up to the SO₂ detector of the Rock-Eval® device, where it is continuously quantified. The solid residue of each sample obtained after conclusion of the pyrolysis sequence is subsequently placed in the oxidation oven

of the Rock-Eval® device and then the sample is heated between 300°C and 850°C, with a temperature gradient of 20°C/min and under a stream of air at 100 ml/min. The SO₂ effluents released are entrained up to an SO₂ detector where they are continuously
 5 quantified by means of the SO₂ detector of the Rock-Eval® device.

Subsequently, the term "effect of the mineral matrix" is used to describe the quantity which is expressed according to a formula of the type:

10

$$E_{Min} = \frac{S_{Pyrol}^{Pyrit,ref} - S_{pyrol}^{Pyrit,Matrix}}{S_{Pyrol}^{Pyrit,ref}} * 100,$$

15

where $S_{Pyrol}^{Pyrit,ref}$ is the pyrolysis pyritic sulfur released by a reference sample (consisting of pure igneous pyrite and of silica) and $S_{pyrol}^{Pyrit,Matrix}$ is the pyrolysis pyritic sulfur released
 by a mixture under consideration (pure igneous pyrite plus a mineral or a mixture of minerals). In order to evaluate this quantity, the content of pyrolysis pyritic sulfur is determined as described in stage 3 above, this being done for a reference
 20 sample $S_{Pyrol}^{Pyrit,ref}$ and for a mixture under consideration $S_{Pyrol}^{Pyrit,Matrix}$.

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Figure 3a presents a histogram representative of the effect E_{Min} of the mineral matrix as a function of the category of mixtures which are under consideration in the case of clay/silicate and carbonate minerals, more precisely for the following categories of mixtures:

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- M1: mixtures consisting of pyrite and of quartz (reference sample);
- M2: mixtures consisting of pyrite and of kaolinite;
- M3: mixtures consisting of pyrite and of illite;
- 35 - M4: mixtures consisting of pyrite and of smectite;
- M5: mixtures consisting of pyrite and of calcite;

- M6: mixtures consisting of pyrite and of dolomite;
- M7: mixtures consisting of pyrite and of siderite.

5

Figure 3b presents a histogram representative of the mean effect E_{Min} of the clays, the carbonates and intermediate formations on the proportion of sulfur of the pyrite released during the pyrolysis for the following mixtures:

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- M8: mixtures consisting of 100% of clays;
- M9: mixtures consisting of 93% of clays and of 7% of carbonates;
- M10: mixtures consisting of 69% of clays and of 31% of carbonates;
- M11: mixtures consisting of 51% of clays and of 49% of carbonates;
- M12: mixtures consisting of 26% of clays and of 74% of carbonates;

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- M13: mixtures consisting of 100% of carbonates.

Figures 3a and 3b also exhibit the error bars for each histogram bar. These error bars were obtained by estimating a standard deviation established from a repetition of the analyses as described above.

30

Thus, the results obtained by the implementation of the method for calibration of the parameter β as described above for the different mixtures described above demonstrate the fact that the mineral matrix can reduce the proportion of sulfur of the pyrite released during the pyrolysis phase. However, this effect is highly variable according to the type of mineral present. The relative reduction in the proportion of sulfur released by the

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pyrite in pyrolysis varies between 0% and 40% in the presence of clay/silicate minerals and between 60% and 98% in the presence of carbonate minerals (cf. Figure 3a). The mean effect of the clays amounts to 6%, whereas that of the carbonates reaches 93% (cf. Figure 3b). Between these two poles, an increasing change in the effect of the matrix E_M as a function of the share of clays and of carbonates in the mixture is observed (cf. Figure 3b).

Figure 3c shows the change in the effect E_{Min} of the mineral matrix as a function of the mineral carbon (denoted MinC below), which is a parameter which can be measured, for example, with the Rock-Eval® device (IFP Energies nouvelles, France) and which is an indicator of the carbonate content of the mixtures. It can be observed, in this figure, that the MinC varies over a range of between 0 wt% and 12 wt%, which corresponds to a calcite equivalent of between 0 wt% and 100 wt%. By virtue of this parameter, three types of lithologies can be defined: clays, marls and limestones. The region (A) of Figure 3c represents the region of the clays, which have carbonate/calcite equivalent contents of between 0 wt% and 30 wt% ($0 \leq \text{MinC clays} < 3.6 \text{ wt\%}$). In this region of the clayey formations, the effect of the matrix on the amount of sulfur of the pyrite released during the pyrolysis phase varies between 6% and 70%, with a mean of 38%. The region (B) of Figure 3c represents the region of the marls, which have carbonate/calcite equivalent contents of between 30% and 70% ($3.6 \leq \text{MinC marls} < 8.4 \text{ wt\%}$). In this region of the marly formations, the mean value of the effect of the matrix on the amount of sulfur of the pyrite released during the pyrolysis phase varies between 70% and 87%, with a mean of 78%. The region (C) of Figure 3c represents the region of the limestones, which have carbonate/calcite equivalent contents of between 70 wt% and 100 wt% ($8.4 \leq \text{MinC limestones} \leq 12 \text{ wt\%}$). In this region of the limestone formations, the mean value of the effect of the matrix on the amount of sulfur of the pyrite released during the pyrolysis phase varies between 87% and 94%, with a mean of 90%.

Thus, the parameter β varies between 0.06 and 0.94 according to

the type of sedimentary formation, and more precisely, in the case of:

- clays: the parameter β has a value on average of 0.38;
- marls: the parameter β has a value on average of 0.78;
- limestones: the parameter β has a value on average of 0.90.

10 • **calibration of the parameter γ**

According to one implementation of the invention, the parameter γ , which represents the impact of the organic matrix on the amount of sulfur released by the pyrite during the pyrolysis phase, is calibrated from at least one mixture consisting of pyrite and of organic matter representative of that present in the rock sample to be studied. In samples of natural rocks, in particular in source rocks and in reservoir rocks, the pyrite is found in the presence of organic matter.

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An example of the calibration of the parameter γ is described below.

According to one implementation of the invention comprising a stage of calibration of the parameter γ for different types of organic matter, mixtures consisting of pyrite and of different types of organic matter, conventionally denoted:

30 - type I: lacustrine organic matter, such as the Green River shales (Eocene, USA);

- type II: marine organic matter, such as the paper shales of the Paris Basin (Toarcian, France);

35 - type IIS: marine organic matter rich in organic sulfur, such as the Phosphoria Formation (Permian, USA);

- type III: terrestrial organic matter, such as the Calvert

Bluff Formation (Paleocene, USA),

are produced.

5 According to one implementation of the invention, it is possible to produce mixtures such:

- mixture of type A: 2 mg of pyrite + 2 mg of organic matter;
- 10 - mixture of type B: 2 mg of pyrite + 4 mg of organic matter.

These mixtures are representative of a typical composition of the kerogens of sedimentary formations.

15 Subsequently, the term "effect of the organic matrix" refers to the quantity which is expressed according to the following formula:

$$E_{Org} = \frac{S_{Pyrol}^{Pyrit+OM\ obtained} - S_{pyrol}^{Pyrit+OM\ expected}}{S_{Pyrol}^{Pyrit+OM\ expected}} \times 100$$

20 where $S_{Pyrol}^{Pyrit+OM\ obtained}$ is the pyrolysis pyritic sulfur obtained after the analysis of the mixture formed of pyrite and of organic matter (as described in stage 3) and $S_{Pyrol}^{Pyrit+OM\ expected}$ is the expected value of pyrolysis pyritic sulfur of the mixture. This
 25 theoretical reference value is calculated as follows:

- each organic matter sample alone is analysed by means of the Rock-Eval® device (IFP Energies nouvelles, France), in order to quantify its content of pyrolysis pyritic sulfur (as
 30 described in stage 3);

- the pyrite alone is analysed by means of the Rock-Eval® device (IFP Energies nouvelles, France), in order to quantify its content of pyrolysis pyritic sulfur (as described in stage
 35 3);

- the pyrolysis pyritic sulfur of the pyrite and the

pyrolysis pyritic sulfur of the organic matter are added proportionally, as a function of the pyrite/organic matter ratio.

5 Figure 4a presents the effect E_{org} of the organic matrix on the amount of sulfur released by the pyrite during the pyrolysis phase for the mixtures of type A, with:

- 10 - MA1: mixture consisting of 100% of pyrite;
- MA2: mixture consisting of 50% of pyrite and of 50% of organic matter of type I;
- 15 - MA3: mixture consisting of 50% of pyrite and of 50% of organic matter of type II;
- MA4: mixture consisting of 50% of pyrite and of 50% of organic matter of type IIS;
- 20 - MA5: mixture consisting of 50% of pyrite and of 50% of organic matter of type III.

Figure 4b presents the effect E_{org} of the organic matrix on the amount of sulfur released by the pyrite during the pyrolysis
25 phase for the mixtures of type B, with:

- MB1: mixture consisting of 100% of pyrite;
- 30 - MB2: mixture consisting of 30% of pyrite and of 70% of organic matter of type I;
- MB3: mixture consisting of 30% of pyrite and of 70% of organic matter of type II;
- 35 - MB4: mixture consisting of 30% of pyrite and of 70% of organic matter of type IIS;
- MB5: mixture consisting of 30% of pyrite and of 70% of

organic matter of type III.

The results obtained by the implementation of the method for calibration of the parameter γ as described above for the
5 different mixtures described above show that there is virtually no effect of the organic matter as regards the types I, II and IIS. This is because the effect of the organic matter is less than 6% for mixtures of this type (cf. Figures 4a and 4b). However, the organic matter of type III appears to have a
10 significant effect on the amount of sulfur of the pyrite released during the pyrolysis phase (cf. Figures 4a and 4b). This is because the effect of the organic matter of type III is 17% on average in the mixture MA5 and 26% in the mixture MB5, a mixture for which the proportion between pyrite and organic matter is
15 the most representative of that of the kerogens of the majority of sedimentary formations (cf. Figures 4a and 4b).

Thus, the parameter γ varies over a range between 0 and 0.29 according to the type of organic matter present, and more
20 precisely, in the case of an organic matter:

- of type I, II or IIS, γ has a value of 0 (Figures 4a and 4b);
- 25 - of type III, γ is between 0.23 and 0.29 and has a value on average of 0.26 (Figure 4b).

According to one implementation of the invention, the stages 1 and 2 described above can be carried out by means of the Rock-Eval® device (IFP Energies nouvelles, France) developed by the
30 Applicant Company and described in particular in Patent EP 2 342 557 (US 8 796 035). This is because the Rock-Eval® device comprises at least:

- 35 - an oven for pyrolysis in a nonoxidizing atmosphere,
- means for oxidization of the pyrolysis sulfur effluents,

- means for continuous measurement of the amount of SO₂ contained in the said effluents after oxidation,

- means for transfer of the pyrolysis residues into an oxidation oven,

- an oven for oxidation in an oxidizing atmosphere,

- means for continuous measurement of the amount of SO₂ contained in the said part after oxidation.

In addition, this device can also comprise means for measurements of the hydrocarbon compounds released during the pyrolysis and also a means for detection of carbon monoxide (CO) and of carbon dioxide (CO₂).

The method can also be carried out by means of a single pyrolysis oven which can operate in a nonoxidizing atmosphere and in an oxidizing atmosphere, cooperating with a device for detection and measurement of the amount of sulfur dioxide (SO₂).

Application examples

The method according to the invention is applied in a first application example to a series of thirteen samples originating from a rock known under the name Grey Shale Member which is located in the Toarcian of the Whitby Mudstone Formation of the Cleveland sedimentary basin in the United Kingdom. The Grey Shale Member is an interval of marine clays deposited in an oxygenated environment, interbedded with three sedimentary levels rich in sulfur (sulfur bands). These three levels were deposited as sediments in an anoxic (oxygen-free) to euxinic (deeper, oxygen-free and under a depth of water rich in sulfides) environment.

The method according to the invention is also applied in a second application example to a sample originating from a rock known under the name Black Band, which is also a clayey interval of

the Toarcian of the Whitby Mudstone Formation.

The method according to the invention is applied in a third application example to a series of eight samples originating from a rock known under the name Kimmeridge Clay Formation of the Wessex-Channel sedimentary basin in Dorset in the United Kingdom. The interval studied, of Kimmeridgian-Tithonian age, consists of an alternation of clays, marls and limestones.

10 The pyritic sulfur and the organic sulfur present in these samples are determined according to the method as described above by means of the Rock-Eval® device (IFP Energies nouvelles, France). More precisely, each sample is placed in the pyrolysis oven of the Rock-Eval® device and then the sample is heated
15 between 300°C and 650°C, with a temperature gradient of 25°C/min and under a stream of nitrogen at 150 ml/min. According to one implementation of the invention, the sulfur effluents released by each sample are entrained by a stream of nitrogen to a combustion chamber (also known as oxidation oven) of the Rock-Eval® device, where they are converted into SO₂ in a continuous stream, and then the SO₂ is entrained up to the SO₂ detector of the Rock-Eval® device, where they are continuously quantified. After conclusion of the pyrolysis, each sample residue is transferred from the pyrolysis oven to the oxidation oven of the
25 Rock-Eval® device and then the sample is heated between 300°C and 850°C or 1200°C according to the implementation, with a temperature gradient of 20°C/min and under a stream of air at 100 ml/min. The SO₂ effluents released by this oxidation are entrained up to the SO₂ detector of the Rock-Eval® device, where
30 they are continuously quantified. The content of pyritic sulfur and the content of organic sulfur of each rock sample analysed are deduced by the use of the method according to the invention. They are then compared with those obtained with the method of the elemental analysis of kerogen as described above (by ICP-AES for the iron and by infrared spectroscopy for the sulfur),
35 known as method according to the prior art subsequently.

Figures 5a, 5b and 5c respectively present the change in content

of total sulfur, of pyritic sulfur and of organic sulfur for each of the samples of the first application example EX1 (i.e., the 13 samples of the Grey Shale Member), for the sample of the second application example EX2 (i.e., the sample of the Black Band) and for each of the samples of the third application example EX3 (i.e., the 8 samples of the Kimmeridge Clay Formation) obtained by the method according to the invention INV, as a function of the content of total sulfur obtained for these same samples by the method according to the prior art AA.

There may be observed, in Figure 5a, a very good correlation between the contents of total sulfur determined from the method according to the invention and by the method according to the prior art (correlation with a slope close to 1), confirming the validity of the determination of the content of total sulfur of a sample by the method according to the invention.

Likewise, there may be observed, in Figure 5b, a very good correlation between the contents of pyritic sulfur, determined from the method according to the invention and by the method according to the prior art (correlation with a slope close to 1), confirming the validity of the determination of the content of pyritic sulfur by the method according to the invention.

Figure 5c shows a poorer correlation line as regards the content of organic sulfur determined by the method according to the invention and by the method according to the prior art. In point of fact, in the method according to the invention, the content of organic sulfur is entirely deduced from the contents of total and pyritic sulfur determined by the method according to the invention (cf. stage 3 above), the values of which are themselves valid (cf. discussion relating to Figures 5a and 5b above). This lack of correlation can be linked to the fact that the samples selected predominantly have a low content of organic sulfur. This is because the content of organic sulfur of the samples selected is predominantly between 0 wt% and 1 wt% (values of the prior art) or between 0 wt% and 3 wt% (values obtained by the method according to the invention) (Figure 5c). Thus, it is

possible that the contents of organic sulfur obtained here are of the order of magnitude of the measurement error of each of the methods. This is because a repetition of the analyses carried out by means of the method according to the invention for
5 different samples shows that the standard deviation with regards to the measurement is, on average, 0.1 wt% for the total sulfur and 0.2 wt% for the pyritic and organic sulfur. Furthermore, a repetition of the analyses carried out by means of the method according to the prior art shows that the standard deviation
10 with regard to the measurement is, on average, 0.1 wt% for the total sulfur, 0.5 wt% for the pyritic sulfur and 0.6 wt% for the organic sulfur. It is thus found that the method according to the prior art appears to be less accurate than the method according to the invention. This can be explained by the fact
15 that the prior art combines two different techniques (ICP-AES and infrared spectroscopy) and thus two possible sources of error and by the fact that this prior art is based on the assumption that all the iron contained in the organic matter is pyritic. In point of fact, if the iron contained in the organic
20 matter is also found in other forms, such as oxides or sulfides other than pyrite, then the content of pyritic sulfur is overestimated and the content of organic sulfur is underestimated. Conversely, the method according to the invention employs only a single type of measurement (measurement
25 of the SO₂ released by a sample) and is based on a total distinction between the pyritic sulfur and the organic sulfur during the pyrolysis phase. Thus, the method according to the invention is less uncertain than the prior art.

30 Furthermore, the method according to the invention is faster since the implementation of the method according to the invention on, for example, the 13 samples of the Grey Shale Member, an application example described above, took place in approximately 15 hours for the 13 samples, whereas the
35 implementation of the method according to the prior art on the same application example took place in approximately 7 days.

Patentkrav

1. Fremgangsmåde til kvantificering af pyritsvovl i en prøve af sedimentær bjergart, hvorved i det mindste de følgende trin anvendes:

A. prøven opvarmes i en inert atmosfære mellem en første temperatur på mellem 100 °C og 320 °C og en anden temperatur på mellem 600 °C og 700 °C ifølge en første temperaturgradient på mellem 1 °C/min og 30 °C/min

B. der oxyderes kontinuerligt i det mindste en del af udløbene fra opvarmningen af prøven i en inert atmosfære, der måles kontinuerligt en første mængde frigivet SO₂ som funktion af tiden for opvarmningen i en inert atmosfære, og der bestemmes i det mindste et indhold af pyrolysesvovl S_{Pyrol} og et indhold af pyrolyse-pyritsvovl

S_{Pyrit}^{Pyrit}

ud fra den første mængde SO₂

C. resten af prøven fra opvarmningen i en inert atmosfære opvarmes i en oxiderende atmosfære mellem en tredje temperatur på mellem 280 °C og 320 °C og en fjerde temperatur, der er større end eller lig med 800 °C, ifølge en anden temperaturgradient på mellem 1 °C/min og 30 °C/min

D. der måles kontinuerligt en anden mængde frigivet SO₂ som funktion af tiden for opvarmningen i en oxiderende atmosfære, der bestemmes i det mindste et indhold af oxidationssvovl S_{Oxy} ud fra den anden mængde SO₂, og der bestemmes i det mindste et samlet svovlindhold S_{Total} som summen af indholdet af pyrolysesvovl S_{Pyrol} og indholdet af oxidationssvovl S_{Oxy} ,

kendetegnet ved, at der bestemmes i det mindste et indhold af pyritsvovl S_{Pyrit}^{Pyrit} indeholdt i prøven ved hjælp af en formel af typen:

$$S_{Pyrit}^{Pyrit} = \rho(\alpha, \beta, \gamma) \cdot S_{Pyrol}^{Pyrit},$$

hvor $\rho(\alpha, \beta, \gamma)$ er en vægtningsfunktion, der afhænger af en parameter α , som angiver en andel af pyrolyse-pyritsvovlet i forhold til det samlede svovl, af en parameter β , som angiver en virkning af mineralmatrixen på forholdet, af en parameter γ , som angiver en virkning af den organiske matrix på andelen, idet værdierne af disse parametre er forud bestemt,

hvilken vægtningsfunktion $\rho(\alpha, \beta, \gamma)$ skrives i formen:

$$p(\alpha, \beta, \gamma) = \frac{(1 + \beta + \gamma)}{\alpha}$$

og hvorved:

- i) parameteren α ligger mellem 0,40 og 0,46 og fortrinsvis har værdien 0,43, og
- ii) parameteren β ligger mellem:
 - 0,04 og 0,7 og fortrinsvis har værdien 0,38, hvis bjergartsprøven er af lertypen, eller
 - 0,7 og 0,9 og fortrinsvis har værdien 0,78, hvis bjergartsprøven er af mergeltypen, eller
 - 0,85 og 0,97 og fortrinsvis har værdien 0,9, hvis bjergartsprøven er af kalktypen, og
- iii) parameteren γ :
 - har værdien 0, hvis bjergartsprøven indeholder et organisk stof af flod-og-sø-oprindelse og/eller marin oprindelse, eller
 - ligger mellem 0,23 og 0,29 og fortrinsvis har værdien 0,26, hvis bjergartsprøven indeholder organisk stof af terrestrisk oprindelse.

2. Fremgangsmåde ifølge krav 1, hvorved prøven er af typen reservoirstejn, og hvorved den første temperatur ligger mellem 100 °C og 200 °C.

3. Fremgangsmåde ifølge krav 1, hvorved prøven er af typen kildestejn, og hvorved den første temperatur ligger mellem 280 °C og 320 °C.

4. Fremgangsmåde ifølge et af de foregående krav, hvorved den fjerde temperatur ligger mellem 800 °C og 900 °C, og hvorved der bestemmes et indhold af organisk svovl S^{Org} ifølge formlen:

$$S^{Org} = S_{Total} - S^{Pyrit}.$$

5. Fremgangsmåde ifølge et af kravene 1 til 3, hvorved den fjerde temperatur er højere end 1150 °C og fortrinsvis lavere end 1250 °C, og hvorved der ydermere bestemmes et indhold af sulfatsvovl

$$S_{Oxy}^{Sulfa}$$

ud fra den anden mængde SO₂, og der udledes et indhold af organisk

svovl derfra ifølge formelen:

$$S^{Org} = S_{Total} - S^{Pyrit} - S_{Oxy}^{Sulfa}.$$

- 5 6. Fremgangsmåde ifølge et af de foregående krav, hvorved indholdet af pyrolysesvovl og/eller indholdet af pyrolysepyritsvovl bestemmes ud fra den første mængde SO₂ og ud fra en kalibreringskoefficient for pyrolysesvovl, der fastsættes på en referenceprøve, hvis svovlindhold er kendt.
- 10 7. Fremgangsmåde ifølge krav 6, hvorved referenceprøven er nativt svovl.
- 15 8. Fremgangsmåde ifølge et af de foregående krav, hvorved indholdet af oxidationssvovl bestemmes ud fra den anden mængde SO₂ og ud fra en kalibreringskoefficient for oxidationssvovl, der fastsættes på en referenceprøve, hvis svovlindhold er kendt.
- 20 9. Fremgangsmåde ifølge krav 8, hvorved referenceprøven er et kul.
10. Fremgangsmåde ifølge et af de foregående krav, hvorved det følgende i øvrigt måles:
 - mængderne af carbonhydridprodukter, af CO og af CO₂, der er indeholdt i udløbene fra opvarmningen af prøven i en inert atmosfære
 - 25 - mængderne af CO og CO₂, der er indeholdt i udløbene fra opvarmningen i en oxiderende atmosfære.

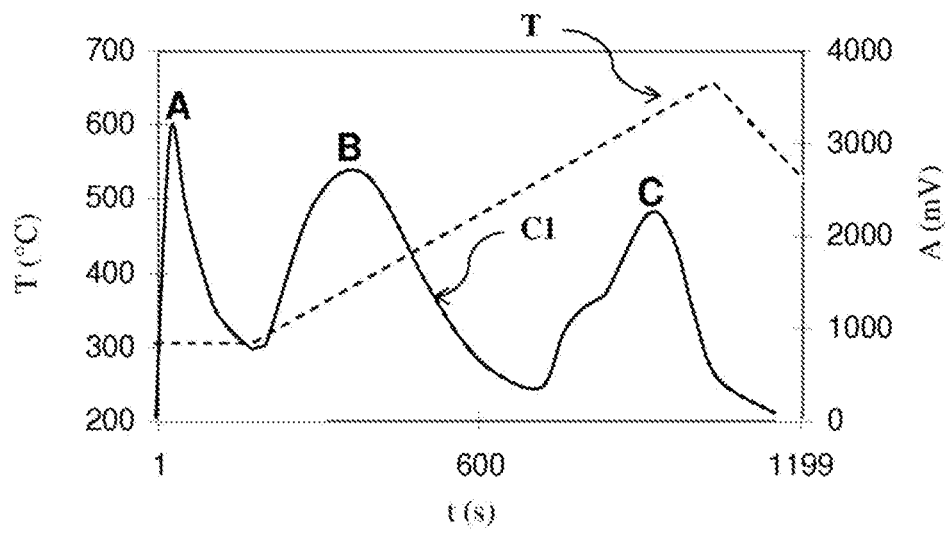


Figure 1a

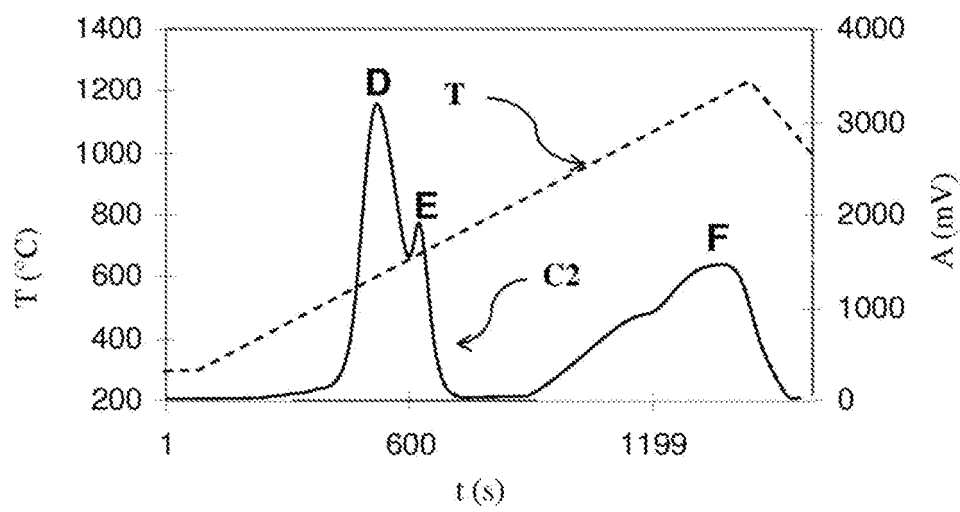


Figure 1b

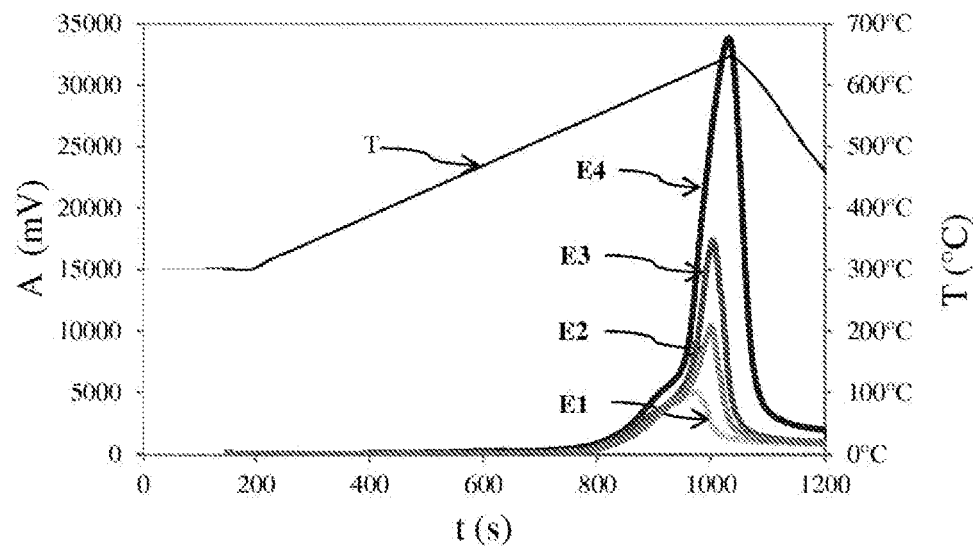


Figure 2

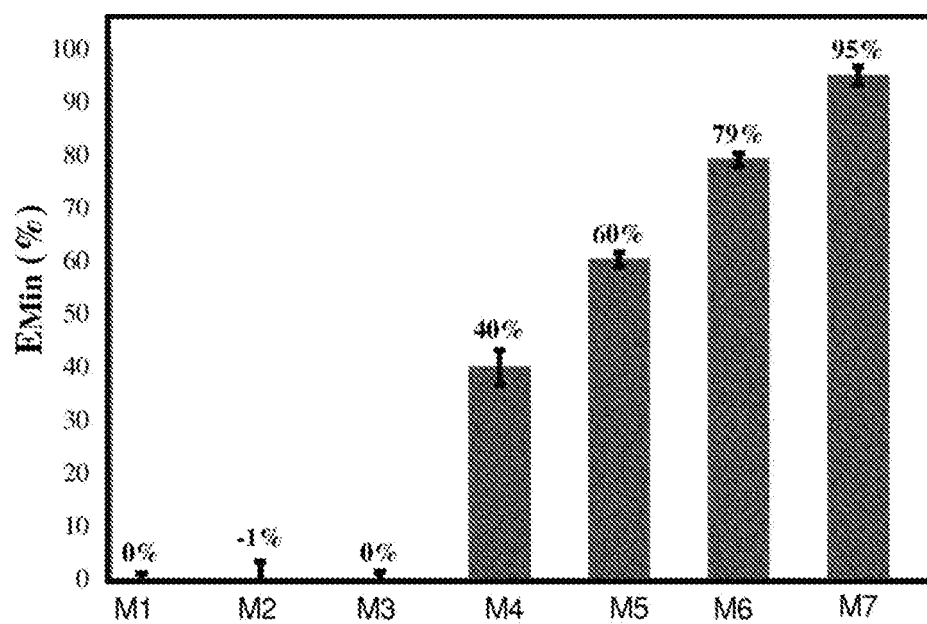


Figure 3a

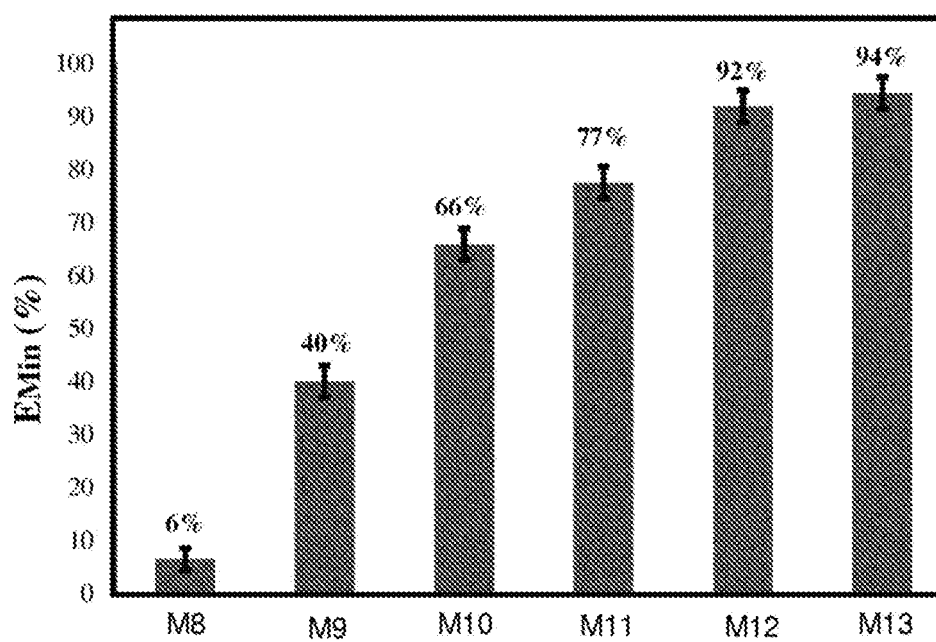


Figure 3b

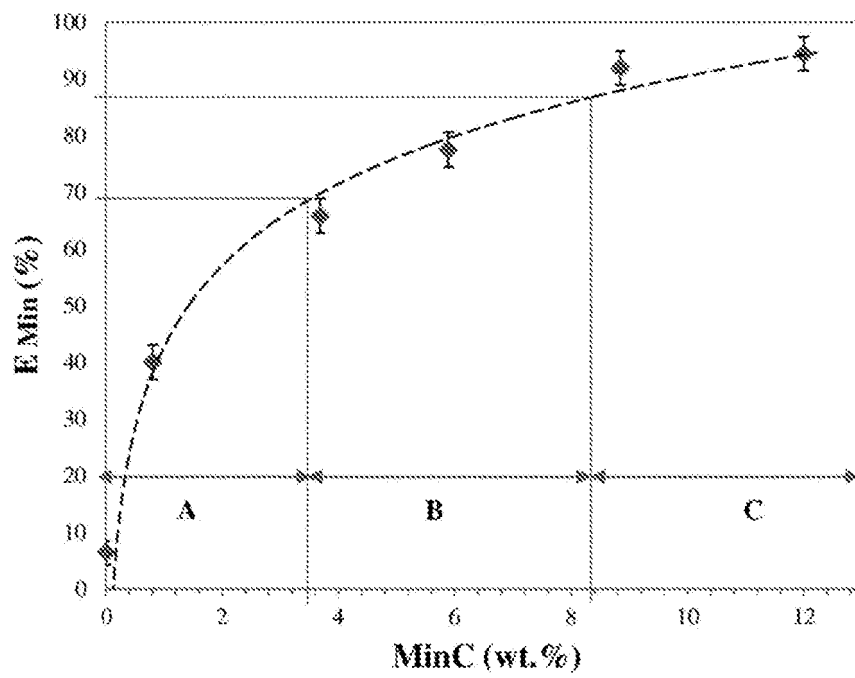


Figure 3c

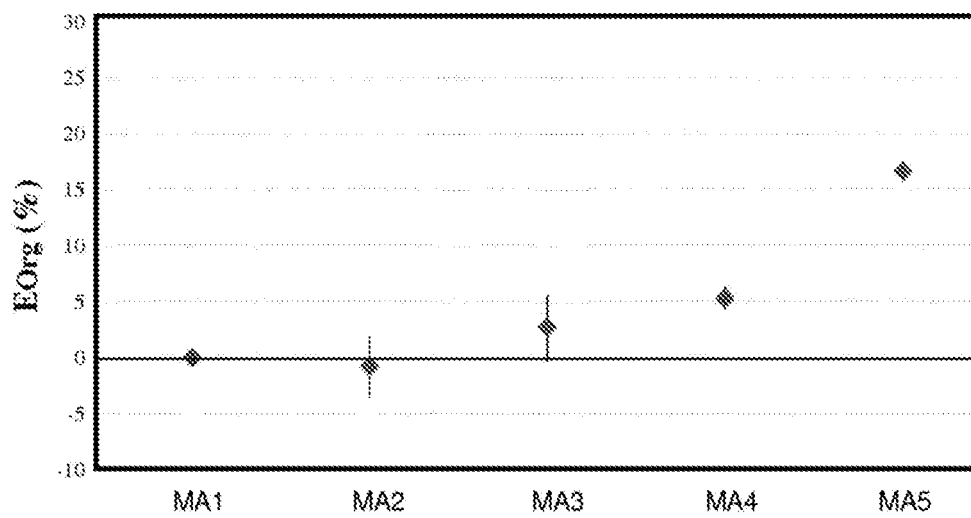


Figure 4a

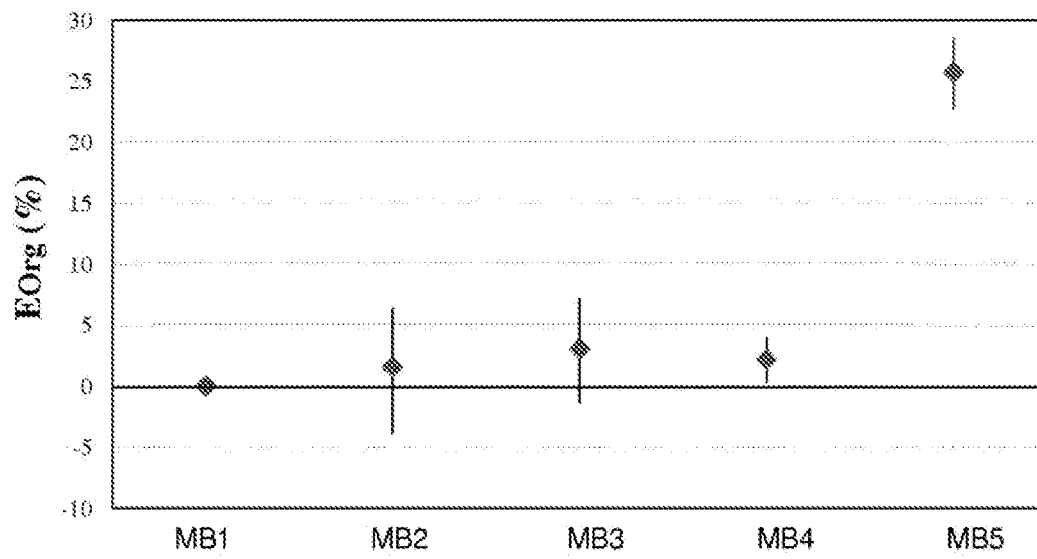


Figure 4b

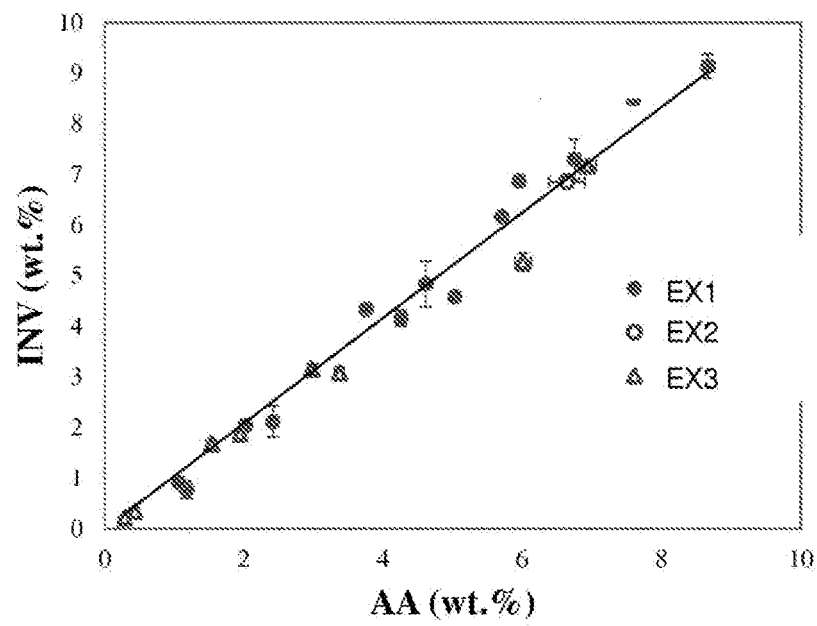


Figure 5a

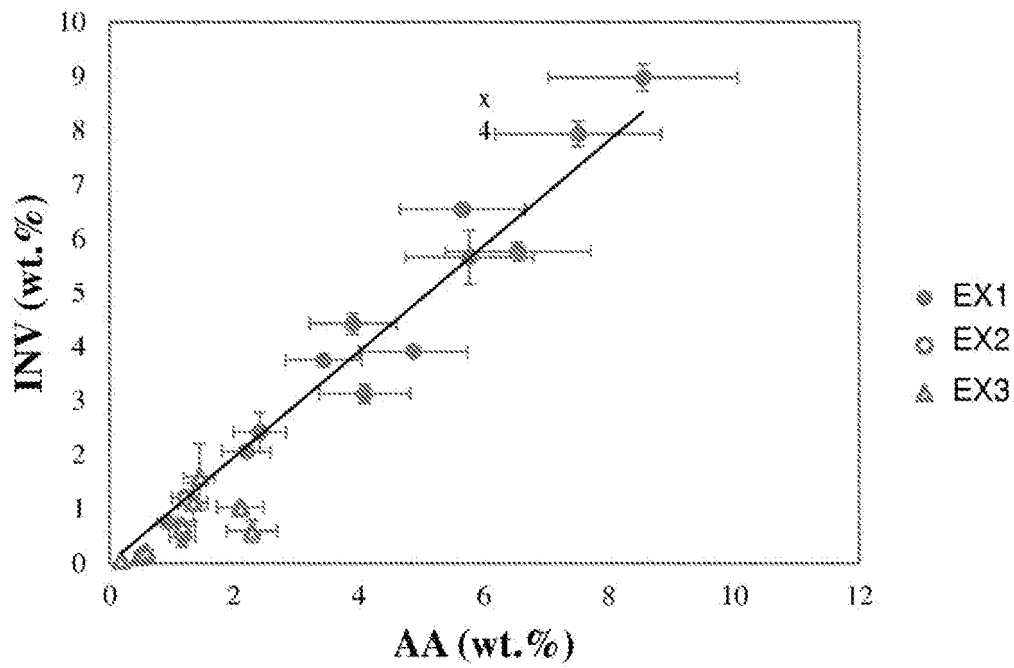


Figure 5b

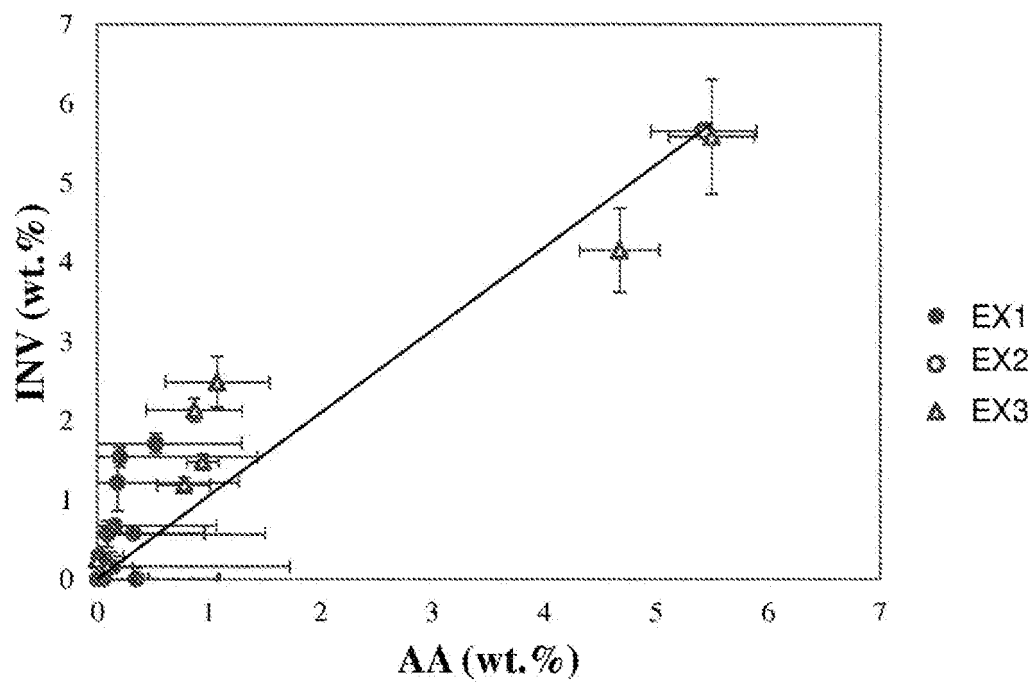


Figure 5c