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— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

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*[Continued on next page]*

(54) Title: A METHOD FOR ANALYSIS BY RAMAN SPECTROSCOPY

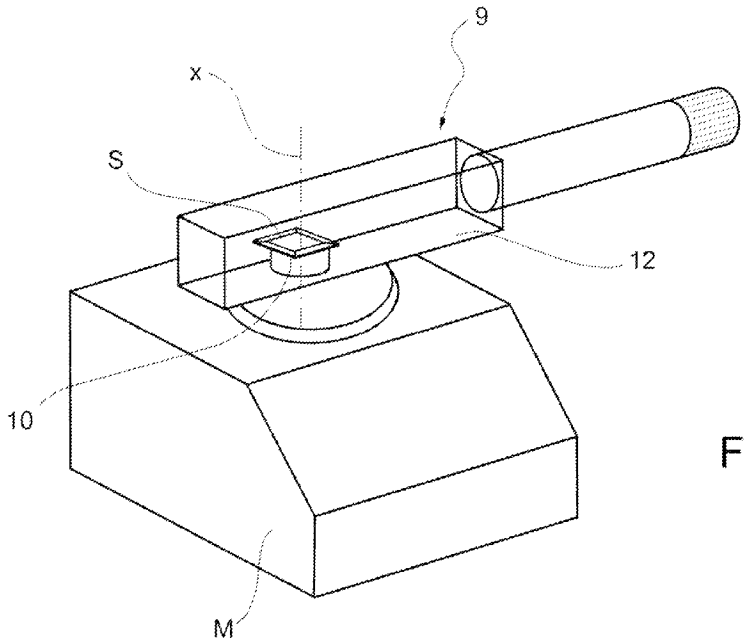


FIG.1

(57) Abstract: A method of analysis by means of Raman spectroscopy comprises the steps for preparing a cell for analysis (9), which includes a container for Raman spectroscopy (12) in which is inserted a sample holder (10), applying to the sample holder (10) an incident radiation beam, and subjecting the sample holder (10) to the action of a magnetic field from outside the container (12), so as to make the sample holder (10) move independently with respect to the container (12) and to the incident radiation beam.

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# A method for analysis by Raman spectroscopy

## Technical sector

The present invention pertains, in general, to the field of systems for spectroscopic analysis. In particular, the invention relates to a cell for Raman spectroscopy analysis.

## Prior art

Raman spectroscopy is an analytical technique that allows vibrational-type information to be obtained.

The physical principle on which the technique is based is the inelastic scattering of light: photons are absorbed by the sample and re-emitted at lower (Stokes scattering) or higher (anti-Stokes scattering) energies.

As the portion of photons arising from inelastic scattering is very limited (when compared with that produced by elastic scattering), it follows that, to obtain a Raman spectrum of acceptable quality and in a reasonable time frame, it is necessary to use an incident radiation with high brilliance, typically produced by a laser source.

The use of sources with high brilliance involves the concentration of high energy densities on the sample, with the result of possible damage to the same.

To work around this problem, one typically proceeds by reducing the power of the incident radiation, with the resulting increase in the measurement time. This aspect is limiting for the application of the technique, since it is virtually impossible to monitor phenomena which involve highly perishable species and/or which occur rapidly (e.g. chemical reactions between small organic molecules).

Alternatively, in the scientific literature, solutions have been proposed for moving the sample during measurement. In this way, individual points on the sample are exposed to

incident radiation for a shorter time, thus avoiding damage to the sample, since the energy of the photons is dispersed over a much larger surface area.

A solution of the type mentioned above is illustrated in the scientific publication W. Kiefer and H. J. Bernstein, Applied Spectroscopy 25 (1971), pages 609-613, which introduces the concept of rotating the sample by means of a mechanical device, so as to prevent decomposition at high powers. However, such a solution allows measurements to be made exclusively in the air and not in a controlled atmosphere.

The scientific publication C. P. Cheng, J. D. Ludowise, and G. L. Schrade, Applied Spectroscopy 34 (1980), pages 146-150, illustrates a solution that allows one to overcome the limitation of application of the previous case, allowing measurements to be made in a controlled atmosphere. In this case, the sample is rotated using mechanical devices inside the cell so that the internal volume of the cell is isolated from the outside.

However, the presence of internal mechanical parts involves a series of technical problems, such as the inability to heat the electro-mechanical elements without damaging them or sealing problems due to the presence of numerous connections with the outside of the cell. Furthermore, a solution thus configured is inherently expensive and technically complex.

Understandably, such limitations are to the detriment of the efficiency and cost effectiveness of the measuring cell.

Summary of the invention

One purpose of the present invention is to overcome the aforementioned limitations by providing a method for analysis by Raman spectroscopy that is easy and inexpensive to implement and that moreover lends itself to a wider range of applications than the solutions provided in the prior art.

In order to ensure the movement of the sample within a cell isolated from the outside environment while avoiding the presence of mechanical parts within the same cell, a

method according to the present invention includes steps for preparing a cell for analysis comprising a cuvette inside of which a magnetic sample holder is inserted, which is moved via the application of a magnetic field generated outside the cell.

Subjected to the action of the external magnetic field, the sample holder moves with respect to the cuvette and the incident radiation beam, so as to avoid damage to the sample.

The sample holder preferably contains a magnetic alloy bar made of AlNiCo V embedded within a hollow stainless steel cylinder on which is fixed a small envelope. The sample, in the form of pellets, is placed within this envelope.

To produce the movement, it is sufficient to apply a rotating magnetic field to the sample holder by means of, for example, a magnetic stirrer. In this way, the magnet of the sample holder will be forced to align with the field applied, producing a continuous rotation of the sample integral to it. This type of sample holder can also be made extremely small in size, such as to allow it to be introduced inside a cell of a restricted volume.

The absence of electrical and/or mechanical connections outside the cell body allows the internal volume to be heated even to high temperatures with the only limitation being to maintain the magnetization of the sample holder.

The cell also allows the sample to be subjected to dynamic vacuum or exposed to a desired pressure of a gas/vapor.

The above and other purposes and advantages are achieved, according to an aspect of the invention, by a cell for analysis through Raman spectroscopy having the characteristics defined in the appended claims.

Brief description of drawings

The functional and structural characteristics of some preferred embodiments of a cell for analysis by Raman spectroscopy according to the invention will now be described. Reference is made to the appended drawings, in which:

- Figure 1 is a schematic perspective view of a cell for analysis by Raman spectroscopy according to one embodiment of the present invention, positioned on a traditional magnetic stirrer; and
- Figure 2 is an enlargement of the cell of Figure 1.

Detailed description

Before explaining in detail a plurality of embodiments of the invention, it should be clarified that the invention is not limited in its application to the details of construction and to the configuration of the components provided in the following description or illustrated in the drawings. The invention may assume other embodiments and may be implemented or achieved in essentially different ways. It should also be understood that the phraseology and terminology have descriptive purposes and should not be construed as limiting.

A method to carry out an analysis by Raman spectroscopy according to the present invention comprises the step of preparing a cell for Raman spectroscopy 9, comprising a container 12 (in the illustrated example, a tubular cuvette for Raman spectroscopy), in which is inserted a sample holder 10, which carries a sample S to be measured.

A container 12 is prepared, of a type known per se, appropriately configured as a cuvette with an elongated shape and a circular or square section. It can be made, for example, of glass, plastic or optical quartz. Preferably, the method includes the step of preparing a cuvette 12 that provides an optical part and a non-optical part. The optical part will be appropriately constructed of very high quality optical quartz, to minimize the interaction with the incident radiation. Quartz is also intrinsically suitable for heating to temperatures even far exceeding those traditionally used (500-600 °C), without losing its properties (if handled with due care). In addition, the optical part will preferably provide a square section so as to properly support the sample holder 10 and position the sample parallel to the

optical window, thus avoiding problems of astigmatism which drastically reduce the quality of the measurement.

The non-optical part will be appropriately made of a suitable material to withstand the treatment temperatures that are to be used. For example, Pyrex glass will be suitable for applications up to 450-500 °C, whereas to use the cell at higher temperatures the body can be made of quartz glass (non-optical and less expensive). In principle, it is possible to make the non-optical part of metal, connecting it to the optical part through a glass-metal weld: although this type of weld is more fragile than a glass-glass weld and results in higher implementation costs, it may nevertheless be useful for some specific applications (for example, with a connection to metallic vacuum systems).

Once the cell 9 is prepared, the method according to the invention comprises the steps for preparing a sample holder 10, which can be moved independently under the action of a magnetic field, and applying a magnetic field, appropriately variable, by means of a magnet M (for example, a traditional magnetic stirrer) outside the container 12. The size of the sample holder 10 will be such as to allow its insertion in the cuvette 12.

Therefore, the sample holder 10, to which is applied a sample S to be analyzed by means of Raman spectroscopy, will be built at least in part of a magnetically responsive material. Preferably, the sample holder 10 incorporates a magnetic alloy bar (not shown), for example one made of AlNiCo V.

The method therefore includes the step of applying an incident radiation beam on the sample S.

The action of the magnetic field will move the sample holder 10 (and, therefore, the sample S) with respect to the container 12 and the incident radiation beam, for example by imparting a rotation around an axis X of the sample holder 10. Depending on parameters such as, for example, intensity and frequency of the magnetic field, it will be possible to impart to the sample holder 10 different movements for direction, speed, etc. Instead of rotation, for example, the specimen holder can move in a reciprocating linear motion. The

different movements of the sample holder 10 can be obtained, for example, by moving the magnet M with respect to the container 12.

According to one embodiment of the present invention, the method includes the step of preparing a sample holder 10 comprising a base 10a (which, in the case illustrated, is a metallic or ceramic cylinder, for example of copper, stainless steel, etc., having an appropriately hollow shape, so that the magnetic bar can be inserted in it), topped by a plate 10b which is applied to the sample S. Appropriately, the plate 10b is made of gold, and can be secured to the base 10a by means of a clip (not illustrated). Sample S, preferably in the form of a tablet, can be secured to the plate 10b, according to the embodiment illustrated in Figure 2, by means of flaps 10c on the sample S. According to an alternative not shown, the flaps 10c can be simple raised edges inside of which the sample S is held, or a combination of rigid, raised edges around the outside and folding tabs, which enclose the sample S.

Depending on the configuration of the plate 10b, the sample S can be applied to the sample holder 10 also in forms other than a tablet, for example in powder or monolithic form.

Once provided with the sample S and positioned inside the tubular container 12, the sample holder 10 is subjected to the action of the magnetic field, so as to move independently, with respect to the container 12 and to the incident radiation beam, in the absence of any mechanism that requires connections to the outside of the container 12. The stirring of the sample S, caused by the movement of the sample holder 10, prevents damage to the sample S even when subjected to high intensity incident radiation.

The absence of connections to the outside of the cuvette 12, made possible by the use of a cell 9 that comprises a magnetically moved sample holder 10, allows an analysis to be performed in a controlled atmosphere without the need for seals and gaskets on the movement devices. The absence, furthermore, of vacuum greases prevents the triggering of undesirable phenomena (such as fluorescence) due to contamination by the hydrocarbons that make up the same greases and which can make the Raman measurement impossible.

The sample measurement is furthermore made possible both at elevated temperatures (for example, through the application of a heating element around the body of the cell) and at low temperatures (for example, by cooling with an appropriate cooling fluid).
Therefore, a method which uses a cell 9 thus configured is simple to manufacture, and can be easily applied, for example, even in the case of analyses carried out in flux, when a second connection for gas, vapor, etc. is applied to the cuvette 12. In this case (not illustrated), it will be possible to carry out the treatment and the measurement of the sample S in the gaseous flux, rather than in static conditions, so as to make a cell 9 that can be used in *operando* conditions.

Ultimately, one achieves the advantages of being able to use the exciter source at maximum power, while avoiding damage to the sample through the movement of the sample holder achieved without the aid of mechanical parts within the cell. The reduction of the measurement time furthermore allows for *in situ* measurements, allowing one to monitor even relatively fast phenomena, and an oil-free design of the cell minimizes the possible contamination caused by elements within the cell itself.

Finally, the embodiment of the device entails considerably lower costs when compared to known technologies.
Various aspects and embodiments of a method for analysis by Raman spectroscopy according to the invention have been described. It is intended that each embodiment may be combined with any other embodiment. The invention, moreover, is not limited to the described embodiments, but may be varied within the scope defined by the appended claims.

# CLAIMS

1. A method of analysis of a sample (S) by Raman spectroscopy, comprising the steps of:

a) preparing a cell for analysis by Raman spectroscopy (9), comprising a container for Raman spectroscopy (12) inside of which is inserted a sample holder (10), which holds the sample (S) to be analyzed, the sample holder (10) being capable of moving independently under the action of a magnetic field;

b) applying an incident radiation beam to the sample (S);

c) subjecting the sample holder (10) to the action of a variable magnetic field, said magnetic field being applied to the container (12) by means of an external magnet (M), so as to make said specimen holder (10) move independently with respect to the container (12) and to the incident radiation beam.

2. Method according to claim 1, wherein the step (c) is performed by moving the magnet (M) with respect to the container (12).

3. Method according to claim 1 or 2, wherein the sample holder (10) incorporates a magnetic alloy bar.

4. Method according to claim 3, wherein the magnetic alloy bar is made of AlNiCo V.

5. Method according to one of the preceding claims, wherein the sample holder (10) comprises a plate (10b) to which the sample (S) can be applied.

6. Method according to claim 5, comprising the step of securing the sample (S) to the plate (10b) by means of flaps (10c).

7. Method according to any of claims 1 to 6, wherein the sample holder (10) comprises a hollow base (10a) made of a metallic material.

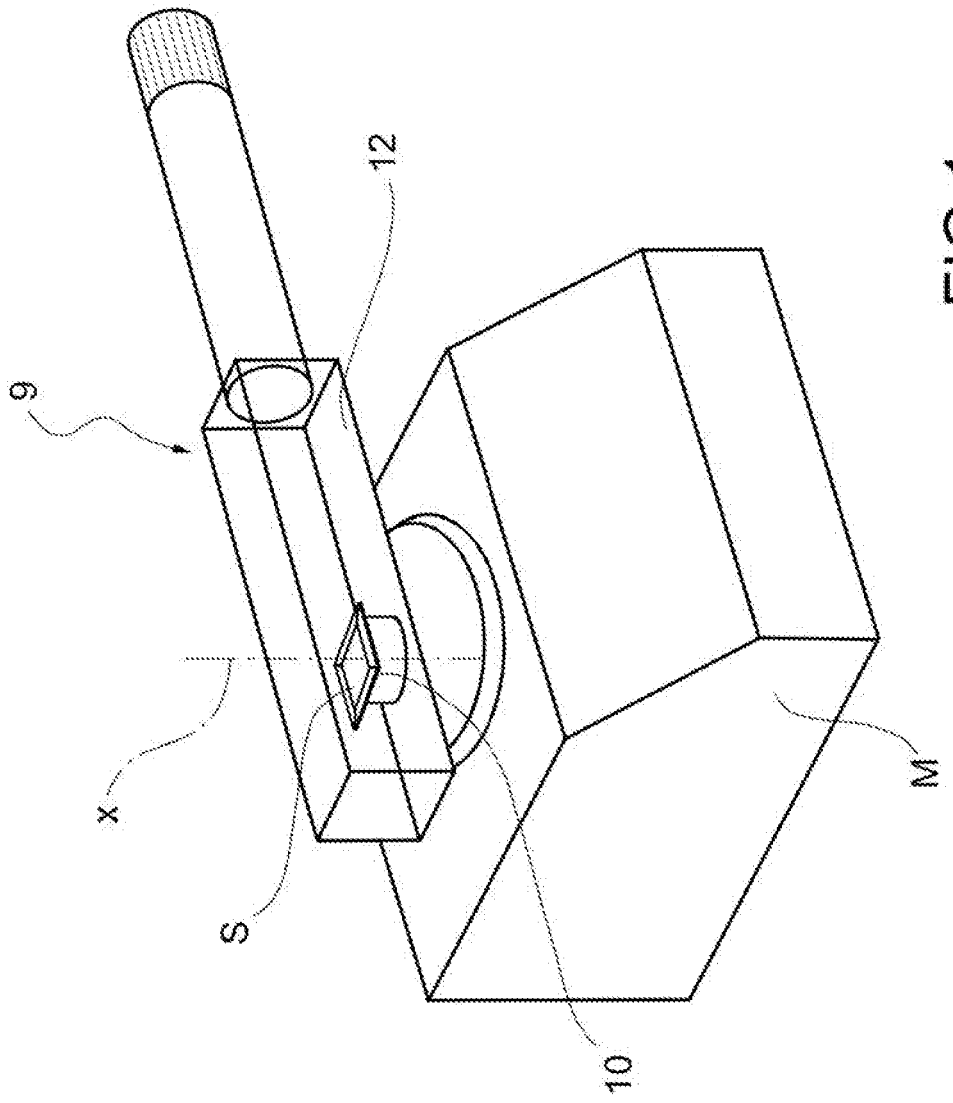


FIG.1

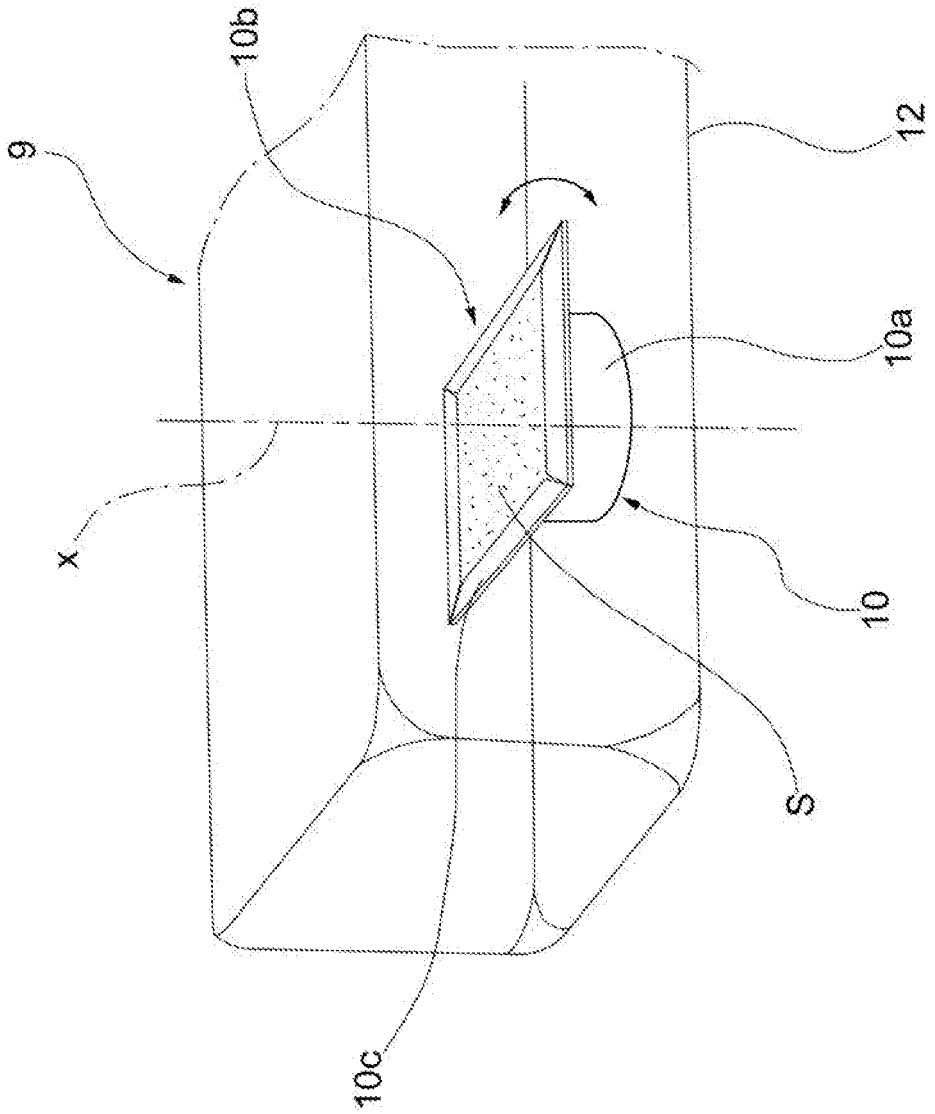


FIG.2

# INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
INV. G01N21/65 G01N21/03 G01J3/44
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)
G01J 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

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 23 February 2017 | 07/03/2017 |

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| European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016 | Mason, William |

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