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(54) **Title**: EQUIPMENT FOR IDENTIFYING MERCURY SPECIES IN SOLIDS

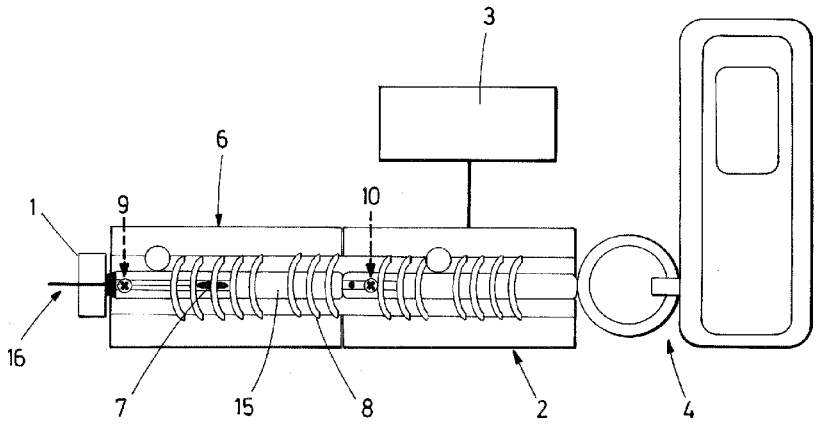

FIG.2

(57) **Abstract**: The analytical device comprises an solid inlet (1) for the solid sample, a commercial oven (2), an analyzer (4) and a control unit (5). It also comprises a laboratory-assembled oven (additional oven) (6) comprising two chambers, a first chamber (7) connected to the solid inlet (1) for the solid sample and a second chamber (8) connected to the commercial oven (2). The equipment is fitted with a first gas inlet (9) for inert gas, that is located in the additional oven (6), and a second gas inlet (10) for air or oxygen, located in the commercial oven (2). The equipment also comprises three temperature controllers; a first temperature controller (3) in the commercial oven (2), a second temperature controller in the first chamber (7) and a third temperature controller in the second chamber (8). The equipment allows analysis of solid samples.

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EQUIPMENT FOR IDENTIFYING MERCURY SPECIES IN SOLIDS

DESCRIPTION

OBJECT OF THE INVENTION

The present invention comes within the technical field of analysis of mercury species in solid samples.

The equipment described allows the mercury species to be identified in products derived from the combustion and conversion of coal and any fuel which has carbonaceous material, in general, any solid contaminated with mercury.

BACKGROUND OF THE INVENTION

The identification and quantification of organic and inorganic compounds of mercury in samples is currently a very important field of study since it is a highly contaminating chemical element which may also be very harmful for human beings.

In order to carry out this determination, several techniques with their corresponding advantages and disadvantages are available. For example, x-ray absorption spectroscopy, which is based on the different absorption of atoms as a function of neighboring atoms. With this technique, characteristic spectrums of each compound can be obtained, but low detection limits are not reached. In addition, in many cases, this method is subject to interferences and the treatment of data is complex.

Alternatively the sequential chemical extraction technique can be used. This allows the mercury species to be separated as a function of their solubility in different sequentially arranged solvents. The technical problems associated with this technique are a result of the fact that a) it has a low selectivity as the complete extraction of each fraction depends on time, b) no distinction is made between the mercury species and c) it is a tedious method that entails numerous sources of uncertainty.

Another known technique for identifying mercury species is thermal desorption which is the method upon which the present invention is based. This technique is generally used for determining the total mercury content in solids rather than for identifying mercury species. Identifying the mercury species is carried out as a function of the desorption temperature thereof such that when the desorption is carried out under controlled temperature, temperature peaks characteristic of each compound are obtained. This method has been used to identify mercury compounds in different types of samples, such as contaminated soils, sediments and airborne particulate matter. In

order to be able to identify the mercury compounds, it is necessary to prepare several reference samples of mercury compounds from which a database is created establishing a temperature peak to each mercury compound present in the solids.

From the state of the art, document US5882381 describes a thermal desorption procedure and system for treating solid residues containing mercury. Thermal desorption is carried out on the contaminant elements and the process takes place in an atmosphere of inert gas. This is designed for continuous solid waste treatment.

US7048779 also describes a method and equipment for removing mercury from a coal fired power plant exhaust gas. The equipment comprises a bulk particle filter to remove coarse particles, followed by the introduction of powdered activated carbon which is separated from the exhaust gas in a fine particle filter to enable subsequent elevated temperature desorption to separate the mercury and inert gas from the powdered activated carbon.

In the document US2012205533, a system and a method are described for quantitatively measuring multiple types of heavy metals which include mercury or other toxic contaminants through concentration on a collection interface, desorption and analysis by mass spectrometry. The samples which can be analyzed with this system and this method are water, air, liquid, ice and snow.

The currently used systems that are based on thermal desorption for identifying mercury species in solid samples have the following associated technical problems:

- they can not be used with coal and carbonaceous samples,
- it is necessary to optimize the variables which affect the widening or overlapping of peaks,
- it is necessary to eliminate possible interferences (the high concentration of organic matter in the samples may interfere with the signal obtained).

DESCRIPTION OF THE INVENTION

The present invention describes an equipment for identifying mercury species in solids that avoids the technical problems generally associated with state-of-the-art thermal desorption equipments.

The equipment for identifying mercury species in solids comprises at least one solid inlet for the solid sample, two ovens with temperature control, one analyzer and a control unit for processing all the data obtained including mercury signal, temperatures, flow rates, etc. The equipment comprises a commercial oven, and an additional oven consisting of two chambers: a first chamber in which the solid sample is placed to

undergo decomposition at a controlled temperature, and a second chamber connected to the commercial oven, to avoid loss of heat. Both chambers may be surrounded by a, for instance, 0.65 mm (Ø) resistance wire which allows high temperatures to be reached quickly and avoids oxidation problems. Each one of the wires is connected to a corresponding temperature controller which allows the first chamber and the second chamber to heat at different temperatures. Similarly, the equipment comprises a first gas inlet through which an inert gas is introduced into the equipment and which is connected to the additional oven. The equipment also comprises a second gas inlet through which air or oxygen is introduced and which is connected to the commercial oven.

The equipment has a temperature controller in the first chamber of the additional oven, which is the element responsible for regulating the temperature ramps applied to the solid sample, and another temperature controller in the second chamber, which is responsible for regulating the temperature so that an appropriate heat transfer is produced, maintaining the temperature between the additional oven and the commercial oven and thus avoiding losses in the recording of the mercury signal.

The equipment allows mercury species to be identified in carbonaceous matrices without interferences resulting from the presence of organic matter with the signal collected in the mercury detector. It is also possible to evaluate the influence of different heating ramps on the sensitivity and selectivity of the desorption curves obtained for the pure mercury compounds.

The inclusion of the additional oven formed by two chambers makes easier to vary the number and type of applicable temperature ramps.

In the additional oven, the desorption of mercury (i.e. is the release of the mercury species) takes place. This additional oven is connected not only to the solid inlet for the sample, which is introduced inside a quartz boat, but also to the first gas inlet, through which an inert carrier gas is introduced, preferably Ar or N_2, so the desorption takes place without any transformation. In order to control the additional oven, a control program that allows the generation of temperature curves between 25 and 700 °C is employed. Breaking down the mercury species at a controlled temperature allows each type of mercury to be correlated with its characteristic desorption temperature.

When the mercury species is released from the solid without having undergone any transformation, it passes to the commercial oven, to which the second gas inlet (through which air or oxygen enters) is connected. As an example in one case, the

temperature of the commercial oven is fixed at 800 °C. The organic compounds of the sample are burned in the commercial oven and the oxidized mercury is reduced to Hg^0 which then passes to the mercury analyzer where it is measured. In the commercial oven, a total breakdown of the sample takes place for mercury determination.

One problem that may arise from the arrangement of the components described is the entrainment of the mercury species in a nitrogen flow inside the commercial oven. This may cause errors in the quantitative determination of the mercury, due to the mercury species reacting with some component of the equipment, producing corrosion and analytical errors. In order to solve this problem, the equipment of the invention contains an internal tube, preferably made of quartz, which passes through the additional oven and the commercial oven and connects them. In addition, this internal tube avoids corrosion and losses of mercury during the analysis.

Another technical problem to be solved is the control of the transfer of heat from the additional oven to the commercial oven since the heat transfer may not be homogeneous. This is solved by installing another temperature controller in the second chamber of the additional oven. This second temperature controller is connected to the first chamber of the additional oven and to the commercial oven to ensure that the heat transfer between them is controlled.

The second gas inlet, through which oxygen or air is introduced, is located inside the quartz tube in the commercial oven to prevent the loss of mercury and to allow a proper quantitative analysis of the sample.

Another problem to be solved is to ensure that the equipment is versatile and allows an accurate, simple and quick analysis of the mercury species. More specifically to ensure a quick functioning of the equipment, a fan has been installed inside the additional oven to reduce the waiting time of the analysis from 5 hours to 3 hours.

With this equipment, the signal can be broken down into several, well differentiated peaks, improving the selectivity of the thermal desorption techniques while allowing more mercury species to be identified than would be possible identifiable with the state-of-the-art devices.

In addition, the equipment for identifying mercury species in solids of the present invention can be used to analyze any type of solid samples and in particular r the products and sub-products derived from the combustion and conversion of coal. Good results are also obtained when analyzing any type of fuel that contains carbonaceous material. The ability to identify the mercury species present in the

different solids of a thermal power plant makes it possible to predict mercury behavior during the process and to assess the risk of the residues and sub-products generated.

Also, with the equipment of the present invention, solids used as mercury sorbents in energy production processes can be examined, which is of paramount importance bearing in mind that the combustion of coal is one of the principal sources of emission of mercury into the environment.

The equipment may also be used for analyzing any solid contaminated by mercury since the fate, the transport and the bioavailability of mercury are dependent on the species present.

DESCRIPTION OF THE DRAWINGS

As a complement to the description and to provide a better understanding of the characteristics of the invention, a set of drawings for illustration are included:

Figure 1 shows a complete view of the equipment of the present invention.

Figure 2 shows a detailed view of the chambers and the ovens.

Figure 3a shows an example of the results obtained from identifying mercury species in a solid sample of coal with an state-of-the-art equipment.

Figure 3b shows an example of the results obtained from identifying mercury species in a solid sample of coal by means of the equipment of this invention.

PREFERRED EMBODIMENT OF THE INVENTION

A detailed description of the present invention is provided below with the aid of Figures 1 to 3.

The proposed equipment for identifying mercury species in solid samples uses the technique of thermal desorption. For this purpose, the equipment comprises at least one solid inlet (1) for the solid sample, a commercially available oven (2) connected to a first temperature controller (3), a mercury analyzer (4) and a control unit (5).

In order to obtain the optimum results for identifying mercury species, the equipment also comprises an additional oven (6) which comprises a first chamber (7) and a second chamber (8) arranged one after the other. This additional oven (6) is connected with the first chamber (7) to the solid inlet (1) for the solid sample and with the second chamber (8) to the commercial oven (2). As has been previously described, the additional oven allows the sample to be subjected to a wider range of temperatures resulting in a larger number and types of curves. This facilitates the correlation of the

mercury species with the specific desorption temperature and enhances the accuracy of the results.

The equipment also comprises two gas inlets, namely a first gas inlet (9), through which an inert gas passes, and which is located in the additional oven (6) and a second gas inlet (10), through which air or oxygen passes, and which is located in the commercial oven (2). The inert gas is used for the desorption of the mercury from the sample in the additional oven (6), avoiding possible interferences while oxygen is used to completely break down the sample in the commercial oven (2).

The equipment is also equipped two further temperature controllers, namely a second temperature controller (11) in the first chamber (7) of the additional oven (6) and a third temperature controller (12) in the second chamber (8) of the additional oven (6).

Additionally, the equipment may comprise a gas station (13) with connections to the two gas inlets (9, 10) and with two gas flow controllers (14) for each connection to the gas inlets (9, 10).

In order to avoid possible mercury leaks when it passes from the additional oven to the commercial oven, the equipment has an internal tube (15) which passes through the additional oven (6) to the commercial oven (2) forming a continuous connection of the commercial oven (2) and the additional oven (6) to each other. Thus the mercury passes through the tube without any leaks or corrosion inside the ovens (6, 2). The internal tube (15) is preferably made of quartz which is a material that resists high temperatures.

Additionally, the equipment can comprise an O-ring configured for sealing the joint between the additional oven and the commercial oven by way of the internal tube (15) which avoids the loss of mercury as it passes from the additional oven (6) to the commercial oven(2). Thus the entire sample is burned well and the mercury species are identified and the total concentration of mercury determined.

In the solid inlet (1) for the solid sample, a sample holder with a thermocouple (16) is configured for continuously measuring the temperature of the sample.

Figures 3a and 3b show the results obtained from the identification of mercury species in a solid sample of coal using equipment of the state of the art (the result is shown in Figure 3a) and using the equipment of this invention (the result is shown in Figure 3b). As can be observed, the data obtained with the equipment of the state of the art are less accurate and less selective. The equipment of the state of the art has not allowed various mercury species to be identified due to the overlapping of signals in

one single peak. In contrast, the equipment of the present invention has led to an increase in the accuracy and selectivity of the results, allowing different mercury species to be identified (shown in the graph in the form of two different temperature peaks).

CLAIMS

1. Equipment for identifying mercury species in solids by means of thermal desorption, the equipment comprising at least:

- one solid inlet (1) for the solid sample,

-one commercial oven (2) with a first temperature controller (3) of the commercial oven (3),

- one analyzer (4),

- one control unit (5) configured for controlling the equipment,

and the equipment being characterized in that it comprises:

- an additional oven (6) which comprises a first chamber (7) and a second chamber (8) arranged one after the other and which is connected via the first chamber (7) to the solid inlet (1) for the solid sample and via the second chamber (8) to the commercial oven (2),

- two gas inlets (9, 10) in:

  - a first gas inlet (9), through which an inert gas passes, is arranged in the additional oven (6) and

  - a second gas inlet (10), through which air or oxygen passes, is arranged in the commercial oven (2),

- a second temperature controller (11) arranged in the first chamber (7) of the additional oven (6),

- a third temperature controller (12) arranged in the second chamber (8) of the additional oven (6).

2. The equipment for identifying mercury species in solids according to claim 1, characterized in that it further comprises a gas station (13) which comprises connections to the two gas inlets (9, 10) and which comprises also two gas flow controllers (14) for each connection to the gas inlets (9, 10).

3. The equipment for identifying mercury species in solids according to any one of the preceding claims, characterized in that it comprises an internal tube (15) which passes through the additional oven (6) to the commercial oven (2) and connects them to each other.

4. The equipment for identifying mercury species in solids according to any one of the preceding claims, characterized in that the internal tube (15) is made of quartz.

5. The equipment for identifying mercury species in solids according to any one of the preceding claims, characterized in that it additionally comprises an O-ring configured for sealing the joint between the additional oven and the commercial oven via the quartz tube (15).

6. The equipment for identifying mercury species in solids according to claim 3, characterized in that the second gas inlet (10) is connected directly to the internal tube (15).

7. The equipment for identifying mercury species in solids according to any one of the preceding claims, characterized in that it comprises, in the inlet for the solid sample (1), a sample holder with a thermocouple (16) configured for continuously measuring the temperature of the sample.

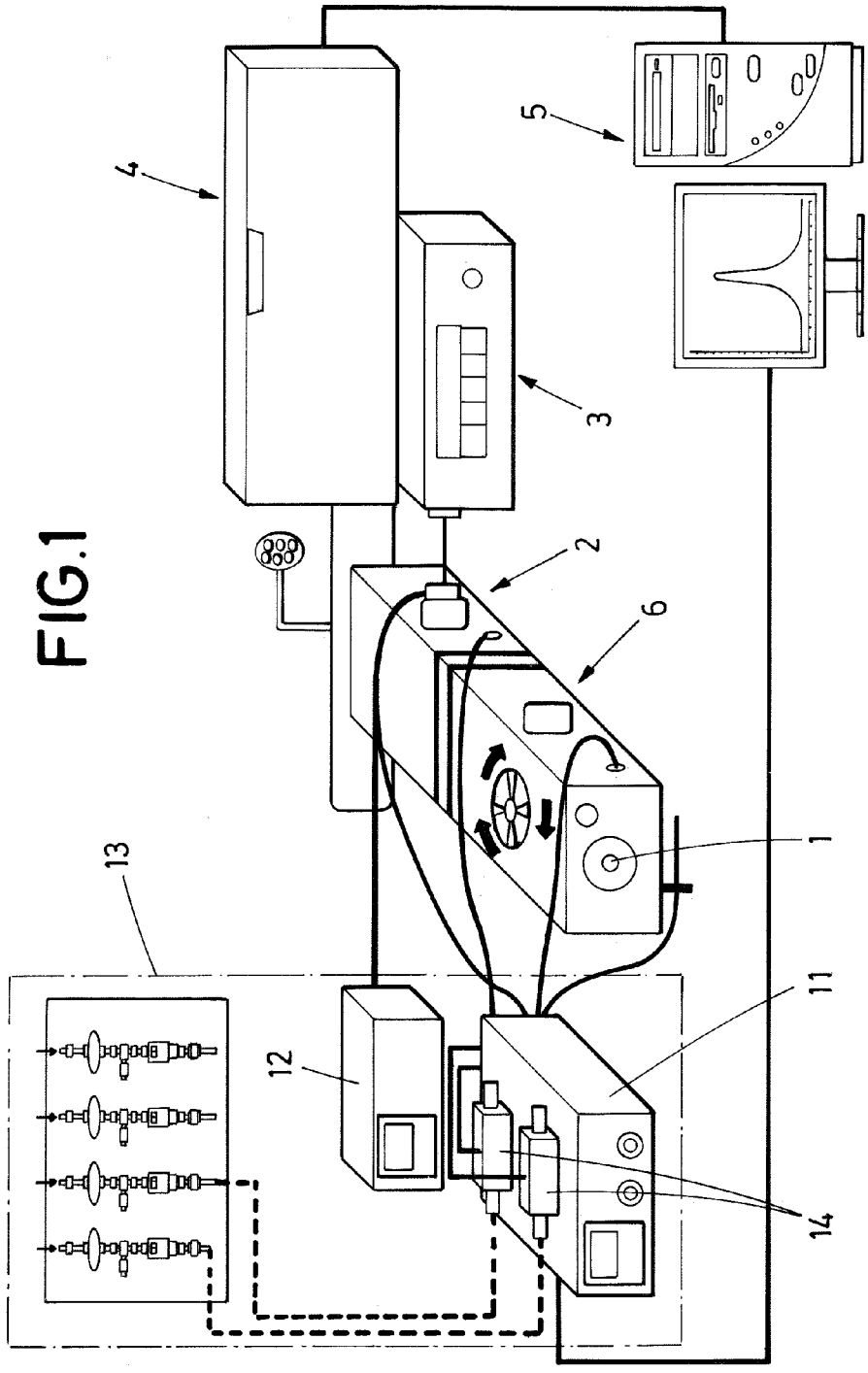

FIG.1

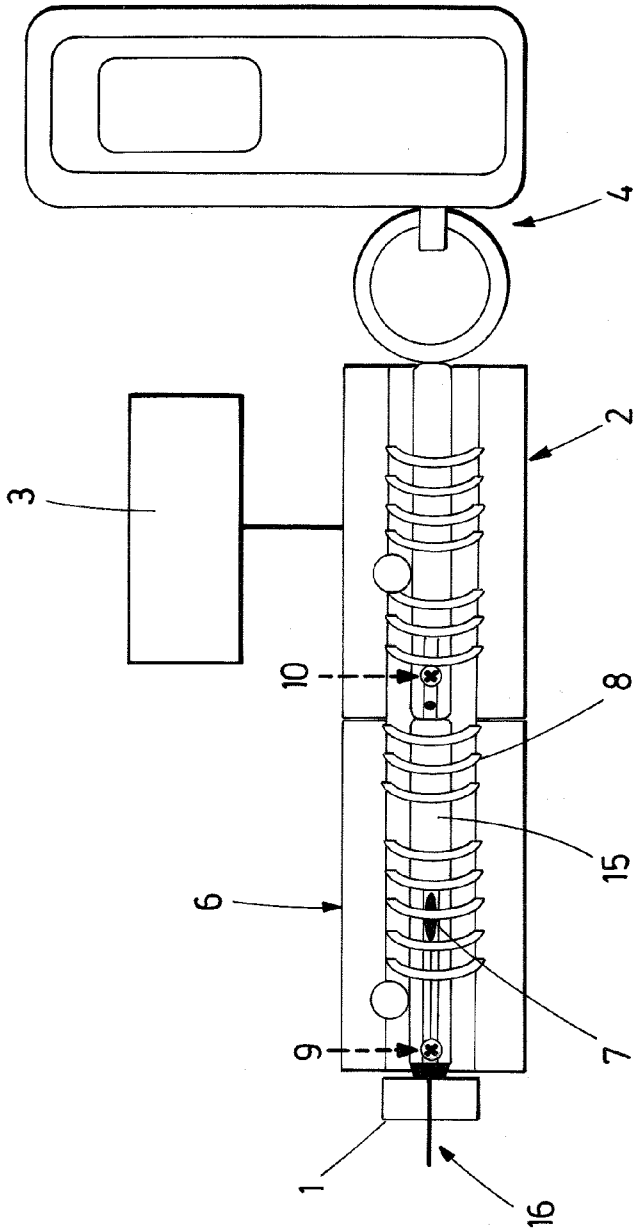

FIG.2

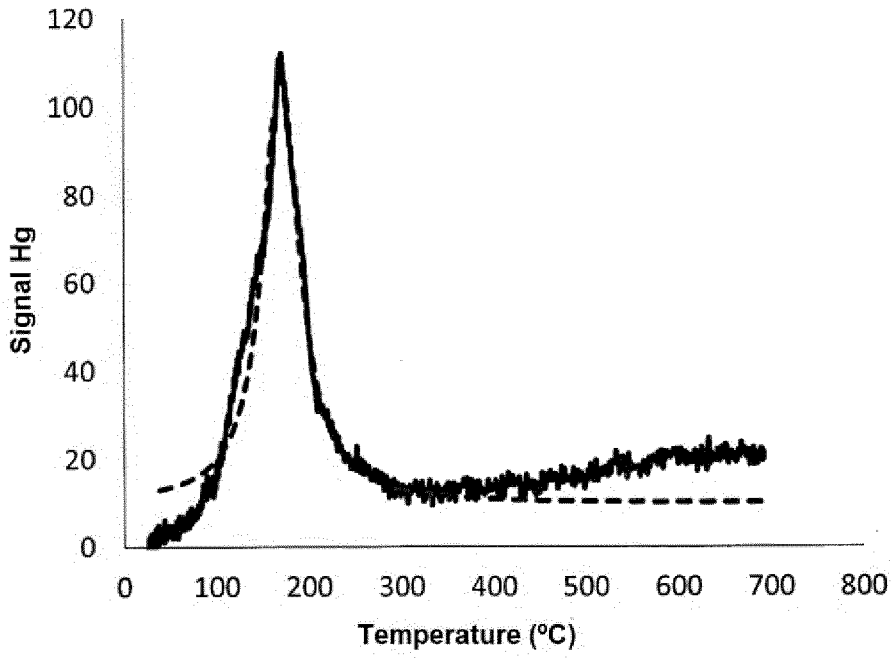
120
100
80
60
40
20
0
Signal Hg
0
100
200
300
400
500
600
700
800
Temperature (°C)

FIG.3a

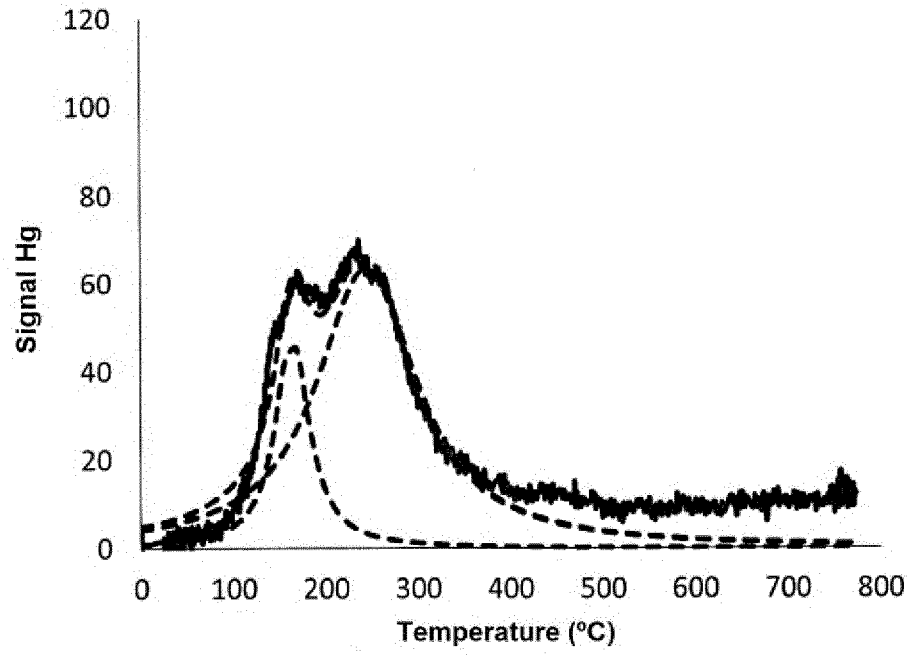
120
100
80
60
40
20
0
Signal Hg
0
100
200
300
400
500
600
700
800
Temperature (°C)

FIG.3b

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/055198

A. CLASSIFICATION OF SUBJECT MATTER
INV. G01N1/40 G01N33/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2013/236361 A1 (WATANABE TOMOAKI [JP] ET AL) 12 September 2013 (2013-09-12)	1,3,4,6
A	figure 5 paragraphs [0029], [0035] - [0037], [0043], [0046], [0051]	2,5
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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
30 May 2016	13/06/2016

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Bockstahl, Frédéric

1

Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	RUMAYOR M ET AL: "Application of thermal desorption for the identification of mercury species in solids derived from coal utilization", CHEMOSPHERE, PERGAMON PRESS, OXFORD, GB, vol. 119, 8 August 2014 (2014-08-08), pages 459-465, XP029109968, ISSN: 0045-6535, DOI: 10.1016/J.CHEMOSPHERE.2014.07.010 abstract 2.1 Thermal desorption procedure for mercury speciation.; page 460	1,4,7

Y	REIS A T ET AL: "Development and validation of a simple thermo-desorption technique for mercury speciation in soils and sediments", TALANTA, vol. 99, 7 June 2012 (2012-06-07), pages 363-368, XP028936838, ISSN: 0039-9140, DOI: 10.1016/J.TALANTA.2012.05.065 abstract 2.2 Mercury speciation by thermo-desorption: development and validation of the technique.; page 364	1,4,7

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2016/055198

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2013236361 A1	12-09-2013	JP 5001419 B2	15-08-2012
		JP 2012117889 A	21-06-2012
		US 2013236361 A1	12-09-2013
		WO 2012073617 A1	07-06-2012