(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
5 October 2017 (05.10.2017)

WIPO | PCT

(10) International Publication Number
WO 2017/168211 A1

(51) International Patent Classification:
G01N 21/71 (2006.01) *G01J 3/443* (2006.01)
B23K 26/02 (2006.01) *G01N 1/28* (2006.01)
B23K 26/08 (2006.01) *G01N 21/03* (2006.01)

(21) International Application Number:
PCT/IB2016/051829

(22) International Filing Date:
31 March 2016 (31.03.2016)

(25) Filing Language: English

(26) Publication Language: English

(71) Applicant: **FOSS ANALYTICAL A/S** [DK/DK]; Foss Allé 1, 3400 Hilleroed (DK).

(72) Inventors: **JENSEN, Allan Kjaergaard**; c/o FOSS Analytical A/S, Foss Alle 1, 3400 Hilleroed (DK). **NIKOLAJSEN, Thomas**; c/o FOSS Analytical A/S, Foss Alle 1, 3400 Hilleroed (DK).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

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

Published:

— *with international search report (Art. 21(3))*

[Continued on next page]

(54) Title: SYSTEM FOR AND METHOD OF PERFORMING LASER INDUCED BREAKDOWN SPECTROSCOPY

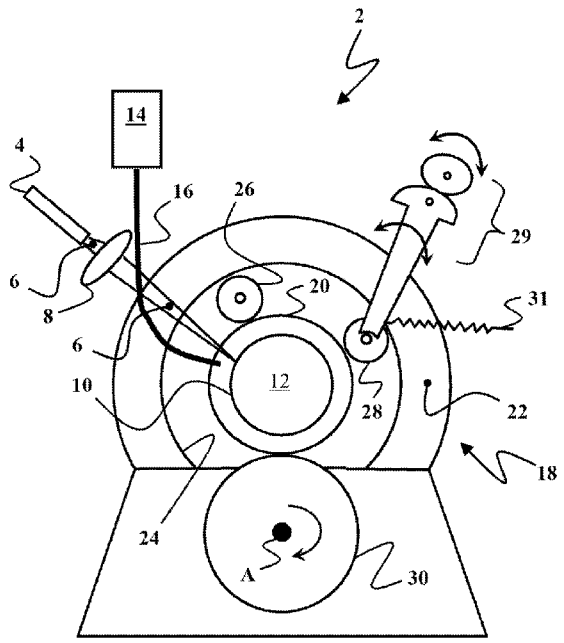


Fig. 1

(57) Abstract: A Laser Induced Breakdown Spectrocopy (LIBS) system (2) for the analysis of a sample pellet (12) of a consolidated granular material retained in a tubular container (20), the system (2) comprising a laser source (4) configured to emit a pulsed laser beam (6) towards an exposed surface of the sample pellet (12); and a sample station (18) configured to hold the tubular container (20) with the sample pellet (12) orientated to present the exposed surface towards the pulsed laser beam and comprising an actuator configured to slide the sample pellet (12) along a movement axis out of the tubular container (20) and thereby present a portion of an outer surface (10) of the sample pellet (12) previously constrained by an inner surface of the tubular container (20) as the exposed surface.

WO 2017/168211 A1

— *with amended claims (Art. 19(1))*

Description

System for and Method of Performing Laser Induced Breakdown Spectrocopy

[0001] The present invention relates to a system for and a method of performing Laser Induced Breakdown Spectrocopy (LIBS) and in particular to a system for and a method of performing LIBS analysis of granular samples.

[0002] LIBS is a known analysis technique which is employed in the measurement of the concentrations of elemental components of a sample. A high energy density laser pulse is used to generate a plasma at the surface of the sample. The plasma contains a mixture of excited atoms representative of the elemental composition of the sample. As the plasma cools the excited atoms emit optical radiation that is characteristic of the atom emitting it. As the intensity of the characteristic radiation is related to the number of atoms in the plasma and ultimately the number of atoms in the sample then spectrophotometric analysis of the so emitted radiation may be employed to provide information on the concentration of elements present in the sample.

[0003] When analysing granular samples it is known, for example from US 2007/0218556, to present the sample for analysis as a single consolidated mass in the form of a pressed pellet. The pellet is made by placing the granular material, that is, material composed of individual or partially agglomerated granules, pieces or particles, for example ground, shredded or pulverised plant or soil material; foodstuff or its intermediate products; or pharmaceutical products; into a cylindrical tubular container and pressing the granular material to consolidate it into the pellet. The pellet in the cylindrical tubular container is then moved into the path of the laser beam for the subsequent LIBS analysis of an exposed upper surface.

[0004] A LIBS analyser, such as disclosed for example in US 5,583,634, in US 2007/0218556 or in US2013/0271761, therefore generally comprises a laser source capable of generating a laser beam pulse of typically between 10 – 500 milliJules (mJ) for the order of 1-10 nanoseconds (ns) at a repetition rate of up to a few tens of hertz ; focussing optics for focusing the laser beam at a spot of around 10 micrometers (μm) diameter on the

exposed surface of the sample; collection optics for collecting optical radiation emitted by the plasma and a sample station configured to hold the sample orientated to present the exposed surface at a distance from the focussing optics. The optical radiation collected via the collection optics may then be provided to a spectrometer which generates wavelength dependent intensity data from the so provided optical radiation and supplies the data for analysis to determine the elemental concentration of the sample.

[0005] The amount of energy produced by such a laser source may also generate relatively large amounts of black body (or 'continuum') radiation, by means of a general heating of the sample. This radiation acts as a background from which the optical radiation emitted by the plasma must be differentiated. Lower energy laser sources may be employed to overcome this problem. However, the use of a lower energy laser source will increase the necessary precision by which the focussing optics must focus the laser beam at the sample in order to ensure a sufficient energy density at its surface for plasma generation. This is especially a problem when investigating granular samples as the surface of the sample presented for interaction with the laser beam tends to present height variations as measured along the optical axis of the focussing optics. Even pelletized samples may present this problem as it has been found that such samples tent to 'relax' causing uneven expansion of any unconfined, that is to say, exposed, surface. Relatively complicated automatically adjustable focussing optics has been proposed, for example in US 2013/0271761, to maintain the laser beam in focus at the surface as a solution to the problem of surface unevenness.

[0006] Additionally, with each plasma formation the laser beam removes a small portion of the surface which creates additional height variations. Eventually a crater is formed which results in the laser beam becoming out of focus in the crater. To mitigate this the sample container is often mounted on a moveable X-Y sample stage and the sample container moved after one or more laser pulses in order to present new portions of the exposed upper surface for LIBS analysis. Movement of the sample stage in the Z direction

may also be provided in order to maintain the laser beam in focus at the surface of the sample.

[0007] According to a first aspect of the present invention there is provided a Laser Induced Breakdown Spectrocopy (LIBS) system for the analysis of a sample pellet of consolidated granular material retained in a tubular, preferably cylindrical, container, the system comprising a laser source configured to emit a pulsed laser beam towards an exposed surface of the sample pellet; and a sample station configured to hold the tubular container with the sample pellet orientated to present the exposed surface towards the pulsed laser beam; wherein the sample station comprises an actuator configured to slide the sample pellet along a movement axis out of the tubular container and thereby present a portion of an outer surface of the sample pellet previously constrained through contact with an inner surface of the tubular container as the exposed surface.

[0008] Thus, by having a system configured to perform LIBS analysis on an outer surface of the sample pellet which was previously constrained by the inner surface of the tubular container relaxation effects are mitigated. This provides an advantage that the focussing of the pulsed laser beam at the exposed surface can be more accurately maintained without the need for complicated adjustments of any focussing optics or of the sample stage.

[0009] In some embodiments the sample station further comprises a rotary drive mechanically connectable to the tubular container to impart a rotational motion thereto to present a plurality of portions of the outer surface as the exposed surface. This facilitates the collection of multiple instances of LIBS spectral data whilst also mitigating the effects of cratering.

[0010] In some embodiments the moving of the sample pellet out of the tubular container and imparting rotational movement to the container is concerted to provide spiral portions of the outer surface of the sample pellet as the exposed surface. Collection of multiple instances of LIBS spectral data from different portions of the same sample is thereby further facilitated.

[0011] According to a second aspect of the present invention there is provided a method of performing LIBS analysis of a sample pellet of a consolidated granular material, preferably employing the system according to the first

aspect of the present invention, the method comprising: locating the granular sample pellet at a distance from focussing optics of a LIBS system; directing laser beam pulses from a laser source onto an exposed surface of the granular sample pellet; wherein locating the granular sample pellet comprise locating a tubular container containing the sample pellet with an outer surface of the sample pellet in contact with an inner surface of the tubular container, the method further comprising moving the sample pellet out of the tubular container linearly along a movement axis to provide a portion of the outer surface previously constrained by the inner surface of the tubular container as the exposed surface.

[0012] Thus, by measuring on an outer surface of the sample pellet which was previously constrained by the inner surface of the tubular container relaxation effects are mitigated. This provides an advantage that the focussing of the pulsed laser beam at the exposed surface can be more accurately maintained without the need for complicated adjustments of any focussing optics or of the sample stage.

[0013] According to a third aspect of the present invention there is provided a sample station useable in the system according to the first aspect of the present invention and with the method according to the second aspect, the sample station configured to hold a sample for LIBS analysis, the sample station comprising an actuator configured to slide the sample pellet along a movement axis out of the tubular container and thereby present a portion of the outer surface of the sample pellet previously constrained by an inner surface of the tubular container as an exposed surface for LIBS analysis.

[0014] These and other advantages and features will be better understood from a consideration of the following description of one or more exemplary embodiments of the method and the system according to the present invention made with reference to the drawings of the accompanying figures, of which:

Fig. 1 Shows schematically an embodiment of a LIBS system according to the present invention; and

Fig. 2 Shows schematically an embodiment of an actuator for use in a LIBS system according to the present invention.

[0015] Considering Fig. 1, an embodiment of a Laser Induced Breakdown Spectrocopy (LIBS) system 2 is illustrated (not to scale) as basically comprising a laser source 4 for emitting a pulsed laser beam 6 towards focussing optics 8 (here simply represented by lens) configured to focus the laser beam 6 onto an exposed portion of an outer surface 10 of a sample pellet 12 of a consolidated granular material, made for example by press-forming the granular material into a consolidated mass. In other embodiments an optical fiber may be employed to couple the laser beam 6 onto the exposed portion of outer surface 10 and focussing optics may be incorporated with the optical fiber. An optical spectrometer 14 is provided and is configured to perform spectral analysis of optical radiation emitted by a plasma produced by the focussed pulsed laser beam 6 on the exposed portion of the outer surface 10 of sample pellet 12 and to generate in a conventional manner LIBS spectral data therefrom. An optical fiber 16 is provided, in the present embodiment and by way of example only, to couple the optical radiation emitted by the plasma into the optical spectrometer 14.

[0016] The LIBS system 2 further comprises a sample station 18 configured to hold a tubular sample container 20 containing the sample pellet 12 of consolidated granular material and to present its outer peripheral surface 10 at a distance from the focussing optics 8, at which distance the laser beam 6 is focussed onto the so presented outer surface 10. The sample station 18 here comprises an open ended cylindrical housing 22 with an inner cylindrical surface 24. A set of rollers, here three, 26,28,30 are provided to hold the sample container 20 within the cylindrical housing 22. The sample station 18 also includes a rotary drive configured to impart rotational motion to the container 20 (hence to the exposed outer surface 10 of the sample pellet 12). This rotary motion has the advantage that multiple new portions of the outer surface 10 may be relatively simply

presented for LIBS analysis. In the present embodiment at least one of the rollers, here roller 30, is driven to rotate, for example using a rotary motor mechanically coupled to an axle on which the roller 30 is mounted, and forms the rotary drive. At least one of the rollers, here roller 28, may be made to engage with and disengage from the container 20 to facilitate its insertion into and removal from the sample station 18. In the present embodiment the roller 28 is mounted at one end of a rocker arm assembly 29 and is biased away from the container using spring bias 31.

[0017] As illustrated in Fig. 2, an actuator 32 is configured to effect relative movement of the sample container 20 and the sample pellet 12 so as to slide the sample pellet 12 along a movement axis 'M' and gradually present different portions (P, P') of the outer surface 10 for exposure to the focussed, pulsed laser beam 6. In the present embodiment the actuator 32 comprises, for example, a piston 34 having a toothed lower portion 36 which engages with teeth of a rotatable cog wheel 38 so that when the cog wheel 38 rotates the piston 34 moves linearly along the movement axis M to contact with an end 40 of the sample pellet 12. Linear movement is thereby transferred to the sample pellet 12. In this manner the pellet 12 is slid out of the sample container 20 which is held stationary as the piston 34 moves through the sample container 20.

[0018] Initially, the outer surface 10 is in contact with and constrained by an inner surface 42 of the sample container 20 and expansion or relaxation of the outer surface 10 is prevented. Moreover, dust or other contamination cannot accumulate on the outer surface 10. This advantageously enables samples to be stored, for example during transportation from remote collection sites, without the sample surface to be exposed to the laser beam during the LIBS analysis relaxing to cause height variations or becoming contaminated.

[0019] Usefully the sample container 20 is a cylindrical tubular container which is open at both ends 20a, 20b. This facilitates the coupling of the movement of the piston 34 to the sample pellet 12 as the piston 34 can directly contact the pellet 12. Furthermore, with this construction the position of the outer surface 12 of the pellet 12 is maintained relative to the focal point of

the laser beam as the container 20 rotates. In some embodiments the sample container 20 may be have different cross-sectional shapes or one end may be formed of a slidable end wall configured to slide along the inner surface 42 of sample container 20 without falling outside of the scope of the invention as claimed.

[0020] In use, the actuator 32 operates to present a portion P of the outer surface 10 of the sample pellet 12 at the focal point of the focussing optics 8. The laser 4 produces a pulsed laser beam 6, typically with an energy of less than 1mJ and preferably between 0.1mJ and 0.5mJ at a repetition rate of greater than 100Hz, which is focussed at the portion P of the outer surface 10 to cause breakdown of that portion P of the outer surface 10 and thereby generating a plasma containing optical radiation. The optical radiation is collected by optical fiber 16 and coupled into the spectrometer 14 for spectral analysis. The actuator 32 and the motorised roller 30 rotary drive are operated in concert to present for LIBS analysis a new portion of the outer surface 10 to the focussed laser beam 6 after one or more laser beam pulses. Thus, a spiral track (illustrated by points P') is traced by the laser beam 6 over the outer surface 10 of the sample pellet 12 during the analysis and collection of multiple instances of LIBS spectral data from the same sample is thereby facilitated.

[0021] By way of example, the LIBS system is configured to operate to provide the sample pellet 12 with three 'virtual' zones. A first zone 44 comprises a portion of the outer surface 10 first presented external of the sample container 20. No analysis is made from this first zone 44 and it is provided to limit the effects on the LIBS measurements of carry over between samples due to residue in the sample press used to form the sample pellets12 . A second zone 46 follows this first zone 44 and represents the portion of the outer surface 10 from which analysis is made and which is exposed to the pulsed laser beam 6 for LIBS analysis. A third zone 48 follows the second zone 46 and represents a holding portion of the sample pellet 12 which remains internal of the sample container 20 throughout the analysis.

[0022] A sample pellet 12 may be formed from a granular sample material through pelletizing the sample in a manner known in the art of LIBS analysis. Typically, the sample container 20 is located in the pellet press with its open ends along a vertical axis. A die is placed co-axially with and on top of the container 20. Sample is placed in the die and a ram, typically a pneumatic ram, applies several tons to consolidate the sample material and a sample pellet 12 of consolidated granular material is formed in the sample container 20.

[0023] In some applications the system may, as is known in the art, include a source of inert gas, such as Argon, for supply to the region at which laser ablation will be performed. This is to provide an inert atmosphere in which the plasma will be formed. In some applications the system may, as is known in the art, include a source of gas, such as compressed air, for cleaning optics of the system in order to remove debris that may collect there.

Claims

1. A Laser Induced Breakdown Spectrocopy (LIBS) system (2) for the analysis of sample pellet (12) of a consolidated granular material retained in a tubular container (20), the system (2) comprising a laser source (4) configured to emit a pulsed laser beam (6) towards an exposed surface (46) of the sample pellet (12); and a sample station (18) configured to hold the tubular container (20) with the sample pellet (12) orientated to present the exposed surface (46) towards the pulsed laser beam (6); wherein the sample station (18) comprises an actuator (32) configured to slide the sample pellet (12) along a movement axis (M) out of the tubular container (20) and thereby present a portion (P) of an outer surface (10) of the sample pellet (12) previously constrained through contact with an inner surface (42) of the tubular container (20) as the exposed surface (46).
2. The LIBS system (2) as claimed in claim 1 wherein the sample station (18) is configured to receive a cylindrical tubular container (20) configured with opposing open ends (20a, 20b).
3. The LIBS system (2) as claimed in claim 2 wherein the actuator (32) comprises a linearly moveable piston (34) configured to pass through a one (20a) of the opposing open ends (20a, 20b) and couple linear movement to the sample pellet (12) along the movement axis (M).
4. The LIBS system (2) as claimed in claim 1 wherein the sample station (18) further comprises a rotary drive (30) mechanically connectable to the cylindrical tubular container (20) to impart a rotational motion thereto and present a plurality of portions (P') of the outer surface (10) as the exposed surface (46).
5. The LIBS system as claimed in claim 4 wherein operation of the actuator (32) and the rotary drive (30) is concerted to present a plurality of spiral portions (P') of the outer surface (10) of the sample pellet as the exposed surface (46).
6. The LIBS system (2) as claimed in claim 1 wherein the laser (4) is adapted to emit laser beam pulses (6) each pulse with an energy of less than 1mJ, preferably between 0.1mJ and 0.5 mJ, at a repetition rate of greater than 100 Hz.

7. The LIBS system (2) as claimed in claim 1 wherein the sample pellet (12) is a pellet of pressed plant matter or soil.
8. A method of performing LIBS analysis of a sample pellet (12) of a consolidated granular material comprising: locating the sample pellet (12) at a distance from focussing optics (8) of a LIBS system (2); directing laser beam pulses (6) from a laser source (4) onto an exposed surface (46) of the sample pellet (12); wherein locating the sample pellet (12) comprise locating a tubular container (20) containing the sample pellet (12) with an outer surface (10) of the sample pellet (12) in contact with an inner surface (42) of the tubular container (20), the method further comprising moving the sample pellet (12) out of the tubular container (20) linearly along a movement axis (M) to provide a portion of the outer surface (10) previously constrained by the inner surface (42) of the tubular container (20) as the exposed surface (46).
9. The method of performing LIBS analysis as claimed in claim 8 wherein moving the sample pellet (12) out of the tubular container (20) comprises moving sequential portions of the outer surface (10) as the exposed surface (46) for different laser beam (6) pulses.
10. The method of performing LIBS analysis as claimed in claim 8 wherein the tubular container (20) is a cylindrical tubular container and the method further comprises imparting a rotational movement to the cylindrical tubular container (20).
11. The method of performing LIBS analysis as claimed in claim 10 wherein the moving the sample pellet (12) out of the cylindrical tubular container (20) and imparting rotational movement to the container is concerted to provide spiral portions (P') of the outer surface (10) of the sample pellet (12) as the exposed surface (46).
12. The method of performing LIBS analysis as claimed in claim 8 further comprising a step of forming the sample pellet (12) by pressing plant matter to form a consolidated mass.
13. A sample station (18) configured to hold a sample for LIBS analysis, the sample station (18) comprising an actuator (32) configured to slide a sample pellet (12) of consolidated granular material along a movement axis (M) out of the tubular container (20) and thereby present a portion (P) of the outer

surface (10) of the sample pellet (12) previously constrained by an inner surface (42) of the tubular container (20) as an exposed surface (46) for LIBS analysis.

AMENDED CLAIMS
received by the International Bureau on 23 Novembre 2016 (23.11.2016)

1. A Laser Induced Breakdown Spectroscopy (LIBS) system (2) comprising a laser source (4) configured to emit a pulsed laser beam (6) ; a cylindrical tubular container (20) for retaining a sample pellet of a consolidated granular material, the container (20) configured with opposing open ends (20a, 20b); and a sample station (18) configured to hold the tubular container (20) orientated to present an exposed surface (46) of a retained sample pellet (12) towards the pulsed laser beam (6); wherein the sample station (18) comprises an actuator (32) having a piston (34) configured to pass through a one (20a) of the opposing open ends (20a, 20b) and moveable along a movement axis (M) between the open ends (20a, 20b) for coupling linear movement along the movement axis (M) to a sample pellet (12) retained in the container (20) and thereby present a portion (P) of an outer surface (10) of the sample pellet (12) previously constrained through contact with an inner surface (42) of the tubular container (20) as the exposed surface (46).
2. The LIBS system (2) as claimed in claim 1 wherein the sample station (18) further comprises a rotary drive (30) mechanically connectable to the cylindrical tubular container (20) to impart a rotational motion thereto and present a plurality of portions (P') of the outer surface (10) as the exposed surface (46).
3. The LIBS system as claimed in claim 2 wherein operation of the actuator (32) and the rotary drive (30) is concerted to present a plurality of spiral portions (P') of the outer surface (10) of the sample pellet as the exposed surface (46).
4. The LIBS system (2) as claimed in claim 1 wherein the laser (4) is adapted to emit laser beam pulses (6) each pulse with an energy of less than 1mJ, preferably between 0.1mJ and 0.5 mJ, at a repetition rate of greater than 100 Hz.
5. A method of performing LIBS analysis of a sample pellet (12) of a consolidated granular material comprising: locating the sample pellet (12) at a distance from focussing optics (8) of a LIBS system (2); directing laser beam pulses (6) from a laser source (4) onto an exposed surface (46) of the sample pellet (12); wherein locating the sample pellet (12) comprise locating a tubular container (20) containing the sample pellet (12) with an outer surface (10) of the sample pellet (12) in contact

with an inner surface (42) of the tubular container (20), the method further comprising moving the sample pellet (12) out of the tubular container (20) linearly along a movement axis (M) to provide a portion of the outer surface (10) previously constrained by the inner surface (42) of the tubular container (20) as the exposed surface (46).

6. The method of performing LIBS analysis as claimed in claim 5 wherein moving the sample pellet (12) out of the tubular container (20) comprises moving sequential portions of the outer surface (10) as the exposed surface (46) for different laser beam (6) pulses.
7. The method of performing LIBS analysis as claimed in claim 5 wherein the tubular container (20) is a cylindrical tubular container and the method further comprises imparting a rotational movement to the cylindrical tubular container (20).
8. The method of performing LIBS analysis as claimed in claim 7 wherein the moving the sample pellet (12) out of the cylindrical tubular container (20) and imparting rotational movement to the container is concerted to provide spiral portions (P') of the outer surface (10) of the sample pellet (12) as the exposed surface (46).

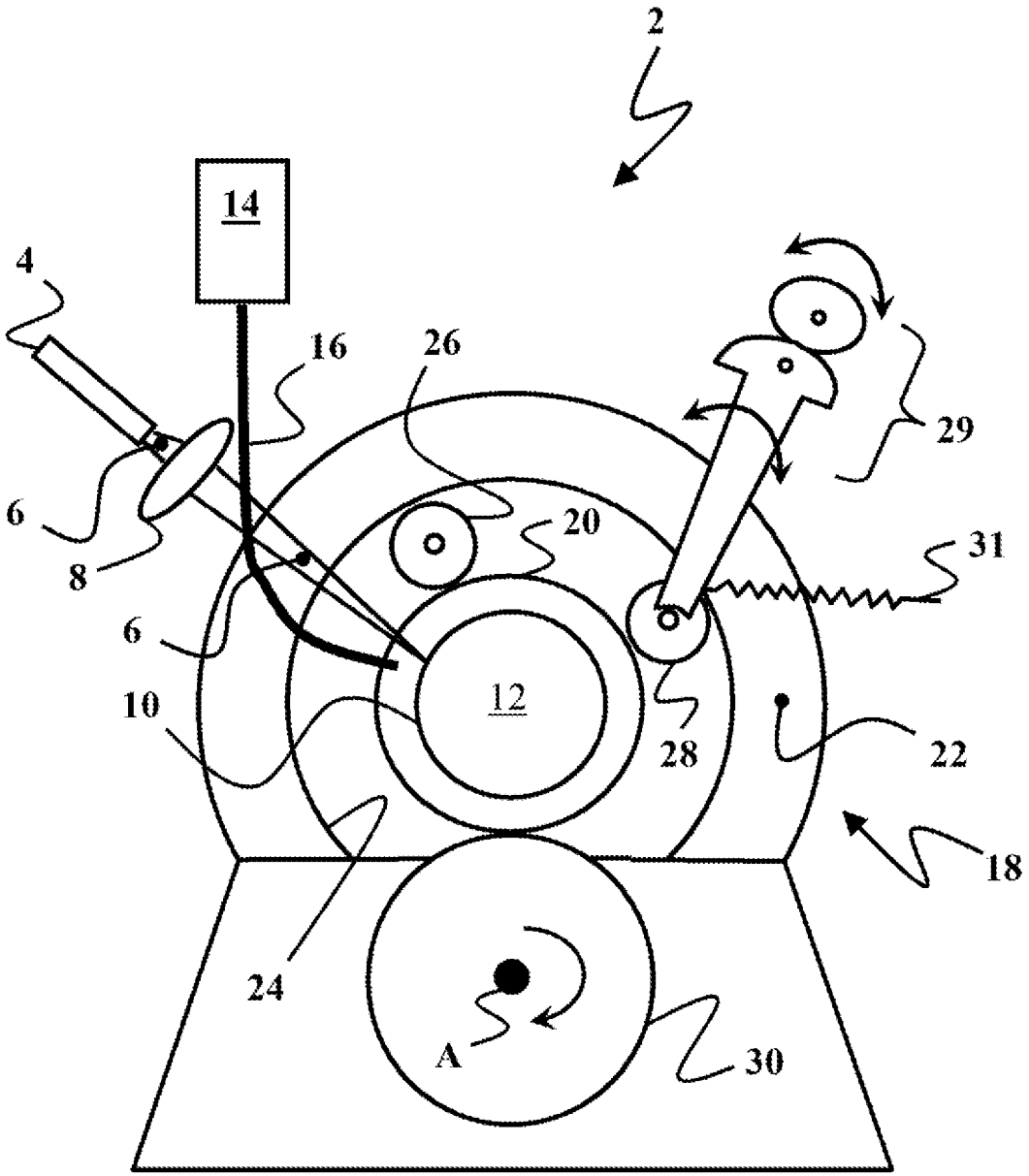


Fig. 1

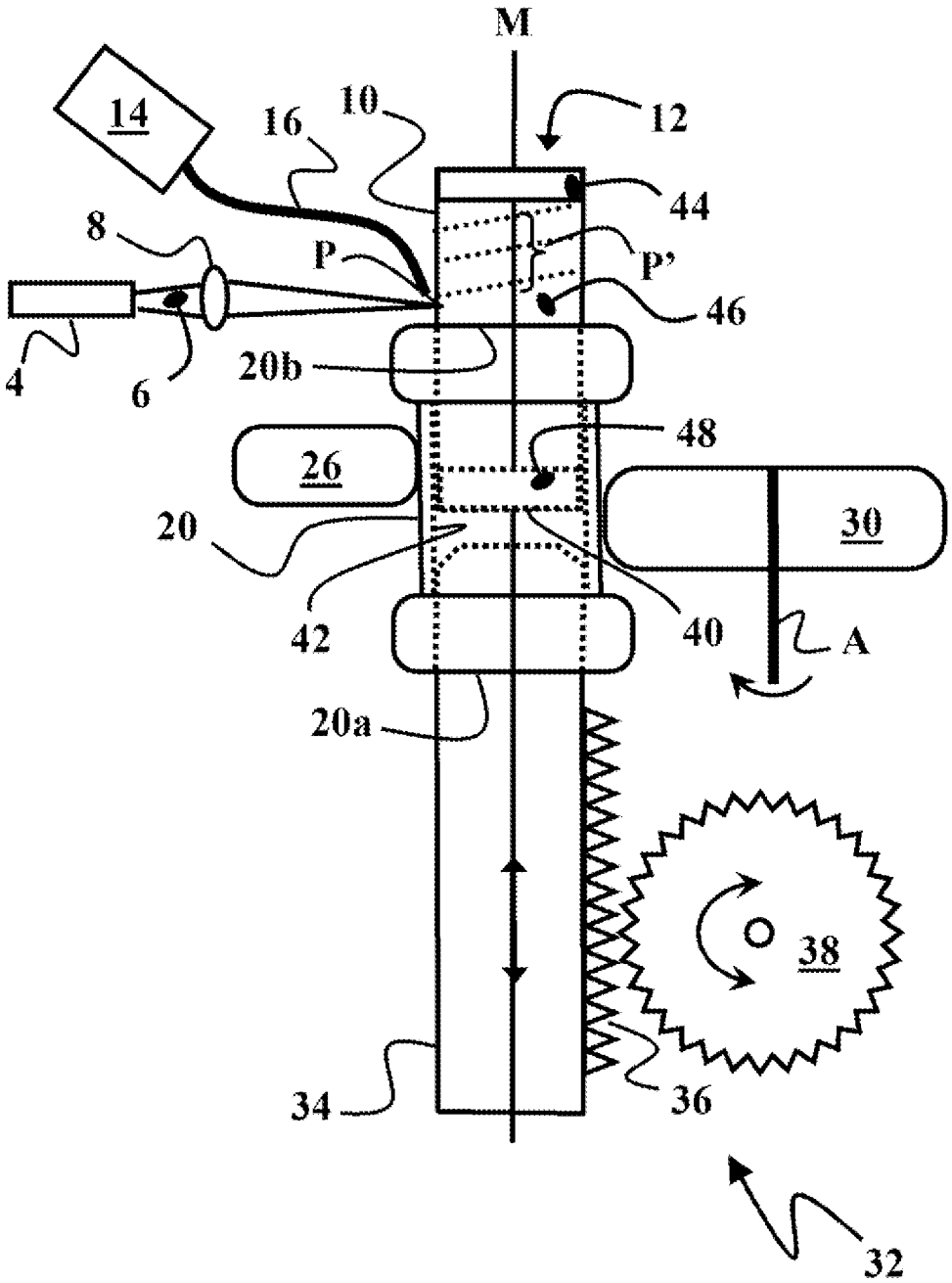


Fig. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2016/051829

A. CLASSIFICATION OF SUBJECT MATTER
INV. G01N21/71 B23K26/02 B23K26/08
ADD. G01J3/443 G01N1/28 G01N21/03

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 B23K G01J

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2005/106458 A2 (TRANSFORM PHARMACEUTICALS INC [US]; KANE NATHAN [US]; MACPHEE MICHAEL) 10 November 2005 (2005-11-10)	13
Y	paragraphs [0002], [0004], [0007], [0029], [0033], [0048], [0050], [0051], [0055] figures 5,8,13	1-12
Y	US 7 692 789 B1 (EBINGER MICHAEL H [US] ET AL) 6 April 2010 (2010-04-06) title column 1, line 35 - line 55 column 5, line 10 - line 35 figures 2,3	1-12

-/--

[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
21 October 2016	31/10/2016

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	Witte, Thomas

1

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

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2016/051829

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2016/018325 A1 (ELSOEE MAJA KIRSTINE [DK] ET AL) 21 January 2016 (2016-01-21) paragraph [0011]	4,5,10, 11
Y	EP 0 168 374 A2 (CENTRE RECH METALLURGIQUE [BE]) 15 January 1986 (1986-01-15) page 3, line 13 - line 32 figure 1	4,5,10, 11
Y	US 2007/218556 A1 (HARRIS RONNY D [US] ET AL) 20 September 2007 (2007-09-20) cited in the application paragraphs [0006], [0007], [0035]	12
A	US 2016/069745 A1 (WANG SEAN XIAOLU [US] ET AL) 10 March 2016 (2016-03-10) paragraph [0013]	6

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IB2016/051829

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2005106458 A2	10-11-2005	EP 1740925 A2	10-01-2007
		US 2009091740 A1	09-04-2009
		WO 2005106458 A2	10-11-2005
US 7692789 B1	06-04-2010	NONE	
US 2016018325 A1	21-01-2016	CN 105008898 A	28-10-2015
		EP 2976620 A1	27-01-2016
		US 2016018325 A1	21-01-2016
		WO 2014146719 A1	25-09-2014
EP 0168374 A2	15-01-1986	BE 902850 A1	10-01-1986
		DE 3582281 D1	02-05-1991
		EP 0168374 A2	15-01-1986
		JP S6182989 A	26-04-1986
		LU 85463 A1	12-02-1986
US 2007218556 A1	20-09-2007	NONE	
US 2016069745 A1	10-03-2016	NONE	