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- (71) Applicant: **BATTELLE MEMORIAL INSTITUTE**
[US/US]; 505 King Avenue, Columbus, OH 43201-2696 (US).
- (72) Inventors; and
- (71) Applicants : **BARTON, Andrew, C.** [US/US]; 133 Springhouse Lane, Pittsburgh, PA 15238 (US). **MORROW, Alex** [US/US]; 126 Walcreek Drive East, Gahanna, OH 43230 (US). **SCHAEFER, Jason, A.** [US/US]; 2728 Wildwood Road, Columbus, OH 43231 (US). **IVANCIC,**

William, A. [US/US]; 909 Cordero Lane, Gahanna, OH 43230 (US). **BARNES, Russell, H.** [US/US]; 1478 Berkshire Road, Columbus, OH 43221 (US).

(74) Agents: **GEGNEHEIMER, Charles Michael** et al.; Battelle Memorial Institute, 505 King Avenue, Columbus, OH 43201-2696 (US).

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(54) Title: IMMERSIBLE METHANE SENSORS

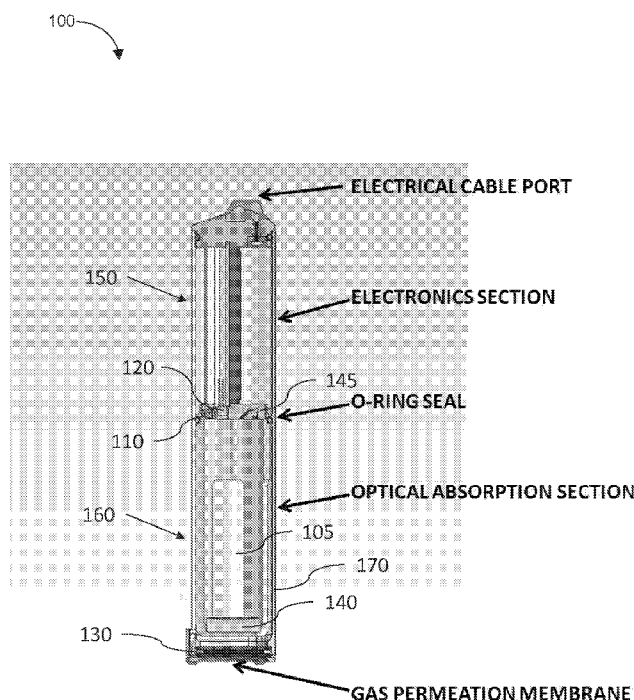


FIG. 1

(57) Abstract: Immersible detection systems (100) and methods for using the same are provided for detecting the existence and concentration of methane gas in a fluid medium. The system comprises a radiation source (110) emitting at a methane absorption wavelength, a methane permeable membrane layer (130) which is e.g. water impermeable, a detector (120) as well as a signal process and control unit (150) connected to the detector to analyse the radiation to determine the concentration of methane in the fluid medium.



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IMMERSIBLE METHANE SENSORS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority from U.S. Provisional Patent Application No. 61/732,822, filed December 3, 2012, which is incorporated by reference herein in its entirety.

BACKGROUND

[0002] Methane, CH₄(g), is a colorless, odorless gas, and is the chief constituent of natural gas. Methane gas is especially prevalent in coal beds, but occurs in non-coal rocks as well. Methane gas occurs naturally in the subsurface, accumulating in voids within the rock and as dissolved gas in groundwater. Methane can enter a well system through damaged or corroded well casing, improperly sealed well casing, uncased formations, and as dissolved gases being released from groundwater present in the well. Because methane may be dissolved in groundwater, it may not leave the well water until it arrives at the faucet, resulting in the accumulation of gas in the home. Thus, a risk exists for methane over-exposure. Symptoms of methane over-exposure may include difficulty breathing, suffocation, dehydration, nausea, vomiting, dizziness, confusion, blurred vision, and increased heart rate. In addition, methane gas is flammable and, in the right mixture with air, can be highly explosive. Thus, detection of methane gas in well systems is important.

[0003] Methane detection systems exist. For example, one conventional methane detection system is the well-known “bottle test.” Other conventional methane detection systems include catalytic combustion detectors, flame ionization detectors, and semiconductor-type detectors. More recently, methane gas has been detected spectroscopically, e.g., by infrared optical analysis.

SUMMARY

[0004] In one embodiment, an immersible detection system is provided for detecting the existence and concentration of methane gas in water. The immersible detection system may include:

- a radiation source, tuned to emit radiation at a wavelength having a linewidth which embraces at least one significant absorption line of the $2\nu_3$ band of methane;

- a detector configured to receive the radiation;

- a gas permeable, water impermeable membrane;

- a multi-pass mirror system configured to direct the radiation emitted by the radiation source to the detector; and

- a signal process and control unit, operatively connected with the detector, for analyzing the received radiation to determine the existence and concentration of methane gas.

[0005] In another embodiment, a water-immersible methane sensor is provided. The water-immersible methane sensor may include:

- a light emitting diode tuned to emit light with a peak wavelength of between about 1.60 μm and about 1.69 μm ;

- a detector configured to receive the light;

- a membrane including a silicone polymer that is substantially gas permeable and substantially water impermeable;

- a multi-pass mirror system configured to direct the light to the detector; and

- a signal process and control unit, operatively connected with the detector, for analyzing the received light to determine the existence and concentration of methane in water.

[0006] In another embodiment, an immersible detection system is provided for detecting the existence and concentration of methane gas in water. The immersible detection system may include:

a gas chamber;

a radiation source operatively connected with the gas chamber and tuned to emit radiation at a wavelength having a linewidth which embraces at least one significant absorption line of the $2\nu_3$ band of methane;

a detector configured to receive the radiation;

a gas permeable, water impermeable membrane layer operatively connected with the gas chamber and configured to allow methane gas to enter the gas chamber;

a multi-pass mirror system contained within the gas chamber; and

a signal process and control unit, operatively connected with the detector, for analyzing the received radiation to determine the existence and concentration of methane gas.

[0007] In another embodiment, a method for detecting the presence and concentration of methane gas in water is provided. The method may include:

immersing at least a portion of a methane detection system in the water. The methane detection system may include:

a light emitting diode tuned to emit light with a peak wavelength of between about 1.60 μm and about 1.69 μm ;

a detector to receive the light;

a gas permeable, water impermeable membrane layer; and

a multi-pass mirror system configured to direct the light emitted by the light emitting diode to the detector; and

analyzing the received light using a signal process and control unit which is operatively connected to the detector.

[0008] In one embodiment, an immersible detection system for determining an existence and concentration of methane included by a fluid medium is provided. The immersible detection system may include a radiation source. The radiation source may be tuned to emit radiation at a wavelength having a linewidth which embraces at least one significant absorption line of a 2v3 band of methane. The immersible detection system may include a methane permeable, water impermeable membrane layer. The methane permeable, water impermeable membrane layer may be configured to admit at least a portion of the methane included by the fluid medium into the immersible detection system. The admitted methane may absorb at least a portion of the radiation at the at least one significant absorption line of the 2v3 band of methane. The immersible detection system may include a detector configured to receive the radiation. The immersible detection system may include a signal process and control unit operatively connected to the detector. The signal process and control unit may be configured to analyze the radiation to determine the existence and concentration of the methane included by the fluid medium according to absorption at the at least one significant absorption line of the 2v3 band of methane.

[0009] In another embodiment, a water-immersible methane sensor for determining an existence and concentration of methane included by a fluid medium is provided. The water-immersible methane sensor may include a light emitting diode. The light emitting diode may be tuned to emit light with a peak wavelength between about 1.60 μm and about 1.69 μm . The water-immersible methane sensor may include a detector configured to receive the light. The water-immersible methane sensor may include a membrane that includes a silicone polymer. The membrane may be permeable to methane and substantially impermeable to water. The membrane may be configured to admit at least a portion of the methane included by the fluid medium into the water-immersible methane sensor. The admitted methane may absorb at least a portion of the light in at least one significant absorption line of a 2v3 band of

methane. The water-immersible methane sensor may include a signal process and control unit operatively connected to the detector. The signal process and control unit may be configured to analyze the light to determine the existence and concentration of the methane included by the fluid medium according to absorption at the at least one significant absorption line of the 2v3 band of methane.

[0010] In one embodiment, an immersible detection system for detecting the existence and concentration of methane included by a fluid medium is provided. The immersible detection system may include a chamber. The immersible detection system may include a radiation source operatively connected with the chamber. The radiation source may be tuned to emit radiation at a wavelength having a linewidth which embraces at least one significant absorption line of methane. . The immersible detection system may include a methane permeable, water impermeable membrane layer. The methane permeable, water impermeable membrane layer may be operatively connected to the chamber. The methane permeable, water impermeable membrane layer may be configured to admit at least a portion of the methane included by the fluid medium to the chamber. The admitted methane may absorb at least a portion of the radiation at the at least one significant absorption line of methane. The immersible detection system may include a detector configured to receive the radiation. The immersible detection system may include a multi-pass mirror system including a concave mirror, e.g., a concave spherical mirror. The multi-pass mirror system may be configured to direct the radiation emitted by the radiation source through the admitted methane in at least two passes. The admitted methane may absorb at least a portion of the radiation at the at least one significant absorption line of methane. The multi-pass mirror system may be configured to direct at least a portion of the radiation not absorbed by the admitted methane to the detector. The immersible detection system may include a signal process and control unit operatively connected to the detector. The signal process and control

unit may be configured to analyze the radiation to determine the existence and concentration of the methane included by the fluid medium according to absorption at the at least one significant absorption line of methane.

[0011] In another embodiment, a method for detecting the presence and concentration of methane included by a fluid medium is provided. The method may include separating at least a portion of the methane from the fluid medium. The method may include directing radiation through the methane separated from the fluid medium in at least two passes. The radiation may be at a wavelength having a linewidth which embraces at least one significant absorption line of a 2v3 band of methane. The admitted methane may absorb at least a portion of the radiation in the at least one significant absorption line of the 2v3 band of methane. The method may include selectively detecting absorption of the radiation at the at least one significant absorption line of the 2v3 band of methane. The method may include determining the existence and concentration of the methane included by the fluid medium according to the selectively detected absorption of the radiation at the at least one significant absorption line of the 2v3 band of methane.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] The accompanying figures, which are incorporated in and constitute a part of the specification, illustrate various example systems, methods, results, and so on, and are used merely to illustrate various example embodiments. Specific dimensions and unclaimed elements are included in the figures for ease of understanding. It is not the intention to restrict or in any way limit the scope of the appended claims to such detail.

[0013] **FIG. 1** is a cross-sectional side view of an example immersible methane sensor **100** showing the electronics and optical absorption sections of the sensor;

[0014] **FIG. 2** illustrates another view of example immersible methane sensor **100** wherein the electronics and optical absorption sections of the sensor are separated from the outer tube;

[0015] **FIG. 3** is a perspective view of example immersible methane sensor **100** showing the electrical cable port and the spherical mirror of the multi-pass optical absorption mirror system;

[0016] **FIG. 4** is a perspective view of the assembled example immersible methane sensor **100** showing o-ring seals and the gas permeation membrane;

[0017] **FIG. 5** illustrates an example IR detector suitable for use with the immersible methane sensors disclosed herein;

[0018] **FIG. 6A** illustrates an exploded view of the electronics section-side of the support block that at least partially divides the electronics section from the optical absorption section of example immersible methane sensor **100**;

[0019] **FIG. 6B** illustrates an exploded view of the optical absorption section-side of the support block that at least partially divides the electronics section from the optical absorption section of example immersible methane sensor **100**;

[0020] **FIG. 7** illustrates the mirror mosaic portion of the multi-pass optical absorption mirror system of example immersible methane sensor **100**;

[0021] **FIG. 8** is a flow chart of an example method for detecting the presence and concentration of methane gas in water;

[0022] **FIG. 9A** is a graph showing methane diffusion into an example sensor in a test fixture as a function of time, the example sensor lacking the membrane layer and a porous stainless steel support; temperature at the example sensor is also shown as a function of time;

[0023] **FIG. 9B** is a graph showing methane diffusion into an example sensor as a function of time, the example sensor including the membrane layer and a porous stainless steel support; temperature at the example sensor is also shown as a function of time;

[0024] **FIG. 9C** is a graph showing a reverse methane diffusion test, where methane loaded into an example sensor exits the sensor as a function of time, the example sensor including the membrane layer and a porous stainless steel support; temperature at the example sensor is also shown as a function of time;

[0025] **FIG. 9D** is a graph showing the forward methane diffusion test of **FIG. 9C**, but with temperature correction applied to the data; and

[0026] **FIG. 9E** is a graph showing the forward methane diffusion test of **FIG. 9D**, but with the temperature corrected voltage signal converted to a dissolved methane concentration.

[0027] **FIG. 9F** is a graph showing temperature-corrected data for the forward methane diffusion test of **FIG. 9D**.

DETAILED DESCRIPTION

[0028] The present embodiments disclose relatively small, compact, inexpensive systems and methods for detecting and determining the concentration of dissolved gases in water, including down-hole detection and determination of the concentration of dissolved methane gas in underground well water. In a general sense, the method of operation for the sensor involves separating dissolved methane gas from the water by gas permeation through a hydrophobic polymer membrane that passes methane gas while rejecting the passage of water. A longpath optical absorption measurement in the near-infrared optical range is used within the sensor to measure the methane collected in the gas phase. The methane measurements are correlated to methane concentration in the surrounding water in contact with the permeation membrane using a Henry's Law mathematical relationship as known in the art.

[0029] Details of example embodiments of the methane sensor are illustrated in **FIGS. 1-7**. In one example embodiment, a cross-sectional side view of which is depicted in **FIG. 1**, an immersible detection system **100** is provided for detecting the existence and concentration of methane gas in water. As shown in **FIG. 1**, immersible detection system **100** may include a gas chamber **105**, a radiation source **110**, tuned to emit radiation through gas chamber **105** at a wavelength having a fluorescence linewidth which embraces at least one significant absorption line of the $2\nu_3$ band of methane; a detector **120** configured to receive the radiation; a gas permeable, water impermeable membrane layer **130**; a multi-pass mirror system including a spherical mirror **140**, located within the gas chamber **105** and configured to direct the radiation emitted by radiation source **110** through gas chamber **105** to detector **120**; and a signal process and control unit (not shown), operatively connected with detector **120**, for analyzing the received radiation to determine the existence and concentration of methane gas. In one embodiment, gas chamber **105** is operatively connected with radiation source **110** and gas permeable, water impermeable membrane layer **130**. In another embodiment, radiation source **110**, detector **120**, and a mirror mosaic portion (not shown) of the multi-pass mirror system are mounted on a mosaic mirror support block **145**.

[0030] In one embodiment, a thermistor may be used to provide the temperature of the methane gas in gas chamber **105** and to correct calculations for temperature variation effects on radiation source **110**, detector **120**, and absorption coefficients for methane.

[0031] Outputs from detector **120** may be processed using signal processing electronics and a microprocessor in the electronics section **150** of sensor **100**. Software in the microprocessor with temperatures from the thermistor converts the spectroscopic measurements to methane pressure, and then through Henry's Law calculates the dissolved methane concentration in water.

[0032] Results from the dissolved methane measurements may be reported from sensor **100** through an electrical cable to an output box at ground level at or near the well-head. A digital display on the output box provides continuous dissolved methane concentrations. Outputs from the box can be relayed by wire or wireless. In one embodiment, an alarm may be triggered if threshold levels of methane gas are present. Electrical power for detection system **100** may be supplied, for example, by an internal battery or remotely by a cable and output box located at the well head.

[0033] In one embodiment, shown in **FIG. 1**, immersible detection system **100** may be configured in two primary sections—electronics section **150** and an optical absorption section **160**. In such an embodiment, a radiation source **110** and detector **120** may be operatively connected with both electronics section **150** and optical absorption section **160** through support block **145**.

[0034] **FIG. 2** illustrates another view of an example immersible methane sensor **100** wherein electronics section **150** and optical absorption section **160** of sensor **100** are separated from an outer tube **170**. **FIG. 3** is a perspective view of an example immersible methane sensor **100** showing an electrical cable port **180** and spherical mirror **140** of the multi-pass optical absorption system.

[0035] In one embodiment, shown in **FIGS. 1, 3, and 4**, electronics section **150** and optical absorption section **160** (which include radiation source **110**, detector **120**, and the multipass mirror system) are sealed in water and gas tight metal or plastic housing **170**, so that immersible detection system **100** may be immersed in water, e.g., well water, to be monitored. Housing **170** may be contoured to allow for pipe travel, as shown in **FIGS. 1-4**. In one embodiment, housing **170** includes a metal cylindrical tube with an outer diameter of less than about 1¾ inches and a length of less than about nine inches. These dimensions are

convenient for insertion into standard well pipes and natural gas wells. It should be noted that when not inserted in water, sensor **100** may be used for gas-phase measurements.

[0036] Other gases commonly dissolved in water, such as carbon dioxide and oxygen, can enter detection system **100**, but are rejected spectroscopically. However, if desired, detection system **100** may be readily adapted, e.g., by use of different wavelengths and corresponding filters, to detect many other gases dissolved in water and other liquids. As an example, additional wavelengths may be emitted and filtered to monitor both methane and carbon dioxide in sea water. Further, detection system **100** may be coupled with other water quality parameter sensors, e.g., TDS, chloride, and pH sensors.

[0037] For ease of understanding the present invention, various example embodiments are now described. It is not the intention to restrict or in any way limit the scope of the appended claims to such detail.

Radiation Source

[0038] Methane has two strong absorption bands, or groups of lines, centered at 3.3 μm (ν_3 band) and 7.6 μm (ν_4 band). Methane has another strong absorption band located at 1.64 to 1.70 μm ($2\nu_3$ band). In particular, the R(3) line ($\lambda = 1.6537 \mu\text{m}$) in the $2\nu_3$ band is suitable for gas leak detection because that line is one of the strongest absorption lines in the $2\nu_3$ band and is relatively free from interference from atmospheric gases.

[0039] Thus, with respect to the embodiments described herein, radiation source **110** may include, for example, a thermal source or a light emitting diode (LED) that emits light at or near the R(3) line ($\lambda = 1.6537 \mu\text{m}$) in the $2\nu_3$ band of methane. In one embodiment, a suitable LED may emit light with a peak wavelength of between about 1.60 μm and about 1.69 μm . In another embodiment, a suitable LED may emit light with a peak wavelength of about 1.65 μm . One example of a suitable LED may be the “LED16FC” manufactured by Roithner

Lasertechnik GmbH in Vienna, Austria. The LED16FC has an output wavelength of from about 1500 to about 1900 nm, with a peak wavelength of between about 1600 nm and about 1690 nm, and particularly at about 1650 nm.

[0040] In one embodiment, radiation source **110** may include an LED with a collection lens on its face. The collection lens helps gather more of the emitted energy and limit the angular extent of the LED's divergence.

Detector

[0041] Detector **120** may include, for example, a single or multi-element detector with separate narrow bandpass optical filters. In one embodiment, detector **120** may be a two element detector with a filter wavelength for the filters of about 1670 nm for the methane absorption channel, and 1550 nm for zero absorbance correction (that is, as reference to correct for instrument drift). The 1670 nm wavelength is associated with the Q-branch manifolds of the $2\nu_3$ vibration band of methane. The zero absorbance channel is between the 1900 and 1400 nm bands of water vapor where water absorbance is minimal.

[0042] In another particular embodiment, detector **120** may be a lead sulfide quad cell (four element) detector as shown in **FIG. 5** and as manufactured by Cal-Sensors, Inc. in Santa Rosa, California. With reference to **FIG. 5**, in one specific embodiment, detector **120** may have a first element having a filter wavelength of between about 1647 nm and 1691 nm, with a center wavelength of about 1670 nm (e.g., a NB-1670-023 optical filter manufactured by Spectrogon in Taby, Sweden); a second element having a filter wavelength of between about 1516.1 nm and 1582.7 nm, with a center wavelength of about 1550 nm (e.g., a NB-1552-031 optical filter manufactured by Spectrogon); a third element having a filter wavelength of between about 1627 nm and 1664 nm, with a center wavelength of about 1646 nm (e.g., a NB-1648-019 optical filter manufactured by Spectrogon); and a fourth element having a filter

wavelength of between about 1699 nm and 1718 nm, with a center wavelength of about 1708 nm (e.g., a NB-1710-009 optical filter manufactured by Spectrogon). The first through fourth elements may be arranged in any order. Further, any of the four elements may be replaced with appropriate filters to detect additional species such as ethane or propane, or to correct for other interfering species.

[0043] In any or all embodiments, detector **120** may further include a collection lens, such as, for example, a TECHSPEC® N-BK7 Half-Ball Lens as manufactured by Edmund Optics Inc. in Barrington, New Jersey. Such a collection lens is shown in **FIG. 5** as item **190**.

[0044] Detection sensitivity for a particular wavelength region may be optimized by adjusting the separation between spherical mirror **140** and the mosaic mirrors of the multi-pass mirror system.

Gas Permeable, Water Impermeable Membrane Layer

[0045] Gas permeable, water impermeable membrane layer **130** allows the transfer of methane into and out of detection system **100**, while rejecting the passage of water. As the dissolved methane concentration in the water varies up and down, methane passes in and out of the gas chamber through the membrane. Thus, membrane layer **130** may include any composition that has a high permeability for methane and high hydrophobicity to reject the passage of water. One example membrane may include a porous, super-hydrophobic silicone polymer manufactured by Millipore Corporation in Billerica, Massachusetts. Another example membrane may include polydimethylsiloxane. The membrane parameters are chosen to balance maximum diffusion of methane with the necessary strength to withstand water pressure and other forces in deep well environments.

Multi-Pass Mirror System

[0046] In one example operation mode, the LED described herein is directed toward a relatively large (e.g., about 1 inch in some embodiments) primary mirror (e.g., spherical mirror **140**), which collects the divergent energy from the LED and focuses it back onto a small mirror back near (but slightly displaced from) the LED. This small mirror redirects the light toward another small mirror, which then redirects the light back toward the primary mirror. This process is repeated multiple times (each reflection off of the primary mirror is pointed toward a different set of small mirrors) and results in the establishment of a long path length through the volume of gas contained in the gas chamber (e.g., gas chamber **105**). At the end of this repeated reflection optical path, the light is directed to the detector (e.g., detector **120**).

[0047] **FIG. 6a** illustrates an exploded view of the electronics section-side of support block **145** that at least partially divides electronics section **150** from optical absorption section **160** of example immersible methane sensor **100**. **FIG. 6b** illustrates an exploded view of the optical absorption section-side of support block **145**. In **FIG. 6b**, an example mirror mosaic **140'** is shown which corresponds to the “small mirrors” described herein. **FIG. 7** illustrates another view of the mirror mosaic portion **140'** of the optical absorption mirror system of example immersible methane sensor **100**.

[0048] In one embodiment, the multi-pass mirror system produces a long optical absorption path length within a small volume (in one embodiment, the gas chamber has a volume of approximately 73 cm³) to provide the detection sensitivity for methane in water in the subparts per million concentration range—a surprisingly good result. In one embodiment, the primary mirror is separated from the mosaic by about 10 cm, with the overall length of the mirror system in the sensor being about 12 cm. Sixteen passes through such a system provides an optical absorption pathlength of about 1.63 meters. The multi-pass mirror system

allows for a compact (and inexpensive) design that can be used to perform down-hole well measurements at very high sensitivity and response time.

[0049] In view of the above description, multiple alternative embodiments are envisioned. For example, in one embodiment, an immersible detection system is provided for detecting the existence and concentration of methane gas in water. The immersible detection system may include: a radiation source, tuned to emit radiation at a wavelength having a fluorescence linewidth which embraces at least one significant absorption line of the $2\nu_3$ band of methane; a detector configured to receive the radiation; a gas permeable, water impermeable membrane; a multi-pass mirror system configured to direct the radiation emitted by the radiation source to the detector; and a signal process and control unit, operatively connected with the detector, for analyzing the received radiation to determine the existence and concentration of methane gas.

[0050] In another embodiment, a water-immersible methane sensor is provided. The water-immersible methane sensor may include: a light emitting diode tuned to emit light with a peak wavelength of between about 1.60 μm and about 1.69 μm ; a detector configured to receive the light; a membrane including a silicone polymer that is substantially gas permeable and substantially water impermeable; a multi-pass mirror system configured to direct the light to the detector; and a signal process and control unit, operatively connected with the detector, for analyzing the received light to determine the existence and concentration of methane in water.

[0051] In another embodiment, an immersible detection system is provided for detecting the existence and concentration of methane gas in water. The immersible detection system may include: a gas chamber; a radiation source operatively connected with the gas chamber and tuned to emit radiation at a wavelength having a fluorescence linewidth which embraces

at least one significant absorption line of the $2\nu_3$ band of methane; a detector configured to receive the radiation; a gas permeable, water impermeable membrane layer operatively connected with the gas chamber and configured to allow methane gas to enter the gas chamber; a multi-pass mirror system contained within the gas chamber; and a signal process and control unit, operatively connected with the detector, for analyzing the received radiation to determine the existence and concentration of methane gas.

[0052] **FIG. 8** is a flow chart of an example method **800** for detecting the presence and concentration of methane gas in water. Thus, at least a portion of a methane detection system (e.g., methane detection system **100**) is immersed in the water (step **810**). The methane detection system may include: a light emitting diode (e.g., radiation source **110**) tuned to emit light with a peak wavelength of between about 1.60 μm and about 1.69 μm ; a detector (e.g., detector **120**) configured to receive the light; a gas permeable, water impermeable membrane layer (e.g., membrane **130**) configured to pass methane gas from the water into a gas chamber (e.g., gas chamber **105**) within the methane detection system, while rejecting the liquid water; and a multi-pass mirror system configured to direct the light emitted by the light emitting diode through the gas chamber to the detector; and analyzing the received light using a signal process and control unit which is operatively connected to the detector (step **820**).

[0053] Thus, dissolved methane released from the water in contact with the surface of the hydrophobic membrane penetrates through the membrane into the gas chamber where the spectroscopic absorption measurement provides a methane pressure which is correlated to a dissolved methane concentration using an established Henry's Law relationship.

[0054] **FIG. 9A** is a graph **900** showing methane diffusion into an example sensor as a function of time. The example sensor for which data is shown in **FIG. 9A** lacks a membrane layer and a porous stainless steel support. The test of **FIG. 9A** was performed in the gas

phase to measure diffusion time through the test fixture and example sensor; here, response time is approximately three hours. Voltage signal **902** represents sensitivity of the example sensor to methane. Voltage **902** may be converted to mg/L of methane, taking into account the effect of temperature **906**, also graphed as a function of time. Dotted line **904** indicates the point in time, about 1.9 hours, when methane was added.

[0055] **FIG. 9B** is a graph **910** showing methane diffusion into an example sensor as a function of time. The example sensor for which data is shown in **FIG. 9B** includes a membrane layer and a porous stainless steel support. The test of **FIG. 9B** was performed in the gas phase to measure diffusion time through the example sensor; here, response time is approximately three hours, taking into account a response time of six hours minus the three hour fixture diffusion time of the experiment in **FIG. 9A**. Voltage signal **912** represents sensitivity of the example sensor to methane. Voltage **912** may be converted to mg/L of methane, taking into account the effect of temperature **916**, also graphed as a function of time. Dotted line **914** indicates the point in time, about 3.7 hours, when methane was added.

[0056] **FIG. 9C** is a graph **920** showing a reverse methane diffusion test, where methane pre-loaded into an example sensor exits the sensor as a function of time. The example sensor for which data is shown in **FIG. 9C** includes a membrane layer and a porous stainless steel support. The test of **FIG. 9C** was performed by pre-loading the example sensor with methane, and placing the example sensor in methane-free water in a nitrogen environment to measure diffusion time out of the example sensor. Increasing voltage signal **922** over time shows that methane was diffusing out of the sensor. Sensor temperature **924** and laboratory temperature **926** are also graphed as a function of time. Voltage signal **922** is not temperature corrected in **FIG. 9C**.

[0057] **FIG. 9D** is a graph **930** showing a forward methane diffusion test, where an example sensor is placed in methane-free water. After about 5 hours, the gas surrounding the water was loaded with methane to create an approximately 10 mg/L methane concentration in the water. The example sensor for which data is shown in **FIG. 9D** includes a membrane layer and a porous stainless steel support. Decreasing voltage signal **932** over time shows that methane was diffusing into the sensor. Sensor temperature **934** and laboratory temperature **936** are also graphed as a function of time. Voltage signal **932** is not temperature corrected in **FIG. 9D**.

[0058] **FIG. 9E** is a graph **940** showing temperature-corrected data for the forward methane diffusion test of **FIG. 9D**, where an example sensor is placed in methane-free water. After about 5 hours, the gas surrounding the water was loaded with methane to create an approximately 10 mg/L methane concentration in the water. The example sensor for which data is shown in **FIG. 9E** includes a membrane layer and a porous stainless steel support. Decreasing voltage signal **942** over time shows that methane was diffusing into the sensor. Sensor temperature **944** and laboratory temperature **946** are also graphed as a function of time. Voltage signal **942** is temperature corrected in **FIG. 9E**.

[0059] **FIG. 9F** is a graph **950** showing temperature-corrected data for the forward methane diffusion test of **FIG. 9D**, where an example sensor is placed in methane-free water. After about 5 hours, the gas surrounding the water was loaded with methane to create an approximately 10 mg/L methane concentration in the water. The example sensor for which data is shown in **FIG. 9E** includes a membrane layer and a porous stainless steel support. Signal **952** corresponds to signal 942 from **FIG. 9E**, but converted to a dissolved methane concentration in mg/L.

[0060] In various embodiments, an immersible detection system for determining an existence and concentration of methane included by a fluid medium is provided. The immersible detection system may include a radiation source. The radiation source may be tuned to emit radiation at a wavelength having a linewidth which embraces at least one significant absorption line of a 2v3 band of methane. The immersible detection system may include a methane permeable, water impermeable membrane layer. The methane permeable, water impermeable membrane layer may be configured to admit at least a portion of the methane included by the fluid medium into the immersible detection system. The admitted methane may absorb at least a portion of the radiation at the at least one significant absorption line of the 2v3 band of methane. The immersible detection system may include a detector configured to receive the radiation. The immersible detection system may include a signal process and control unit operatively connected to the detector. The signal process and control unit may be configured to analyze the radiation to determine the existence and concentration of the methane included by the fluid medium according to absorption at the at least one significant absorption line of the 2v3 band of methane.

[0061] In some embodiments, the immersible detection system may include a multi-pass mirror system. The multi-pass mirror system may be configured to direct the radiation emitted by the radiation source through the admitted methane. The radiation emitted by the radiation source may be directed through the admitted methane in at least two passes such that the admitted methane absorbs at least a portion of the radiation at the at least one significant absorption line of the 2v3 band of methane. The multi-pass mirror system may be configured to direct at least a portion of the radiation not absorbed by the methane to the detector. The multi-pass mirror system may further include a concave mirror, e.g., a concave spherical mirror.

[0062] In several embodiments, the signal process and control unit may be configured to analyze the radiation to determine the existence and concentration of the methane included by the fluid medium selectively according to absorption at the at least one significant absorption line of the 2v3 band of methane.

[0063] In various embodiments, the radiation source may include a light emitting diode. The light emitting diode may be tuned to emit light with a peak wavelength of about 1.60 μm , 1.61 μm , 1.62 μm , 1.63 μm , 1.64 μm , 1.65 μm , 1.66 μm , 1.67 μm , 1.68 μm , 1.69 μm , or a range between about any two of the preceding values, for example, between about 1.60 μm and about 1.69 μm . The light emitting diode may be tuned to emit light with a peak wavelength of about any one of the preceding values, for example, about 1.65 μm .

[0064] In some embodiments, the detector may include a filter configured to reject at least some radiation outside of the absorption line of the 2v3 band of methane. In some embodiments, detector may include at least two filter elements. The first filter element may include a filter center wavelength of about 1.67 μm . The second filter element may include a filter center wavelength of about 1.55 μm . In some embodiments, the detector may include at least four filter elements. The first filter element may include a filter wavelength of between about 1647 nm and 1691 nm. The second filter element may include a filter wavelength of between about 1516 nm and 1582 nm. The third filter element may include a filter wavelength of between about 1627 nm and 1664 nm. The fourth filter element may include a filter wavelength of between about 1699 nm and 1718 nm.

[0065] In several embodiments, the methane permeable, water impermeable membrane layer may include a polydimethylsiloxane compound. The methane permeable, water impermeable membrane layer may be supported by an underlying porous, gas permeable substrate.

[0066] In various embodiments, the fluid medium may include one or more of: a gaseous mixture of the methane in air or the methane dissolved in an aqueous solution. The fluid medium may include a gaseous mixture of the methane in air. The fluid medium may include the methane dissolved in an aqueous solution. The fluid medium may include one or more of: a liquid, a gas, a vapor, a subcritical fluid, or a supercritical fluid. The fluid medium may include a liquid. The fluid medium may include a gas. The fluid medium may include a vapor. The fluid medium may include a subcritical fluid. The fluid medium may include a supercritical fluid.

[0067] In some embodiments, the detector and signal process and control unit may be configured to determine the existence and concentration of the methane included by the fluid medium. The fluid medium may be sampled to evaluate water quality associated with one or more of: conventional or unconventional oil and gas development, coal mining, landfill operations, wastewater treatment, chemical manufacturing, or industrial processes.

[0068] The fluid medium may be sampled to evaluate water quality associated with conventional oil and gas development. The fluid medium may be sampled to evaluate water quality associated with unconventional oil and gas development. The fluid medium may be sampled to evaluate water quality associated with coal mining. The fluid medium may be sampled to evaluate water quality associated with landfill operations. The fluid medium may be sampled to evaluate water quality associated with wastewater treatment. The fluid medium may be sampled to evaluate water quality associated with chemical manufacturing, or industrial processes.

[0069] In several embodiments, the immersible detection system may be configured to fit within a cylinder having a diameter in inches of about 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, or 5, or any range between about any two of the preceding values, for example, between about 1 inch and

about 4 inches. The cylinder may have a diameter about any of the preceding values, for example, about two inches. The cylinder may have a length in inches of about 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, or 16, or any range between about any two of the preceding values, for example, between about 7 inches and about 12 inches. The cylinder may have a diameter about any of the preceding values, for example, about 8 inches. The cylinder may have a combination of any of the preceding values for the diameter and length, for example, a diameter of about 2 inches and a length of about eight inches.

[0070] In some embodiments, the immersible detection system may include a lower methane detection limit in the fluid medium in mg/mL of at least about 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 1.1, 1.2, 1.3, 1.4, 1.5, or any range between about any two of the preceding values, for example, between about 0.01 mg/mL and about 0.1 mg/mL. The immersible detection system may include a lower methane detection limit in the fluid medium of about any of the preceding values, for example, about 0.01 mg/ml; about 0.1 mg/mL; or about 1 mg/mL.

[0071] In various embodiments, the immersible detection system may be configured to operate at a pressure in pounds per square inch absolute (psia) of about 0, 10, 25, 50, 75, 100, 125, 150, 175, 200, 225, 250, 275, 300, 325, 350, 375, 400, or any range between about any two of the preceding values, for example, between about 10 psia and 200 psia.

[0072] In various embodiments, the immersible detection system may be configured to operate at a temperature in °C of about 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, or any range between about any two of the preceding values, for example, between about 0 °C and about 50 °C, or between about 5 °C and about 30 °C.

[0073] In some embodiments, the immersible detection system may also include a heater configured to reduce condensation in the immersible detection system, for example, a resistive or thin film heater.

[0074] In various embodiments, a water-immersible methane sensor for determining an existence and concentration of methane included by a fluid medium is provided. The water-immersible methane sensor may include a light emitting diode. The light emitting diode may be tuned to emit light with a peak wavelength between about 1.60 μm and about 1.69 μm . The water-immersible methane sensor may include a detector configured to receive the light. The water-immersible methane sensor may include a membrane that includes a silicone polymer. The membrane may be permeable to methane and substantially impermeable to water. The membrane may be configured to admit at least a portion of the methane included by the fluid medium into the water-immersible methane sensor. The admitted methane may absorb at least a portion of the light in at least one significant absorption line of a 2v3 band of methane. The water-immersible methane sensor may include a signal process and control unit operatively connected to the detector. The signal process and control unit may be configured to analyze the light to determine the existence and concentration of the methane included by the fluid medium according to absorption at the at least one significant absorption line of the 2v3 band of methane.

[0075] In some embodiments, the water-immersible methane sensor may include a multi-pass mirror system. The multi-pass mirror system may be configured to direct the radiation emitted by the radiation source to the admitted methane. The admitted methane may absorb at least a portion of the radiation at the at least one significant absorption line of the 2v3 band of methane. The multi-pass mirror system may be configured to direct at least a portion of the radiation not absorbed by the methane to the detector. The multi-pass mirror system may include a concave mirror, e.g., a concave spherical mirror.

[0076] In several embodiments, the signal process and control unit may be configured to analyze the radiation to determine the existence and concentration of the methane included by the fluid medium selectively according to absorption at the at least one significant absorption line of the 2v3 band of methane.

[0077] In various embodiments, the light emitting diode may be tuned to emit light with a peak wavelength of about 1.60 μm , 1.61 μm , 1.62 μm , 1.63 μm , 1.64 μm , 1.65 μm , 1.66 μm , 1.67 μm , 1.68 μm , 1.69 μm , or a range between about any two of the preceding values, for example, between about 1.60 μm and about 1.69 μm . The light emitting diode may be tuned to emit light with a peak wavelength of about any one of the preceding values, for example, about 1.65 μm .

[0078] In some embodiments, the detector may include a filter configured to reject at least some radiation outside of the absorption line of the 2v3 band of methane. In some embodiments, the detector may include at least two filter elements. The first filter element may include a filter center wavelength of about 1.67 μm . The second filter element may include a filter center wavelength of about 1.55 μm . In some embodiments, the detector may include at least four filter elements. The first filter element may include a filter wavelength of between about 1647 nm and 1691 nm. The second filter element may include a filter wavelength of between about 1516 nm and 1582 nm. The third filter element may include a filter wavelength of between about 1627 nm and 1664 nm. The fourth filter element may include a filter wavelength of between about 1699 nm and 1718 nm.

[0079] In several embodiments, the membrane may include a polydimethylsiloxane compound. The membrane may be supported by an underlying porous, gas permeable substrate.

[0080] In some embodiments, the fluid medium may include one or more of: a gaseous mixture of the methane in air or the methane dissolved in an aqueous solution. The fluid medium may include a gaseous mixture of the methane in air. The fluid medium may include the methane dissolved in an aqueous solution. The fluid medium may include one or more of: a liquid, a gas, a vapor, a subcritical fluid, or a supercritical fluid. The fluid medium may include a liquid. The fluid medium may include a gas. The fluid medium may include a vapor. The fluid medium may include a subcritical fluid. The fluid medium may include a supercritical fluid.

[0081] In several embodiments, the detector and signal process and control unit may be configured to determine the existence and concentration of the methane included by the fluid medium. The fluid medium may be sampled to evaluate water quality associated with one or more of: conventional or unconventional oil and gas development, coal mining, landfill operations, wastewater treatment, chemical manufacturing, or industrial processes. The fluid medium may be sampled to evaluate water quality associated with conventional oil and gas development. The fluid medium may be sampled to evaluate water quality associated with unconventional oil and gas development. The fluid medium may be sampled to evaluate water quality associated with coal mining. The fluid medium may be sampled to evaluate water quality associated with landfill operations. The fluid medium may be sampled to evaluate water quality associated with wastewater treatment. The fluid medium may be sampled to evaluate water quality associated with chemical manufacturing. The fluid medium may be sampled to evaluate water quality associated with industrial processes.

[0082] In several embodiments, the water-immersible methane sensor may be configured to fit within a cylinder having a diameter in inches of about 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, or 5, or any range between about any two of the preceding values, for example, between about 1 inch and about 4 inches. The cylinder may have a diameter about any of the preceding

values, for example, about two inches. The cylinder may have a length in inches of about 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, or 16, or any range between about any two of the preceding values, for example, between about 7 inches and about 12 inches. The cylinder may have a diameter about any of the preceding values, for example, about 8 inches. The cylinder may have a combination of any of the preceding values for the diameter and length, for example, a diameter of about 2 inches and a length of about eight inches.

[0083] In some embodiments, the water-immersible methane sensor may include a lower methane detection limit in the fluid medium in mg/mL of at least about 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 1.1, 1.2., 1.3, 1.4, 1.5, or any range between about any two of the preceding values, for example, between about 0.01 mg/mL and about 0.1 mg/mL. The immersible detection system may include a lower methane detection limit in the fluid medium of about any of the preceding values, for example, about 0.01 mg/ml; about 0.1 mg/mL; or about 1 mg/mL.

[0084] In various embodiments, the water-immersible methane sensor may be configured to operate at a pressure in pounds per square inch absolute (psia) of about 0, 10, 25, 50, 75, 100, 125, 150, 175, 200, 225, 250, 275, 300, 325, 350, 375, 400, or any range between about any two of the preceding values, for example, between about between about 10 psia and 200 psia.

[0085] In various embodiments, the water-immersible methane sensor may be configured to operate at a temperature in °C of about 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, or any range between about any two of the preceding values, for example, between about between about 0 °C and about 50 °C, or between about 5 °C and about 30 °C.

[0086] In some embodiments, the water-immersible methane sensor may also include a heater configured to reduce condensation in the immersible detection system, for example, a resistive or thin film heater.

[0087] In various embodiments, an immersible detection system for detecting the existence and concentration of methane included by a fluid medium is provided. The immersible detection system may include a chamber. The immersible detection system may include a radiation source operatively connected with the chamber. The radiation source may be tuned to emit radiation at a wavelength having a linewidth which embraces at least one significant absorption line of methane. . The immersible detection system may include a methane permeable, water impermeable membrane layer. The methane permeable, water impermeable membrane layer may be operatively connected to the chamber. The methane permeable, water impermeable membrane layer may be configured to admit at least a portion of the methane included by the fluid medium to the chamber. The admitted methane may absorb at least a portion of the radiation at the at least one significant absorption line of methane. The immersible detection system may include a detector configured to receive the radiation. The immersible detection system may include a multi-pass mirror system including a concave mirror, e.g., a concave spherical mirror. The multi-pass mirror system may be configured to direct the radiation emitted by the radiation source through the admitted methane in at least two passes. The admitted methane may absorb at least a portion of the radiation at the at least one significant absorption line of methane. The multi-pass mirror system may be configured to direct at least a portion of the radiation not absorbed by the admitted methane to the detector. The immersible detection system may include a signal process and control unit operatively connected to the detector. The signal process and control unit may be configured to analyze the radiation to determine the existence and concentration

of the methane included by the fluid medium according to absorption at the at least one significant absorption line of methane.

[0088] In various embodiments, a method for detecting the presence and concentration of methane included by a fluid medium is provided. The method may include separating at least a portion of the methane from the fluid medium. The method may include directing radiation through the methane separated from the fluid medium in at least two passes. The radiation may be at a wavelength having a linewidth which embraces at least one significant absorption line of a $2\nu_3$ band of methane. The admitted methane may absorb at least a portion of the radiation in the at least one significant absorption line of the $2\nu_3$ band of methane. The method may include selectively detecting absorption of the radiation at the at least one significant absorption line of the $2\nu_3$ band of methane. The method may include determining the existence and concentration of the methane included by the fluid medium according to the selectively detected absorption of the radiation at the at least one significant absorption line of the $2\nu_3$ band of methane.

[0089] In some embodiments, the fluid medium may include one or more of: a gaseous mixture of the methane in air or the methane dissolved in an aqueous solution. The fluid medium may include a gaseous mixture of the methane in air. The fluid medium may include the methane dissolved in an aqueous solution. The fluid medium may include one or more of: a liquid, a gas, a vapor, a subcritical fluid, or a supercritical fluid. The fluid medium may include a liquid. The fluid medium may include a gas. The fluid medium may include a vapor. The fluid medium may include a subcritical fluid. The fluid medium may include a supercritical fluid.

[0090] In several embodiments, the method may include sampling or extracting the fluid medium to evaluate water quality. The water quality may be associated with one or more of:

conventional or unconventional oil and gas development, coal mining, landfill operations, wastewater treatment, chemical manufacturing, or industrial processes. The water quality may be associated with conventional oil and gas development. The water quality may be associated with unconventional oil and gas development. The water quality may be associated with coal mining. The water quality may be associated with landfill operations. The water quality may be associated with wastewater treatment. The water quality may be associated with chemical manufacturing. The water quality may be associated with industrial processes.

[0091] In various embodiments, the method may include detecting methane included by the fluid medium at a lower methane detection limit of at least about 0.01 mg/L. The lower methane detection limit in the fluid medium in mg/mL may be at least about 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 1.1, 1.2., 1.3, 1.4, 1.5, or any range between about any two of the preceding values, for example, between about 0.01 mg/mL and about 0.1 mg/mL. The method may include detecting methane included by the fluid medium at a lower methane detection limit of about any of the preceding values, for example, about 0.01 mg/ml; about 0.1 mg/mL; or about 1 mg/mL.

[0092] In some embodiments, the method may include operating in a pressure range in pounds per square inch absolute (psia) of between about 10 psia and 200 psia. The method may include operating at a pressure in pounds per square inch absolute (psia) of about 0, 10, 25, 50, 75, 100, 125, 150, 175, 200, 225, 250, 275, 300, 325, 350, 375, 400, or any range between about any two of the preceding values, for example, between about 10 psia and 200 psia.

[0093] In several embodiments, the method may include operating in a temperature range of between about 0 °C and 50 °C. The method may include operating at a temperature in °C

of about 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, or any range between about any two of the preceding values, for example, between about 0 °C and about 50 °C, or between about 5 °C and about 30 °C.

[0094] In some embodiments, the directing radiation through the methane separated from the fluid medium in at least two passes may further include using a concave mirror, e.g., a concave spherical mirror. In several embodiments, the method may also include reducing condensation by heating one or more of a detector, a filter, a multi-pass mirror system, or a radiation source.

[0095] While the present application has been illustrated by the description of embodiments thereof, and while the embodiments have been described in considerable detail, it is not the intention to restrict or in any way limit the scope of the appended claims to such detail. Additional advantages and modifications will readily appear to those skilled in the art, having the benefit of the present application. Therefore, the application, in its broader aspects, is not limited to the specific details, illustrative embodiments shown, or any apparatus referred to. Departures may be made from such details, examples, and apparatuses without departing from the spirit or scope of the general inventive concept.

[0096] To the extent that the term “includes” or “including” is used in the specification or the claims, it is intended to be inclusive in a manner similar to the term “comprising” as that term is interpreted when employed as a transitional word in a claim. Furthermore, to the extent that the term “or” is employed (e.g., A or B) it is intended to mean “A or B or both.” When the applicants intend to indicate “only A or B but not both” then the term “only A or B but not both” will be employed. Thus, use of the term “or” herein is the inclusive, and not the exclusive use. See Bryan A. Garner, *A Dictionary of Modern Legal Usage* 624 (2d. Ed. 1995). Also, to the extent that the terms “in” or “into” are used in the specification or the

claims, it is intended to additionally mean “on” or “onto,” and vice-versa. To the extent that the term “operatively connected” is used in the specification or the claims, it is intended to mean that the identified components are connected in a way to perform a designated function. As used in the specification and the claims, the singular forms “a,” “an,” and “the” include the plural. Finally, where the term “about” is used in conjunction with a number, it is intended to include $\pm 10\%$ of the number. In other words, “about 10” may mean from 9 to 11.

CLAIMS

What is claimed is:

1. An immersible detection system for determining an existence and concentration of methane comprised by a fluid medium, the immersible detection system comprising:

a radiation source tuned to emit radiation at a wavelength having a linewidth which embraces at least one significant absorption line of a 2v3 band of methane;

a methane permeable, water impermeable membrane layer configured to admit at least a portion of the methane comprised by the fluid medium into the immersible detection system such that the admitted methane absorbs at least a portion of the radiation at the at least one significant absorption line of the 2v3 band of methane;

a detector configured to receive the radiation; and

a signal process and control unit operatively connected to the detector, the signal process and control unit configured to analyze the radiation to determine the existence and concentration of the methane comprised by the fluid medium according to absorption at the at least one significant absorption line of the 2v3 band of methane.

2. The immersible detection system of claim 1, further comprising a multi-pass mirror system, the multi-pass mirror system being configured to:

direct the radiation emitted by the radiation source through the admitted methane in at least two passes such that the admitted methane absorbs at least a portion of the radiation at the at least one significant absorption line of the 2v3 band of methane; and

direct at least a portion of the radiation not absorbed by the methane to the detector.

3. The immersible detection system of claim 2, the multi-pass mirror system further comprising a concave mirror.

4. The immersible detection system of claim 1, the signal process and control unit being configured to analyze the radiation to determine the existence and concentration of the

methane comprised by the fluid medium selectively according to absorption at the at least one significant absorption line of the 2v₃ band of methane.

5. The immersible detection system of claim 1, wherein the radiation source comprises a light emitting diode.

6. The immersible detection system of claim 1, wherein the radiation source comprises a light emitting diode tuned to emit light with a peak wavelength of between about 1.60 μm and about 1.69 μm.

7. The immersible detection system of claim 1, wherein the radiation source comprises a light emitting diode tuned to emit light with a peak wavelength of about 1.65 μm.

8. The immersible detection system of claim 1, wherein the detector comprises a filter configured to reject at least some radiation outside of the absorption line of the 2v₃ band of methane.

9. The immersible detection system of claim 1, wherein the detector comprises at least two filter elements, the first filter element having a filter center wavelength of about 1.67 μm and the second filter element having a filter center wavelength of about 1.55 μm.

10. The immersible detection system of claim 1, wherein the detector comprises at least four filter elements, the first filter element having a filter wavelength of between about 1647 nm and about 1691 nm, the second filter element having a filter wavelength of between about 1516 nm and about 1582 nm, the third filter element having a filter wavelength of between about 1627 nm and about 1664 nm, and the fourth filter element having a filter wavelength of between about 1699 nm and about 1718 nm.

11. The immersible detection system of claim 1, wherein the methane permeable, water impermeable membrane layer comprises a polydimethylsiloxane compound.

12. The immersible detection system of claim 1, the methane permeable, water impermeable membrane layer being supported by an underlying porous, gas permeable substrate.
13. The immersible detection system of claim 1, wherein the fluid medium comprises one or more of: a gaseous mixture of the methane in air or the methane dissolved in an aqueous solution.
14. The immersible detection system of claim 1, wherein the fluid medium comprises one or more of: a liquid, a gas, a vapor, a subcritical fluid, or a supercritical fluid.
15. The immersible detection system of claim 1, the detector and signal process and control unit being configured to determine the existence and concentration of the methane comprised by the fluid medium, the fluid medium being sampled to evaluate water quality associated with one or more of: conventional or unconventional oil and gas development, coal mining, landfill operations, wastewater treatment, chemical manufacturing, or industrial processes.
16. The immersible detection system of claim 1, configured to fit within a cylinder having a diameter of about two inches and a length of about eight inches.
17. The immersible detection system of claim 1, comprising a lower methane detection limit in the fluid medium of at least about 0.01 mg/L.
18. The immersible detection system of claim 1, configured to operate in a pressure range in pounds per square inch absolute (psia) of between about 10 psia and about 200 psia.
19. The immersible detection system of claim 1, configured to operate in a temperature range of between about 0 °C and about 50 °C.
20. The immersible detection system of claim 1, further comprising a heater configured to reduce condensation in the immersible detection system.

21. A water-immersible methane sensor for determining an existence and concentration of methane comprised by a fluid medium, the water-immersible methane sensor comprising:

a light emitting diode tuned to emit light with a peak wavelength between about 1.60 μm and about 1.69 μm ;

a detector configured to receive the light;

a membrane comprising a silicone polymer that is permeable to methane and substantially impermeable to water, the membrane being configured to admit at least a portion of the methane comprised by the fluid medium into the water-immersible methane sensor such that the admitted methane absorbs at least a portion of the light in at least one significant absorption line of a 2v3 band of methane; and

a signal process and control unit operatively connected to the detector, the signal process and control unit configured to analyze the light to determine the existence and concentration of the methane comprised by the fluid medium according to absorption at the at least one significant absorption line of the 2v3 band of methane.

22. The water-immersible methane sensor of claim 21, further comprising a multi-pass mirror system, the multi-pass mirror system being configured to:

direct the radiation emitted by the radiation source to the admitted methane such that the admitted methane absorbs at least a portion of the radiation at the at least one significant absorption line of the 2v3 band of methane; and

direct at least a portion of the radiation not absorbed by the methane to the detector.

23. The water-immersible methane sensor of claim 21, the multi-pass mirror system further comprising a concave mirror.

24. The water-immersible methane sensor of claim 21, the signal process and control unit being configured to analyze the radiation to determine the existence and concentration of the

methane comprised by the fluid medium selectively according to absorption at the at least one significant absorption line of the 2v₃ band of methane.

25. The water-immersible methane sensor of claim 21, wherein the light emitting diode is tuned to emit light with a peak wavelength of about 1.65 μm .

26. The water-immersible methane sensor of claim 21, wherein the detector comprises a filter configured to reject at least some radiation outside of the absorption line of the 2v₃ band of methane.

27. The water-immersible methane sensor of claim 21, wherein the detector comprises at least two filter elements, the first filter element having a filter center wavelength of about 1.67 μm and the second filter element having a filter center wavelength of about 1.55 μm .

28. The water-immersible methane sensor of claim 21, wherein the detector comprises at least four filter elements, the first filter element having a filter wavelength of between about 1647 nm and about 1691 nm, the second filter element having a filter wavelength of between about 1516 nm and about 1582 nm, the third filter element having a filter wavelength of between about 1627 nm and about 1664 nm, and the fourth filter element having a filter wavelength of between about 1699 nm and about 1718 nm.

29. The water-immersible methane sensor of claim 21, wherein the membrane comprises a polydimethylsiloxane compound.

30. The water-immersible methane sensor of claim 21, the membrane being supported by an underlying porous, gas permeable substrate.

31. The water-immersible methane sensor of claim 21, wherein the fluid medium comprises one or more of: a gaseous mixture of the methane in air or the methane dissolved in an aqueous solution.

32. The water-immersible methane sensor of claim 21, wherein the fluid medium comprises one or more of: a liquid, a gas, a vapor, a subcritical fluid, or a supercritical fluid.

33. The water-immersible methane sensor of claim 21, the detector and signal process and control unit being configured to determine the existence and concentration of the methane comprised by the fluid medium, the fluid medium being sampled to evaluate water quality associated with one or more of: conventional or unconventional oil and gas development, coal mining, landfill operations, wastewater treatment, chemical manufacturing, or industrial processes.
34. The water-immersible methane sensor of claim 21, configured to fit within a cylinder having a diameter of about two inches and a length of about eight inches.
35. The water-immersible methane sensor of claim 21, comprising a lower methane detection limit in the fluid medium of at least about 0.01 mg/L.
36. The water-immersible methane sensor of claim 21, configured to operate in a pressure range in pounds per square inch absolute (psia) of between about 10 psia and about 200 psia.
37. The water-immersible methane sensor of claim 21, configured to operate in a temperature range of between about 0 °C and about 50 °C.
38. The water-immersible methane sensor of claim 1, further comprising a heater configured to reduce condensation in the water-immersible methane sensor.
39. An immersible detection system for detecting the existence and concentration of methane comprised by a fluid medium, the immersible detection system comprising:
- a chamber;
 - a radiation source operatively connected with the chamber and tuned to emit radiation at a wavelength having a linewidth which embraces at least one significant absorption line of methane;
 - a methane permeable, water impermeable membrane layer operatively connected to the chamber, the methane permeable, water impermeable membrane layer configured to admit at least a portion of the methane comprised by the fluid medium to the chamber such

that the admitted methane absorbs at least a portion of the radiation at the at least one significant absorption line of methane;

a detector configured to receive the radiation;

a multi-pass mirror system comprising a concave mirror, the multi-pass mirror system being configured to:

direct the radiation emitted by the radiation source through the admitted methane in at least two passes such that the admitted methane absorbs at least a portion of the radiation at the at least one significant absorption line of methane; and

direct at least a portion of the radiation not absorbed by the admitted methane to the detector; and

a signal process and control unit operatively connected to the detector, the signal process and control unit configured to analyze the radiation to determine the existence and concentration of the methane comprised by the fluid medium according to absorption at the at least one significant absorption line of methane.

40. A method for detecting the presence and concentration of methane comprised by a fluid medium, the method comprising:

separating at least a portion of the methane from the fluid medium;

directing radiation through the methane separated from the fluid medium in at least two passes, the radiation being at a wavelength having a linewidth which embraces at least one significant absorption line of a $2\nu_3$ band of methane, such that the admitted methane absorbs at least a portion of the radiation in the at least one significant absorption line of the $2\nu_3$ band of methane;

selectively detecting absorption of the radiation at the at least one significant absorption line of the $2\nu_3$ band of methane; and

determining the existence and concentration of the methane comprised by the fluid medium according to the selectively detected absorption of the radiation at the at least one significant absorption line of the 2v3 band of methane.

41. The method of claim 40, wherein the fluid medium comprises one or more of: a gaseous mixture of the methane in air or the methane dissolved in an aqueous solution.
42. The method of claim 40, wherein the fluid medium comprises one or more of: a liquid, a gas, a vapor, a subcritical fluid, or a supercritical fluid.
43. The method of claim 40, further comprising sampling or extracting the fluid medium to evaluate water quality associated with one or more of: conventional or unconventional oil and gas development, coal mining, landfill operations, wastewater treatment, chemical manufacturing, or industrial processes.
44. The method of claim 40, further comprising detecting methane comprised by the fluid medium at a lower methane detection limit of at least about 0.01 mg/L.
45. The method of claim 40, further comprising operating in a pressure range in pounds per square inch absolute (psia) of between about 10 psia and about 200 psia.
46. The method of claim 40, further comprising operating in a temperature range of between about 0 °C and about 50 °C.
47. The method of claim 40, the directing radiation through the methane separated from the fluid medium in at least two passes further comprising using a concave mirror.
48. The method of claim 40, further comprising reducing condensation by heating one or more of a detector, a filter, a multi-pass mirror system, or a radiation source.

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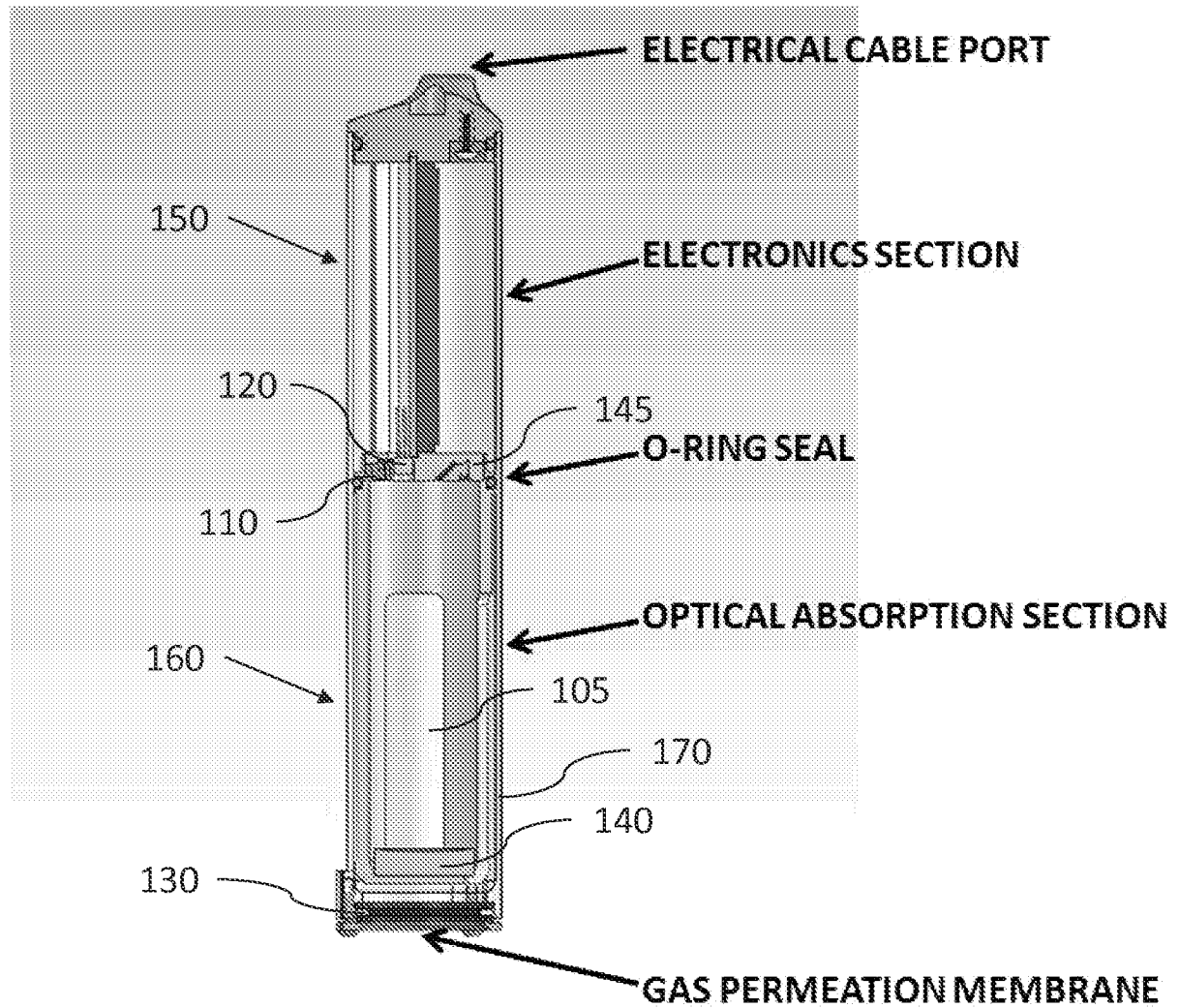


FIG. 1

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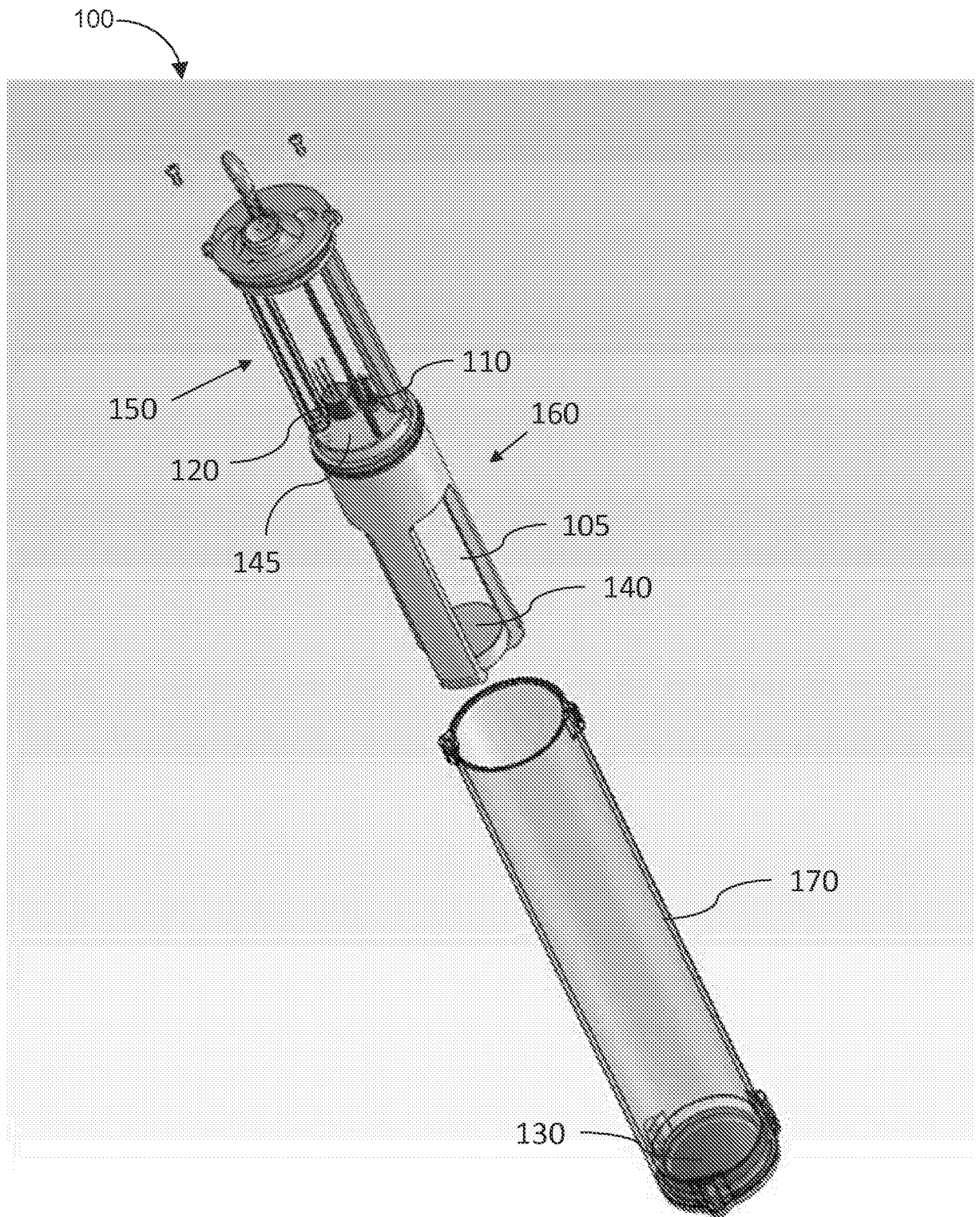


FIG. 2

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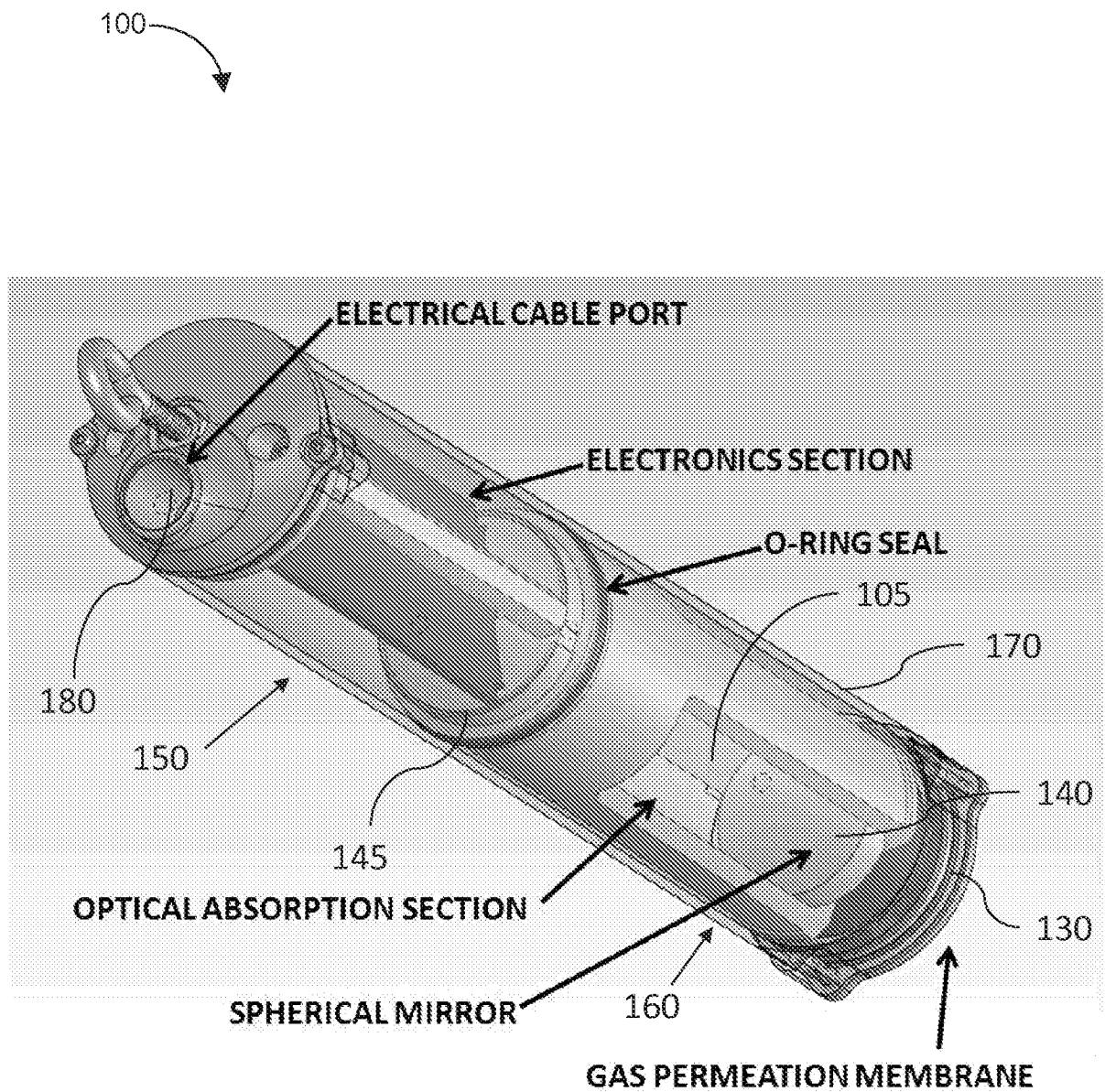


FIG. 3

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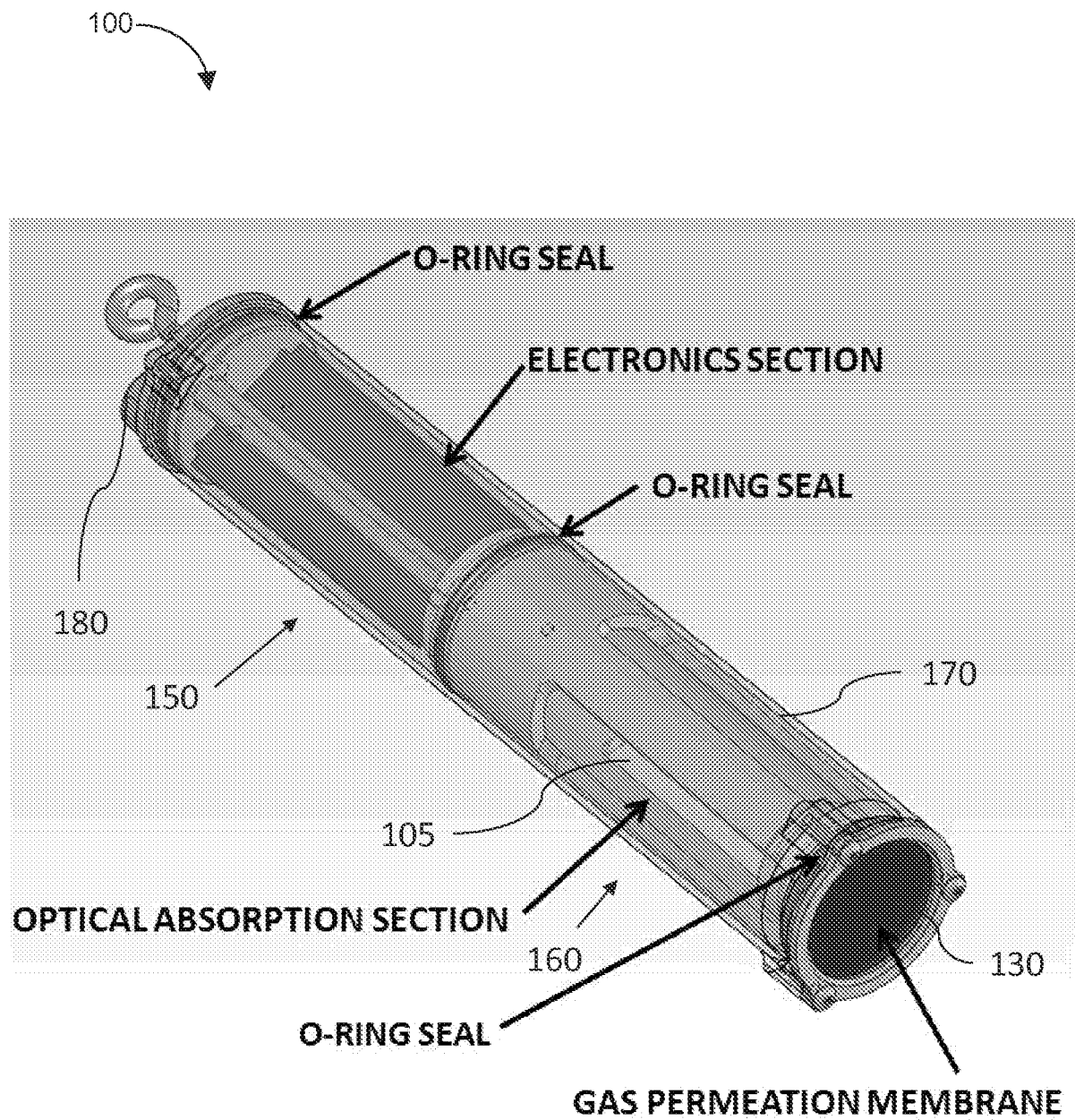


FIG. 4

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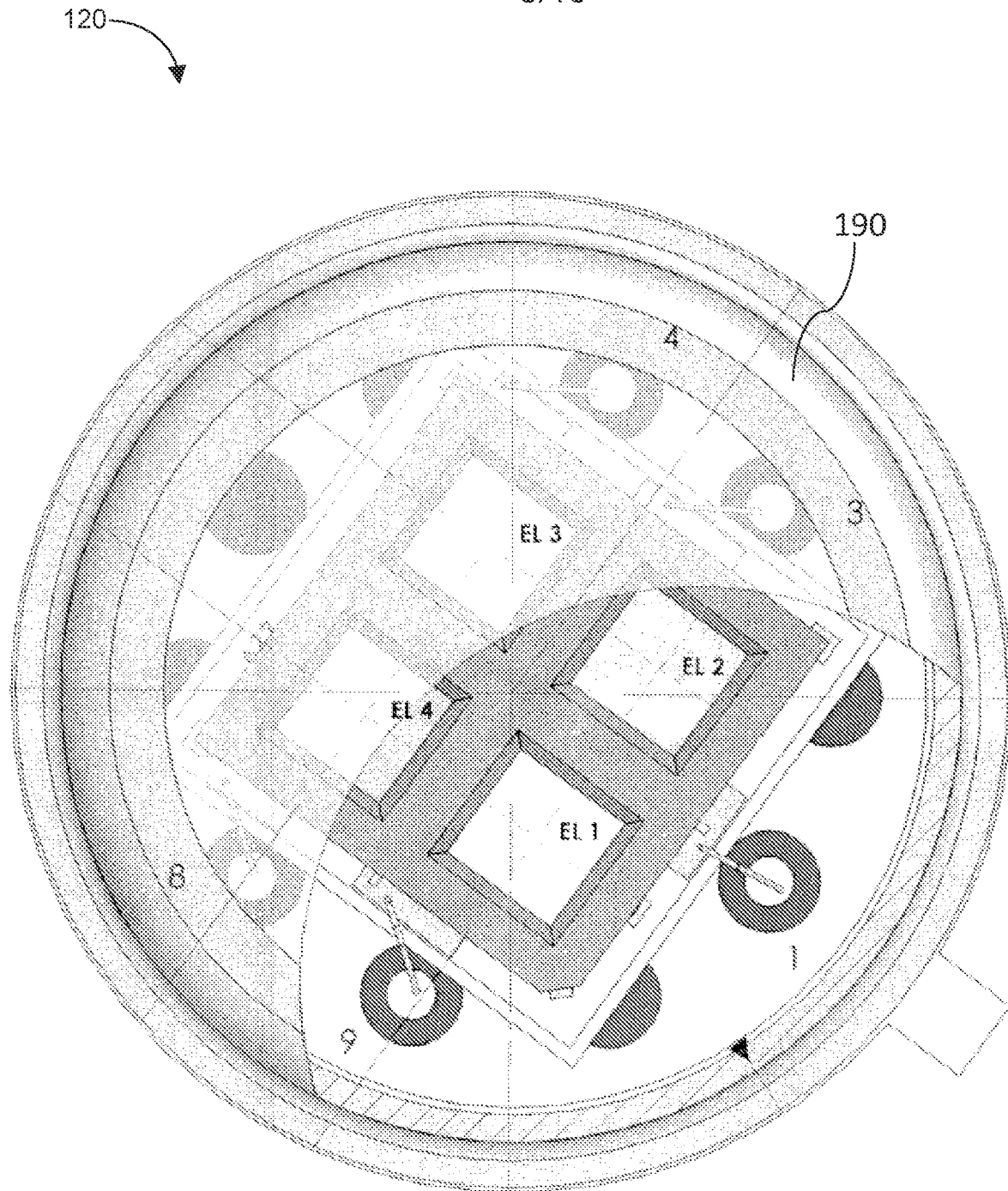


FIG. 5

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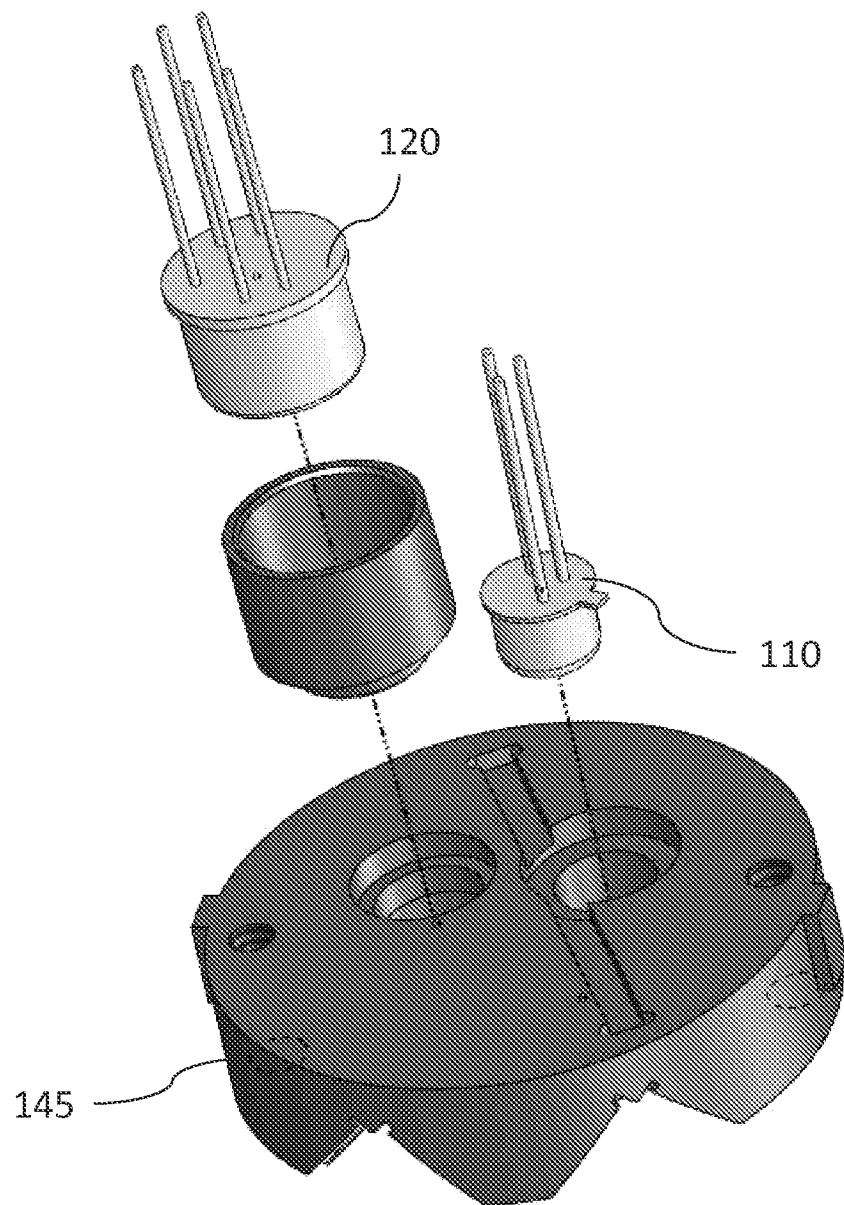


FIG. 6A

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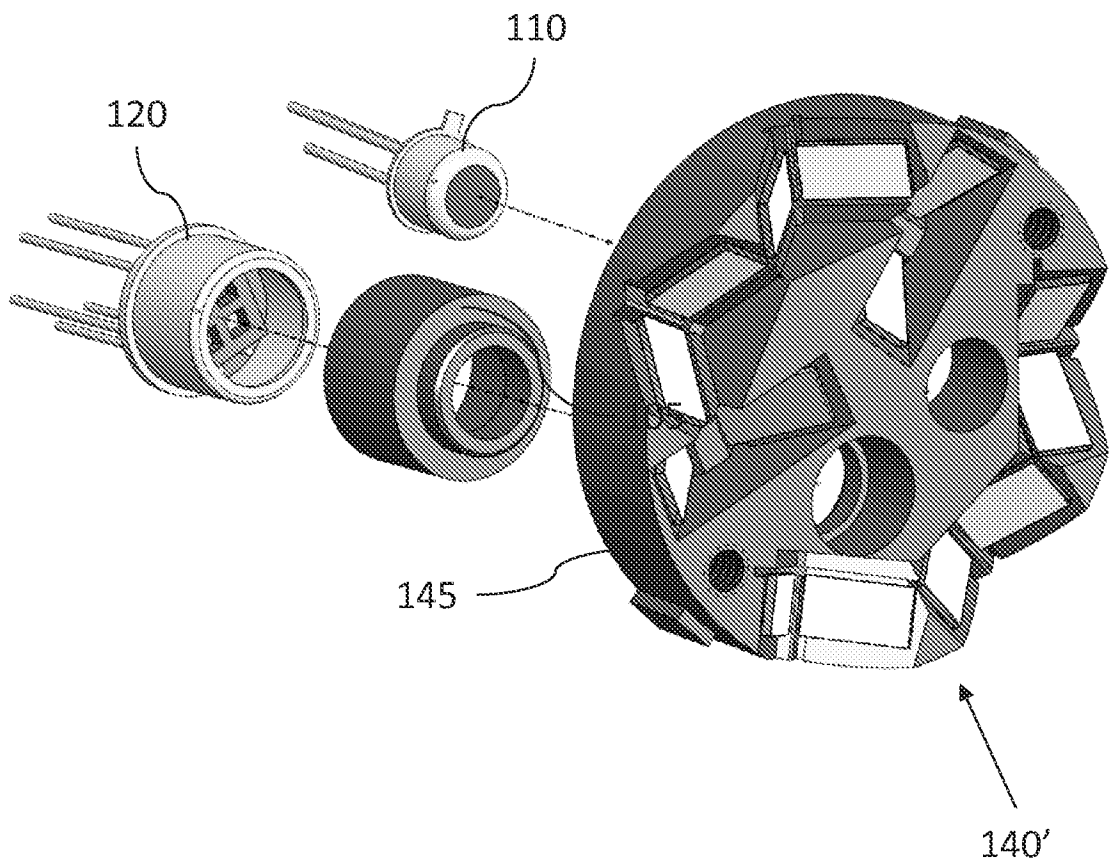


FIG. 6B

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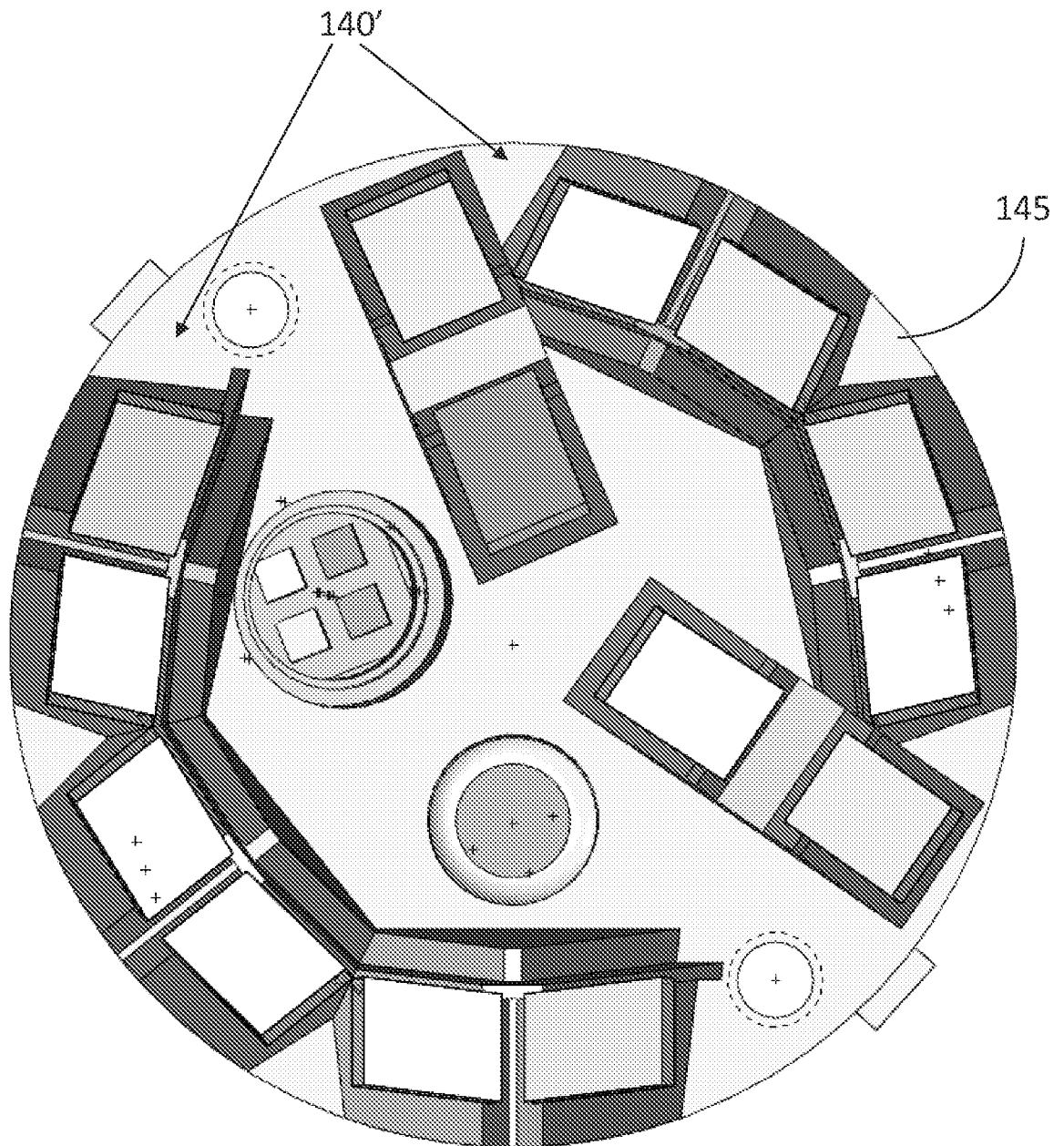


FIG. 7

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Immerse at least a portion of the methane detection system in water, the methane detection system comprising: a light emitting diode tuned to emit light with a peak wavelength of between about 1.60 μm and about 1.69 μm ; a detector configured to receive the light; a gas permeable, water impermeable membrane layer configured to pass methane gas from the water into a gas chamber within the methane detection system, while rejecting the liquid water; and a multi-pass mirror system configured to direct the light emitted by the light emitting diode through the gas chamber to the detector

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Analyze the received light using a signal process and control unit which is operatively connected to the detector

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FIG. 8

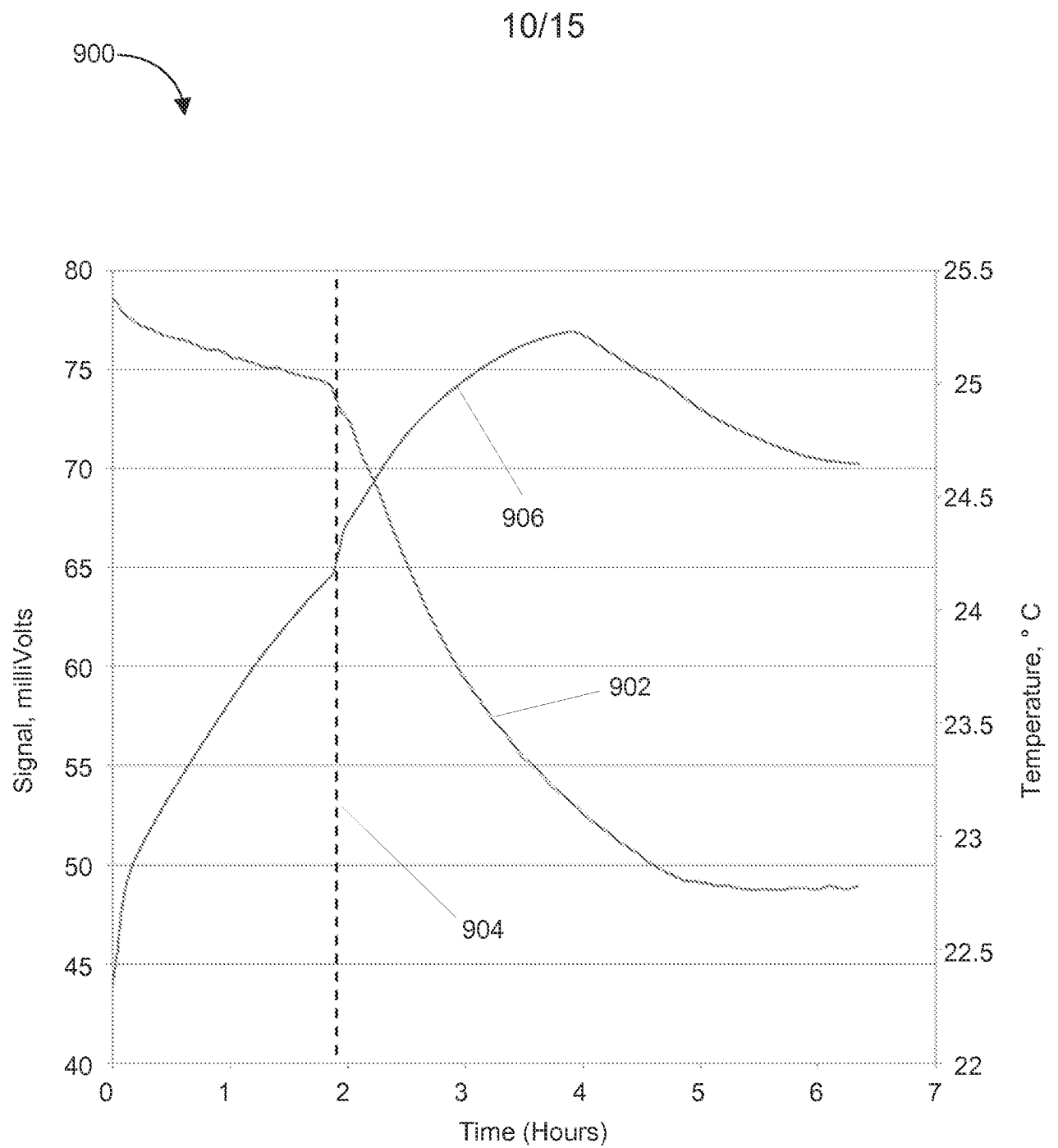


FIG. 9A

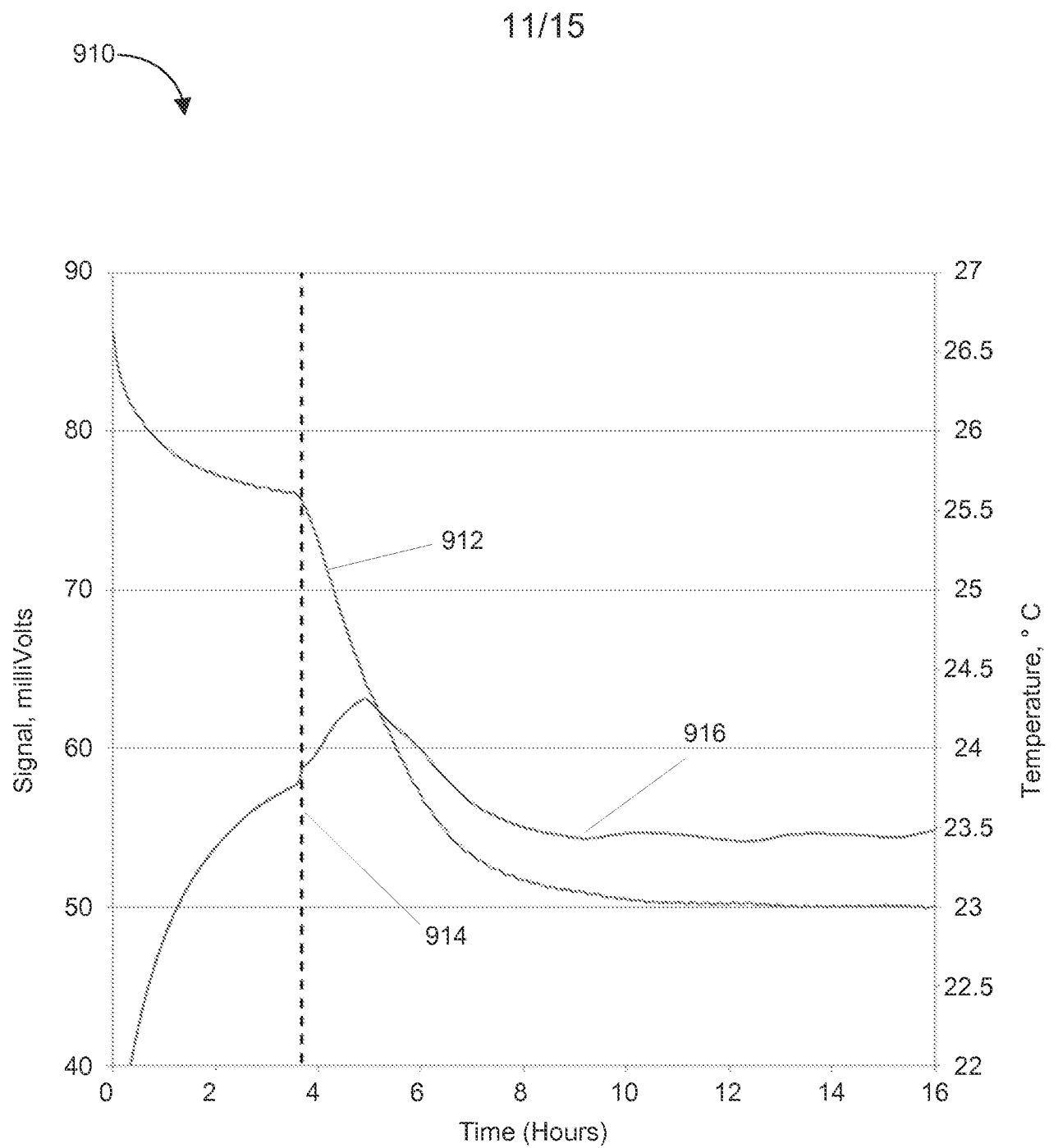


FIG. 9B

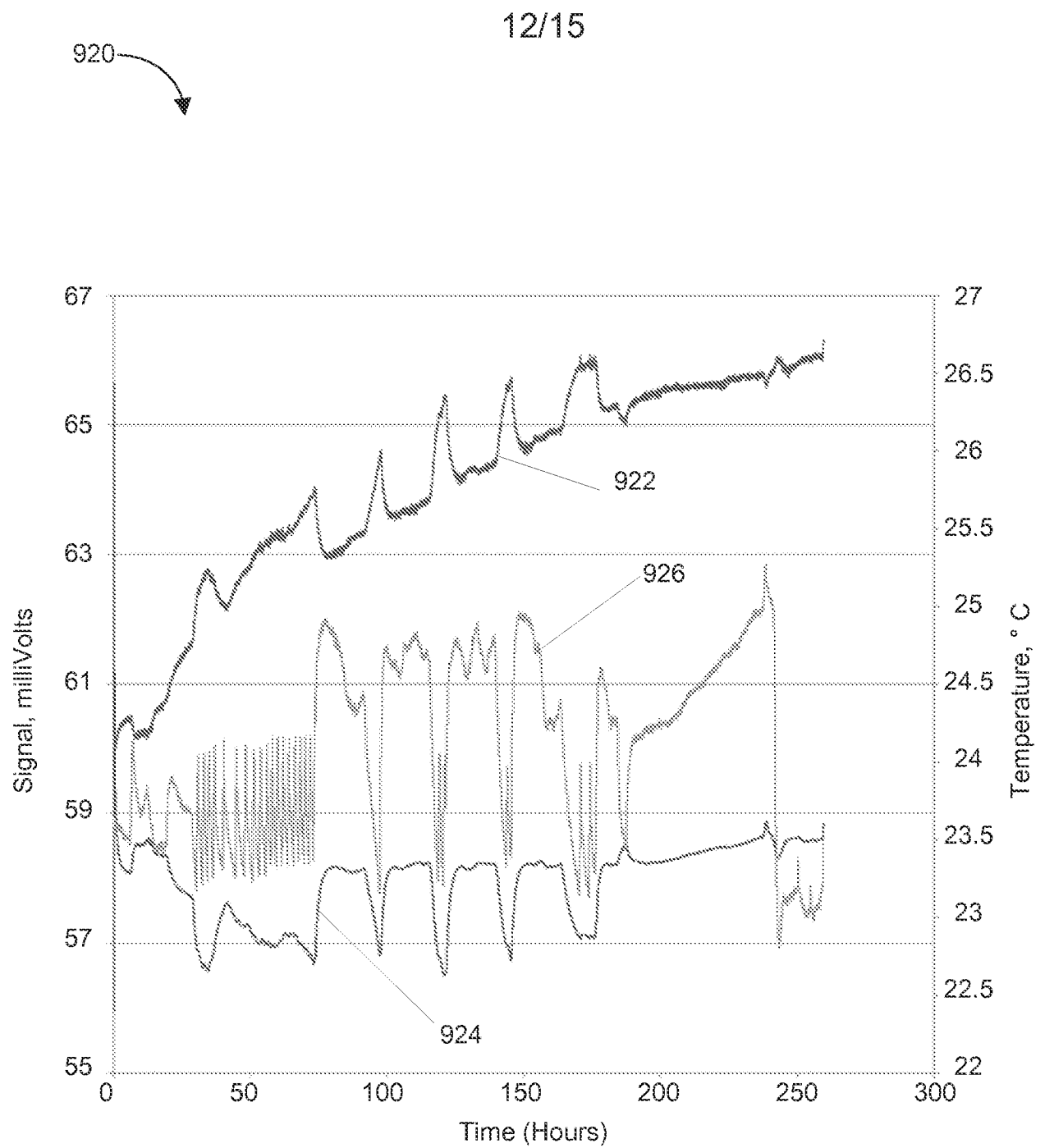


FIG. 9C

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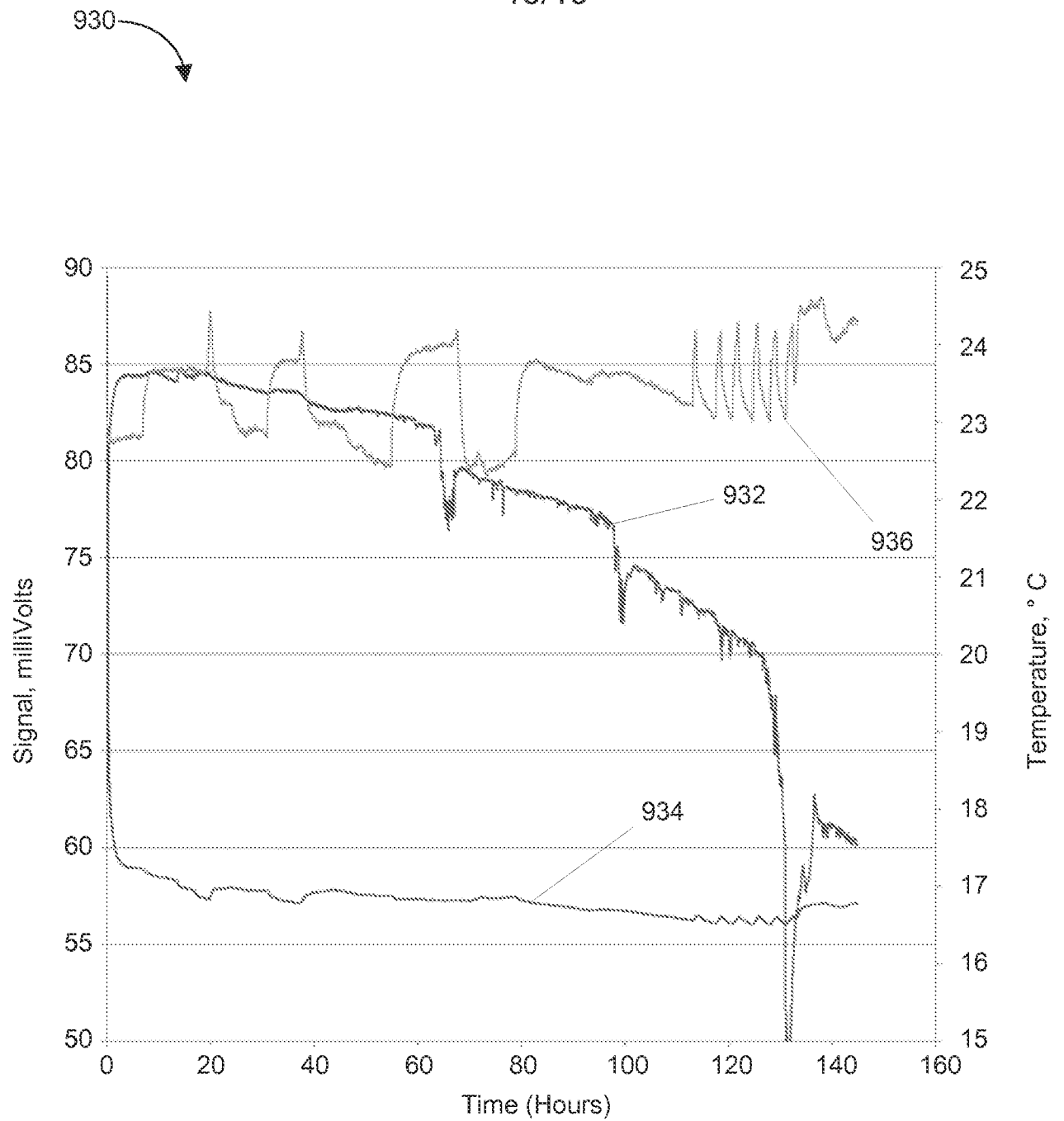


FIG. 9D

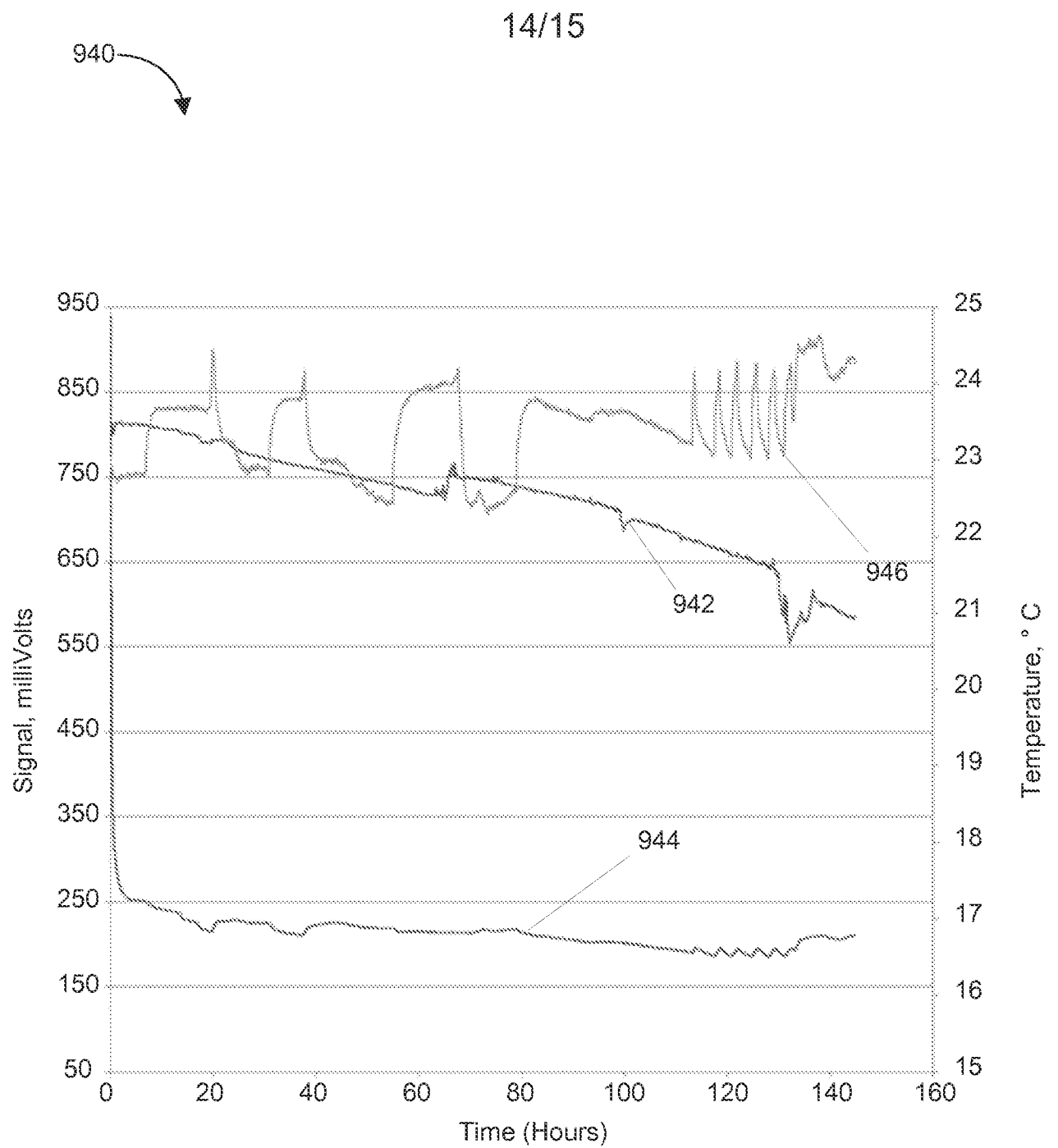


FIG. 9E

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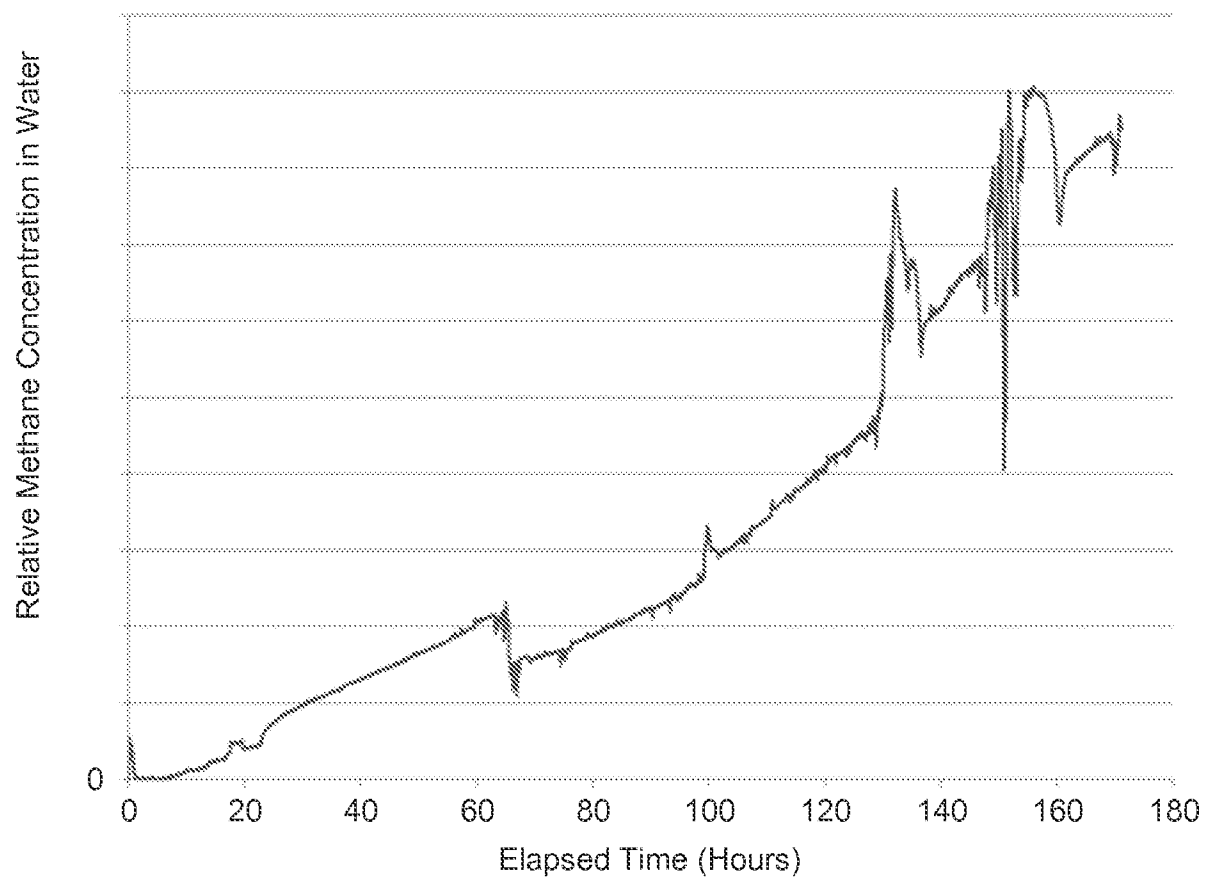


FIG. 9F

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/072920

A. CLASSIFICATION OF SUBJECT MATTER INV. G01N21/35 G01N21/03 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) G01N		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, COMPENDEX, INSPEC, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2007 192638 A (NEW COSMOS ELECTRIC CO) 2 August 2007 (2007-08-02)	1,2,4-7, 12-14, 16-19, 22,24, 25, 30-37, 40-42, 44-46
Y	[0001]-[0009], [0020]-[0022], [0037]; figures 1, 12, 14 ----- -/--	3,8-11, 15,20, 21,23, 26-29, 38,39, 43,47,48
☒ Further documents are listed in the continuation of Box C. ☒ 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
18 March 2014		25/03/2014
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Mason, William

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/072920

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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