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G01N 21/3504 (2014.01) ***G01N 21/3577*** (2014.01)

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US 6627873 A

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Other: **ONLINE: WPI, EPODOC**

(54) Title of the Invention: **Mid-infrared carbon dioxide sensor**
Abstract Title: **Mid-infrared carbon dioxide sensor**

(57) A sensor for monitoring carbon dioxide in a fluid regardless of the phase properties of the fluid, i.e. regardless of whether the fluid contacting the window is a liquid water- based phase, a liquid oil-based phase, a mixture of liquid water and liquid oil-based phases, or a gas phase. The sensor includes an internal reflection window 4 for contacting with the fluid. A mid-infrared light source 1 directs a beam of mid-infrared radiation into the window and the beam is internally reflected at an interface between the window and the fluid. The reflected beam is passed through three narrow bandpass filters 5 which preferentially transmit mid-infrared radiation over bands of wavelengths corresponding to absorbance peaks of water, oil and CO_2. The amount of CO_2 is determined from the intensities of the mid-infrared radiation passing through the three filters. In another aspect a method of determining CO_2 is provided wherein the amount of CO_2 is determined by calculating the phase of the fluid and the measured intensity of the radiation.

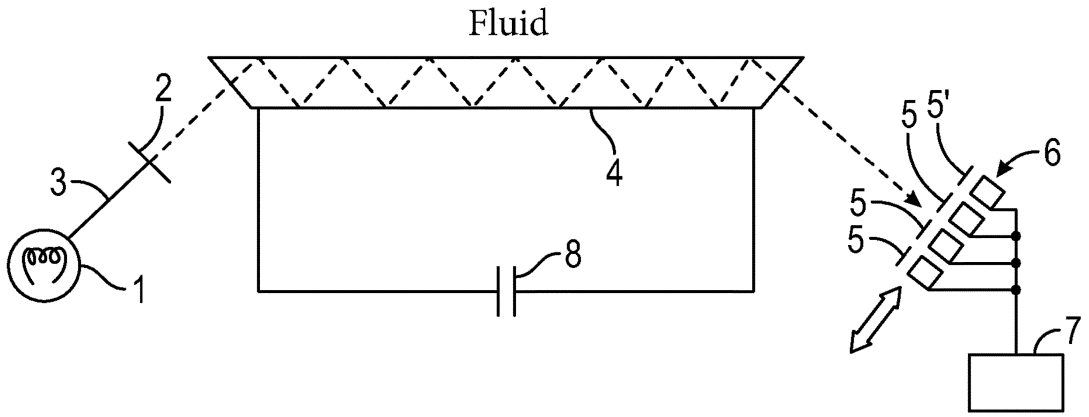

FIG. 1A

GB 2530485 A

At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

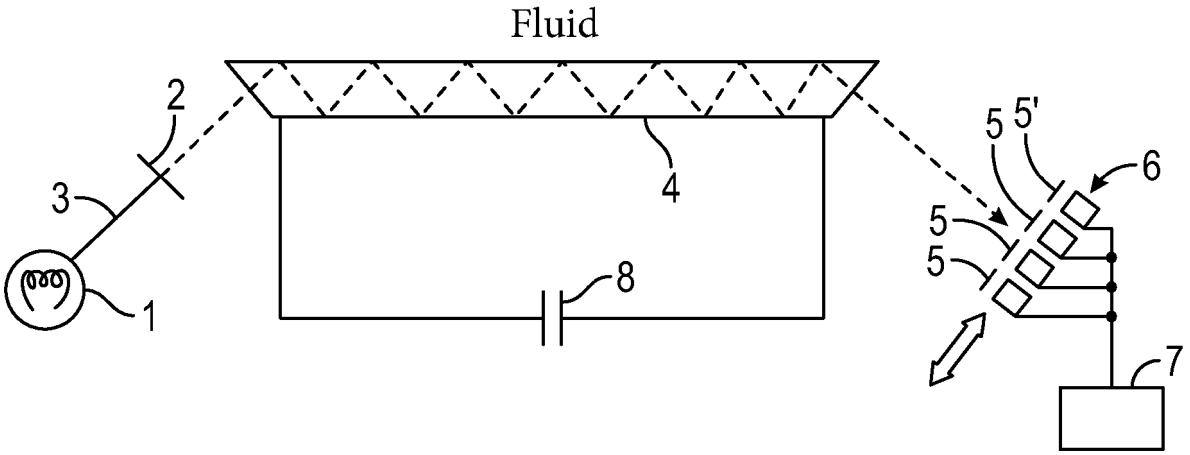

FIG. 1A

16 02 16

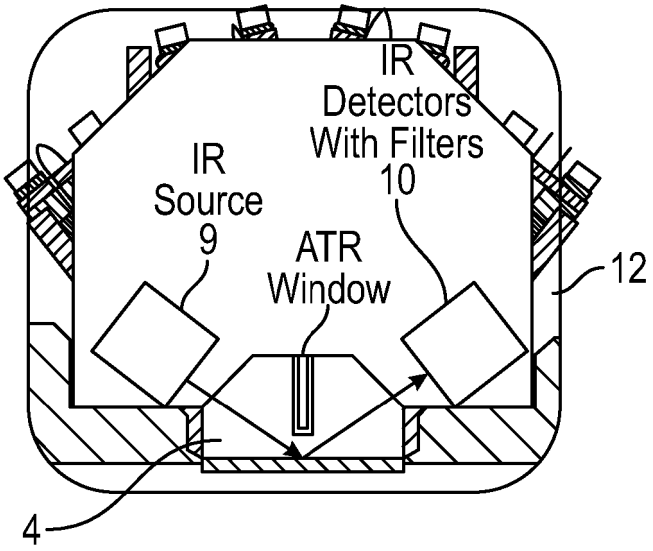

FIG. 1B

02 02 16

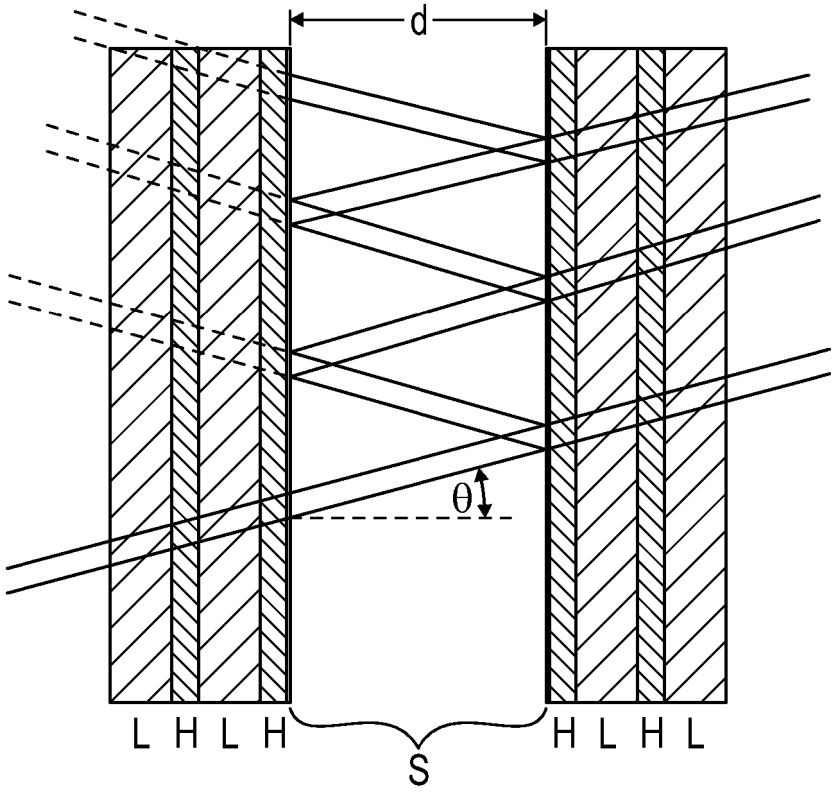

FIG. 2

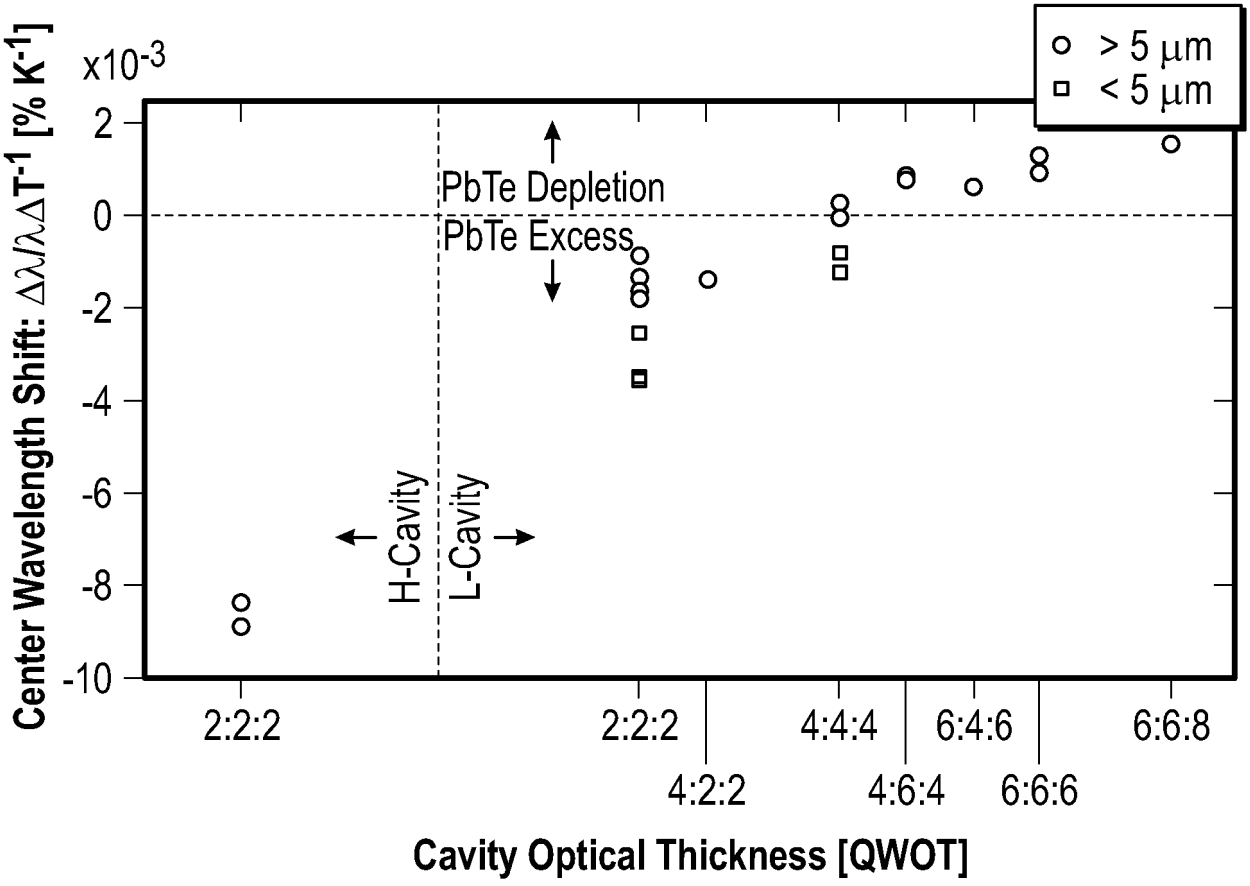

FIG. 3

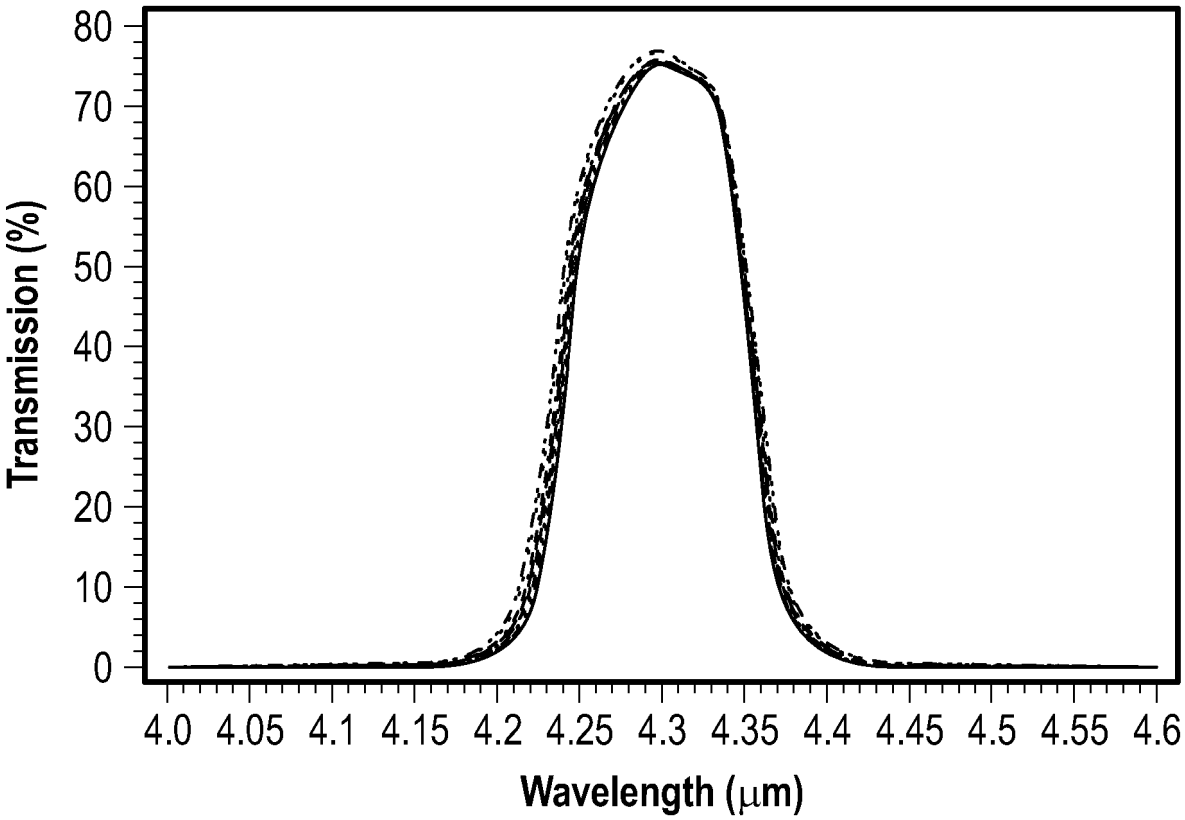

FIG. 4A

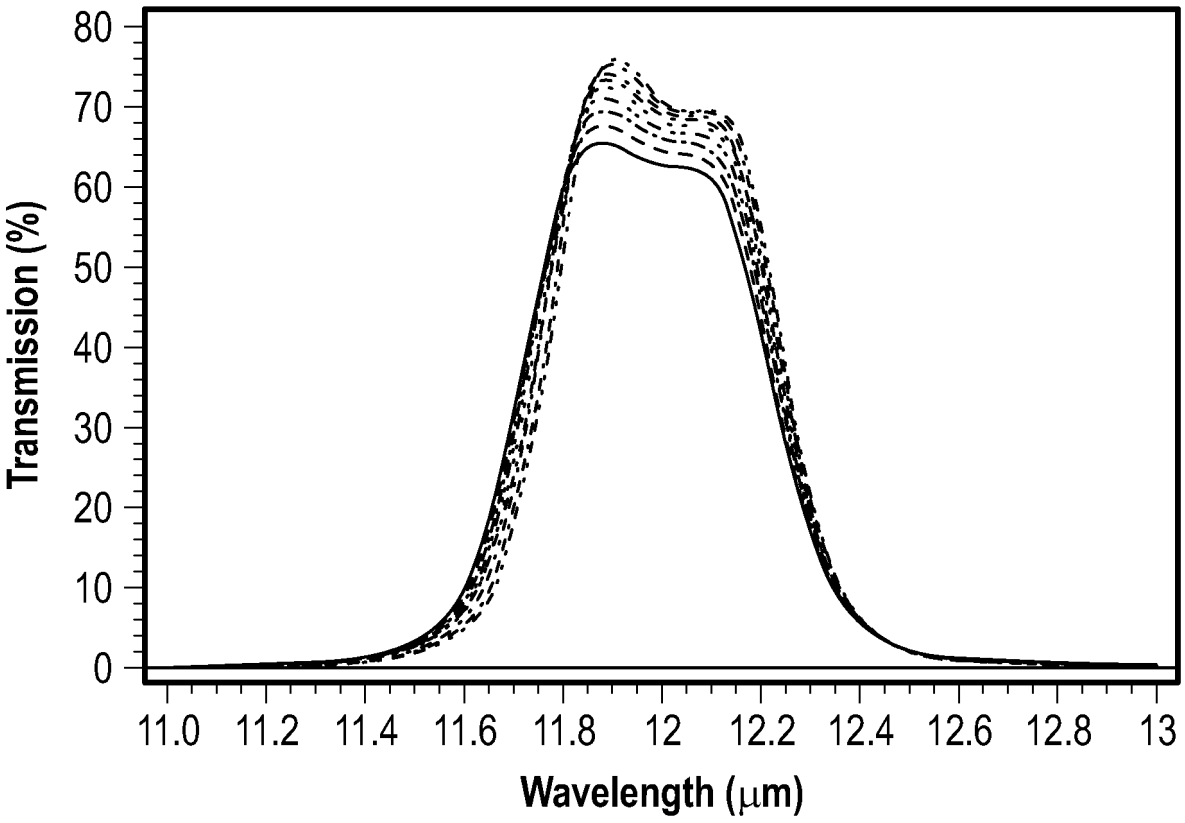

FIG. 4B

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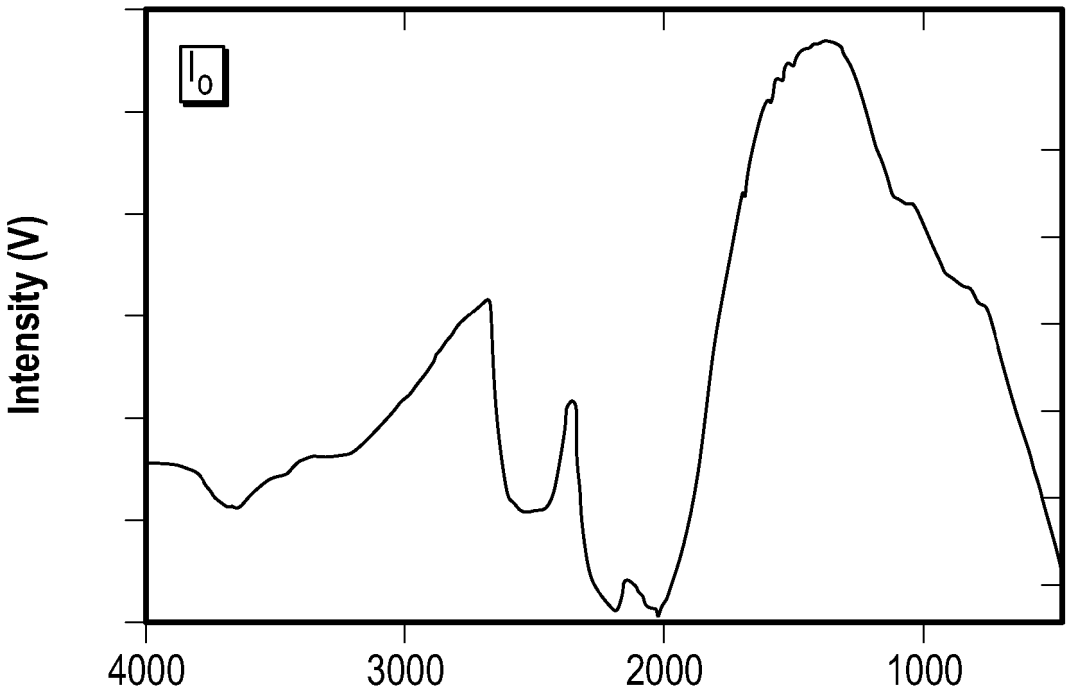

FIG. 5A

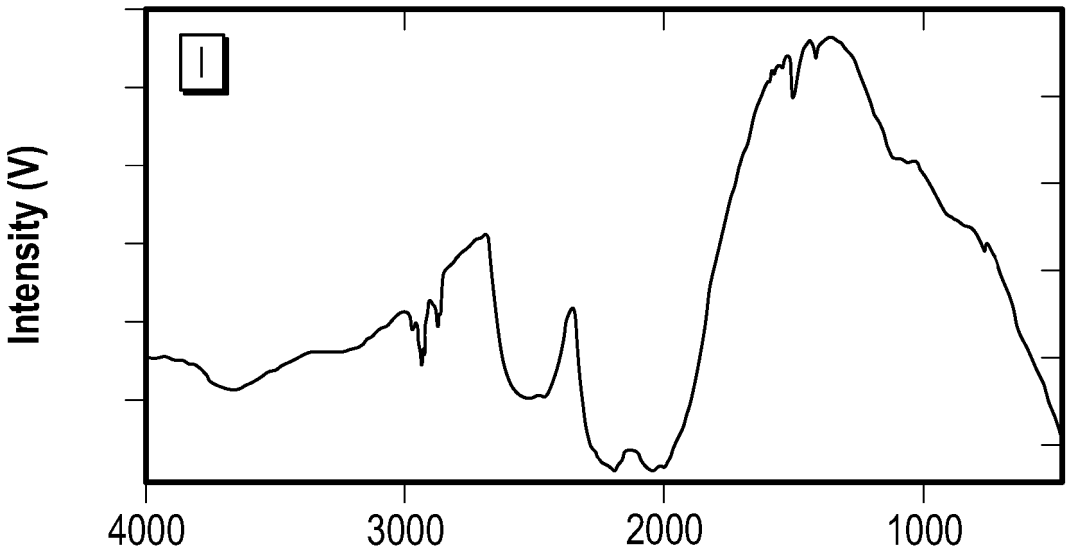

FIG. 5B

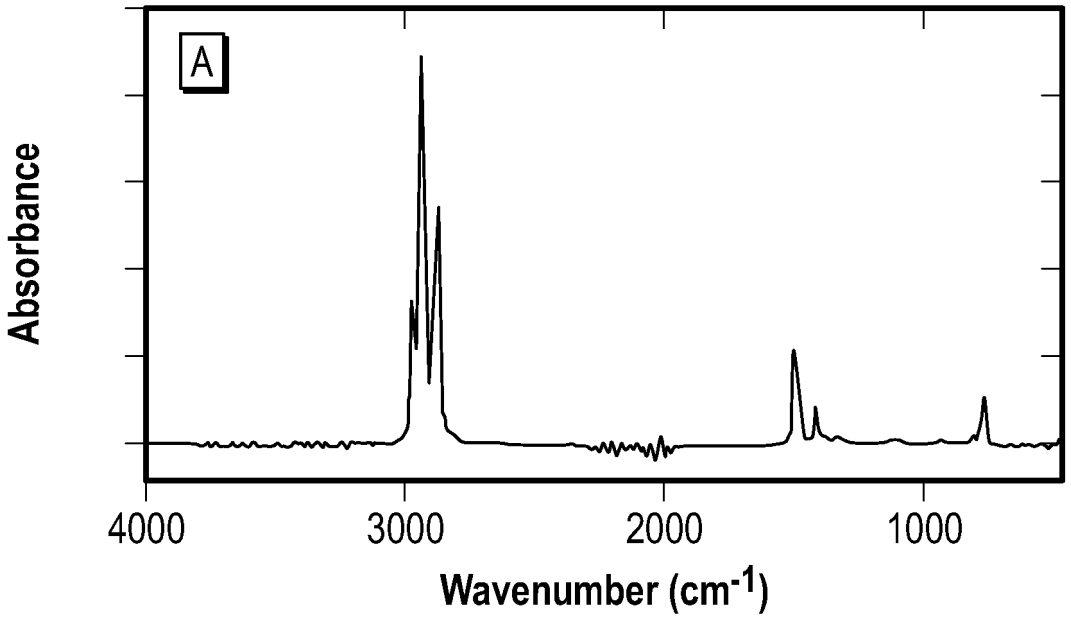

FIG. 5C

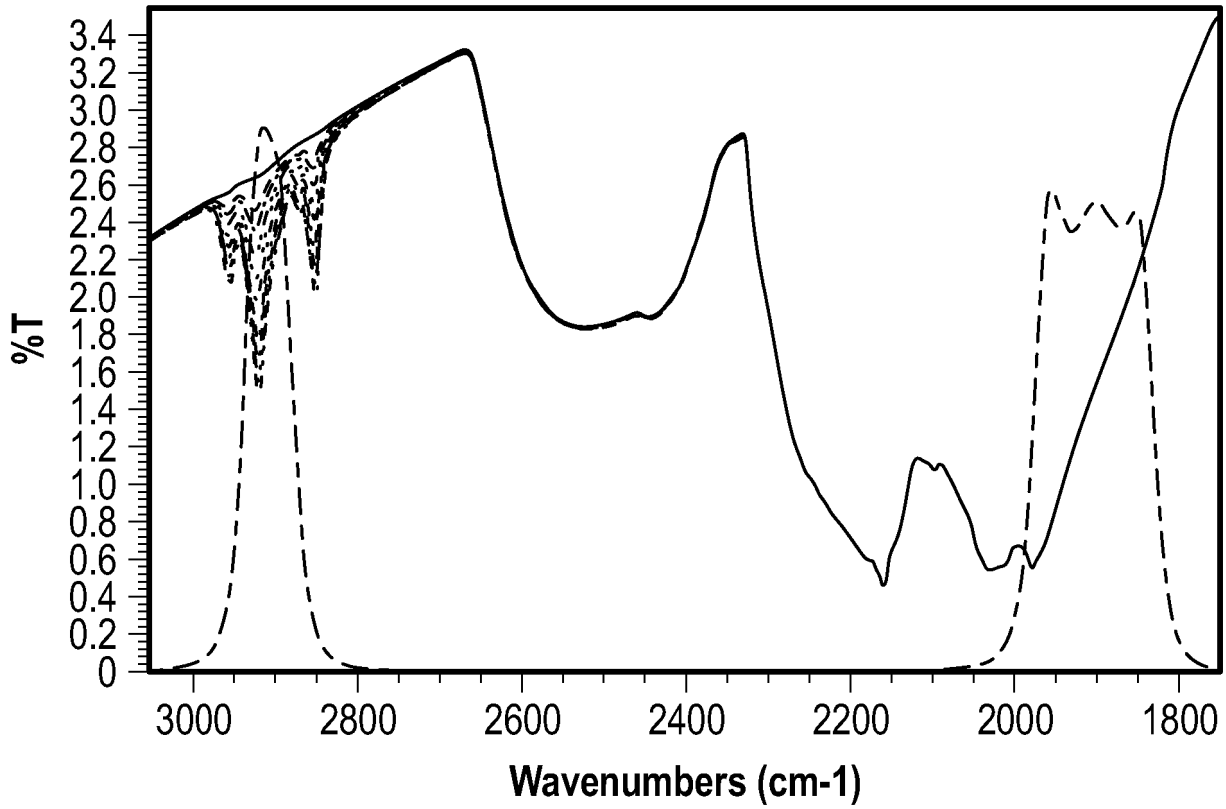

FIG. 6

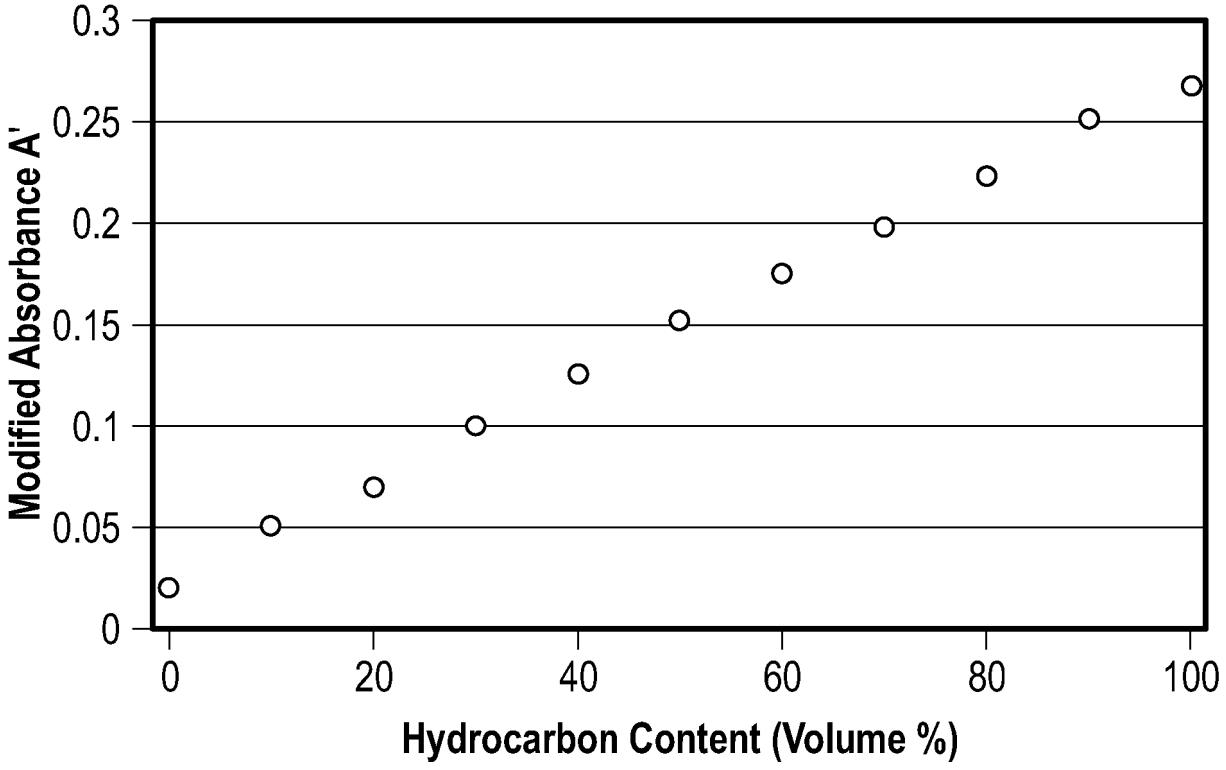

FIG. 7

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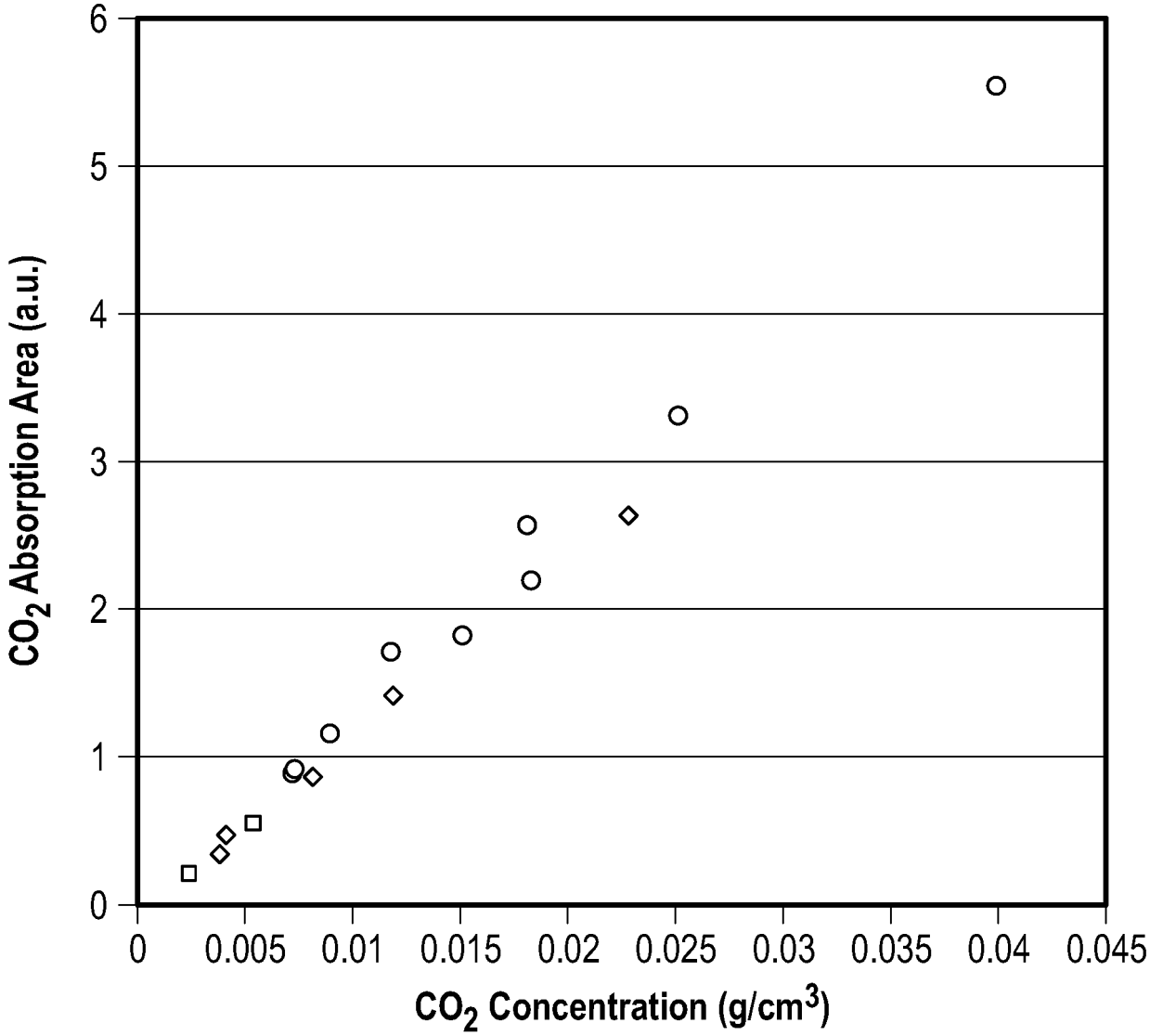
6
5
4
3
2
1
0
CO_2 Absorption Area (a.u.)
0
0.005
0.01
0.015
0.02
0.025
0.03
0.035
0.04
0.045
CO_2 Concentration (g/cm^3)

FIG. 8

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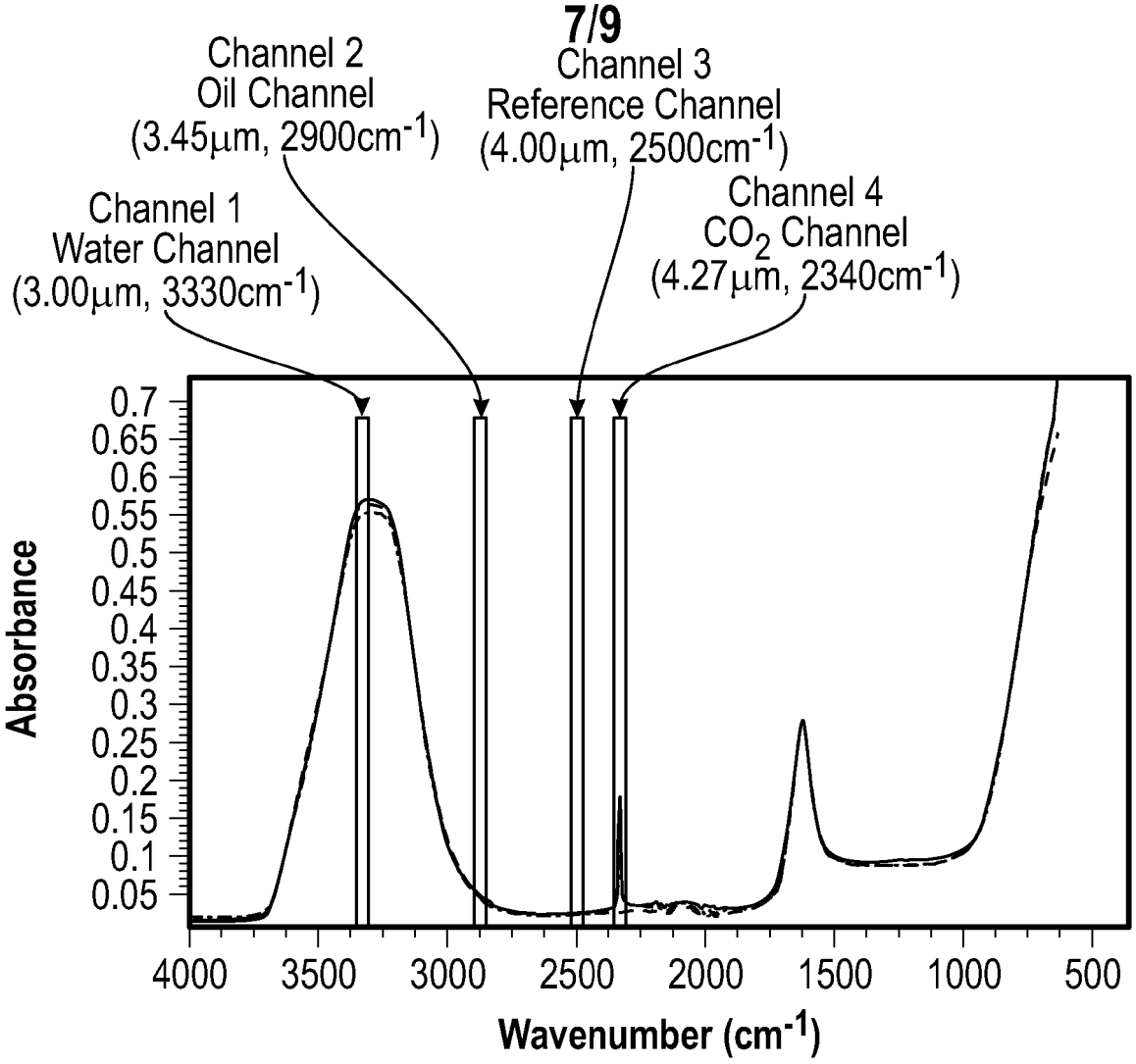

FIG. 9A

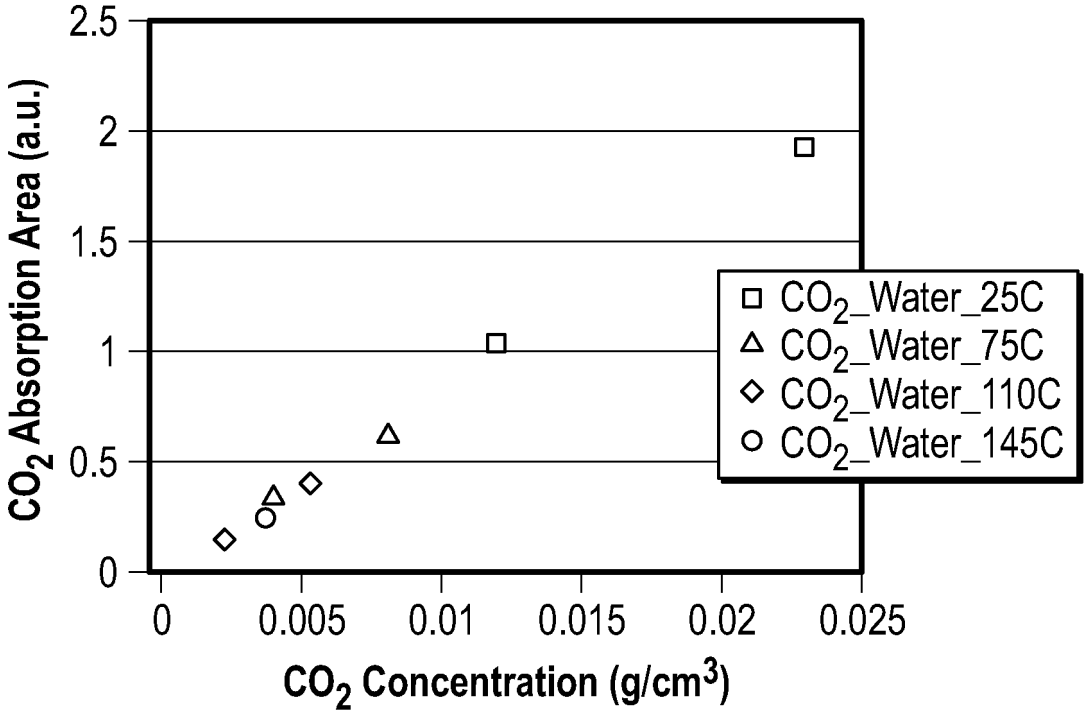

FIG. 9B

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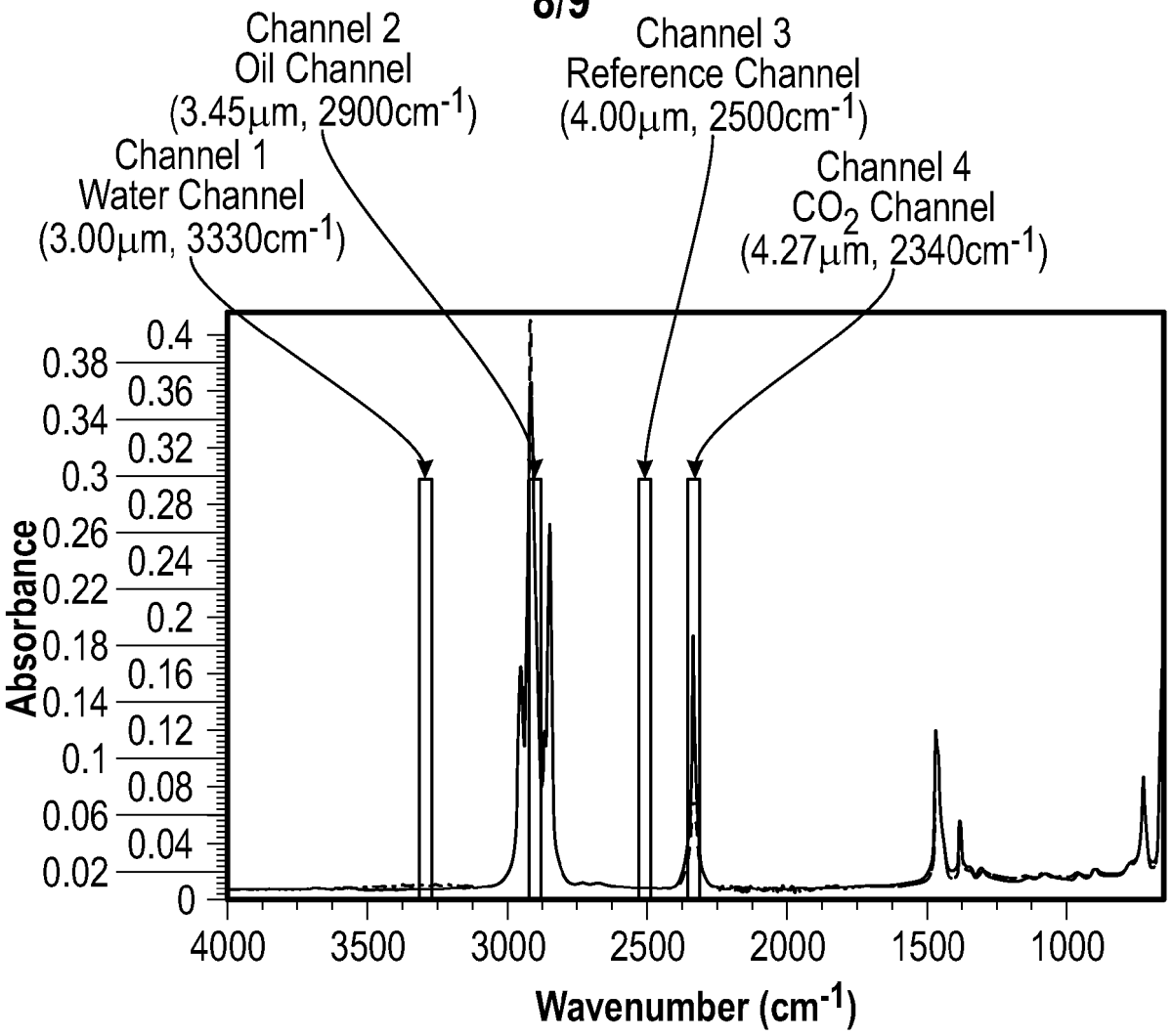

FIG. 10A

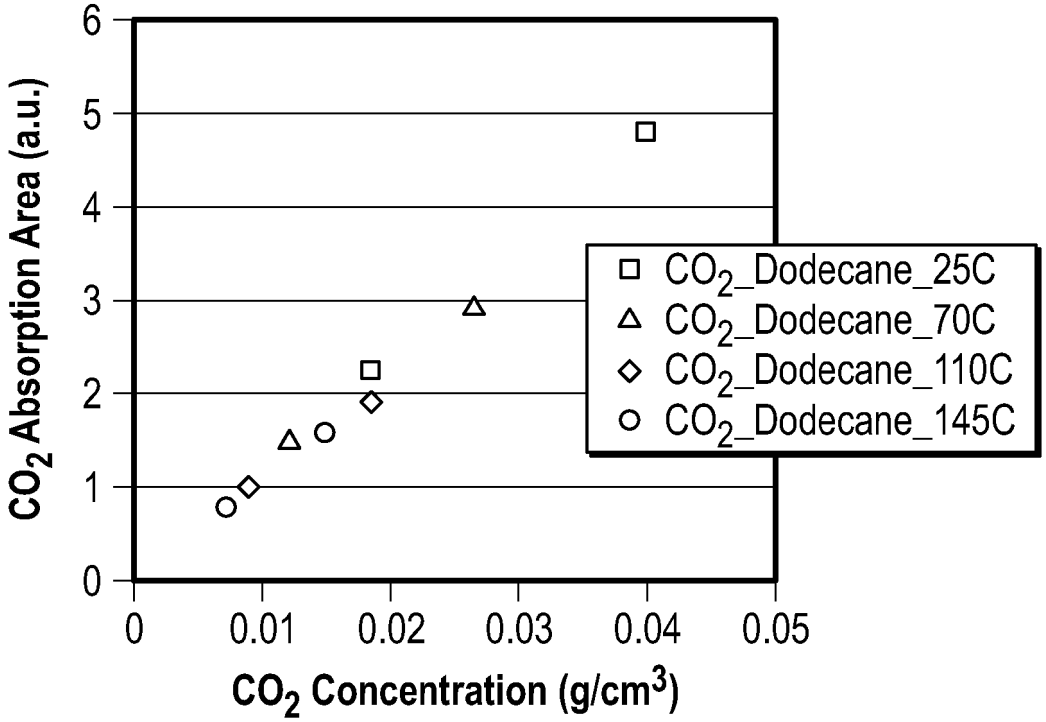

FIG. 10B

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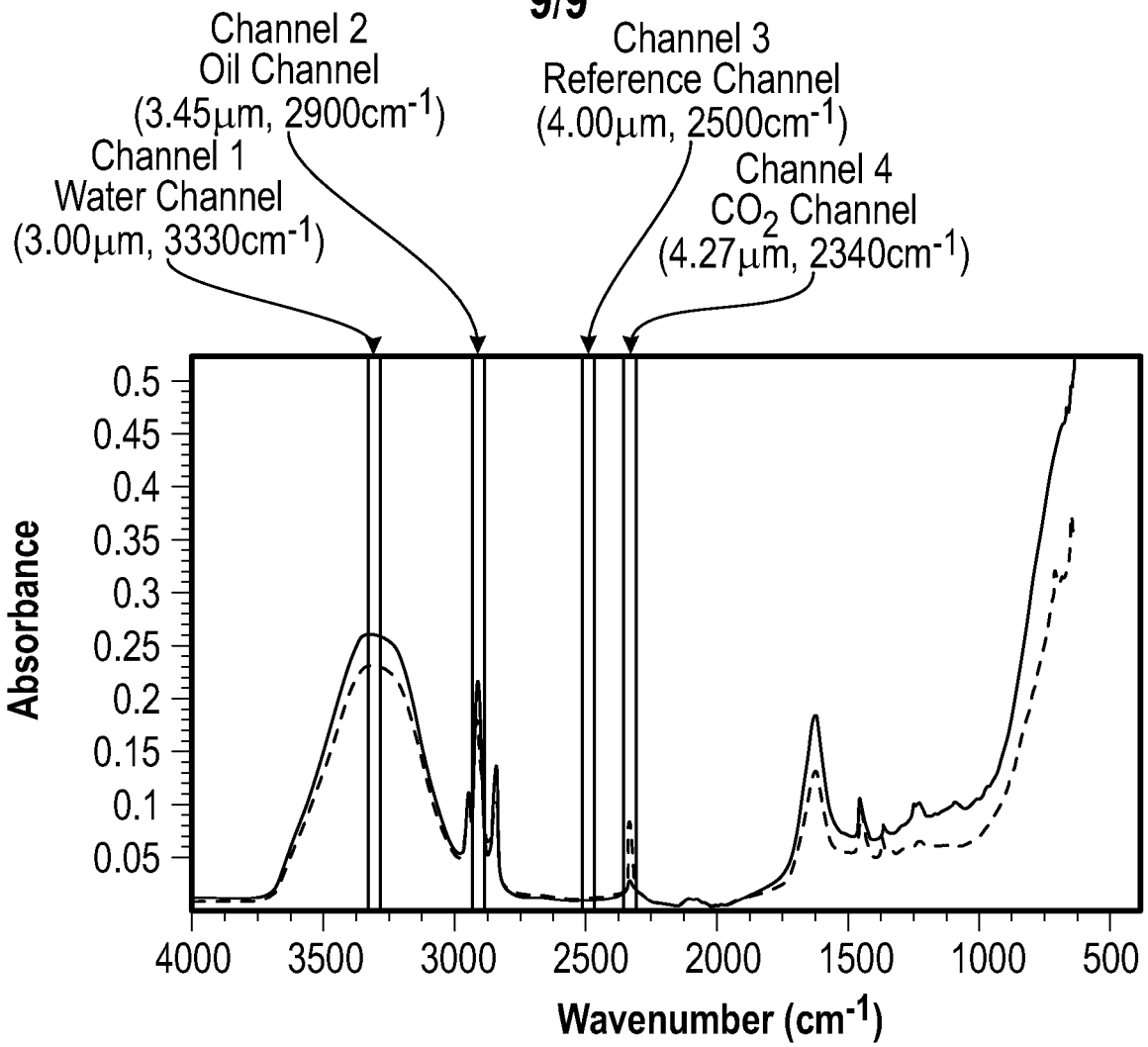

FIG. 11

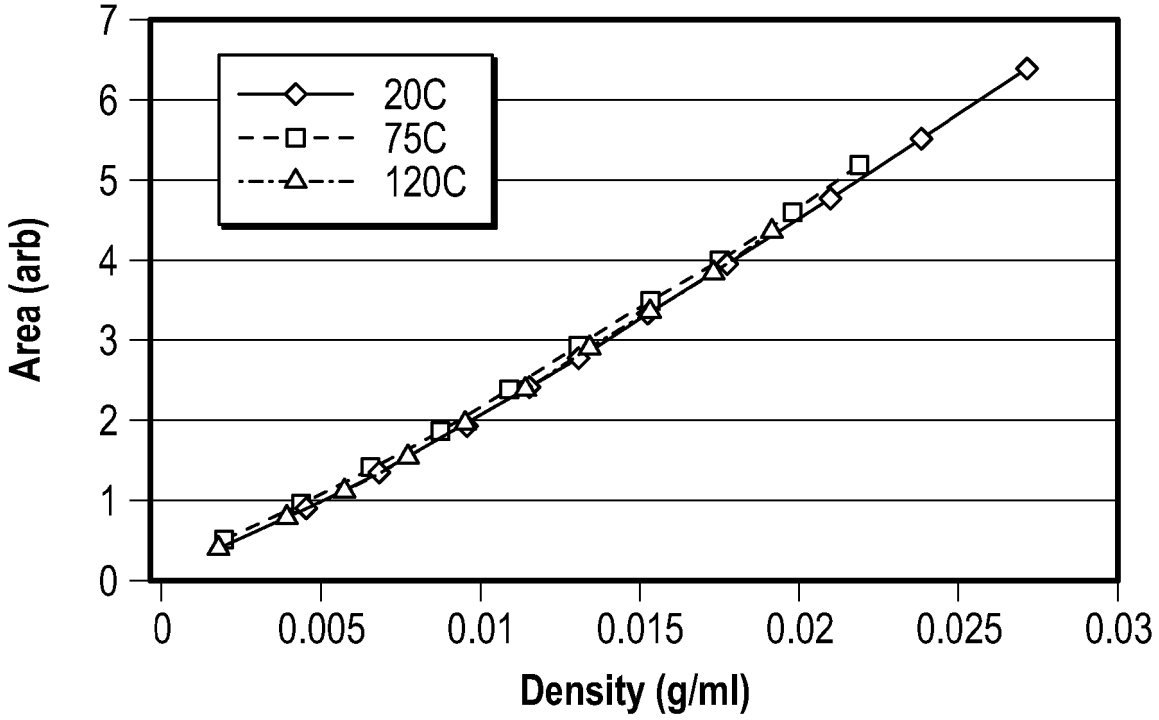

FIG. 12

MID-INFRARED CARBON DIOXIDE SENSOR

BACKGROUND

Embodiments of the present disclosure relate to mid-infrared sensing, and more particularly but not by way of limitation to a mid-infrared sensor for monitoring carbon dioxide (CO_2) in a fluid.

The analysis of chemical composition of fluid samples from hydrocarbon wells for the determination of phase behaviour and chemical composition is a critical step in the monitoring and management of a hydrocarbon well as well as the evaluation of the producibility and economic value of the hydrocarbon reserves. Similarly, the monitoring of fluid composition during production or other operations can have an important bearing on reservoir management decisions. Similarly, determination of phase behaviour and chemical composition is important in pipelines and the like used to convey/transport hydrocarbons from the wellhead, including subsea pipelines.

Several disclosures have described analysis of specific gases in borehole fluids in the downhole environment using near-infrared (*e.g.* λ = 1–2.5μm) spectral measurements. For example, U.S. Patent No. 5,859,430 describes the use of near-infrared spectroscopy to determine quantitatively the presence of methane, ethane and other simple hydrocarbons in the gas phase. The gases were detected using the absorption of near-infrared radiation by the overtone/combination vibrational modes of the molecules in the spectral region 1.64—1.75 μm.

More recently, U.S. Patent No. 6,995,360 describes the use of mid-infrared radiation with a wavelength λ = 3—5μm to monitor gases in downhole environments, and U.S. Patent Publication No. 2012/0290208 proposes the use of mid-infrared radiation to monitor sequestered carbon dioxide dissolved into the liquid solutions of saline aquifers.

There are however many technical problems with using mid-infrared sensors in the hydrocarbon industry and processing information from such sensors. Additionally,

much of the utility of mid-infrared spectroscopy for CO_2 monitoring has not previously been recognized.

SUMMARY

Accordingly, in a first aspect, in accordance with an embodiment of the present disclosure, a sensor for monitoring CO_2 in a fluid is provided, where the sensor includes:

an internal reflection window for contacting with the fluid;

a mid-infrared radiation source for directing a beam of mid-infrared radiation into said window, where the beam undergoes attenuated internal reflection at an interface between the window and the fluid;

a set of three first-narrow-bandpass filters, where the narrow bandpass filters are each configured to preferentially transmit mid-infrared radiation over bands of wavelengths corresponding to respective absorbance peaks of water, oil and CO_2 to filter the internally reflected mid-infrared radiation received from the window;

one or more infrared detectors for detecting the filtered mid-infrared radiation that is transmitted through the set of filters; and

a processor that is configured to process/measures the intensities of the detected mid-infrared radiation transmitted through the set of filters, and determine therefrom an amount (*e.g.* a concentration) of CO_2 in the fluid.

By using a set of three filters in the first aspect, the sensor can measure the CO_2 whether the fluid contacting the window is a liquid water-based phase, a liquid oil-based phase, a mixture of liquid water and liquid oil-based phases, or a gas phase. Such a sensor is highly flexible as it is not necessary for a determination of CO_2 concentration that the window is in contact with a liquid, *i.e.* it can be in contact with a liquid or a gas. In general, attenuated total reflection mid-infrared sensing can only be used to sense condensed phases, but a sensor in accordance with an embodiment of the present disclosure may measure CO_2 in uncondensed phases, because the CO_2 is strongly absorbing in the mid-infrared at a wavelength of about 4.3 μm.

As discussed below, the sensor may be part of a sensor arrangement *e.g.* with a further similar sensor for obtaining a reference intensity.

In a second aspect, in accordance with an embodiment of the present disclosure, the use of the sensor, or sensor arrangement, of the first aspect is provided to determine an amount (*e.g.* a concentration) of CO_2 in a fluid. Thus, a method of monitoring CO_2 in a fluid may include: providing the sensor of the first aspect such that the internal reflection window is in direct contact with the fluid; and operating the sensor to determine an amount (*e.g.* a concentration) of CO_2 in the fluid.

In a third aspect, in accordance with an embodiment of the present disclosure, a well tool is provided (such as a drilling, production well or wireline sampling tool) including the sensor, or sensor arrangement, of the first aspect.

Optional features of embodiments of the present disclosure will now be set out. These are applicable singly or in any combination with any aspect of the embodiments of the present disclosure.

In accordance with an embodiment of the present disclosure, the transmission band of the first filters may be located at about 3330 cm^{-1} (water), 2900 cm^{-1} (oil) and 2340 cm^{-1} (CO_2).

In accordance with an embodiment of the present disclosure, the fluid may be a production fluid, drilling fluid, completion fluid or a servicing fluid. The fluid may in some embodiments comprise a liquid/gas mixture.

"Mid-infrared radiation," as used herein means that the radiation has a wavelength in the range from about 2 to 20μm. In some embodiments, mid-infrared radiation be in the range from about 3 to 12 μm or from 3 to 10 μm.

In some embodiments of the present disclosure, each first narrow bandpass filter may be configured such that its wavelength transmission band is substantially temperature invariant over temperatures in the range from about 25 to 150°C. Temperatures in downhole environments can vary greatly, *e.g.* from room temperature up to about 150°C or 200°C. By using such a temperature invariant

filter, the sensitivity of the sensor to shifts in temperature of its surroundings can be greatly reduced, providing for detection of CO_2 in the downhole environment and/or accurate measurement of the amount of CO_2.

To cover a greater range of downhole temperatures, the wavelength transmission band of the each first narrow bandpass filter may be substantially temperature invariant over all temperatures in the range from about 25 to 200°C. To cover both downhole and subsea conditions (where ambient temperatures can be in the range from about -25 to 25°C), the wavelength transmission band of each first narrow bandpass filter may be substantially temperature invariant over all temperatures in the range from about -25 to 150 or 200°C.

"Substantially temperature invariant" as used herein means that the variance is at most about 0.1 nm/°C. In some embodiments of the present disclosure, the temperature invariance may be at most about 0.05, 0.03, 0.02 or 0.01 nm/°C.

In embodiments of the present disclosure, each filter may comprise an interference filter. Merely by way of example, in some embodiments of the present disclosure, each filter may include a substrate, formed of Si, SiO_2, Al_2O_3, Ge or ZnSe and/or the like, and at each opposing side of the substrate alternating high and low refractive index layers may be formed. In some embodiments of the present disclosure, the high refractive index layers can be formed of PbTe, PbSe or PbS and the low refractive index layers can be formed of ZnS, ZnSe and/or the like.

In embodiments of the present disclosure, each filter may have three or more half wavelength cavities. Many conventional filters display unacceptably high band shifts with increasing temperature. For example, shifts in the range 0.2 to 0.6 nm/°C are typical. Transmissivities also tend to reduce with increasing temperature. These properties, have prevented/limited development of mid-infrared sensors. However, in accordance with embodiments of the present disclosure, by using a PbTe-based, a PbSe-based, a PbS-based interference filter and/or the like it is possible to substantially reduce band shifts and transmissivity reductions. For example, a PbTe-based interference filter, in accordance with an embodiment of the present disclosure, may have a band shift of only about 0.03

nm/°C or less. As an alternative to PbTe, PbSe, PbS or the like, the high refractive index layers can be formed, in some embodiments of the present disclosure, of Ge or the like.

In some embodiments of the present disclosure, a reference intensity may be used in the determination of the amount of the CO_2 in the fluid. Thus, a sensor arrangement, in accordance with an embodiment of the present disclosure, may include the sensor of the first aspect and a further similar sensor which can be used to obtain this reference intensity. The further sensor can have similar features as the first sensor except that its narrow bandpass filter transmits mid-infrared radiation over a band of wavelengths corresponding to a reference portion of the absorbance spectrum of the fluid. In such a scenario, the processor arrangement can be a shared processor arrangement of both sensors.

Another option, however, is to obtain the reference intensity using the first sensor. For example, the sensor, in accordance with an embodiment of the present disclosure, may further include a second narrow bandpass filter configured to transmit mid-infrared radiation over a band of wavelengths corresponding to a reference portion of the absorbance spectrum of the fluid. In such embodiments, the or a further infrared detector may be used to detect filtered mid-infrared radiation transmitted through the second filter, and the processor arrangement may measure the reference intensity of the detected mid-infrared radiation transmitted through the second filter and use the measured reference intensity in the determination of the amount of the CO_2 in the fluid.

In some embodiments of the present disclosure, the first and second filters may be selectably positionable between a single detector and the window, or each of the first and second filters can have a respective detector. The second narrow bandpass filter may be configured such that its wavelength transmission band is substantially temperature invariant over all temperatures in the range from about 25 to 150°C. Other optional features of the first narrow bandpass filters pertain also to the second narrow bandpass filter. The transmission band of the second filter may be located at about 2500 cm^{-1}.

In some embodiments of the present disclosure, the beam of mid-infrared radiation may be pulsed. This can be achieved, for example, in some embodiments of the present disclosure, by providing a mechanical chopper between the source and the window, or by pulsing the source.

In some embodiments of the present disclosure, the source may be a broad band thermal source or a narrower band source such as a light emitting diode or a laser.

In some embodiments of the present disclosure, the detector may be a thermopile, a pyroelectric or (particularly in subsea applications, where the low ambient temperatures can provide cooling) a photodiode detector.

In some embodiments of the present disclosure, the window may comprise a diamond window or a sapphire window. In some embodiments of the present disclosure, the diamond windows can be formed by chemical vapour deposition. Sapphire has a cut off for mid-infrared radiation at wavelengths of about 5 to 6 microns, but sapphire windows can generally be formed more cheaply than diamond windows. Thus, for absorption peaks below the cut off (such as the CO_2 absorption peak at about 4.3 microns), sapphire may be a useful alternative to diamond. In particular, for a given cost a larger window can be formed.

In some embodiments of the present disclosure, the sensor may further include a heater which is operable to locally heat the window, thereby cleaning the surface of the window in contact with the fluid. For example, in some embodiments of the present disclosure, if the window includes a conductive or semiconductive material (*e.g.* an area of semiconductive boron-doped diamond), the heater can con comprise an electrical power supply which sends a current through the window to induce resistive heating thereof. For example, in some embodiments of the present disclosure, a diamond window can have a central mid-infrared transmissive (*e.g.* undoped) area and an encircling area of semiconductive boron-doped diamond. The heater can induce resistive heating of the encircling area, and the central area can then be heated by conduction of heat from the encircling area. In some embodiments of the present disclosure, the heater may heats the window to a peak temperature of at least 400°C. In some embodiments of the

present disclosure, the heater may maintain a peak temperature for less than one microsecond.

Alternatively or additionally, in some embodiments of the present disclosure, the sensor may further include an ultrasonic cleaner which is operable to ultrasonically clean the surface of the window in contact with the fluid. As another option, the sensor may be provided with a pressure pulse arrangement which is operable to produce a pressure pulse in the fluid at the window, thereby cleaning the surface of the window in contact with the fluid. In some embodiments of the present disclosure, the arrangement may produce a pressure pulse of at least about 1000 psi (6.9 MPa) in the fluid.

In some embodiments of the present disclosure, the sensor may be located downhole.

To determine the amount of CO_2 in the fluid, in some embodiments of the present disclosure, the processor arrangement may calculate from the measured intensities of the mid-infrared radiation transmitted through the water and oil first filters the phase of the fluid, and may then calculate from the phase of the fluid and the measured intensity of the mid-infrared radiation transmitted through the CO_2 first filter the amount of CO_2 in the fluid. More particularly, in some embodiments of the present disclosure, the processor arrangement may use the refractive index of the fluid, derived from the phase of the fluid, in the calculation of the amount of CO_2 in the fluid.

Indeed more generally, in a fourth aspect, in accordance with an embodiment of the present disclosure, a method of determining an amount of CO_2 in a fluid is provided, including:

receiving respective measured intensities of mid-infrared radiation filtered by three narrow bandpass filters that are configured to preferentially transmit mid-infrared radiation over bands of wavelengths corresponding to respective absorbance peaks of water, oil and CO_2, where the mid-infrared radiation, prior to filtering, is produced by directing a beam of mid-infrared radiation

into an internal reflection window for attenuated internal reflection at an interface between the window and a fluid in direct contact with the window;

calculating from the measured intensities of the mid-infrared radiation filtered by the water and oil filters the phase of the fluid, and

calculating from the phase of the fluid and the measured intensity of the mid-infrared filtered by the CO_2 filter the amount of CO_2 in the fluid.

The method may further include: deriving the refractive index of the fluid from the calculated phase of the fluid. The refractive index can then be used in the calculation of the amount of CO_2 in the fluid.

Further aspects of embodiments of the present disclosure provide: a computer program comprising code which, when run on a computer, causes the computer to perform the method of the fourth aspect; a computer readable medium storing a computer program comprising code which, when run on a computer, causes the computer to perform the method of the fourth aspect; and a computer system programmed to perform the method of the fourth aspect.

BRIEF DESCRIPTION OF THE DRAWINGS

Embodiments of the invention will now be described by way of example with reference to the accompanying drawings in which:

Figure 1 shows schematically, in accordance with embodiments of the present disclosure: (a) a mid-infrared sensor, and (b) the sensor implemented as a module in a toolstring;

Figure 2 shows schematically a narrow bandpass filter based on Fabry-Perot interferometry, in accordance with an embodiment of the present disclosure;

Figure 3 shows variation of $d\lambda_m/\lambda_m dT$ for a suite of filters fabricated with ZnSe as the low refractive index material and PbTe as the high refractive index material, in accordance with an embodiment of the present disclosure;

Figure 4 shows plots of transmissivity against wavelength at a range of temperatures from 25 to 200°C for (a) a PbTe-based filter having a pass band centred at 4.26 μm, and (b) a PbTe-based filter having a pass band centred at 12.1 μm, in accordance with embodiments of the present disclosure;

Figure 5 shows (a) a reference intensity spectrum I_0 obtained from a fluid not containing a given species, (b) an intensity spectrum I obtained from the fluid containing the species, and (c) the absorbance spectrum of the species;

Figure 6 shows intensity spectra obtained for dodecane dissolved in deuterated chloroform for increasing concentrations of dodecane, the spectra being superimposed with transmissivity plots for a first filter having a pass band of 3000 to 2800 cm^{-1}, and a second filter having a pass band of 2000 to 1800 cm^{-1};

Figure 7 shows a plot of modified absorbance A' against hydrocarbon content for dodecane dissolved in deuterated chloroform;

Figure 8 shows a plot of absorbance against dissolved CO_2 concentration in water or hydrocarbon;

Figure 9 shows (a) a mid-infrared absorbance spectrum for a water phase and CO_2, and (b) a corresponding plot of absorbance against CO_2 concentration for CO_2 in H_2O;

Figure 10 shows (a) a mid-infrared absorbance spectrum for an oil phase and CO_2, and (b) a corresponding plot of absorbance against CO_2 concentration for CO_2 in oil;

Figure 11 shows a mid-infrared absorbance spectrum for a water phase, an oil phase and CO_2; and

Figure 12 shows a plot of absorbance against CO_2 concentration for CO_2 in gas phase.

In the appended figures, similar components and/or features may have the same reference label. Further, various components of the same type may be

distinguished by following the reference label by a dash and a second label that distinguishes among the similar components. If only the first reference label is used in the specification, the description is applicable to any one of the similar components having the same first reference label irrespective of the second reference label.

DETAILED DESCRIPTION

The ensuing description provides preferred exemplary embodiment(s) only, and is not intended to limit the scope, applicability or configuration of the invention. Rather, the ensuing description of the preferred exemplary embodiment(s) will provide those skilled in the art with an enabling description for implementing a preferred exemplary embodiment of the invention, it being understood that various changes may be made in the function and arrangement of elements without departing from the scope of the invention.

Specific details are given in the following description to provide a thorough understanding of the embodiments. However, it will be understood by one of ordinary skill in the art that embodiments maybe practiced without these specific details. For example, well-known circuits, processes, algorithms, structures, and techniques may be shown without unnecessary detail in order to avoid obscuring the embodiments.

Also, it is noted that the embodiments may be described as a process which is depicted as a flowchart, a flow diagram, a data flow diagram, a structure diagram, or a block diagram. Although a flowchart may describe the operations as a sequential process, many of the operations can be performed in parallel or concurrently. In addition, the order of the operations may be re-arranged. A process is terminated when its operations are completed, but could have additional steps not included in the figure. A process may correspond to a method, a function, a procedure, a subroutine, a subprogram, etc. When a process corresponds to a function, its termination corresponds to a return of the function to the calling function or the main function.

Moreover, as disclosed herein, the term "storage medium" may represent one or more devices for storing data, including read only memory (ROM), random access memory (RAM), magnetic RAM, core memory, magnetic disk storage mediums, optical storage mediums, flash memory devices and/or other machine readable mediums for storing information. The term "computer-readable medium" includes, but is not limited to portable or fixed storage devices, optical storage devices, wireless channels and various other mediums capable of storing, containing or carrying instruction(s) and/or data.

Furthermore, embodiments may be implemented by hardware, software, firmware, middleware, microcode, hardware description languages, or any combination thereof. When implemented in software, firmware, middleware or microcode, the program code or code segments to perform the necessary tasks may be stored in a machine readable medium such as storage medium. A processor(s) may perform the necessary tasks. A code segment may represent a procedure, a function, a subprogram, a program, a routine, a subroutine, a module, a software package, a class, or any combination of instructions, data structures, or program statements. A code segment may be coupled to another code segment or a hardware circuit by passing and/or receiving information, data, arguments, parameters, or memory contents. Information, arguments, parameters, data, etc. may be passed, forwarded, or transmitted via any suitable means including memory sharing, message passing, token passing, network transmission, etc.

It is to be understood that the following disclosure provides many different embodiments, or examples, for implementing different features of various embodiments. Specific examples of components and arrangements are described below to simplify the present disclosure. These are, of course, merely examples and are not intended to be limiting. In addition, the present disclosure may repeat reference numerals and/or letters in the various examples. This repetition is for the purpose of simplicity and clarity and does not in itself dictate a relationship between the various embodiments and/or configurations discussed. Moreover, the formation of a first feature over or on a second feature in the description that follows may include embodiments in which the first and second features are

formed in direct contact, and may also include embodiments in which additional features may be formed interposing the first and second features, such that the first and second features may not be in direct contact.

Figure 1(a) shows schematically a mid-infrared sensor, in accordance with an embodiment of the present disclosure, having a thermal broad band mid-infrared source 1, a mechanical chopper 2 that pulses a beam 3 of mid-infrared radiation which issues from the source, a diamond window 4, a set of selectively movable first narrow bandpass filters 5 and a second narrow bandpass filter 5', respective mid-infrared detectors 6 for the filters, and a processor arrangement 7. In some embodiments, the sensor may be encased in a protective housing allowing the sensor to be deployed downhole, the window 4 being positioned for contact with the fluid to be monitored. Mid-infrared waveguides (not shown) optically connect the source, window and the detectors. Suitable waveguides can be formed from optical fibres (*e.g.* hollow fibres or chalcogenide fibres), solid light pipes (*e.g.* sapphire pipes), or hollow light pipes (*e.g.* air or vacuum filled) with a reflective (*e.g.* gold) coating.

As the detector 6 changes its output with its temperature, even small changes in temperature can cause a large drift in signal output. However, in accordance with an embodiment of the present disclosure, pulsing the beam 3 allows the output signal of the detector to be frequency modulated, enabling removal of the environmental temperature effects from the signal. More particularly, the environment effects can be largely removed electronically by a high pass filter, because the time constant for environment effects tends to be much longer than the signal frequency. In some embodiments of the present disclosure, the detector output is AC-coupled to an amplifier. The desired signal can then be extracted *e.g.* electronically by lock-in amplification or computationally by Fourier transformation.

Instead of the thermal source 1 and the mechanical chopper 2, in some embodiments of the present disclosure, the pulsed beam 3 may be produced *e.g.* by a pulsable thermal source, light emitting diode or laser source. Pulsing the source in this way can give the same benefit of frequency modulation measurement, plus it can reduce resistive heating effects.

The beam 3 enters at one edge of the window 4, and undergoes a number of total internal reflections before emerging from the opposite edge. The total internal reflection of the infrared radiation at the fluid side of the window is accompanied by the propagation of an evanescent wave into the fluid. As the fluid preferentially absorbs certain wavelengths, depending on its chemical composition, this causes the emerging beam to have a characteristic variation in intensity with wavelength.

In some embodiments of the present disclosure, the window 4 is mechanically able to withstand the high pressures and temperatures typically encountered downhole. It is chemically stable to fluids encountered downhole and is transparent in the mid-IR wavelength region. In some embodiments of the present disclosure, the window may comprise diamond, sapphire and/or the like.

In accordance with an embodiment of the present disclosure, the first narrow bandpass filters 5 each transmit mid-infrared radiation over a band of wavelengths corresponding to an absorbance peak of a respective species in the fluid, while the second narrow bandpass filter 5' transmits mid-infrared radiation over a band of wavelengths corresponding to a reference portion of the absorbance spectrum of the fluid. The beam 3 then passes through a selected one of the narrow bandpass filters and is detected at the respective detector 6. Instead of having a plurality of detectors, each movable with its corresponding filter (as indicated by the double-headed arrow), in some embodiments of the present disclosure, a single detector is provided in front of which the filters are selectively movable.

In some embodiments of the present disclosure, the detector 6 may comprise. semiconductor photo-diodes (particularly in subsea applications), thermopiles or pyroelectric detectors.

The processor arrangement 7 receives a signal from the respective detector 6, which it processes to measure the intensity of the detected mid-infrared radiation transmitted through each filter 5, 5', and, as discussed in more detail below, determines therefrom an amount of the respective species in the fluid.

Also discussed in more detail below, the sensor may have a heater 8 which is operable to locally heat the window 4, thereby cleaning the surface of the window in contact with the fluid. Other options, however, are to clean the window ultrasonically (as described for example in U.S. Patent No. 7,804,598), or with a mechanical wiper.

Figure 1(b) shows schematically how, in accordance with an embodiment of the present disclosure, the sensor can be implemented as a module in a toolstring. In some embodiments of the present disclosure, the source 1 and chopper 2 are contained in a source unit 9 and filters 5, 5' and detectors 6 are contained in a detector unit 10. These may be located close to the window 4 that is in contact with a tool flowline 11. The sensor may be packaged in a protective metal chassis 12 to withstand the high pressure of the fluid in the flowline. The window may be sealed into the chassis also to withstand the high pressures, and its packaging ensures no direct source light strays into the detectors.

Narrow Bandpass Filters

In embodiments of the present disclosure, the narrow bandpass filters 5, 5' may be based on Fabry-Perot interferometry. As shown in Figure 2, each filter may have a substrate S of low refractive index and thickness d. On opposing surfaces of the substrate are stacked alternating high-reflectivity dielectric layers of high H and low L refractive index deposited onto the substrate using techniques such as ion-beam sputtering or radical-assisted sputtering. In some embodiments of the present disclosure, each layer in the stacks of alternating layers of high H and low L refractive index has an optical thickness of a quarter wavelength.

The optical thickness $ndcos\theta$ of the substrate S, where n is the refractive index of the substrate, is equal to an integer number of half wavelengths λ_m, where λ_m is the peak transmission wavelength, corresponding approximately to the centre wavelength of the pass band of the filter. The condition for the transmission of radiation of wavelength λ_m through the filter is thus $m\lambda_m/2 = ndcos\theta$, where m is an integer.

The spectral region of conventional narrow bandpass dielectric filters designed to operate in the mid-infrared spectral regions shifts systematically to longer wavelengths with increasing temperature. The origin of the change in λ_m with temperature is a change in the material properties with temperature of the dielecric materials that comprise the layers of the filter.

However, an approach described below, in accordance with an embodiment of the present disclosure, provides for the configuration and fabrication of mid-infrared narrow bandpass filters that have substantially temperature invariant optical properties over a wide temperature range.

The approach can be considered by the design of the filter:

$$(LH)^{x1}(LL)^{y1}(HL)^{x2}(LL)^{y2}\ldots\ldots(LL)^{yN}(HL)^{xN+1}$$

consisting of a total of y half wavelength spacers (cavities) LL of low refractive index material in N cycles ($y=\sum y_i$), LH being the stacks of x_i quarter wavelength layers of alternating of high and low refractive index material in the N cycles. The reflections wavelength of the quarter wavelength reflector stack (which is the only reflection to undergo constructive interference), irrespective of the values of x_i and N, can be expressed as:

$$\lambda_m=2(n_L d_L+n_H d_H)$$

for first order reflections (m=0). The temperature variation of the wavelength in the reflector stack $d\lambda_m/dT|_s$ can be expressed as:

$$\left.\frac{d\lambda_m}{dT}\right|_s = 2n_L d_L\left(C_L+\frac{dn_L}{n_L dT}\right)+2n_H d_H\left(C_H+\frac{dn_H}{n_H dT}\right)$$

where C_L and C_H are the coefficients of linear expansion of the low and high refractive index materials, respectively. From eqn.[1] for first order reflection and normal incidence (*i.e.*, m=1 and $\theta=0^o$), the corresponding temperature dependence $d\lambda_m/dT|_c$ of the cavity layer of low refractive index material is given by:

$$\left.\frac{d\lambda_m}{dT}\right|_c = 2yn_L d_L\left(C_L + \frac{dn_L}{n_L dT}\right)$$

noting that y is the total number of half wavelength cavity layers. The total change in wavelength with temperature $d\lambda_m/dT|_T$ is given by the sum of $d\lambda_m/dT|_c$ and $d\lambda_m/dT|_s$:

$$\left.\frac{d\lambda_m}{dT}\right|_T = 2(1+y)n_L d_L\left(C_L + \frac{dn_L}{n_L dT}\right) + 2n_H d_H\left(C_H + \frac{dn_H}{n_H dT}\right)$$

or

$$\left.\frac{d\lambda_m}{\lambda_m dT}\right|_T = (1+y)\left(C_L + \frac{dn_L}{n_L dT}\right) + \left(C_H + \frac{dn_H}{n_H dT}\right)$$

noting that $n_L d_L = n_H d_H$ at the temperature for which the filter is designed for use. Clearly $d\lambda_m/dT|_T$ can only be zero if the value of dn/dT for one of the materials is negative. This condition can be fulfilled by high refractive index materials such as PbTe, PbSe or PbS. For close matching of the value of $d\lambda_m/dT|_T$ to zero, the wavelength dependence of n_i temperature and wavelength dependence of dn_i/dT can be taken into account.

The condition $d\lambda_m/dT|_T = 0$ is given approximately by:

$$\frac{dn_H}{n_H dT} = -(1+y)\frac{dn_L}{n_L dT}$$

noting that C_i is considerably smaller than $dn_i/n_i dT$ for most materials used in mid-infrared filters. The term (1+y) can be chosen to satisfy the above expression depending on the choice of low refractive index material. For example, with ZnSe and PbTe for the low and high refractive index materials, respectively, and using the material values of bulk phases $n_L = 2.43$, $n_H = 6.10$, $dn_L/dT = 6.3 \times 10^{-5}\ K^{-1}$ and $dn_H/dT = -2.1 \times 10^{-3}\ K^{-1}$ for $\lambda_m = 3.4\ \mu m$, the expression is satisfied with y=13.3, i.e.,

approximately 13 half wavelength cavity layers are required to achieve the condition $d\lambda_m/dT|_T=0$.

There is considerable variation in the values of the material properties (n_H, dn_H/dT, C_H, etc.) that appear in for thin films in a multilayer structure and therefore in the predicted value of $d\lambda_m/\lambda_m dT$ or the value of y required to achieve the condition $d\lambda_m/\lambda_m dT=0$. The uncertainty is particularly severe for the value of dn_H/dT for PbTe in view of its magnitude and influence on the value of y. For example, the value of dn/dT for PbTe at λ_m=5 μm has been reported to be $-1.5x10^{-3}$ K^{-1} by Zemel, J.N., Jensen, J.D. and Schoolar, R.B., "ELECTRICAL AND OPTICAL PROPERTIES OF EPITAXIAL FILMS OF PBS, PBSE, PBTE AND SNTE", *Phys. Rev.* **140**, A330-A343 (1965), $-2.7x10^{-3}$ K^{-1} by Piccioli, N., Besson, J.M. and Balkanski, M., "OPTICAL CONSTANTS AND BAND GAP OF PBTE FROM THIN FILM STUDIES BETWEEN 25 AND 300°K", *J. Phys. Chem. Solids*, **35**, 971-977 (1974), and $-2.8x10^{-3}$ K^{-1} by Weiting, F. and Yixun, Y., "TEMPERATURE EFFECTS ON THE REFRACTIVE INDEX OF LEAD TELLURIDE AND ZINC SELENIDE", *Infrared Phys.*, **30**, 371-373 (1990). From the above expression, the corresponding values of y (to the nearest integer) are 9, 17 and 18, respectively.

In view of the uncertainties in the value of dn/dT for PbTe and therefore the number of low refractive index half wavelength spacers required to achieve $d\lambda_m/dT=0$, a more useful approach is to determine the experimental value of $d\lambda_m/dT$ as a function of the optical thickness of the low refractive index cavities for a suite of filters fabricated by the same method. Figure 3 shows the variation of $d\lambda_m/\lambda_m dT$ for a suite of filters fabricated with ZnSe as the low refractive index material and PbTe as the high refractive index material. The plot shows that a particular value of $d\lambda_m/\lambda_m dT$ can be achieved by controlling the ratio of low to high refractive index materials in the filter (i.e., a parameter similar to y in the above expression). Figure 3 shows that for λ_m<5 μm, the condition $d\lambda_m/\lambda_m dT=0$ is met by a 4:4:4 (i.e., 3 full wavelength or 6 half wavelength cavities (y=6)) filter, while for λ_m>5 μm a 6:4:6 (y=8) filter is required.

The approach illustrated by Figure 3 can be used, in accordance with an embodiment of the present disclosure, to fabricate substantially temperature

invariant filters over the entire mid-infrared spectral range. In some embodiments of the present disclosure, the substrate may be formed of Si, SiO_2, Al_2O_3, Ge or ZnSe. In some embodiments of the present disclosure, high refractive index layers can be formed of PbTe, PbSe or PbS, although Ge is also an option. In some embodiments of the present disclosure, the low refractive index layers can be formed of ZnS or ZnSe.

Figure 4 shows plots of transmissivity against wavelength at a range of temperatures from 25 to 200°C for (a) a PbTe-based filter having a pass band centred at 4.26 μm with optimum optical matching to the substrate and 3 full wavelength thickness cavities (4:4:4), and (b) a degenerate PbTe-based filter having a pass band centred at 12.1 μm with 3 half wavelength cavities (2:2:2). Similar filters can be produced having pass bands centred at other mid-infrared wavelengths. The value of $d\lambda_m/dT$ for the λ_m=4.26 μm (4:4:4) filter varies from -0.04 nm/K at 20°C to + 0.03 nm/K at 200°C and is essentially zero over the temperature range 80-160°C. The value of $d\lambda_m/dT$ for the λ_m=12.1 μm (2:2:2) filter is -0.21 nm/K, over the temperature range 20-200°C.. This allows such filters to deployed downhole, where temperatures can vary from about 25 to 200°C, without the pass band of the filter shifting to such an extent that it no longer corresponds to the absorbance peak of its respective species.

Spectroscopy

The Beer-Lambert law applied to the sensor of Figure 1 provides that:

$$A = -\log_{10}(I/I_0)$$

where A is the absorbance spectrum by a species in the fluid having an absorbance peak at a wavelengths corresponding to the pass band of the filter 5, I is the intensity spectrum of the infrared radiation detected by the detector 6, and I_0 is a reference intensity spectrum. For example, Figure 5 shows (a) a reference intensity spectrum I_0 obtained from a fluid not containing a given species, (b) an intensity spectrum I obtained from the fluid containing the species, and (c) the absorbance spectrum of the species.

Figure 6 shows intensity spectra obtained for dodecane dissolved in deuterated chloroform for increasing concentrations of dodecane. With increasing hydrocarbon content there is increased absorption in a first wavenumber range of 3000 to 2800 cm^{-1}. Conversely, the increasing hydrocarbon content has substantially no effect on absorption in a second wavenumber range of 2000 to 1800 cm^{-1}. The second range can thus be used as the reference to the first range. Superimposed on Figure 6 are transmissivity plots for a first filter having a pass band of 3000 to 2800 cm^{-1}, and a second filter having a pass band of 2000 to 1800 cm^{-1}. Two spectra are thus, in effect, detected by the filters, the first spectrum being the unfiltered spectrum multiplied by the transmissivity of the first filter and the second sub-spectrum being the unfiltered spectrum multiplied by the transmissivity of the second filter. The pass band areas of the spectra (as determined by the strengths of the signals received by the photodiode detectors), correspond to respective intensity measurements BA and BA_0. These are thus used to calculate a modified absorbance A' for dodecane dissolved in deuterated chloroform which is $\ln(BA/BA_0)$.

Figure 7 shows a plot of modified absorbance A' against hydrocarbon content for dodecane dissolved in deuterated chloroform. The plot exhibits an approximately linear relationship between A' and hydrocarbon content.

Other species can be monitored in this way. For example, Figure 8 shows a plot of absorbance against dissolved CO_2 concentration in water or hydrocarbon under the high partial pressures and temperatures typical of oil field wellbore conditions.

Carbon Dioxide Concentration

The analysis of fluid samples from hydrocarbon wells for the determination of phase behaviour and chemical composition is a critical step in the evaluation of the producibility and economic value of the hydrocarbon reserves. An important factor in determining the economic value of gas and liquid hydrocarbon reserves is their chemical composition, particularly the concentration of gaseous components, such as carbon dioxide. Similarly, the monitoring of fluid composition during production operations can have an important bearing on reservoir management decisions,

such as ceasing production from certain zones or applying chemical treatments to producing wells.

A mid-infrared sensor, of the type discussed above, in accordance with an embodiment of the present disclosure, may be used to monitor CO_2 concentrations downhole. In particular, in some embodiments of the present disclosure, the sensor may comprise three narrow bandpass filters 5 corresponding to respective absorbance peaks of water, oil and CO_2, and a second narrow bandpass filter 5' for a reference portion of the absorbance spectrum. Such an arrangement allows the CO_2 concentration to be determined when the window 4 is wetted by a liquid water phase, a liquid oil phase, a mixture of liquid water and liquid oil phases, or when the window is dry.

For example, Figure 9(a) shows an absorbance spectrum for the case where the window 4 is wetted by a water phase. The spectrum is characterised by high absorption by water at 3.00 μm, almost no absorption by oil at 3.45 μm. The CO_2 concentration is proportional to the net CO_2 absorption, which is the difference between the CO_2 channel at 4.27 μm and the reference channel at 4.00 μm. The proportionality constant allowing CO_2 concentration in the water phase to be determined from CO_2 absorption can be obtained from an experimental plot of CO_2 absorbance against dissolved CO_2 concentration in water, such as shown in Figure 9(b).

Similarly, Figure 10(a) shows an absorbance spectrum for the case where the window 4 is wetted by an oil phase. The spectrum is characterised by high absorption by oil at 3.45 um μm almost no absorption by water at 3.00 μm. Again, the CO_2 concentration is proportional to the net CO_2 absorption, which is the difference between the CO_2 channel at 4.27 μm and the reference channel at 4.00 μm. The proportionality constant allowing CO_2 concentration in the oil phase to be determined from CO_2 absorption can be obtained from an experimental plot of CO_2 absorbance against dissolved CO_2 concentration in oil, such as shown in Figure 10(b).

Next, Figure 11 shows an absorbance spectrum for the case where the window 4 is wetted by a mixture of water and oil phases. The spectrum is characterised by absorption by water at 3.00 μm and by oil at 3.45 μm. Again the CO_2 concentration is proportional to the net CO_2 absorption, which is the difference between the CO_2 channel at 4.27 μm and the reference channel at 4.00 μm. However, the proportionality constant is slightly different for water and for oil because their refractive indices, and thus their depths of investigation, are different. Specifically, oil has higher refractive index than water, thus its depth of investigation is deeper and potentially more CO_2 is sensed by the sensor in oil than in water. Thus, when the window is wetted by a mixture of both water and oil phase, the mixture proportionality constant is between those of water and oil, but can be calculated from therefrom. For example, In some embodiments of the present disclosure, a "lever rule" may be used, whereby if the water peak height is X% of its full height and the oil peak height is (100-X)% of its full height, the mixture proportionality constant is the sum of X% of the water proportionality constant and (100-X)% of the oil proportionality constant. More elaborate schemes can be used, in other embodiments, but the simple "lever rule" approach works reasonably well because the difference between the water and oil proportionality constants is in any event not great.

Under some circumstances, the sensor window 5 may be dry. The spectrum is characterised by almost no absorption by water at 3.00 μm or by oil at 3.45 μm. CO_2 concentration is proportional to the net CO_2 absorption, which is the difference between the CO_2 channel at 4.27 μm and the reference channel at 4.00 μm. The proportionality constant allowing CO_2 concentration in the gas phase to be determined from CO_2 absorption can, in accordance with an embodiment of the present disclosure, be obtained from an experimental plot of CO_2 absorbance against CO_2 concentration in gas phase, such as shown in Figure 12.

Monitoring of CO_2 concentration can be particularly useful when performed in combination with monitoring of mineral acid concentrations. In particular, a mineral acid sensor can provide a measure of how much acid is being deployed to

stimulate a carbonate formation, and the CO_2 sensor, by measuring the amount of CO_2 produced, can provide a measure of the effectiveness of that acid deployment.

Heater

As mentioned above, the sensor of Figure 1 may, in some embodiments of the present disclosure, comprise a heater 8 that is operable to locally heat the window 4, thereby cleaning the surface of the window in contact with the fluid.

Cleaning the window in this manner may be particularly effective, compared to other techniques such as ultrasonic cleaning or mechanical wiper cleaning.

The window 4 can be formed, for example, in some embodiments of the present disclosure, of diamond (*e.g.* by chemical vapour deposition). A central (typically undoped) area of the window may be mid-infrared transmissive, while an annular encircling area of the window may be made semiconductive, *e.g.* by boron doping that part of the window. The heater 8 can then be a simple electrical power source which sends a current through the window to induce resistive heating of the encircling area. The central area of the window is then heated by thermal conduction from the encircling area. Boron-doping of diamond components is discussed in U.S. Patent No. 7,407,566.

In some embodiments of the present disclosure, the heater 8 may be able to heat the window to at least 400°C. This is higher than the 374°C super-critical point for water, where super-critical water comprises a good cleaner and oxidiser. In some embodiments of the present disclosure, it is unnecessary to keep the window at high temperature for a long time period. In particular, less than a microsecond at peak temperature may be enough for cleaning purposes, with longer periods requiring more power and increasing the risk of overheating of other parts of the sensor.

Pressure Pulse Cleaner

In addition, or as an alternative, to the above heater, cleaning of the window 4 may, in some embodiments of the present disclosure, be performed by providing the

sensor with a pressure pulse arrangement. For example, the sensor may be located on a fluid flow line between a pump for the fluid and an exit port from the flow line. With the exit port in a closed position, the fluid pressure can be increased in front of the window to above hydrostatic pressure by the pump. Subsequent of opening the exit port creates a sudden pressure difference that flushes the flowline fluid, *e.g.* to the borehole. The sudden movement of dense fluid in front of the window dislodges and carries away window contamination. A 1000 psi (6.9 MPa) pressure pulse is generally sufficient in most cases.

All references referred to above are hereby incorporated by reference.

The foregoing outlines features of several embodiments so that those skilled in the art may better understand the aspects of the present disclosure. Those skilled in the art should appreciate that they may readily use the present disclosure as a basis for designing or modifying other processes and structures for carrying out the same purposes and/or achieving the same advantages of the embodiments introduced herein. Those skilled in the art should also realize that such equivalent constructions do not depart from the scope of the present disclosure, and that they may make various changes, substitutions and alterations herein without departing from such scope.

CLAIMS

1. A sensor for monitoring CO_2 in a fluid, the sensor comprising:

an internal reflection window (4) configured in use to contact the fluid;

a mid-infrared light source (1) configured to directs a beam (3) of mid-infrared radiation into said window to provide for attenuated internal reflection of the beam (3) of mid-infrared radiation at an interface between the window and the fluid;

a set of three narrow bandpass filters (5) configured to filter the internally reflected mid-infrared radiation received from the window wherein:

a first of the set of three narrow bandpass filters comprises a water filter and is configured to preferentially transmit mid-infrared radiation over a band of wavelengths corresponding to respective absorbance peaks of water;

a second of the set of three narrow bandpass filters comprises an oil filter and is configured to preferentially transmit mid-infrared radiation over a band of wavelengths corresponding to respective absorbance peaks of oil; and

a third of the set of three narrow bandpass filters comprise a CO_2 filter and is configured to preferentially transmit mid-infrared radiation over a band of wavelengths corresponding to respective absorbance peaks of CO_2;

one or more infrared detectors (6) configured to detect filtered mid-infrared radiation transmitted through set of three narrow bandpass filters; and

a processor arrangement (7), operably coupled to the one or more infrared detector and configured to measure intensities of the detected mid-infrared radiation transmitted through the set of three narrow bandpass filters and determine therefrom an amount of CO_2 in the fluid, notwithstanding whether the fluid contacting the window is a liquid water-based phase, a liquid oil-based phase, a mixture of liquid water and liquid oil-based phases, or a gas phase.

2. A sensor according to claim 1, wherein the set of three narrow bandpass filters preferentially transmit mid-infrared radiation over respective bands of wavelengths corresponding to: a 3330 cm^{-1} absorbance peak for water, a 2900 cm^{-1} absorbance peak for oil, and a 2340 cm^{-1} absorbance peak for CO_2.

3. A sensor according to claim 1 or 2, wherein, to determine the amount of CO_2 in the fluid, the processor arrangement calculates the phase of the fluid from the measured intensities of the mid-infrared radiation transmitted through the water and oil filters, and then calculates from the phase of the fluid and the measured intensity of the mid-infrared radiation transmitted through the CO_2 filter the amount of CO_2 in the fluid.

4. A sensor according to claim 3, wherein the processor arrangement uses the refractive index of the fluid, derived from the phase of the fluid, in the calculation of the amount of CO_2 in the fluid.

5. A sensor according to any of the preceding claims, wherein each of the set of three narrow bandpass filters (5) is configured such that its wavelength transmission band is substantially temperature invariant over all temperatures in the range from about 25 to 150°C;

6. A sensor according to claim 5, wherein each of the narrow bandpass filters comprises an interference filter having a substrate and at each opposing side of the substrate alternating high and low refractive index layers.

7. A sensor according to any one of the previous claims, further comprising:

a reference narrow bandpass filter (5') configured to transmit mid-infrared radiation over a band of wavelengths corresponding to a reference portion of the absorbance spectrum of the fluid, wherein the or a further infrared detector is configured to detect filtered mid-infrared radiation transmitted through the reference filter, and wherein the processor arrangement is configured to measure a reference intensity of the detected mid-infrared radiation transmitted through the

reference filter and use the measured reference intensity in the determination of the amount of the CO_2 in the fluid.

8. A sensor according to any one of the previous claims, wherein the beam of mid-infrared radiation is pulsed.

9. A sensor according to any one of the previous claims, wherein the window comprises one of a diamond window or a sapphire window.

10. A sensor according to any one of the previous claims further comprising:

a heater (8) configured to heat the window and cleaning a surface of the window in contact with the fluid.

11. A sensor according to any one of the previous claims further comprising:

a pressure pulse arrangement configured to produce a pressure pulse in the fluid at the window and clean the surface of the window in contact with the fluid.

12. A sensor according to any one of the previous claims which is located downhole.

13. Use of the sensor of any one of the previous claims to determine an amount of CO_2 in a fluid.

14. A method of monitoring CO_2 in a fluid, the method including:

providing the sensor of any one of claims 1 to 10 such that the internal reflection window is in direct contact with the fluid; and

operating the sensor to determine an amount of CO_2 in the fluid.

15. A method of determining an amount of CO_2 in a fluid, the method including:

receiving respective measured intensities of mid-infrared radiation filtered by three narrow bandpass filters (5) which preferentially transmit mid-infrared radiation over bands of wavelengths corresponding to respective absorbance peaks of water, oil and CO_2, the mid-infrared radiation, prior to filtering, being produced by directing a beam (3) of mid-infrared radiation into an internal reflection window (4) for attenuated internal reflection at an interface between the window and a fluid in direct contact with window;

calculating from the measured intensities of the mid-infrared radiation filtered by the water and oil filters the phase of the fluid, and

calculating from the phase of the fluid and the measured intensity of the mid-infrared filtered by the CO_2 filter the amount of CO_2 in the fluid.

16. A well tool including the sensor of any one of claims 1 to 12.

17. A method for detecting or measuring CO_2 in a fluid, comprising:

directing a beam (3) of mid-infrared radiation into a window in contact with the fluid;

passing an attenuated internal reflection of the beam (3) of mid-infrared radiation at an interface between the window and the fluid through a set of three narrow bandpass filters (5) configured to filter the internally reflected mid-infrared radiation received from the window wherein:

a first of the set of three narrow bandpass filters comprises a water filter and is configured to preferentially transmit mid-infrared radiation over a band of wavelengths corresponding to respective absorbance peaks of water;

a second of the set of three narrow bandpass filters comprises an oil filter and is configured to preferentially transmit mid-infrared radiation over a band of wavelengths corresponding to respective absorbance peaks of oil; and

a third of the set of three narrow bandpass filters comprise a CO_2 filter and is configured to preferentially transmit mid-infrared radiation over a band of wavelengths corresponding to respective absorbance peaks of CO_2;

using one or more infrared detectors (6) to detect the mid-infrared radiation passing through each of the set of three narrow bandpass filters;

measuring intensities of the detected mid-infrared radiation passed through the set of three narrow bandpass filters; and

determining an amount of CO_2 in the fluid from the measured intensities, characterized in that the step of determining the amount of CO_2 in the fluid from the measured intensities is not dependant on whether the fluid contacting the window is a liquid water-based phase, a liquid oil-based phase, a mixture of liquid water and liquid oil-based phases, or a gas phase.

18. The method of claim 17, wherein determining the amount of CO_2 in the fluid comprises determining the phase of the fluid from the measured intensities of the mid-infrared radiation transmitted through the water and oil filters and calculates from the phase of the fluid and the measured intensity of the mid-infrared radiation transmitted through the CO_2 filter the amount of CO_2 in the fluid.

19. The method of claim 18, wherein a refractive index of the fluid that is derived from the phase of the fluid is used to determine the amount of CO_2 in the fluid.

20. A The method of claim 17, wherein each of the set of three narrow bandpass filters (5) is configured such that its wavelength transmission band is substantially temperature invariant over all temperatures in the range from about 25 to 150°C;

21. The method of claim 17, further comprising:

passing the attenuated internal reflection of the beam (3) of mid-infrared radiation through a reference narrow bandpass filter (5') configured to transmit mid-

infrared radiation over a band of wavelengths corresponding to a reference portion of the absorbance spectrum of the fluid,

measuring an intensity of the reflected mid-infrared radiation transmitted through the reference filter; and

using the measured reference intensity in the determination of the amount of the CO_2 in the fluid.

22. The method of claim 17, wherein the beam of mid-infrared radiation is pulsed.

Intellectual Property Office

Application No:	GB1416256.4	**Examiner:**	Megan Jones
Claims searched:	1-22	**Date of search:**	13 March 2015

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
A	-	US6627873 A (BAKER HUGHES INC) See para.37
A	-	EP0795744 A1 (INSTRUMENTARIUM) See WPI abstract
A	-	CN101893558 A (HEFEI KEDA LI AN SAFETY TECHNOLOGY) See WPI abstract

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC^{X} :

Worldwide search of patent documents classified in the following areas of the IPC

E21B; G01N

The following online and other databases have been used in the preparation of this search report

WPI, EPODOC

International Classification:

Subclass	Subgroup	Valid From
G01N	0021/3504	01/01/2014
G01N	0021/3577	01/01/2014