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(54) **MASS SPECTROMETER AND METHOD FOR MASS SPECTROMETRY**

(57) A mass spectrometry method and a spectrometer to carry out said method are hereby provided. Both are based on the generation of ions by means of laser-matter interaction, in a region namely ionization region at atmospheric pressure conditions. Once the ions are generated, they are guided into the body of a mass spectrometer working at high vacuum conditions by means of electrical fields. At the end of the spectrometer a charged particle detector provides the signal. The detection region is separated from the ionization region by one or several orifices of respective membranes arranged in the body of the spectrometer that allow differential pumping using respective vacuum systems.

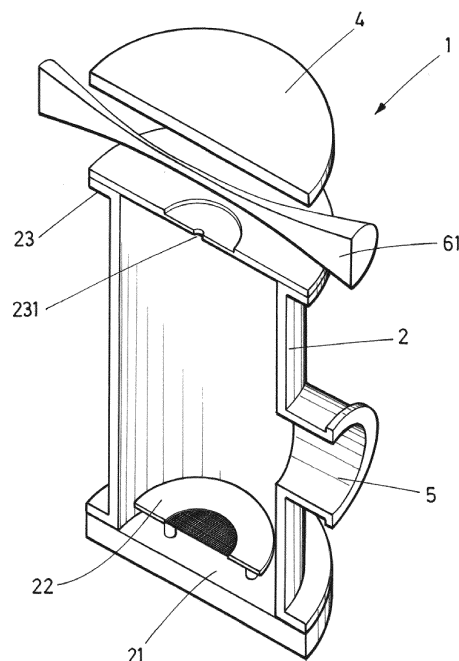


FIG.1

Description

OBJECT OF THE INVENTION

[0001] The invention is aimed to in situ analysis of complex gaseous samples using optical means.

[0002] More specifically, the invention is directed to a mass spectrometer device capable to work without the isolation of the sample from the surrounding medium, and a method for mass spectrometry that uses the said mass spectrometer.

BACKGROUND OF THE INVENTION

[0003] During the last decades the non-stopping development of laser technology has allowed the discovery of new unexpected phenomena that have attracted a considerable attention not only for their scientific interest, but also for their possible practical applications.

[0004] Within the multiple possible examples, laser filamentation can be considered a paradigm that clearly gathers both interests mentioned before. Filamentation has its origin in the balance between two different phenomena: self focusing of the laser pulse when it propagates through a positive Kerr medium and defocusing due to the properties of the plasma created by the concentration of energy in space and time. It was not until the development of intense femtosecond pulsed lasers that filamentation was observed in the atmosphere. Laser filaments have some applications like the control of lighting and rainfalls, the guiding of high power microwaves using the ionization channel created by the filament, or the remote sensing of pollutants in air using molecular fluorescence and LIDAR (Laser Illuminated Detection And Ranging). Nevertheless a successful implementation of such techniques requires a complete understanding of the process of laser filamentation and, more importantly, of the subsequent plasma dynamics. Thus, questions like which species are formed inside of the filament channel, at what time after the formation of the filament new species are generated, or at what time after the pulse the plasma density becomes negligible and the species can move freely, need to be addressed to provide predictable and reliable models of filamentation. Some approaches using spectroscopy techniques like Raman spectroscopy, have been provided by: M. Plewicki and R. J. Levis, J. Opt. Soc. Am. B 25, 1714, 2008, J. H. Odnher, D. A. Romanov, and R. J. Levis, Phys. Rev. Lett. 103, 075005, 2009. or A. Talebpour, M. Abdel-Fattah, A. D. Bandrauk, and S.L. Chin, Laser Phys.. 11, 1, 68-76, 2001; these approaches yielded useful information regarding the process dynamics, however these analysis rely on the correct identification of the fluorescence lines of the plasma which is usually a difficult and arduous task.

DESCRIPTION OF THE INVENTION

[0005] In one aspect of the invention a mass spectrom-

eter is provided, more specifically a TOF (Time of Flight) spectrometer.

[0006] In typical mass spectrometers the ionization process and the detection of the ionized particles take place in high vacuum conditions. This is so because on one hand the most usual ionization techniques in this field like electron impact ionization have low efficiency, being this proportional to the vacuum level. On the other hand the typical ions detectors require high vacuum conditions for their correct operation. In this proposed spectrometer the ionization is produced by a laser. In this way a much higher ionization yield is obtained making it possible to work at atmospheric pressure. Furthermore, the use of lasers allows a possible selective ionization of a certain species from a complex sample. Another advantage is the possibility to study a sample without isolating it from the surrounding medium. This is extremely important for different applications like the biological ones.

[0007] A second aspect of the invention embraces a spectrometry method using the spectrometer of the first aspect of the invention. In order to carry out the second aspect of the invention an ionization source is provided. Said ionization source must fulfil the requirement of providing at least 10^9 W/cm^2 ; in a preferred embodiment of the second aspect of the invention the ionization source is a laser system.

[0008] The spectrometer of the invention is able to work at atmospheric pressure conditions and, in a preferred embodiment, it comprises a preferably cylinder shaped vacuum chamber which provides the required differential vacuum between the atmospheric pressure of the ionization region and the body of the spectrometer. In an alternative embodiment of the invention the spectrometer comprises at least two, preferably cylinder shaped; vacuum chambers that means two stages of differential vacuum. In the alternative embodiment of the first aspect of the invention, a high vacuum chamber and a low vacuum chamber are provided. In any one of the embodiments provided, the vacuum chambers are respectively connected to vacuum systems and when more than one vacuum chamber is provided they are duly separated by pierced vacuum membranes (pierced standing for provided with an orifice for differential vacuum). A second pierced vacuum membrane is also provided with an orifice for differential vacuum, said second vacuum membrane being provided as a closing wall of the low vacuum chamber whilst the high vacuum chamber is closed by a base comprising a charged particles detector.

[0009] A repeller for positive ions is provided opposite to the second vacuum membrane and separated thereof by a distance defining a passage through which the laser beam will flow; being a portion of said passage, that closer to the repeller, the ionization region under a pressure of 1013 mbar approximately, namely at atmospheric conditions. Said repeller may be a plate at a positive high voltage, which drives the ionized particles inside the hollow body into the detection region.

[0010] Hence the detection region is separated from

the ionization region by one or several orifices, those of the membranes that allow differential pumping. This is of critical importance because charged particle detectors need to operate in high vacuum conditions. For guiding the ions through the body of the mass spectrometer electrostatic lenses can be also incorporated. These spectrometer electrostatic lenses are arranged inside the vacuum chamber, although their exact position will depend on their number and the applied voltages, nonetheless and regardless of their position, said electrostatic lenses may have voltages in the range of hundreds of Volts.

DESCRIPTION OF THE DRAWINGS

[0011] To complement the description being made, and in order to aid towards a better understanding of the characteristics of the invention, in accordance with a preferred example of practical embodiment, a set of drawings is attached as an integral part of said description wherein, with illustrative and non-limiting character, the following has been represented:

Figure 1.- Shows a sectional view of the preferred embodiment of the spectrometer of the invention.

Figure 2.- Shows a sectional view of an alternative embodiment of the spectrometer of the invention.

Figure 3.- Depicts the method of the invention by means of an illustration where the laser filament is represented generating the ions that fly till contact the base of the body of the spectrometer, which is in turn a charged particle detector.

PREFERRED EMBODIMENT OF THE INVENTION

[0012] In a preferred embodiment of one aspect of the invention directed to a mass spectrometer (1), depicted in figure 1 where it is shown the hollow body (2) of the mass spectrometer (1) with a vacuum chamber (3, 31, 32) therein. In this preferred embodiment said vacuum chamber (3, 31, 32) is defined by a base (21), which comprises a charged particle detector (22) arranged at distal end of the hollow body (21), the inner wall of the hollow body (2) and a vacuum membrane (23) provided with a first pinhole (231) and arranged at the proximal end of the hollow body (2). In order to generate vacuum conditions inside the chamber (3, 31, 32), the vacuum chamber (3, 31, 32) is connected to a vacuum generation system by means of at least one orifice (5, 51, 52).

[0013] A repeller (4) is arranged opposite to the vacuum membrane (23) at a distance thereof defining a passage through which a laser beam will flow generating a plasma producing ions, as depicted either in figure 1 or 2.

[0014] In an alternative embodiment of the first aspect of the invention the mass spectrometer (1) comprises more than one vacuum chamber (3), for example, and not being a limitative number, two. This is achieved by adding separation elements, like equipping the hollow body (2) with at least an additional vacuum membrane

(24) which is provided with a second pinhole and arranged inside the hollow body (2) so that said additional vacuum membrane (24) splits the vacuum chamber (3) into a high vacuum chamber (31) and a low vacuum chamber (32); hence the high vacuum chamber (31) is defined by the base (21), which comprises a charged particle detector (22) arranged at distal end of the hollow body (21), the inner wall of the hollow body (2) and the additional vacuum membrane (24), whereas the low vacuum chamber (32) is defined by the additional vacuum membrane (24) which is pinholed, the inner wall of the hollow body (2) and the vacuum membrane (23).

[0015] In yet an alternative embodiment of the first aspect of the invention, the mass spectrometer of either the preferred or the alternative embodiment earlier described may be furnished with one or more electrostatic lenses inside the hollow body (2) for guiding electrons through the hollow body (2), said electrostatic lenses are meant to be charged with a voltage up to 100 Volts.

[0016] A second aspect of the invention is that of a mass spectrometry method using the mass spectrometer (1) of the first aspect of the invention. For this embodiment a possible ionization source (5) may be one of the three different exits, with peak powers of 20 TW, 200 TW and 1 PW respectively, of a Ti-Sapphire laser system. The used 200 TW exit delivers pulses of 30 fs, up to 6 J of energy per pulse, 800 nm of central wavelength, a beam diameter of 10 cm, and a repetition rate of 10 Hz was used. However, in other embodiments, when required, an attenuation of the energy per pulse to 30 mJ could be made in order to work at atmospheric pressure conditions after laser compression. Nonetheless any ionization system providing sufficient intensity may be used as an ionization source (5), for example: an 800 nm wavelength laser beam with a cross section of 3 cm of diameter, delivering pulses of 120 fs with a repetition rate of 1 kHz being the energy per pulse of 2.2 mJ, furnished with a 50 cm focal lens.

[0017] The laser pulses generated were focused by the combination of a spherical mirror and a plano-convex lens with focal lengths of 1 m and 20 cm respectively. The effective focal length of the whole system was 28 cm. In these conditions, in the vicinity of the focal plane a filament (61) is created. Any other focalization system that provides the required peak intensity (larger than 10^9 W/cm²) can be used. This invention was designed and constructed in order to have access to the plasma dynamics and the different species generated once the laser-matter interaction ceased. In this spectrometer (1) the interaction region at atmospheric pressure, and the body (2) of the spectrometer (1) at a vacuum level lower than 10^{-4} mbar (this vacuum is required for a properly functioning of the spectrometer (1)) are separated by a first pinhole (231) with diameter in the order of tens of microns, and a thickness of around 10 microns. The ions generated in an ionization zone (61) generated by the ionization source (6) are directed towards the first pinhole (231) by the repeller (4) plate at a positive voltage of the

order of 1kV. The ionization zone (61), directed from the ionization source (6), is separated at a distance comprised between 0.5 mm and 20 mm from first pinhole (231) and a distance comprised between 0.5 mm and 10 cm from the repeller (4).

[0018] Once the ions enter in the spectrometer (1) they travel freely, i.e., there are no further acceleration stages, towards the charged particle detector (22). To avoid a charge accumulation in the body of the spectrometer (1), the outer structure must be properly connected to ground. The signal from the charged particle detector (22) is collected and integrated in an oscilloscope triggered by the laser.

[0019] The integration time was approximately five minutes due to the small size of the first pinhole (231) and the low repetition rate of the laser. A larger first pinhole (231), with sizes up to 25 microns may be used, although a larger first pinhole (231) would make measurements faster, it would decrease the vacuum level to a non-safe value for the correct function of the spectrometer (1), producing unwanted sparks in the charged particle detector (22) that would ruin any useful data, and could risk the integrity of the detector. For using larger pinholes new steps of differential vacuum must be added to the spectrometer or to correctly remodel the vacuum pumping system. The alignment of the ionization zone (61) with respect to the first pinhole (231) was carried out maximizing the UV light detected by the the charged particle detector (22) of the spectrometer (1), which is a MCP that is sensitive to UV, at time zero.

[0020] Regardless of the possible embodiment of this second aspect of the invention, the ionization zone (61) is arranged at a distance comprised between 0.5 mm and 20 mm from the pinhole of the second vacuum membrane (24) and at a distance comprised between 0.5 mm and 10 cm to the repeller (4).

Claims

1. Mass spectrometer (1) **characterised by** comprising:

- a hollow body (2) comprising in turn:

- a base (21) of the hollow body (2), which is arranged at distal end of the hollow body (21) and comprises a charged particle detector (22),

- a vacuum chamber (3, 31, 32) defined by:

- the base (21) of the hollow body (2),
- the inner wall of the hollow body (2) and,

- a vacuum membrane (23) provided with a first pinhole (231) and arranged at the proximal end of the hollow body (2), and

- at least one orifice (5, 51, 52) connecting the vacuum chamber (3, 31, 32) to a vacuum generation system,

- a repeller (4) arranged opposite to the vacuum membrane (23) at a distance thereof defining a passage through which a laser beam will flow generating ions.

2. Mass spectrometer (1) according to claim 1 wherein the hollow body (2) comprises at least an additional vacuum membrane (24) which is pinholed and arranged inside the hollow body (2) so that said additional vacuum membrane (24) splits the vacuum chamber (3) into a high vacuum chamber (31) and a low vacuum chamber (32); wherein:

- the low vacuum chamber (32) is defined by the additional vacuum membrane (24) which is pinholed, the inner wall of the hollow body (2) and the vacuum membrane (23), and

- the high vacuum chamber (31) is defined by the base (21), the inner wall of the hollow body (2) and additional vacuum membrane (24).

3. Mass spectrometer (1) according to claim 1 further comprising electrostatic lenses inside the hollow body (2) for guiding electrons through the hollow body (2).

4. Mass spectrometer (1) according to claim 3 wherein the electrostatic lenses are charged with a voltage comprised between 0 Volts and 100 Volts.

5. Mass spectrometer (1) according to claim 1 wherein the pinholes of the membranes (23, 24) have a diameter comprised between 10 and 100 microns.

6. Mass spectrometer (1) according to claim 1 wherein the repeller (4) is a plate with positive voltage in the range of 0.5 kV to 5 KV.

7. Mass spectrometry method using the mass spectrometer (1) of any of claims 1 to 6 and a ionization source (6), the method comprising:

- generating a vacuum in the vacuum chamber (22) by means of the respective vacuum systems,

- generating an ionization zone (61) by means of laser-matter interaction and the ionization source (6), and

- guiding the ionization zone (61) so that it passes between the repeller (4) and the pinhole (231) of the first vacuum membrane (23) producing ions that are driven towards the inside part of the hollow body (2) since they are repelled by the repeller (4).

8. Mass spectrometry method according to claim 7 wherein the ionization zone (61) is respectively separated at a distance comprised between 0.5 mm and 20 mm from the first pinhole (231) and at a distance comprised between 0.5 mm and 10 cm from the repeller (4). 5
9. Mass spectrometry method according to claim 7 or 8 wherein the ionization source (6) comprises a laser system which delivers pulses of 30 fs, up to 6 J of energy per pulse, 800 nm of central wavelength, a beam diameter of 10 cm, and a repetition rate of 10 Hz. 10
10. Mass spectrometry method according to any one of claims 7 to 9 further comprising attenuating the energy per pulse of the ionization source (6) to 30 mJ in order to work at atmospheric pressure conditions. 15
11. Mass spectrometry method according to any one of claims 7 to 10 wherein the ionization source (6) is capable to reach an intensity of at least 10^9 Wcm^{-2} . 20

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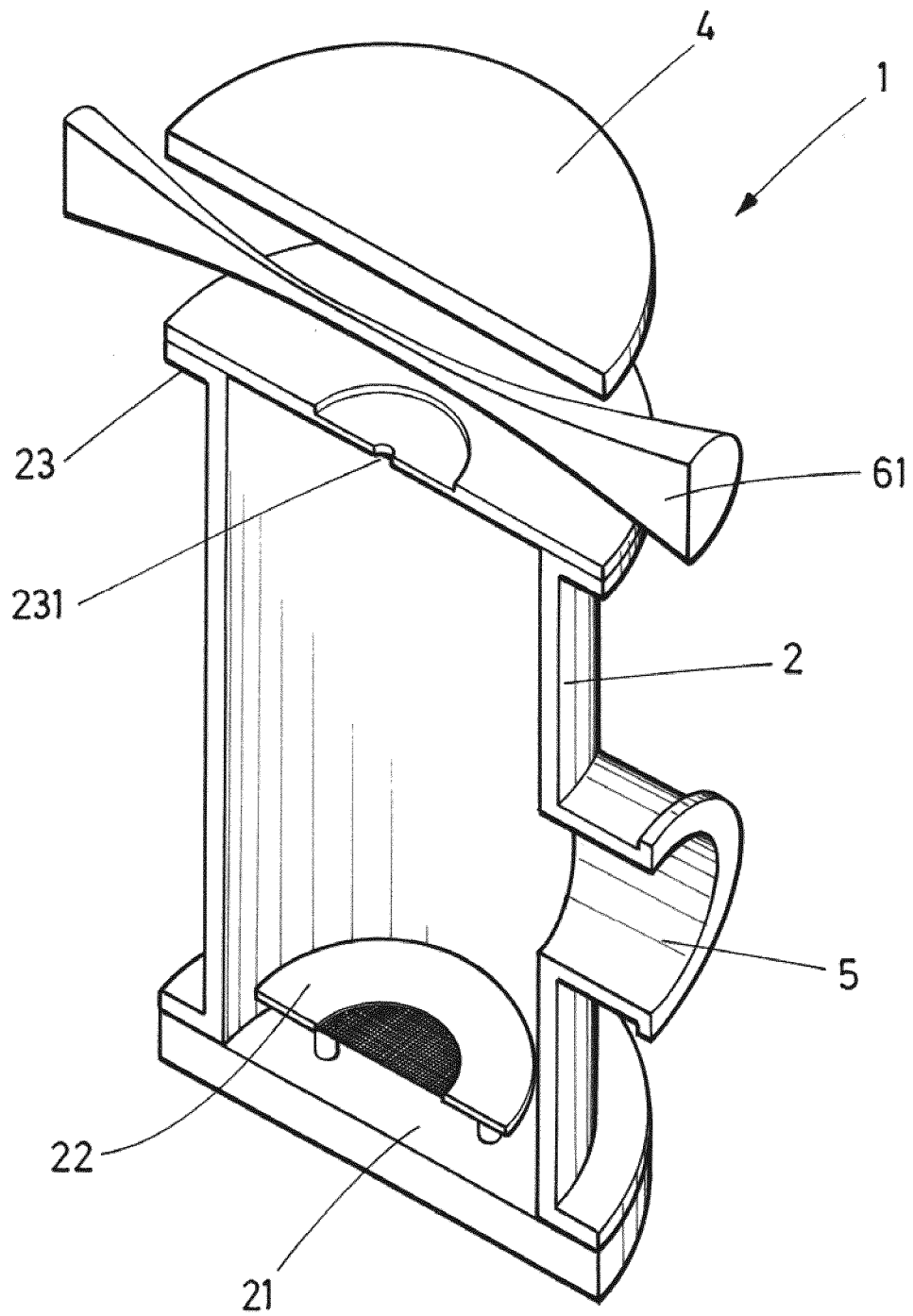


FIG.1

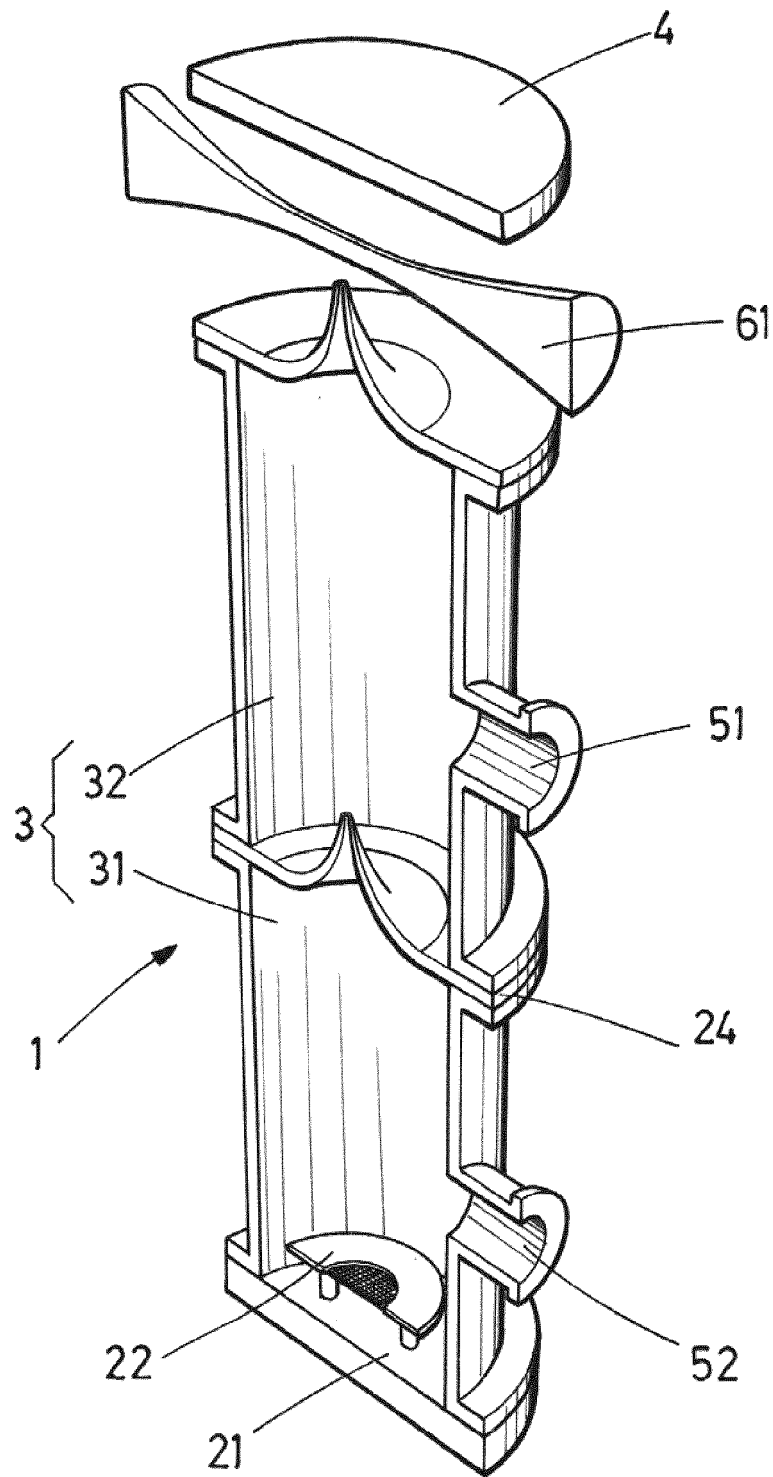


FIG.2

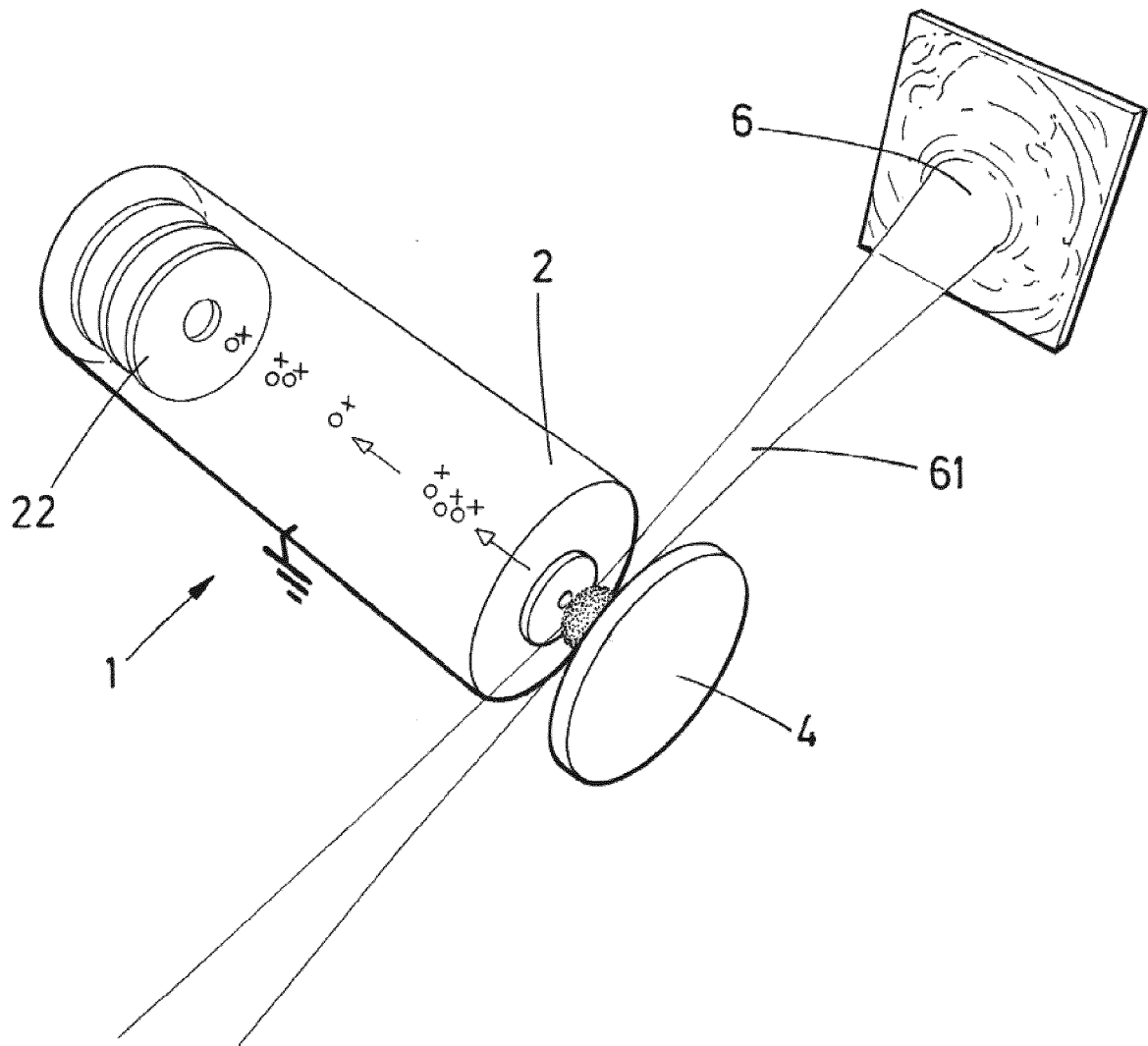


FIG.3



EUROPEAN SEARCH REPORT

Application Number
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Place of search The Hague		Date of completion of the search 22 October 2015	Examiner Cornelussen, Ronald
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The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
The Hague		22 October 2015	Cornelussen, Ronald
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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

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5 This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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