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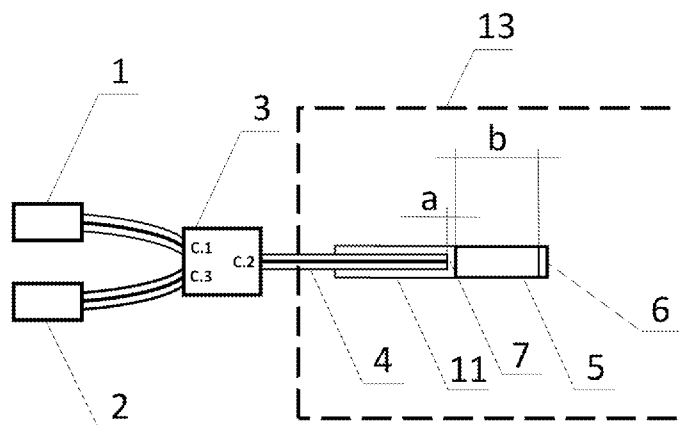


Fig. 1a

(57) Abstract: Disclosed is an interferometric fiber optic sensor for detecting chemical substances comprising a light source (1, 1.1, 1.2, 1.3), a detector (2, 2.1, 2.2, 2.3) and an optical path arranged between the light source (1, 1.1, 1.2, 1.3) and the detector (2, 2.1, 2.2, 2.3) further comprising a light dividing element (3, 3.1, 3.2, 3.3) to which the detector (2, 2.1, 2.2, 2.3) and the light source (1, 1.1, 1.2, 1.3) are connected, as well as optical fiber segment (4), with a measuring element (5) constituting resonant cavity, having a face (6) adapted to come into contact with a chemical substance to be detected, the optical fiber segment (4) and the measuring element (5) being squeezed together so that there is only a residual cavity (7) between them. The optical fiber segment (4) is at least along part of its length contained within a capillary (11). A first end part of the capillary (11) is joined with the measuring element (5) while other portion of the capillary (11) is clenched on the optical fiber segment (4), so that the capillary (11), the optical fiber segment (4) and the measuring element (5) constitute together a fiber optic measuring probe (13) being a part of the optical path. The capillary has a length of at least 5 mm. The disclosure further concerns a probe and a method for detecting a chemical substance with said interferometric fiber optic sensor.

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**Interferometric fiber optic sensor, fiber optic probe
and method of detection of chemical substance**

[0001] The invention concerns interferometric fiber optic sensor, fiber optic probe and method of detection of chemical substance using Interferometric fiber optic sensor with fiber optic probe.

[0002] Interferometric fiber optic sensors for measurement parameters such as temperature, strain or detection of substances are known in the art.

[0003] Publication WO2018106134 of international patent application discloses interferometric fiber optic sensor including Michelson interferometer with one arm covered with active substance adapted to interact with a substance to be detected. A result of this interaction is a change of thickness or optical thickness of the active substance, refractive index or attenuation at the end of measurement arm. Such interferometric fiber optic sensor can be used to detect presence of a substance in the environment surrounding measurement arm. Particularly measurement arm can be immersed in the unknown substance to detect if this substance includes predefined substance or substances. Active substance can be selected so that it reacts with only one substance to be detected or a group of substances to be detected. A method of detection consists in observation of interference fringes before contact with environment or unknown substance and after contact with environment or unknown substance. Presence of predefined substance is detected if particular shift of interference fringes is detected.

[0004] In the state of the art there are known also other configurations of the interferometric sensors. Fabry-Perot interferometer is one of the so called multibeam interferometers and is used for examination of light waves and utilizes a phenomenon of multiple reflection of light beam between two parallel and partially transparent mirrors.

[0005] An example of such construction is fuel level sensor disclosed in description of EP 3054272 may act as an example, in which an optical cavity is made on the optical fiber with a semiconductor material, e.g. gallium arsenide. An optical
5 cavity is attached to a lower surface of a diaphragm and the change of dimensions resulting from the changes of pressure of diaphragm on the cavity make possible interpretation of the result as a state of fuel reserve.

[0006] US patent application no US2005254062 discloses
10 interferometric sensor and method for detecting the presence or amount or rate of binding of an analyte. Sensor works in Fabry-Perrot configuration and has light source, detector with optical path between them comprising light dividing element and measuring element probe in which optical fiber delivers
15 light to a first and second optical element, via air gap. Second optical element is covered with substance capable of binding analyte. Analyte is analyzed with observation of the spectrum of reflected light. Document discloses multiple applications allowing detection and measurements of particular
20 substances - analytes, in particular antigens. The disclosure is not devoid of disadvantages. It requires high precision of manufacturing of the first and the second optical element and - particularly - precise definition of air gap. It is non-optional requirement for the probes to be repeatable and for
25 the spectral changes to be properly observed. It comes at the cost of complicating mathematical model. Replacing of the probe is also a problem as well as manufacturing thereof.

[0007] Sensors known in the art are difficult in mass
30 production, have parameters difficult to be repeated and are a bit cumbersome with small samples. On the other hand industrial sensors like fluid level sensors give only limited information about certain condition that has been met. Consequently there is a need for sensor that can be applied in large amounts of repeatable testing and examination. It is an

object of the invention to provide interferometric fiber optic sensor, fiber optic probe and method of using thereof devoid of the disadvantages of the state of the art mentioned above.

[0008] Interferometric fiber optic sensor according to the invention, for detecting chemical substances comprising a light source, a detector and an optical path arranged between the light source and the detector. It further comprises a light dividing element to which the detector and the light source are connected, as well as optical fiber segment, with a measuring element constituting resonant cavity, having a face adapted to come into contact with chemical substance to be detected. The optical fiber segment and the measuring element are squeezed together so that there is only a residual cavity between them. The optical fiber segment is at least along part of its length contained within a capillary. A first ending part of the capillary is joined with the measuring element while other portion of the capillary is clenched on the optical fiber segment, so that the capillary, the optical fiber segment and the measuring element constitute together a fiber optic measuring probe being a part of the optical path. Capillary has length of at least 5 mm. Positive result of such construction of the sensor is that residual cavity can be neglected in calculations. It has low impact on the measurement results and is easy to manufacture in stable and repeatable manner. Length of capillary of 5 mm or greater enables shifting a point of clenching on the optical fibre segment away from the residual cavity far enough for its parameters not to be affected in the process. Consequently sensor according to the invention can be considered as having a single measurement resonant cavity constituted by the surfaces of the faces of the measuring element. It results in linear measurement and simple interpretation of measurement results. Probe with a capillary can be easily replaced by cutting and welding a new one or using a fiber optic connectors. Sensor is applicable in

particular but not only to detect substances within a group including acetone, refrigerants, ethanol vapours, hydrochloric acid, poly(allylamine hydrochloride), allylamines, proteins, biomarkers and antigens. Additional advantage of the invention is that substance to be detected interact with a face of measuring element being in front of the optical fiber. This configuration improves measurement dynamics in comparison to the probes in which substance to be detected interacts with side surface of the optical fiber or measuring element.

[0009] Advantageously a ratio between optical length $a \cdot n_1$ of the residual cavity and optical length $b \cdot n_2$ of the measuring element falls into a range of 0 to 0.4. Providing ratio between the length of resonant cavity and residual cavity within a range of 0 to 0.4 results in high frequency of interference fringes and simplifies analysis. This ratio makes it easier to use single cavity model in the analysis. Spectrum of the reflected signal from the residual cavity is far wider than the spectrum of measurement signal originating from cavity formed by measuring element. In mathematical model it corresponds to multiplication of two sinusoidal signals having different periods. Providing given ratio makes it easier to consider impact to the spectrum originating from the residual cavity constant and neglect it.

[0010] Advantageously the measuring element has face at least partly covered with substance adhesive to the substance to be detected. This configuration makes it easy to capture the sample of the substance to be detected.

[0011] Alternatively the measuring element has face at least partly covered with substance that loses its adhesiveness when exposed to the substance to be detected. In this configuration substance it is possible to detected result of exposition of the face of the measuring element to the predefined substance and consequently to detect the substance itself.

[0012] Alternatively the measuring element has face at least partly covered with substance that changes its optical parameters when exposed to the substance to be detected. Application of covers with multiple substances interacting with respective particular substances to be detected makes it possible to detect multiple substances in single measurement with the same detector and light source. Attachment/detachment of the substance or change of parameters of the substance on the face of measuring element or change of the parameters of the element itself after exposition to the external factors changes length of the optical path in the interferometer. In result a shift of interference fringes can be observed.

[0013] Measuring element advantageously is a tile made of material comprising a substance selected of a group including glass, silica glass SiO_2 , lead glass, ZBLAN glass and polymers.

[0014] Optical fiber segment advantageously is a single mode fiber within an operating range of the detector.

[0015] An end of the optical fiber segment inside the capillary is advantageously oblique and inclined by an angle within a range of 4° to 20° with respect to the axis of the optical fiber segment. Best effects were obtained for range of 7° to 8° .

[0016] A first surface of optical fiber segment confining residual cavity from the first side has a reflection coefficient R_1 and a second surface of a measuring element confining the residual cavity from the opposite side has a reflection coefficient R_2 and reflection coefficients advantageously meet condition $\frac{R_1}{R_2} \leq 0,5$.

[0017] Advantageously optical fiber segment is a multicore fiber segment and is connected to fan-in/fan-out being in the optical path, wherein interferometer has a first light source and a first detector connected with fan-in/fan-out device via a first light dividing element and a second light source and a second detector connected with fan-in/fan-out device via a second light dividing element. This configuration makes it

possible to simultaneously observe shifts on different wavelengths and improvement of sensitivity and specificity of detection or simultaneous detection of two different substances.

5 [0018] Advantageously the interferometer further has a third light source and a third detector connected with fan-in/fan-out device via a third light dividing element. Application of greater number of sources and detectors operating at various wavelengths further improves sensitivity and specificity, yet
10 is connected with high complication of the sensor.

[0019] Advantageously least one light source selected from a group including:

- supercontinuum source,
- halogen lamp emitting light within a wavelength range of
15 400–700 nm,
- superluminescent diode having a central wavelength of 1310 nm,
- superluminescent diode having a central wavelength of 1400 nm,
- 20 • superluminescent diode having a central wavelength of 1450 nm,
- superluminescent diode having a central wavelength of 1550 nm,
- narrowband light source having a central wavelength within
25 a range 1310 do 1550 nm tunable within a range of 20 nm or wider.

[0020] Generally good results were obtained with sources working within a range of wavelength of 400 ÷ 1600 nm. Having selected a source and mechanism of interaction of the face of
30 measuring element with substance to be detected it is possible easily to select length of the measuring element to obtain fringe at desired wavelength corresponding to selected source so that shift of the fringe can be easily observed.

[0021] Fiber optic measuring probe comprising an optical fiber segment and a measuring element having a face for contacting substances according to the invention has the optical fiber segment and the measuring element are squeezed together so that there is only a residual cavity between them, and an optical fiber segment is at least along part of its length contained within a capillary, wherein first ending part of the capillary is joined with the measuring element while other portion of the capillary is clenched on the optical fiber segment. Probe according to the invention can be located remote from the light source and detector. It is easily replaceable. Can be easily sterilized and adapted to subsequent use.

[0022] Advantageously a ratio between optical length $a \cdot n_1$ of the residual cavity and optical length $b \cdot n_2$ of the measuring element falls into a range of 0 to 0.4. Providing ratio between the length of resonant cavity and residual cavity within a range of 0 to 0.4 results in high frequency of interference fringes and simplifies analysis. This ratio makes it easier to use single cavity model in the analysis. Measurement fringes are far narrower than the ones originating from residual cavity.

[0023] Advantageously the measuring element has face at least partly covered with substance adhesive to the substance to be detected. This configuration makes it easy to capture the sample of the substance to be detected.

[0024] Alternatively the measuring element has face at least partly covered with substance that loses its adhesiveness when exposed to the substance to be detected. In this configuration substance it is possible to detected result of exposition of the face of the measuring element to the predefined substance and consequently to detect the substance itself.

[0025] Alternatively the measuring element has face at least partly covered with substance that changes its optical parameters when exposed to the substance to be detected.

Application of covers with multiple substances interacting with respective particular substances to be detected makes it possible to detect multiple substances in single measurement with the same detector and light source. Attachment/detachment of the substance or change of parameters of the substance on the face of measuring element or change of the parameters of the element itself after exposition to the external factors changes length of the optical path in the interferometer. In result a shift of interference fringes can be observed.

[0026] Measuring element advantageously is a tile made of material comprising a substance selected of a group including glass, silica glass, lead glass, ZBLAN glass and polymers.

[0027] An end of the optical fiber segment inside the capillary is advantageously oblique and inclined by an angle within a range of 4° to 20° with respect to the axis of the optical fiber segment.

[0028] A first surface of optical fiber segment confining residual cavity from the first side has a reflection coefficient R_1 and a second surface of a measuring element confining the residual cavity from the opposite side has a reflection coefficient R_2 and reflection coefficients advantageously meet condition $\frac{R_1}{R_2} \leq 0,5$.

[0029] Advantageously, when difference between refraction index of the medium within capillary n_1 and refraction index of material of measurement element n_2 is greater than 30% i.e.:

$$\frac{|n_2 - n_1|}{n_1} \geq 0,3$$

[0030] Fiber optic measuring probe advantageously has a connector provided on an end of the optical fiber segment, opposite that the measuring element is located.

[0031] Advantageously optical fiber segment in the measurement probe has more than one core. It enables use of the probe within an interferometer with multiple detectors and/or sources providing better sensitivity and specificity.

[0032] Method of detecting chemical substance using interferometer having optical path with detector, light source and fiber optic measuring probe included in the optical path, guiding light to substance to be detected, in which substance
5 is considered as detected if shift of predefined interference fringe is observed on detector, characterized in that interferometer is an interferometer according to the invention. As the measurement element constitutes resonant cavity it is possible to register interference fringes in the
10 wavelength domain. In case to the external surface of the cavity a substance is attached or thickness of the substance already attached is increased interference fringes are shifted towards greater wavelength. Size of the shift can be used to determine thickness change. Alternatively if layer is detached
15 interference fringes move towards shorter wavelengths and reduction of thickness can be determined.

Description of drawings

[0033] Embodiments of the invention has been described below in detail, with reference to the following figures wherein
20 Fig. 1a shows a block diagram of an interferometric fiber optic sensors according to a first, a second and a third embodiment of the invention, Fig. 1b shows schematically configuration of a probe according an embodiment of the invention, Fig. 1c shows schematically configuration of a probe according another
25 embodiment of the invention, Fig. 1d shows schematically configuration of a probe according yet another embodiment of the invention, Fig. 2a and Fig. 2b show a shift of interferometric fringes due to exposition to substance under test in the first embodiment of the invention, Fig. 3 shows a
30 block diagram of a sensor according to a fourth embodiment of the invention with multicore - three core - fiber, while Fig. .4 shows cross-sectional view of this three core fiber.

Embodiments of the invention

Example 1

[0034] Block diagram of an interferometer in this embodiment is presented in fig. 1.a. Superluminescent diode with a central wavelength of 1400 nm and a full width at half maximum equal to 50 nm, constituting the light source 1 is connected through a single mode optical fiber to the first port C.1 of a circulator constituting a dividing element 3. A measuring probe 13 according to the invention is connected to the second circulator port C.2 with a single-mode fiber end 4. In the structure of the measuring probe 13, the other end of the optical fiber 4 is enclosed in a silica glass capillary 11 and pushed to the measuring element 5 attached to the capillary 11 by splicing.

[0035] Alternatively, the capillary can be clamped on the measuring element 5.

[0036] The end of the optical fiber 4 located in the capillary is cut at an angle $\alpha = 8^\circ$. As a result, between the end of optical fiber 4 and the measuring element 5 there is an air gap forming a residual cavity 7 with an effective width from $a = 0 \text{ }\mu\text{m}$ to $a = 2 \text{ }\mu\text{m}$. Measuring element 5 has a length of 20 μm .

[0037] Further tests has shown that effect of attenuation of reflected signals can be obtained to some extent in whole range of cutting angles from 4° to 20° .

[0038] To the third port C.3 of a circulator there is connected an optical spectrum analyzer used in this embodiment of the invention as a detector 2.

[0039] Light from source 1, through a circulator constituting a dividing element 3 gets to the optical fiber 4, where through an air gap of a width "a" it gets to the measuring element 5 having the face 6. This way a Fabry-Perot interferometer is obtained. On the detector 2 one can observe interference fringes in the spectral domain. A shift of fringes and/or contrast depend on changes of the parameters of the cavities

formed along the optical path. In practice, the changes the surface at the boundary of the cavity established between the face 6 and the opposite end of the measuring element 5 is useful in measurements. The best results are obtained if the optical path contains only one cavity. Each connection, and each border of medias introduces an additional cavity. In the construction of the interferometer according to the invention, the number of cavities is limited. The residual cavity 7 is negligible due to its small size. Additionally, its contribution to the measurement result is limited thanks to oblique cut of the fiber section 4 and providing an adequate ratio of reflection coefficients at the boundaries of the cavity:

$$\frac{R_1}{R_2} \leq 0.5$$

Where:

- R_1 is the reflection factor from the end of the optical fiber,
- R_2 is the reflection coefficient from the surface of the measuring element facing the capillary.

The difference between the refractive indices n_1 of the medium in the capillary and n_2 of the material of the measuring element is greater than 30%, i.e. $\frac{|n_2 - n_1|}{n_1} \geq 0,3$, which allows for better dynamics of measurement.

[0040] The measuring element 5 is a tile in the form of a glass cylinder with a height of 20 μm . The face 6 of the measuring element 5 is coated with a perfluorinated polymer with a refractive index of approximately 1.33. Coating is provided by immersing measuring element 5 in a polymer solution. As a result of exposing the face 6 to detected substances - refrigerants, which are compounds of carbon, chlorine and fluorine, like 1,1,2-trichloro-1,2,2-trifluoroethane the layer of polymer swells. In this configuration swelling contributes to a change of the substance thickness by 10 nm, which

corresponds to shift of interference fringes in a proximity of 1410 nm by 0.6 nm – as shown in Fig. 2a and Fig. 2b, showing reflection coefficient S_{11} as a function of wavelength before and after exposure of the measuring element to refrigerants.

5 **[0041]** Based on the obtained spectral plots shown in Fig. 2a and Fig. 2b, the thickness of the layer covering the face 6 and changing its thickness is determined.

[0042] The first step is to measure the thickness of the measuring element 5 by determining the difference in wavelength
10 for neighboring interference fringes during the measurement before exposure to the measuring substance. These fringes are shown in Fig. 2a. Thus, the calibration of the interferometer is carried out by determining the difference of optical paths in the interferometer and considering the refractive index for
15 the cavity formed by the surfaces of the measuring element 5 and taking into account that the optical signal passes through the cavity twice.

[0043] Next, the face 6 is exposed to the measured substance and one of the interference fringes is analyzed; a difference
20 in wavelength corresponding to the fringes before and after exposure is determined. Fig. 2b shows the fringes before and after exposure. Shift of the fringes occurred due to a change in the thickness of the layer which had been attached to the face 6 of the measuring element 5.

25 **[0044]** After determining the difference of the wavelength corresponding to said interference fringe before and after exposure, knowing the refractive index of the layer covering the face 6 of the measuring element 5, a change in the layer thickness ΔL is calculated:

$$30 \quad \Delta L = \frac{(L_2 n_2 + L_3 n_3)}{n_2} \left(\frac{\lambda + \Delta \lambda}{\lambda} - 1 \right)$$

Where:

L_2 , n_2 denote the thickness and refractive index of the measuring element 5, respectively,

L_3 , n_3 denote the thickness and refractive index of the layer of perfluorinated polymer covering the face 6 of the measuring element 5, respectively,

λ is wavelength of analysed fringe before and after swelling of the layer,

$\Delta\lambda$ - is the difference in wavelength for the analyzed interference fringe before and after the layer swelling.

[0045] If the change in wavelength $\Delta\lambda$ of the interference fringe is in a range (0.1 nm, 16.8 nm) towards longer wavelengths, detection of the refrigerant is acknowledged. The range was selected experimentally. In other embodiments of the invention, other ranges and other active substances are suitable for selection to detect other substances. Selection can be done in routine tests. The skilled person is able to easily offer other active substances and measure appropriate ranges.

[0046] In the present embodiment, the configuration of the measuring probe 13 according to the invention makes it possible to effectively shorten the residual optical cavity 7. The probe 13 is shown schematically in Fig. 1b. The end of optical fiber 4 and measuring element 5 are placed in a glass capillary having a U-section in the cross-section. The fiber end 4 is cut at an angle of 20° and press to the measuring element 5. The capillary is sealed by welding at both ends on measuring element 5 and optical fiber 4. Connecting point capillary 11 with optical fiber 4 should be moved away from the residual optical cavity 7 to prevent accidental increase of the reflection of one of the layers. This was achieved using a 5 mm long capillary 11.

Example 2

[0047] An interferometer according to the second embodiment of the invention was made according to the same block diagram illustrated in Fig. 1a. The light source 1 is a narrowband tunable light source with a central wavelength of 1550 nm

tunable in a range of 50 nm. The source 1 is connected to the first port C.1 of circulator via single-mode fiber. A measuring probe 13 is connected to the second port C.2 of the circulator.

[0048] A measuring probe according to this embodiment of the invention is shown schematically in Fig. 1c. It is interconnected into the optical path of the interferometer with an end of the single-mode optical fiber 4 provided with a connector which is not shown in the figure. The other end of the optical fiber 4 is enclosed in the capillary 11 and pushed against the measuring element 5. The end of the optical fiber 4 housed in the capillary is cut at an angle of 8° . A weld is made between the capillary 11 and the measuring element 5. As a result, between the end of the optical fiber 4 and the measuring element 5, there is an air gap forming a residual cavity 7 with an effective width $a = 2 \mu\text{m}$. The measuring element 5 has a length of $b = 20 \mu\text{m}$. The face 6 of the measuring element 5 is covered with the same substance as in example 1.

[0049] Detector 2 is connected to the third port C.3 of the circulator.

Example 3

[0050] Block diagram of an interferometer according to the third embodiment of the invention is the same as in the first and the second embodiment. It is shown in Fig. 1a. The light source 1 being a halogen lamp emitting light in a wavelength range from the 400–700 μm , is connected through a birefringent optical fiber – maintaining polarization, and a single mode in the operational wavelength band of the source 1 – to the first port C.1 of a circulator. Circulator maintaining polarization has a function of dividing element 3. The second port C.2 of the circulator is connected with measuring probe (13). Optical fiber segment 4 of the optical probe 13 is birefringent and has a beat length of 3 mm at wavelength $\lambda = 550 \text{ nm}$. It maintains polarization and is single mode in the wavelength operational band of the source 1. Measuring element (5) is made of lead

glass having a refractive index equal to 1.8. Third port C.3 of the circulator is connected to spectroscope constituting the detector 2.

[0051] Measurement probe 13 shown schematically in Fig. 1d comprises capillary 11 having an O-shaped cross-section and length of 5 mm, into which there is inserted a segment of optical fiber 4 maintaining polarization and measuring element 5 made of a lead glass and having a length of $b = 200 \mu\text{m}$. Residual cavity 7 obtained in this configuration has a length $a = 0,1 \mu\text{m}$.

[0052] Alternatively measuring element 5 can be made of other substances selected from a group including glass, silica glass, lead glass, ZBLAN glass and polymers, which also provide relatively low losses.

[0053] Silica glass is particularly convenient in processing. Using silica glass, it is convenient to manufacture cylindrical measuring element 5 having desired length and smooth surface as well as bases parallel to each other and perpendicular to the axis.

[0054] Adhesion of the substance to be detected to the face 6 of the measuring element 5 is obtained by placing face 6 in the piranha solution, that is a solution comprising concentrated sulfuric acid and 30% hydrogen peroxide mixed in volume proportion of 3:1. Thusly processed face 6 is active enough to attract and be covered with a layer of polymer having a refractive index of 1.5 and 2 nm thick when exposed to poly(allylamine hydrochloride).

[0055] Surface of the lead glass has chemical bonds O-Si-O-Si-O. After exposure to the piranha solution structures Si-O-Si are transformed to 2x Si-OH which have more polar character and consequently attachment of ion polymers to the surface is easier.

[0056] Layer of 2 nm of substance having refractive index of 1.5 to the face 6 of the measuring element 5 results in shift

of spectral refractive fringes by 5 pm at wavelength of 550 nm. Consequently the sensor in this embodiment is applicable for detection of poly(allylamine hydrochloride), presence of which is acknowledged when spectral interference
5 fringes are shifted by a value between 2 pm and 0,2 nm towards longer wavelengths.

Example 4

[0057] In Fig. 3 there is shown a block diagram of a fourth embodiment of the invention. Use of measuring probe 9 with a
10 multi-core section of the fiber 4 makes it possible to simultaneously observe the spectrum for different wavelengths of the light source. In the present example, a three-core optical fiber is shown schematically in cross-section in Fig. 4 and a set of three light sources.

15 **[0058]** In the set of light sources (1.1, 1.2, 1.3), three wide-spectral superluminescent diodes with wavelengths of 1310 nm, 1450 nm and 1550 nm, respectively, and 50 nm full width were used. Each of the sources is connected to the detector 2.1, 2.2, 2.3 connected to it via the circulator 3.1, 3.2, 3.3 in
20 the configuration of the reflection measurement. As the detectors 2.1, 2.2, 2.3, a spectrometer was used. The free ports of circulators 3.1, 3.2, 3.3 are connected to the ports of the Fan-In/Fan-out device 8 connecting these ports to the cores of the three-core section of optical fiber 4 of the
25 measuring probe 9.

[0059] The measuring element 5 has a length $b = 50 \mu\text{m}$ and is made of glass ZBLAN ($\text{ZrF}_4\text{-BaF}_2\text{-LaF}_3\text{-AlF}_3\text{-NaF}$). Between the ZBLAN glass and the input multi-core fiber 4 there is an air gap - residual cavity 7 with length $a = 1 \mu\text{m}$. In this configuration,
30 a Fabry-Perot resonator is formed for each of the cores 9.1, 9.2, 9.3.

[0060] The face 6 of the measuring element 5 is sensitized to the detection of acetone as a result of immersion in a 1% solution of polystyrene in dichloromethane. The active layer

remaining on the face 6 after drying has certain property: it swells as a result of contact with acetone. Consequently, a sensor according to the invention equipped with such a layer can be used as an acetone sensor.

5 **[0061]** The skilled person is able to easily offer other sets of sources with other mid-wavelengths and other spectral widths that allow measurements in the range from 1300 to 1500 nm, in which the sensor of the invention has been able to detect and measure the desired substances.

10 **[0062]** Light from sources through single-mode optical fibers is directed to circulators 3 and then to a fan-in/fan-out device 8 to the input three-core fiber 4. This optical fiber has a cross-section of the triangular set out of the cores 9.1, 9.2, 9.3 shown in Fig. 3, and the lattice constant $\Lambda =$
15 80 μm . Cores 9.1, 9.2, 9.3 have diameters of 8.2 μm and numerical apertures of 0.12. From the optical fiber 4 the light is directed to the air filled residual cavity 7 and the measuring element 5. Light reflected from the edge of the measuring element, returns via a fiber segment 4, through a
20 fan-in/fan-out element, through single-mode optical fibers and circulators to detectors on which the fringes resulting from interference of light reflected from opposite ends of measuring element 5 are observed. The immersion in acetone at room temperature causes a change in the thickness of the layer on
25 the measuring probe by approx. 200 nm and causes the fringes shift in the vicinity of the 1550 nm wavelength by approx. 6.4 nm, adjacent to the wavelength of 1450 nm at 6 nm, in the vicinity of the wavelength of 1310 nm by about 5.4 nm. It is acknowledged that acetone was detected if the interference
30 fringe shift obtained at all source wavelengths lies within the range of 0.1 nm to 8.0 nm. Thus, an increase in the specificity of the detection method has been achieved.

[0063] Use of a fan-in/fan-out element makes it possible to observe shifts of all of these fringes simultaneously.

Improvement of the sensor's operation - higher sensitivity and specificity - is obtained already when observing two fringes. For some of the substances detected, it is advisable to use a fiber with more than three cores and a correspondingly greater number of light sources - up to ten, 12 or more.

[0064] In embodiments of the sensor according to the invention, multi-core fiber sections 4 having a greater number of cores and a corresponding number of light sources and detectors can be used. Such sensor systems and measuring probes are more complicated but they give the possibility to identify the detected substance with more certainty.

[0065] In some embodiments of the invention, a fiber optic section may be used as the measuring element 5. Due to the use of the optical fiber segment as a measuring element 5, the diffraction of beam is avoided - due to the presence of the core in the optical fiber. The use of optical fiber with a positive dispersion in the light source's bandwidths avoids the occurrence of non-linear phenomena.

[0066] The person skilled in the art is able to routinely propose other advantageous modifications of the optical path between source and detector in some circumstances, without however departing from the invention as defined by the claims. For example, circulators used in the embodiments above can be easily replaced with couplers.

[0067] Similarly, one skilled in the art familiarized with the description above is able to propose without difficulty various methods for coating or sensitizing the face 6 of the measuring element 5 to various detected substances and also to select appropriate optical parameters of the source and optical path. Sensitivity to hydrochloric acid can be obtained by preparing a measuring element made of silica glass with a small porosity and refractive index of approx. 1.8 and covering its face with yttrium oxide, e.g. by laser warming of yttrium oxide and depositing on glass. Contact of a dissected element with

hydrochloric acid causes the fringes shift at a wavelength of 1550 nm by approx. 4 nm.

[0068] The person skilled in the art is also able to propose various techniques for connecting the measuring probe to the optical path, in particular by splicing the fibers and with
5 dedicated fiber optic connector.

[0069] The person skilled in the art can easily select the length of the measuring element to the light source band and replace the sources mentioned in the description with various
10 substitutes. The creators have also successfully used various sources, including:

- Supercontinuum source
- Halogen lamp emitting light from the range of 400-700 nm,
- Superluminescent diode with central wavelength on 1310 nm,
- 15 • Superluminescent diode with central wavelength on 1400 nm,
- Superluminescent diode with central wavelength on 1450 nm,
- Superluminescent diode with central wavelength on 1550 nm,
- Narrowband tuned source with central wavelength from range 1310-1550 nm and range of tuning at least 20 nm.

20 [0070] The invention may be embodied using various measuring techniques known to those skilled in the art. Broadband light sources such as SLED diodes, supercontinuum sources, or halogen can be used, and as a detector, a spectrum analyzer or spectrometer. Alternatively, one tunable source can be used,
25 switched during the measurement to the next wavelength. In this configuration, more primitive detectors can be used. There is possibility of analyzing one broadband light signal with several detectors or several sources of narrowband light sources to analyze with one broadband detector.

30 [0071] Embodiments should be read as illustrating the invention but not limiting.

Claims

1. Interferometric fiber optic sensor for detecting chemical substances comprising a light source (1, 1.1, 1.2, 1.3), a detector (2, 2.1, 2.2, 2.3) and an optical path arranged between the light source (1, 1.1, 1.2, 1.3) and the detector (2, 2.1, 2.2, 2.3) further comprising a light dividing element (3, 3.1, 3.2, 3.3) to which the detector (2, 2.1, 2.2, 2.3) and the light source (1, 1.1, 1.2, 1.3) are connected, as well as optical fiber segment (4), with a measuring element (5) constituting resonant cavity, having a face (6) adapted to come into contact with chemical substance to be detected,

characterized in that

the optical fiber segment (4) and the measuring element (5) are squeezed together so that there is only a residual cavity (7) between them, and the optical fiber segment (4) is at least along part of its length contained within a capillary (11), wherein first ending part of the capillary (11) is joined with the measuring element (5) while other portion of the capillary (11) is clenched on the optical fiber segment (4), so that the capillary (11), the optical fiber segment (4) and the measuring element (5) constitute together a fiber optic measuring probe (13) being a part of the optical path wherein the capillary (11) has length of at least 5 mm.

2. Interferometer according to claim 1, characterized in that a ratio between optical length $a \cdot n_1$ of the residual cavity (7) and optical length $b \cdot n_2$ of the measuring element (5) falls into a range of 0 to 0.4.

3. Interferometer according to claim 1 or 2, characterized in that the measuring element (5) has the face (6) at least

partly covered with substance adhesive to the substance to be detected.

4. Interferometer according to claim 1 or 2, characterized in that the measuring element (5) has the face (6) at least partly covered with substance that loses its adhesiveness when exposed to the substance to be detected.

5. Interferometer according to claim 1 or 2 or 3, characterized in that the measuring element (5) has the face (6) at least partly covered with substance that changes its optical parameters when exposed to the substance to be detected.

6. Interferometer according to any of claims 1-5, characterized in that the measuring element (5) is a tile made of material comprising a substance selected of a group including glass, silica glass, lead glass, ZBLAN glass and polymers.

7. Interferometer according to any of claims 1-6, characterized in that the optical fiber segment (4) is a single mode fiber within an operating range of the detector (2).

8. Interferometer according to any of claims 1-7, characterized in that an end of the optical fiber segment (4) inside the capillary (11) is oblique and inclined by an angle within a range of 4° to 20° with respect to the axis of the optical fiber segment (4).

9. Interferometer according to claim 8, characterized in that a first surface of optical fiber segment (4) confining residual cavity from the first side has a reflection coefficient R_1 and a second surface of a measuring element (5) confining the residual cavity from the opposite side has a reflection coefficient R_2 and reflection coefficients meet condition $\frac{R_1}{R_2} \leq 0,5$.

10. Interferometer according to any of claims 1-9, characterized in that the optical fiber segment (4) is a multicore fiber segment and is connected to fan-in/fan-out (8) being in the optical path, wherein interferometer has a first (1.1) light source and a first (2.1) detector connected with fan-in/fan-out device (8) via a first light dividing element (3.1) and a second (1.2) light source and a second (2.2) detector connected with fan-in/fan-out device (8) via a second light dividing element (3.2).

11. Interferometer according to claim 10, characterized in that it has a third (1.3) light source and a third (2.3) detector connected with fan-in/fan-out device (8) via a third light dividing element (3.3).

12. Interferometer according to any of claims 1-11, characterized in that it has at least one light source (1, 1.1, 1.2, 1.3) selected from a group including:

- supercontinuum source,
- halogen lamp emitting light within a wavelength range of 400-700 nm,
- superluminescent diode having a central wavelength of 1310 nm,
- superluminescent diode having a central wavelength of 1400 nm,
- superluminescent diode having a central wavelength of 1450 nm,
- superluminescent diode having a central wavelength of 1550 nm,
- narrowband light source having a central wavelength within a range 1310 do 1550 nm tunable within a range of 20 nm or wider.

13. Fiber optic measuring probe comprising a optical fiber segment (4) and a measuring element (5) having a face (6),

characterized in that the optical fiber segment (4) and the measuring element (5) are squeezed together so that there is only a residual cavity (7) between them, and the optical fiber segment (4) is at least along part of its length contained within a capillary (11), wherein first ending part of the capillary (11) is joined with the measuring element (5) while other portion of the capillary (11) is clenched on the optical fiber segment (4).

14. Fiber optic measuring probe according to claim 13, characterized in that a ratio between optical length $a \cdot n_1$ of the residual cavity (7) and optical length $b \cdot n_2$ of the measuring element (5) falls into a range of 0 to 0.4.

15. Fiber optic measuring probe according to claim 13 or 14, characterized in that the measuring element (5) has the face (6) at least partly covered with substance adhesive to the substance to be detected.

16. Fiber optic measuring probe according to claim 13 or 14, characterized in that the measuring element (5) has the face (6) at least partly covered with substance that loses its adhesiveness when exposed to the substance to be detected.

17. Fiber optic measuring probe according to claim 13 or 14, characterized in that the measuring element (5) has the face (6) at least partly covered with substance that changes its optical parameters when exposed to the substance to be detected.

18. Fiber optic measuring probe according to any of claims 13-17, characterized in that the measuring element (5) is a tile made of material comprising a substance selected of a group including glass, silica glass, lead glass, ZBLAN glass and polymers.

19. Fiber optic measuring probe according to any of claims 13-18, characterized in that an end of the optical fiber

segment (4) inside the capillary (11) is oblique and inclined by an angle within a range of 4° to 20° with respect to the axis of the optical fiber segment (4).

20. Fiber optic measuring probe according to any of claims 13-19, characterized in that a reflection coefficient R_1 from a first surface of optical fiber segment (4) confining residual cavity (7) from the first side and a reflection coefficient R_2 from a second surface of a measuring element (5) confining the residual cavity (7) from the opposite side meet condition $\frac{R_1}{R_2} \leq 0,5$.

21. Fiber optic measuring probe according to any of claims 13-20, characterized in that it has a connector provided on an end of the optical fiber segment (4), opposite that the measuring element (5) is located.

22. Fiber optic measuring probe according to any of claims 13-20, characterized in that the optical fiber segment (4), has more than one core (9.1, 9.2, 9.3).

23. Method of detecting chemical substance using interferometer is equipped with optical path with detector, light source and fiber optic measuring probe included in optical path, leading light to detected substance, in which substance is considered as detected if shift of predefined interference fringe is observed on detector, characterized in that the interferometer is the interferometric fiber optic sensor according to any of claims 1-12 is applied.

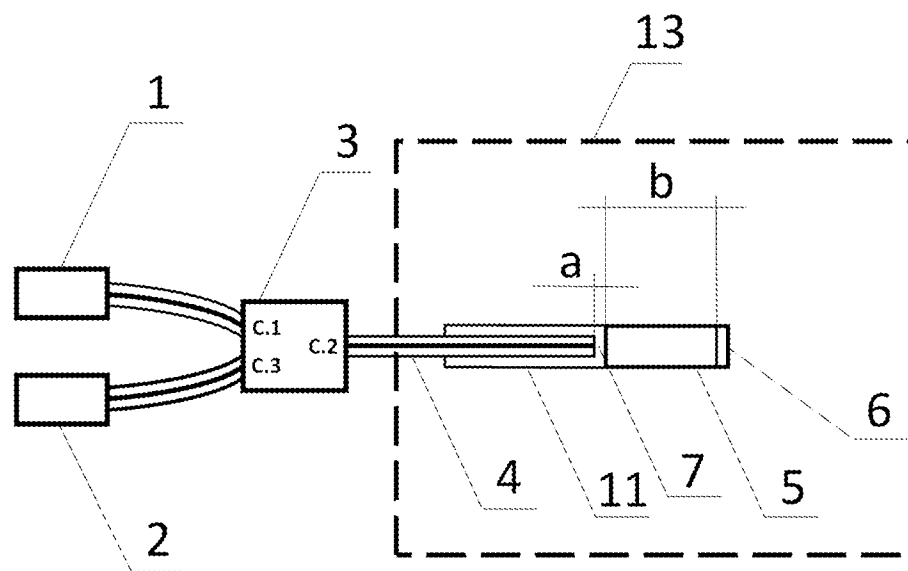


Fig. 1a

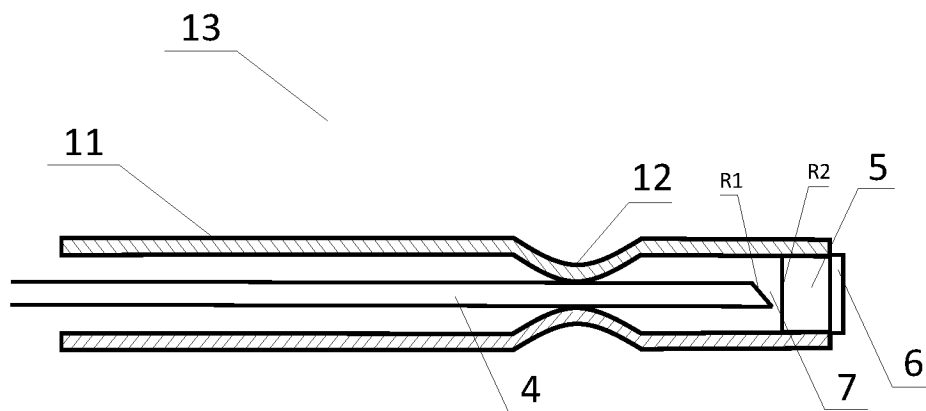


Fig. 1b

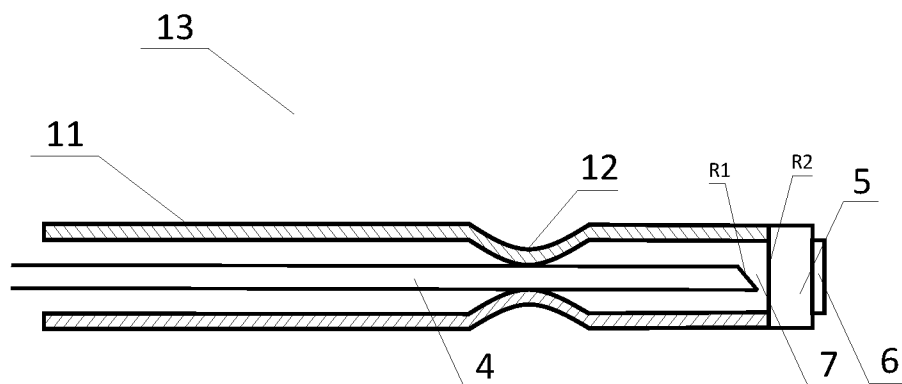


Fig. 1c

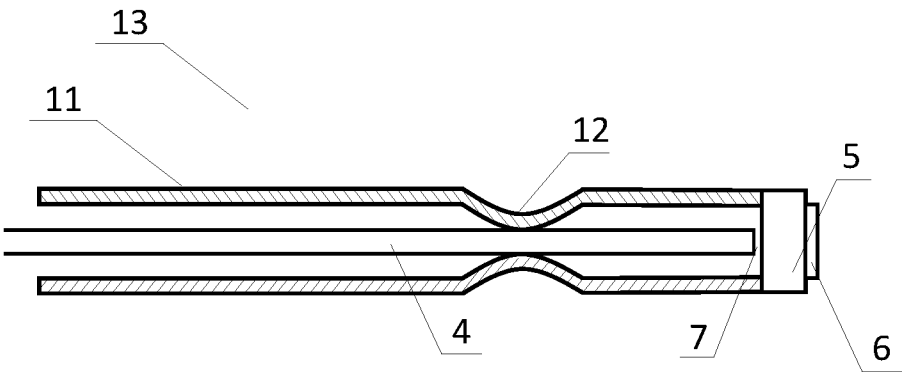


Fig. 1d

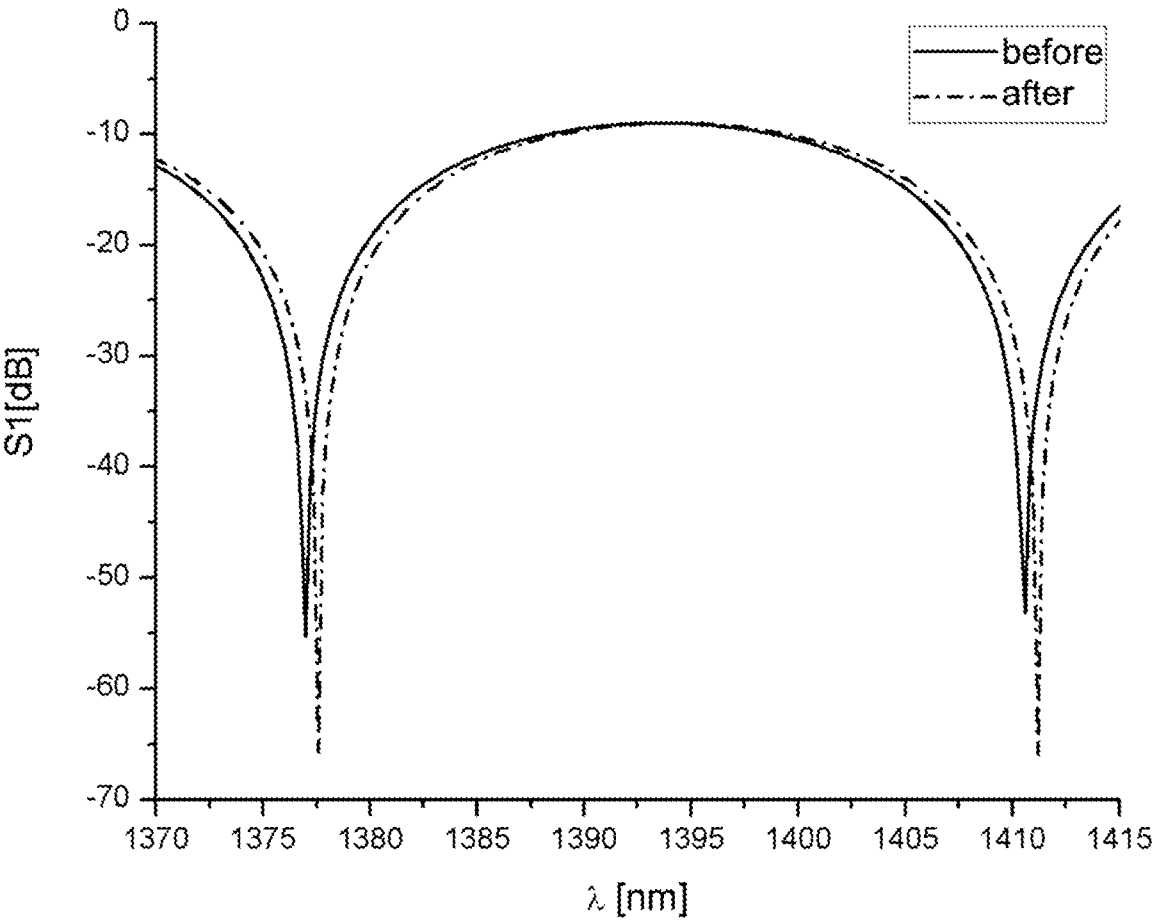


Fig. 2a

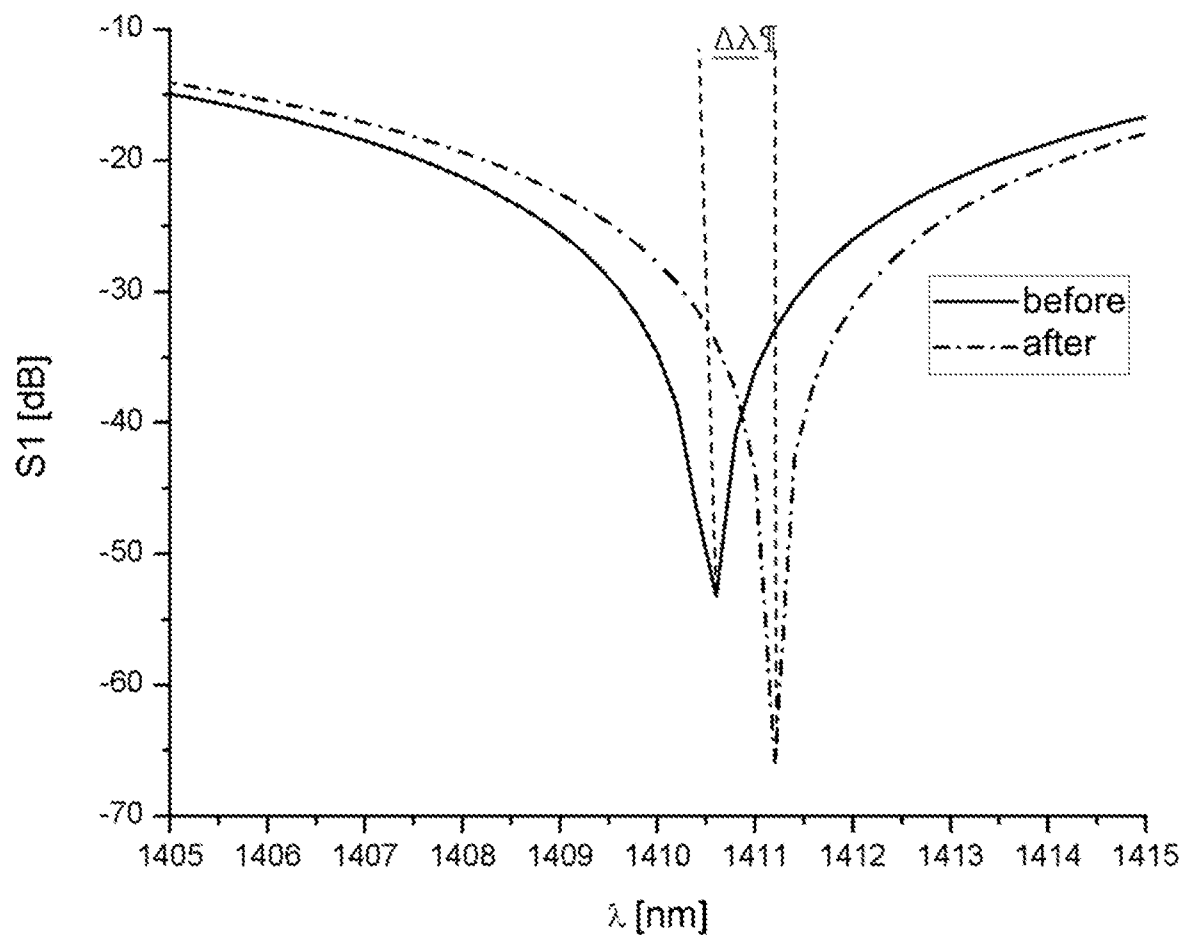


Fig. 2b

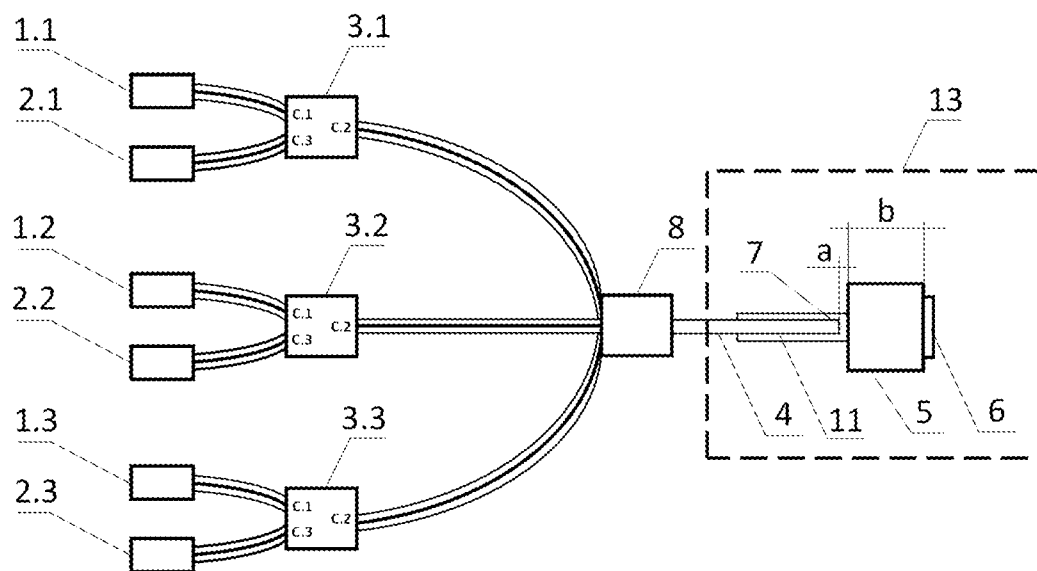


Fig. 3

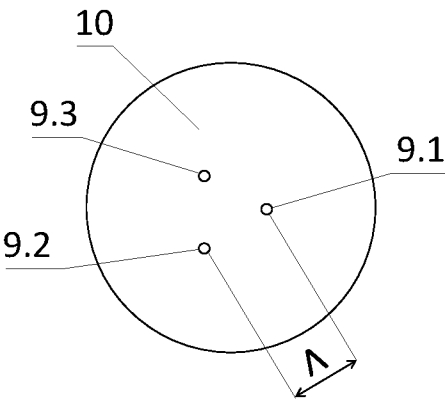


Fig.4

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2019/055062

A. CLASSIFICATION OF SUBJECT MATTER
INV. G01N21/77
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 G01B

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, INSPEC, COMPENDEX, BIOSIS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	W0 2013/139783 A1 (UNIV LIMERICK [IE]) 26 September 2013 (2013-09-26)	1,3-8, 12,13, 15-19, 21,23
Y	abstract page 6, line 12 - page 13, line 18 figures 1-3, 8	10,11,22
Y	W0 2018/106134 A1 (INPHOTECH SP Z O O [PL]) 14 June 2018 (2018-06-14) cited in the application figures 3-12 ----- -/--	10,11,22



Further documents are listed in the continuation of Box C.



See patent family annex.

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

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"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

17 September 2019

Date of mailing of the international search report

27/09/2019

Name and mailing address of the ISA/

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Authorized officer

Sauerer, Christof

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2019/055062

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	YU FEN ET AL: "Envelope-based demodulation for temperature sensing with cascaded fiber Fabry-Perot interferometers", 2017 16TH INTERNATIONAL CONFERENCE ON OPTICAL COMMUNICATIONS AND NETWORKS (ICOON), IEEE, 7 August 2017 (2017-08-07), pages 1-3, XP033270205, DOI: 10.1109/ICOON.2017.8121442 ISBN: 978-1-5386-3271-0 [retrieved on 2017-11-27] the whole document	1-23
A	US 2013/294975 A1 (SONG YONG WON [KR] ET AL) 7 November 2013 (2013-11-07) figures 2-4 paragraph [0037] - paragraph [0113]	1-23
A	CN 105 181 112 A (HARBIN INST OF TECHNOLOGY) 23 December 2015 (2015-12-23) figures 1, 2	1-23
A	WO 2016/043850 A2 (LUNA INNOVATIONS INC [US]) 24 March 2016 (2016-03-24) paragraph [0059] - paragraph [0087] figures 9-11	10,11

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2019/055062

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2013139783 A1	26-09-2013	EP 2828622 A1 US 2015077736 A1 WO 2013139783 A1	28-01-2015 19-03-2015 26-09-2013
WO 2018106134 A1	14-06-2018	AU 2017373550 A1 EP 3551963 A1 KR 20190092456 A WO 2018106134 A1	27-06-2019 16-10-2019 07-08-2019 14-06-2018
US 2013294975 A1	07-11-2013	KR 20130119767 A US 2013294975 A1	01-11-2013 07-11-2013
CN 105181112 A	23-12-2015	NONE	
WO 2016043850 A2	24-03-2016	US 2017268909 A1 WO 2016043850 A2	21-09-2017 24-03-2016