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(54) METHOD AND DEVICE FOR DETERMINING THE PRESENCE OF A SPILL OF A PETROLEUM PRODUCT BY THE DETECTION OF A PETROLEUM-DERIVED VOLATILE ORGANIC COMPOUND

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G01N 21/65	(2006.01)

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(58) **Field of Classification Search**
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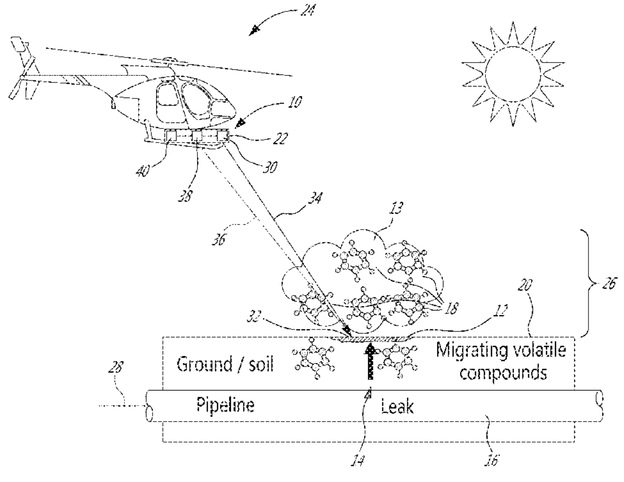
(57) ABSTRACT

The method of determining the presence of a spill of a petroleum product by the detection of a petroleum-derived volatile organic compound (VOC) generally has a step of providing an ultraviolet (UV) radiation generator and a receiver assembly aimed at a scene; a step of illuminating a distant target in the scene with a UV radiation beam, the UV radiation beam having an excitation wavelength being tuned to a resonance Raman excitation wavelength of the petroleum derived VOC; a step of receiving a return signal from the distant target; and a step of determining the presence of the petroleum-derived VOC upon detecting Raman scattering in the received return signal, the Raman scattering being indicative of a resonance Raman interaction between the UV radiation beam and molecules of the petroleum-derived VOC.

17 Claims, 10 Drawing Sheets



(51) **Int. Cl.**
G01M 3/18 (2006.01)
G01J 3/44 (2006.01)
G01M 3/38 (2006.01)
G01N 21/94 (2006.01)
G01N 21/17 (2006.01)

(52) **U.S. Cl.**
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(58) **Field of Classification Search**
USPC 250/372
See application file for complete search history.

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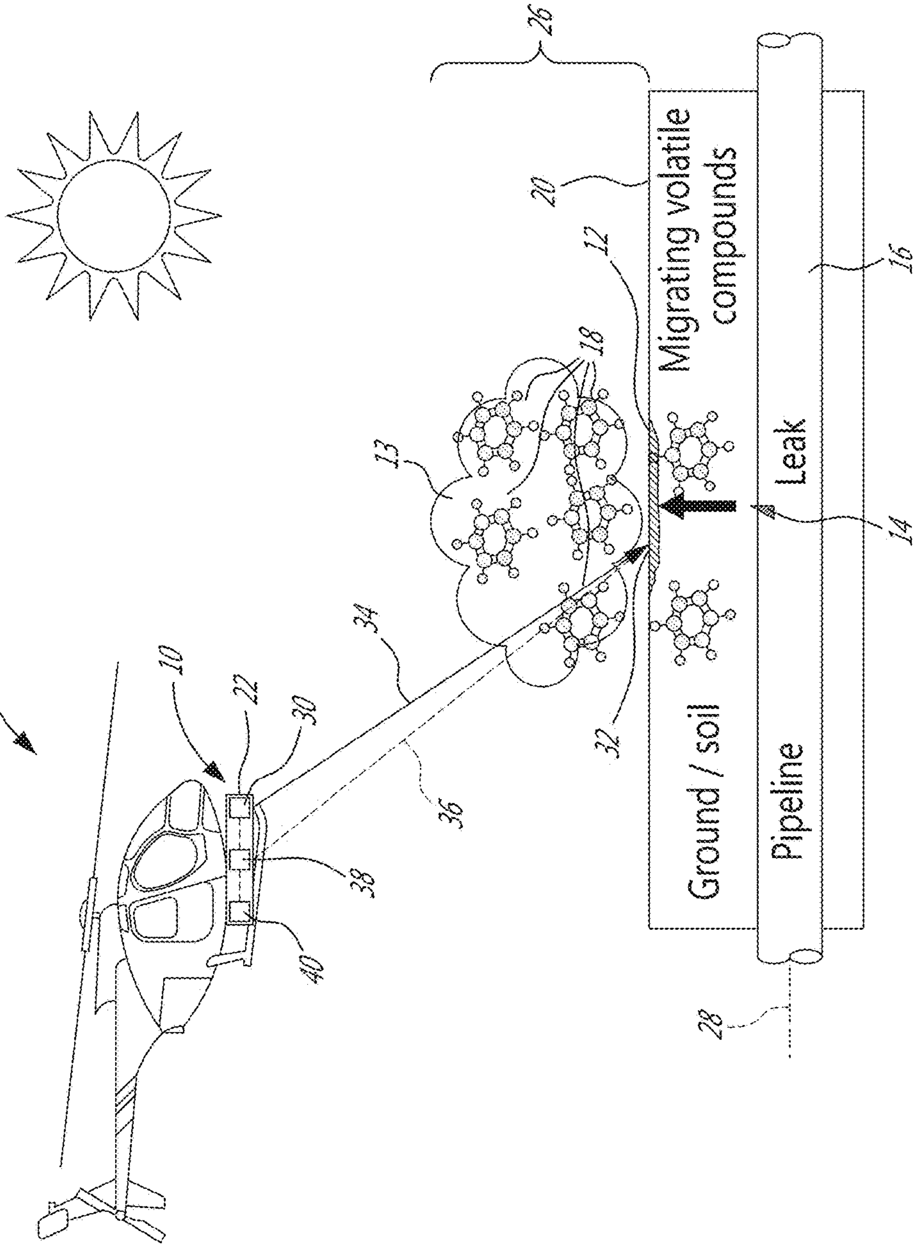
24
10
22
30
34
36
38
40
32
13
18
12
20
26
Migrating volatile compounds
Ground / soil
Pipeline
Leak
14
16
28

FIG. 1

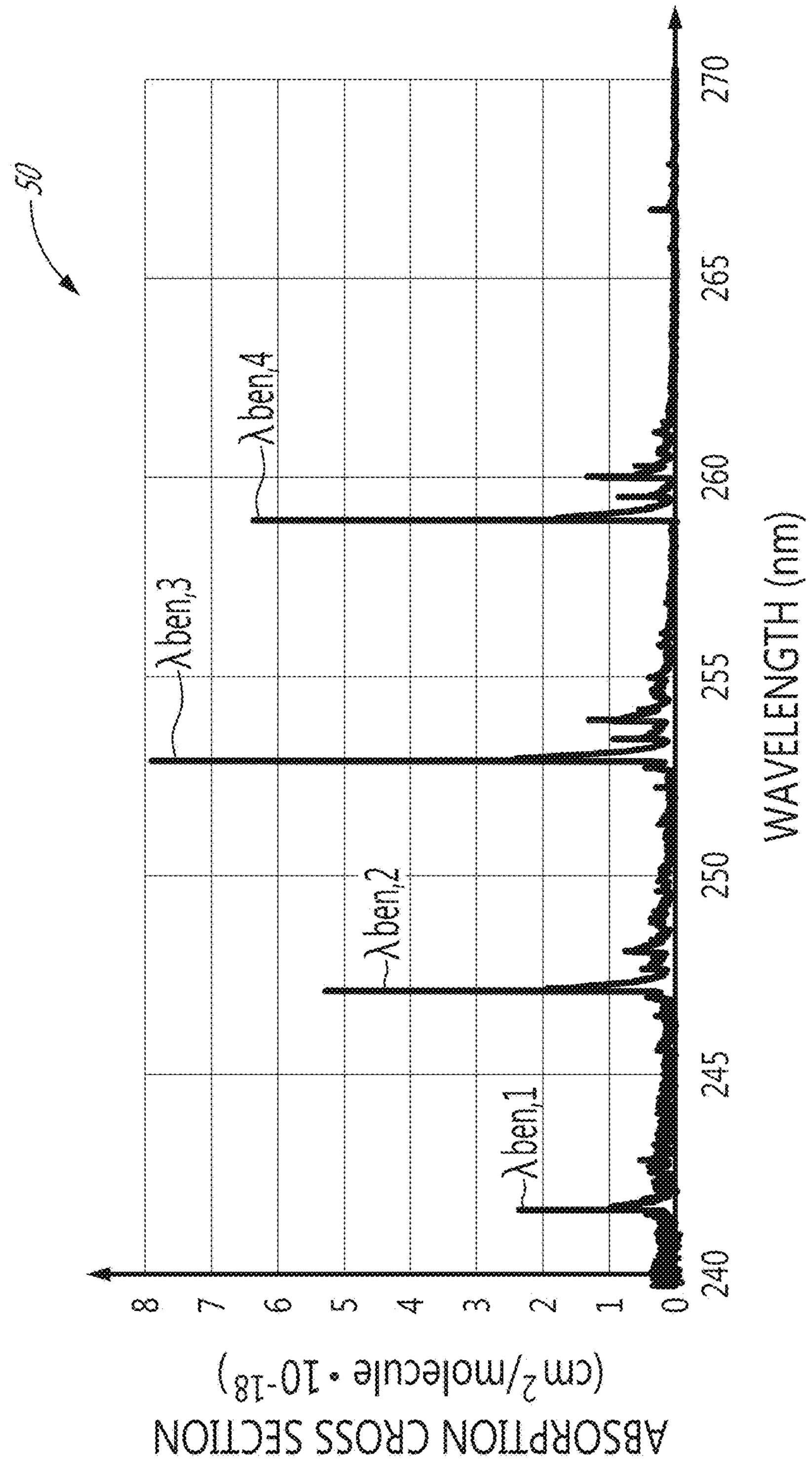
50
λben,1
λben,2
λben,3
λben,4
ABSORPTION CROSS SECTION
(cm²/molecule • 10-18)
0
1
2
3
4
5
6
7
8
240
245
250
255
260
265
270
WAVELENGTH (nm)

FIG. 2

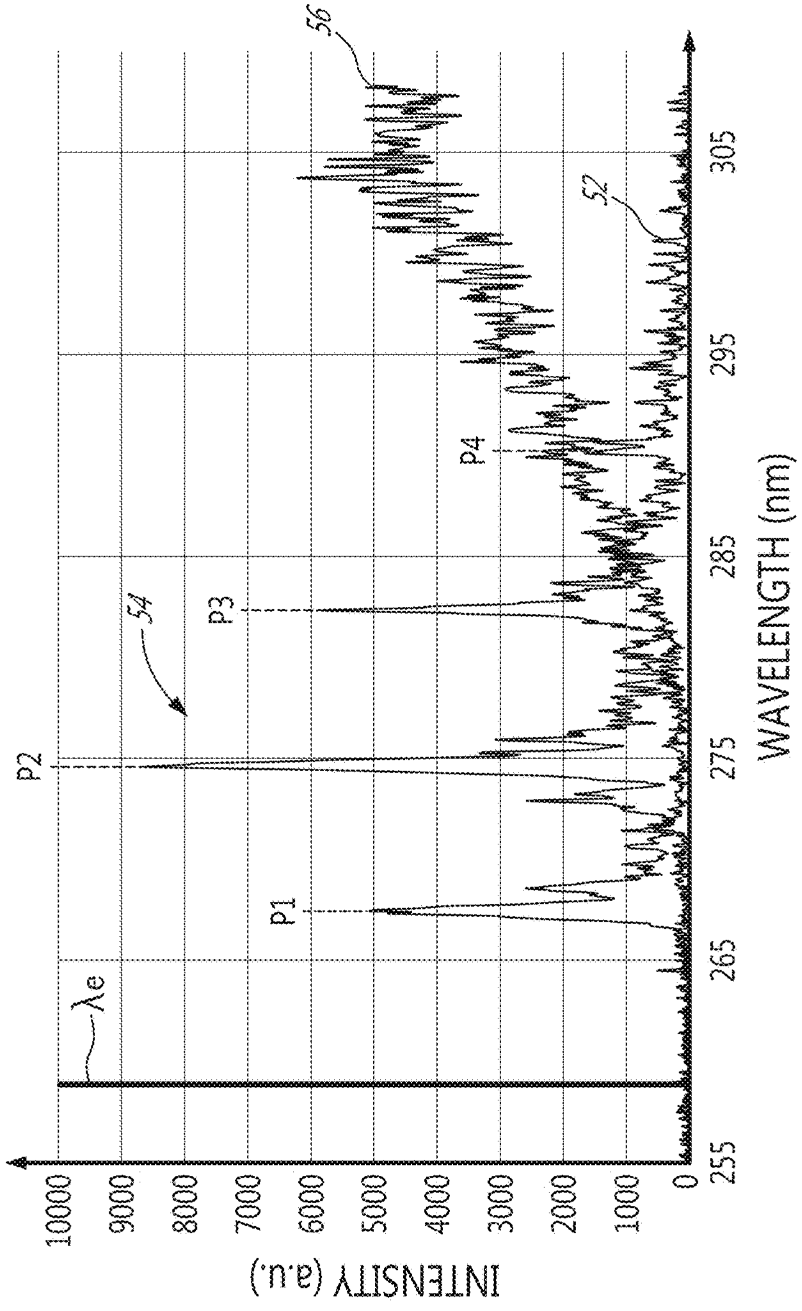
INTENSITY (a.u.)
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
255
265
275
285
295
305
WAVELENGTH (nm)
λe
P1
P2
P3
P4
54
52
56

FIG. 3

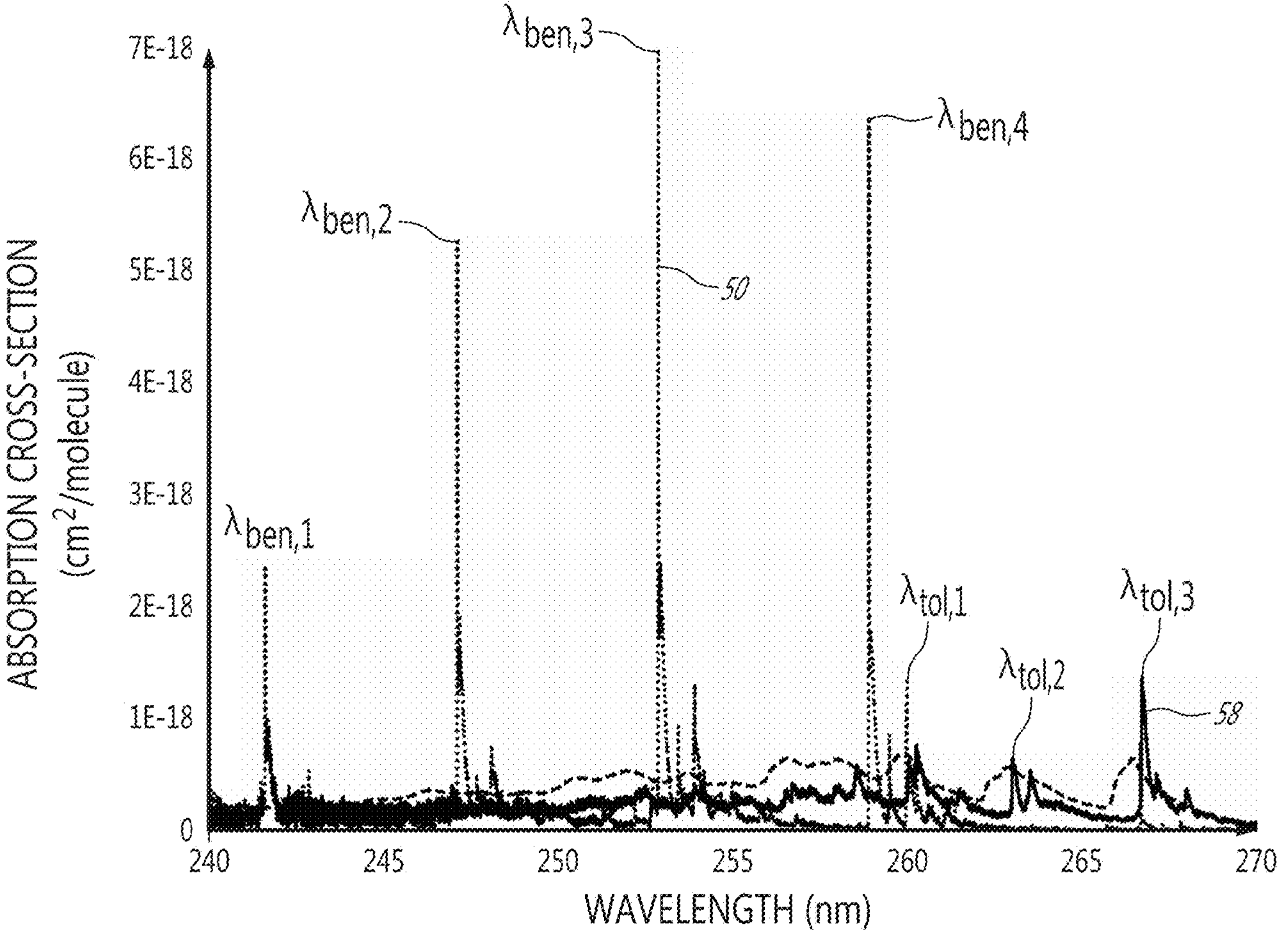
ABSORPTION CROSS-SECTION
(cm²/molecule)
7E-18
6E-18
5E-18
4E-18
3E-18
2E-18
1E-18
0
240
245
250
255
260
265
270
WAVELENGTH (nm)
λben,1
λben,2
λben,3
λben,4
50
λtol,1
λtol,2
λtol,3
58

FIG. 4

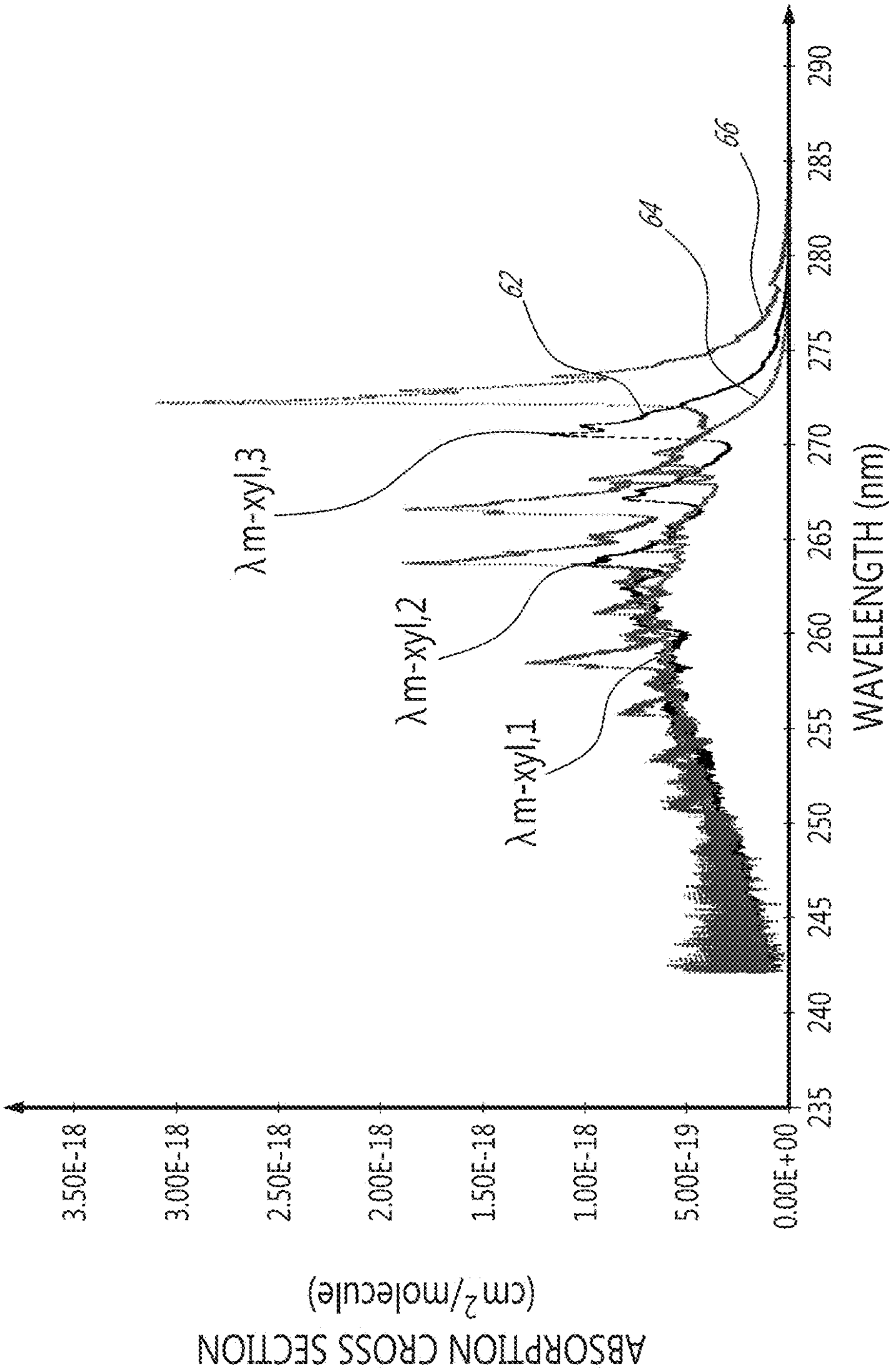
ABSORPTION CROSS SECTION
(cm²/molecule)
3.50E-18
3.00E-18
2.50E-18
2.00E-18
1.50E-18
1.00E-18
5.00E-19
0.00E+00
WAVELENGTH (nm)
235
240
245
250
255
260
265
270
275
280
285
290
λm-xyl,1
λm-xyl,2
λm-xyl,3
62
64
66

FIG. 5

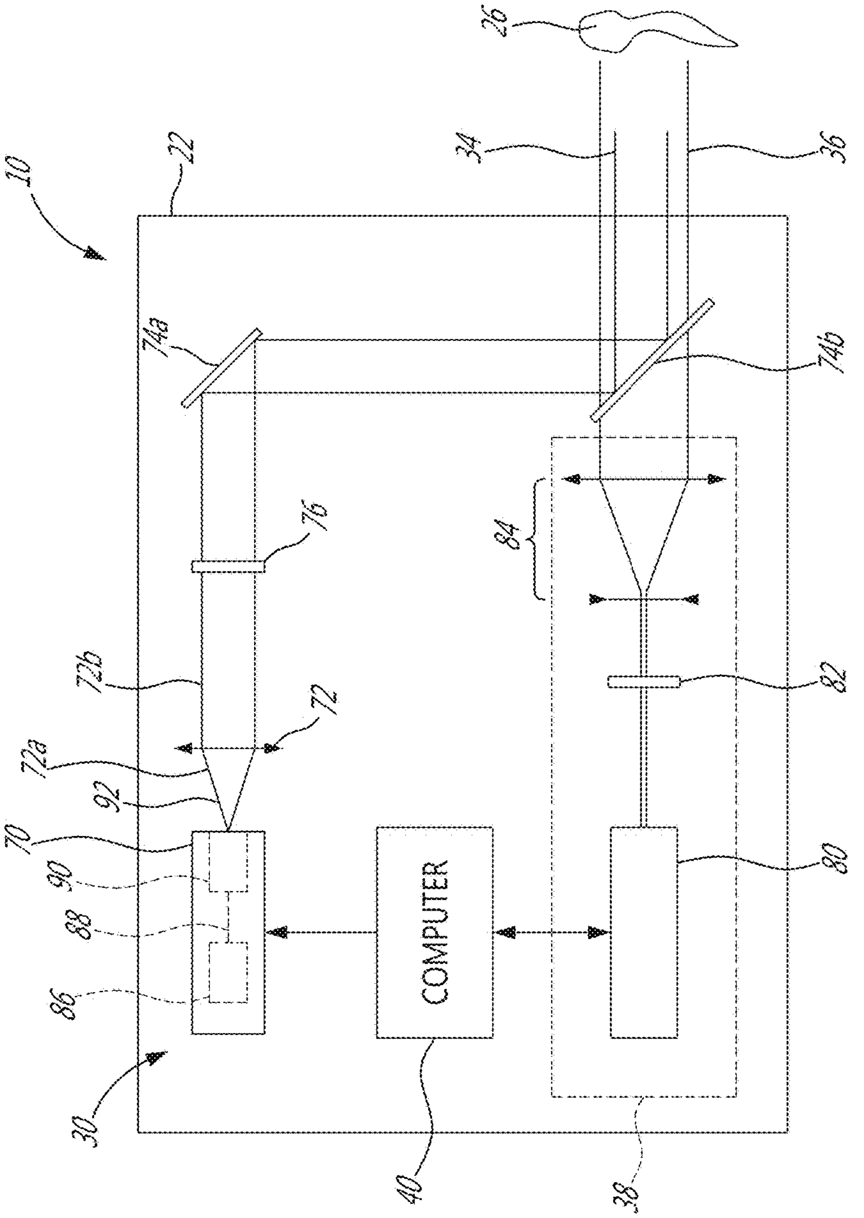
10
22
26
34
36
74a
74b
76
84
72b
72
72a
92
70
90
88
86
82
80
COMPUTER
30
40
38

FIG. 6

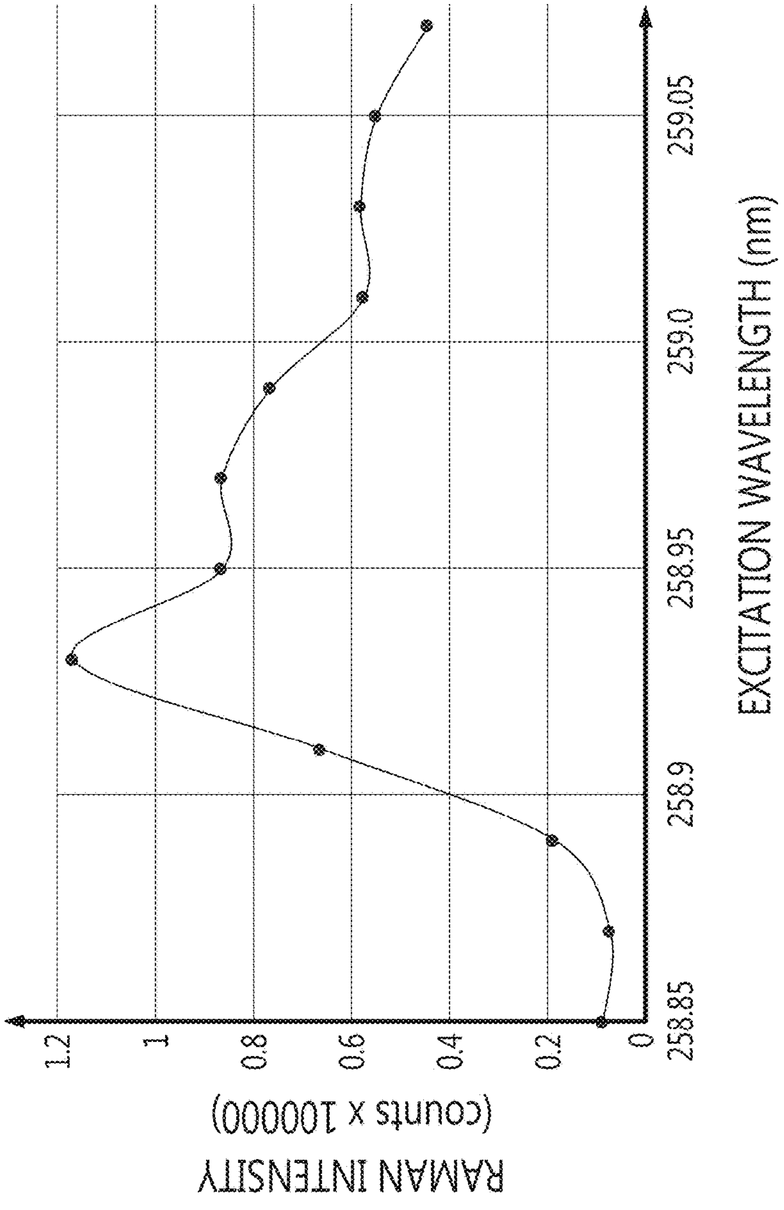
RAMAN INTENSITY
(counts x 100000)
1.2
1
0.8
0.6
0.4
0.2
0
258.85
258.9
258.95
259.0
259.05
EXCITATION WAVELENGTH (nm)

FIG. 7

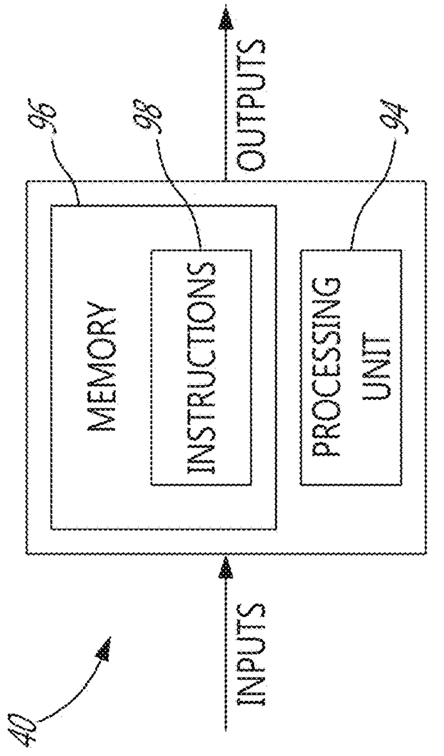
40
INPUTS
OUTPUTS
96
MEMORY
98
INSTRUCTIONS
94
PROCESSING UNIT

FIG. 8

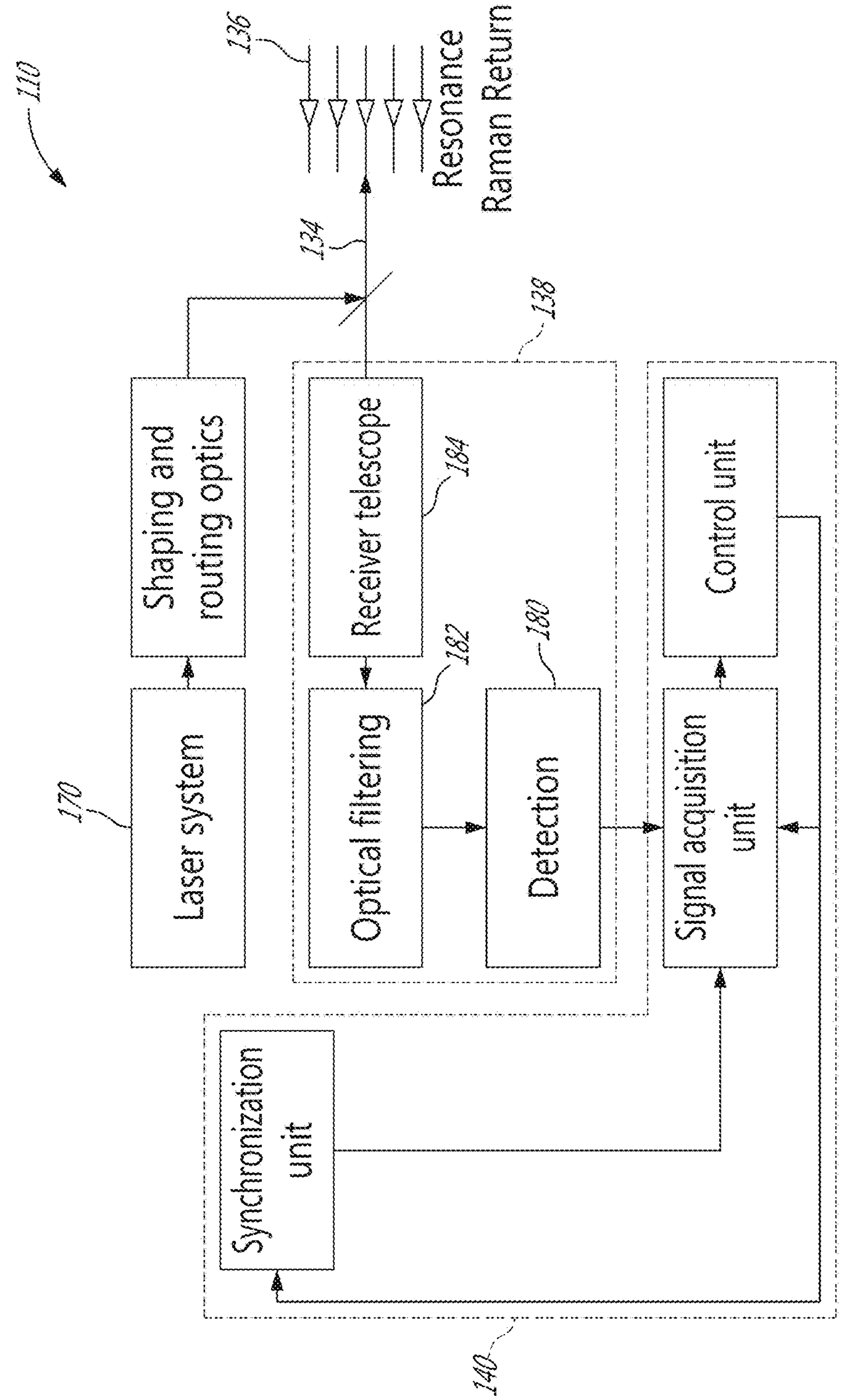
110
136
Resonance
Raman Return
134
138
Shaping and
routing optics
Receiver telescope
184
Control unit
170
Laser system
Optical filtering
182
Detection
180
Signal acquisition
unit
Synchronization
unit
140

Fig-9

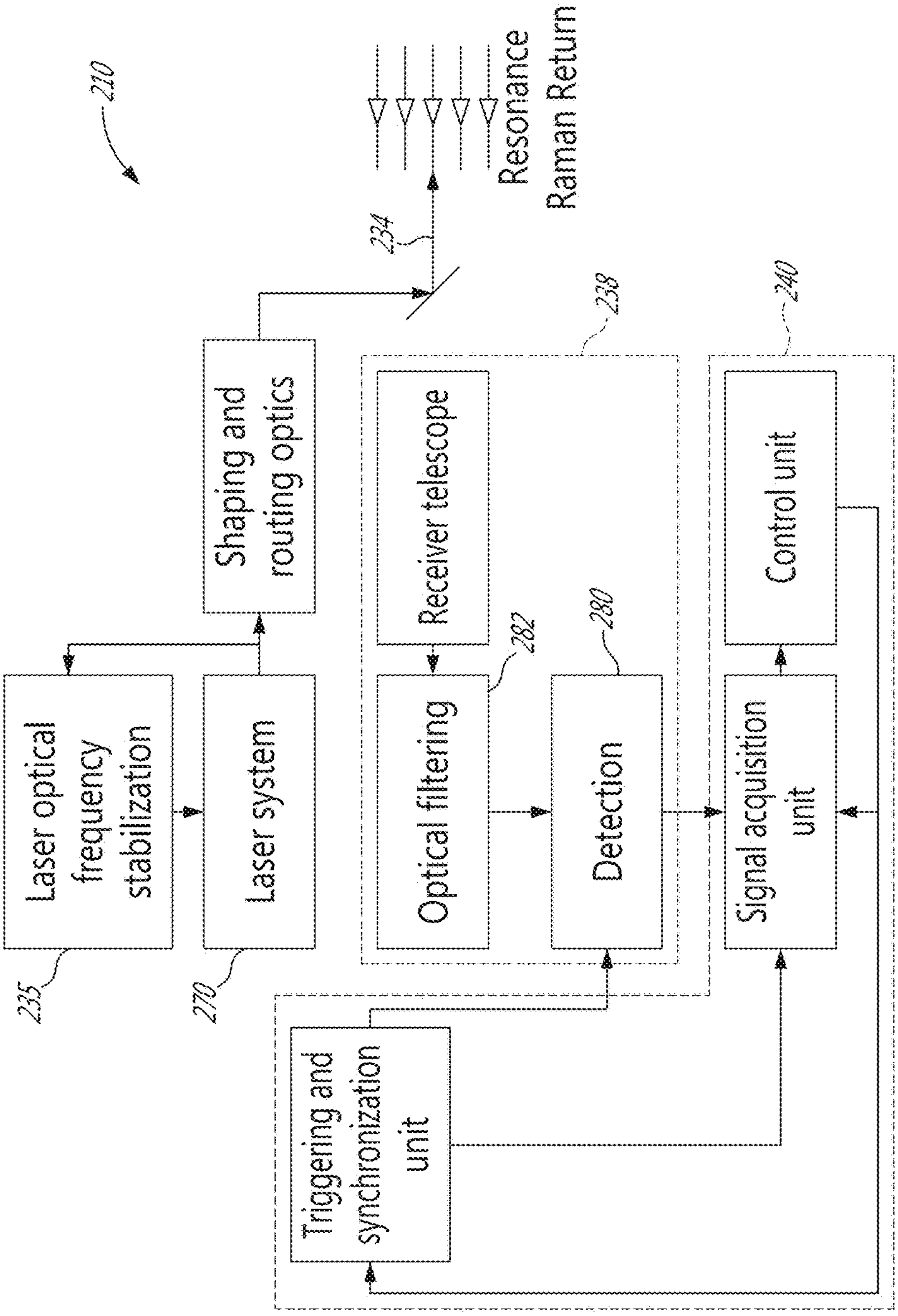
210
Laser optical frequency stabilization
235
Laser system
270
Shaping and routing optics
234
Resonance Raman Return
238
Receiver telescope
Optical filtering
282
Detection
280
240
Signal acquisition unit
Control unit
Triggering and synchronization unit

FIG. 10

METHOD AND DEVICE FOR DETERMINING THE PRESENCE OF A SPILL OF A PETROLEUM PRODUCT BY THE DETECTION OF A PETROLEUM-DERIVED VOLATILE ORGANIC COMPOUND

FIELD

The improvements generally relate to the field of trace contaminant or pollutant detection and more specifically relate to detectors involving Raman scattering.

BACKGROUND

The oil and gas industry has developed multiple techniques to detect spills of petroleum products. One significant source of spills is pipeline leaks. One technique pertaining to pipelines involves monitoring pressure drops along a pipeline using pressure sensors all along the pipeline. One other technique involves moving an acoustic detection apparatus above the pipeline while listening for a sound indicative of a leak.

As can be understood, preventing a pipeline from leaking, no matter how small the leak may be, is of great interest, both from environmental and economic perspectives. Although the existing spill detection techniques are satisfactory to a certain degree, there remains room for improvement.

SUMMARY

In accordance with one aspect, there is provided a system and method to detect spills of petroleum products. It is to be understood that spills encompass petroleum products in any phase of matter, solid, liquid or vapor. The system and method can include using a device. The device can include a UV radiation generator, such as a UV laser, having a wavelength selected specifically (tuned) to target a resonance Raman excitation wavelength of a molecule which is known to be indicative of a petroleum product spill. The device can also include a detector which is used to detect a return signal from an area which is subjected to the UV radiation beam. The detection of emissions from the area at a wavelength which corresponds to Raman scattering from the resonance Raman excitation radiation can then be associated to the presence of a petroleum product spill. The device can be embodied in various forms to detect spills from correspondingly various sources. For instance, the device can be mounted to an aircraft or to another form of vehicle (e.g. boat) to detect and/or monitor the presence of a spill on a greater area of land or sea. Alternately, the device can be mounted to a fixed structure and either be aimed at a fixed location or moved (e.g. rotated) to scan a given area.

In accordance with one aspect, there is provided a method of determining the presence of a spill of a petroleum product by the detection of a petroleum-derived volatile organic compound (VOC), the method comprising: providing an ultraviolet (UV) radiation generator and a receiver assembly aimed at a scene; the UV radiation generator illuminating a distant target in the scene with a UV radiation beam, the UV radiation beam having an excitation wavelength being tuned to a resonance Raman excitation wavelength of the petroleum derived VOC; the receiver assembly receiving a return signal from the distant target; and determining the spill of the petroleum product upon detecting Raman scattering in the received return signal, the Raman scattering being indicative of a resonance Raman interaction between the UV radiation beam and molecules of the petroleum-derived VOC.

In accordance with another aspect, there is provided a device for determining the presence of a spill of a petroleum product by the detection of a petroleum-derived VOC, the device comprising: a housing; an UV radiation generator mounted to the housing and adapted to illuminate a distant target in a scene with a UV radiation beam, the UV radiation emitter being adapted to generate the UV radiation beam at an emission wavelength tuned to a resonance Raman wavelength of the petroleum-derived VOC; a receiver assembly mounted to the housing and adapted to receive a return signal from the distant target; and a computer configured to operate the UV radiation emitter and the receiver to determine the presence of the spill of the petroleum product upon identifying Raman scattering in the received return signal, the Raman scattering being indicative of a resonance Raman interaction between the UV radiation beam and molecules of the petroleum-derived VOC. Such a device may be used to detect the presence of a spill of petroleum product by the detection of a petroleum-derived VOC.

In accordance with another aspect, there is provided a computer-implemented method of determining the presence of a spill of a petroleum product by the detection of a petroleum-derived VOC, the computer-implemented method comprising: instructing an UV radiation generator to generate a UV radiation beam aimed at a distant target, the UV radiation beam having an excitation wavelength being tuned to a resonance Raman wavelength of the petroleum-derived VOC; operating a receiver assembly to receive a return signal from the distant target; and determining the presence of the spill of the petroleum product based on the received return signal when the received return signal includes Raman scattering being indicative of a Raman resonance interaction between the UV radiation beam and molecules of the petroleum-derived VOC.

Many further features and combinations thereof concerning the present improvements will appear to those skilled in the art following a reading of the instant disclosure.

DESCRIPTION OF THE FIGURES

In the figures,

FIG. **1** is a schematic view of an example of a device for determining the presence of a spill of petroleum product using the presence of a VOC contained in the spill, in accordance with an embodiment;

FIG. **2** is a graph showing an example of an absorption spectrum of a benzene molecule, in vapor form, in accordance with an embodiment;

FIG. **3** is a graph showing an example of a return signal including Raman scattering, in accordance with an embodiment;

FIG. **4** is a graph showing exemplary absorption spectrums of a benzene molecule, a toluene molecule and an ethylbenzene molecule, in accordance with an embodiment;

FIG. **5** is a graph shown exemplary absorption spectrums of an m-xylene molecule, an o-xylene molecule and a p-xylene molecule, in accordance with an embodiment;

FIG. **6** is a schematic view of the device of FIG. **1**, in accordance with an embodiment;

FIG. **7** is a graph showing example Raman emission intensity integrated over a Raman scattering band when molecules of benzene are excited with a radiation beam having one of a plurality of excitation wavelengths;

FIG. **8** is a schematic view of an hardware and soft implementation of a computer of the device of FIG. **1**, in accordance with an embodiment;

FIG. **9** is a schematic view of another example of a device for determining the presence of petroleum-derived VOC, in accordance with an embodiment; and

FIG. **10** is a schematic view of another example of a device for determining the presence of a petroleum-derived VOC, shown with a laser optical frequency stabilization subsystem, in accordance with an embodiment.

DETAILED DESCRIPTION

FIG. **1** shows an example of a device **10** for determining the presence of a distant spill **12** of liquid petroleum product via the presence of a vapor plume **13** of petroleum-derived volatile organic compound (VOC). In this disclosure, the term spill is used so as to encompass any kind of spill such as pools, slicks and gas/vapor leaks. The spill can be caused by a leak in a pipeline, buried or above ground, in a storage facility (tank, tank farm, truck, ship and the like), by spilling a product in transfer operations, or from vapors originating from open liquid/solid containers or leaks in vapor phase storage containers. Examples of petroleum-derived VOCs can include benzene, toluene, ethylbenzene, xylene, naphthalene, styrene and any other VOC that may derive from the petroleum product.

In some embodiments, such as the one depicted in FIG. **1**, the spill **12** originates from a leak **14** along a buried pipeline **16**. In such an example, molecules **18** of the leaked petroleum-derived VOC gradually migrate through the ground and collectively form part of the spill **12** as they break the surface **20**. A plume **13** of the petroleum-derived VOC may be present.

It is understood that, however, in some other embodiments, the origin of the spill of petroleum can differ. For instance, the spill can originate from an underground spill or an open-air spill such as an aboveground spill, a sea level spill and the like. The spill can originate from a leaked pipeline or from a failure of an oil delivery vehicle.

As depicted in this example, the device **10** has a housing **22** mountable to an aircraft **24**. In some embodiments, the aircraft **24** is a manned aircraft such as an airplane or a helicopter. In some other embodiments, the aircraft **24** is an unmanned aircraft such as a drone. Any other suitable type of aircraft can be used.

The aircraft **24** is used to fly the device **10** over a scene **26**. For instance, the aircraft **24** can fly the device **10** at multiple tens of kilometers per hour at an altitude of about 100 meters above the surface **20**, and without disrupting normal operation of the buried pipeline **16**.

As depicted in the illustrated embodiment, the aircraft **24** is used to fly the device **10** over a pipeline path **28** of the buried pipeline **16**. In alternate embodiments, the aircraft **24** is used to fly the device **10** over a land, a sea or any other area that may present spills of petroleum products.

The device **10** has an ultraviolet (UV) radiation generator **30** mounted to the housing **22**. The UV radiation generator **30** is adapted to illuminate a distant target **32** in the scene **26** with a UV radiation beam **34** as the aircraft **24** flies over the scene **26**. In FIG. **1**, the distant target **32** is illustrated to coincide with the spill of petroleum product. However, in some other embodiments, it is understood that the distant target can coincide with a plume of petroleum-derived VOC, i.e. a point above the surface **20**. Any point in space can be a distant target as long as the point in space is in the field-of-operation of the device **10**.

More specifically, the UV radiation generator **30** is adapted to generate the UV radiation beam **34** at an excitation wavelength λe that is tuned to a resonance Raman excitation wavelength of the petroleum-derived VOC under examination. A receiver assembly **38** is mounted to the housing **22** and adapted to receive a return signal **36** from the distant target **32**. A computer **40** is provided to determine the presence of a distant spill **12** of petroleum product via the presence of petroleum-derived VOC upon detecting Raman scattering in the received return signal **36**.

In some embodiments, the receiver assembly **38** includes a spectrometer. In these embodiments, the detected Raman scattering corresponds to a Raman spectrum of the petroleum-derived VOC. For instance, the detected Raman spectrum can have at least one Raman peak at a given Raman shift for the UV radiation beam **34** used which is indicative of the presence of the petroleum-derived VOC under examination.

In some other embodiments, the receiver assembly **38** includes an intensity detector. In these embodiments, the detected Raman scattering corresponds to a given intensity (e.g., above a threshold) in an expected Raman scattering band for the UV radiation beam **34** used. As will be understood, the expected Raman scattering band can vary as a function of the resonance Raman excitation wavelength.

In some embodiments, the computer **40** operates the UV radiation generator and the receiver assembly in a synchronized manner allowing to determine a spill **12** of petroleum-derived VOC at a predetermined range. For instance, the UV radiation generator **30** and the receiver assembly **38** may be used in a light detection and ranging (LIDAR) configuration. In this way, the measurement can be said to be spatially-resolved or time-resolved.

The Raman scattering is indicative of a resonance Raman interaction between the UV radiation beam **34** and molecules **18** of the petroleum-derived VOC.

As will be understood, a resonance Raman interaction refers to a type of Raman scattering interaction wherein the excitation wavelength λe is selected so as to be close in energy to an electronic transition of the petroleum-derived VOC under examination. The near coincidence between the excitation wavelength λe and the resonance Raman excitation wavelength can lead to greatly enhanced intensity of the Raman scattering, which may facilitate detection of petroleum-derived VOC, even at low concentrations.

In this way, when a spill **12** of petroleum-derived VOC is present across the UV radiation beam **34**, the UV radiation beam **34** interacts with the molecules **18** of the petroleum-derived VOC to generate a return signal **36** having Raman scattering resulting from the resonance Raman interaction. However, when no molecules **18** of petroleum-derived VOC interacts with the UV radiation beam **34**, the return signal **36** lacks the Raman scattering and no spill **12** of petroleum-derived VOC is present across the UV radiation beam **34**.

In some embodiments, it is envisaged that leaks having a flow rate of 0.1 L/min or less can be detected using the device **10**. In some other embodiments, the computer **40** can be used to signal the presence of the spill **12** of petroleum-derived VOC in quasi real time, which can limit the damage to the environment when the pipeline **16** has a leak, for instance.

As will be understood via the examples presented herebelow, the UV radiation generator **30** can be adapted to generate a UV radiation beam **34** having an excitation wavelength λe tuned to any resonance Raman excitation wavelength of any petroleum-derived VOC under examination, depending on the embodiment. A device may be adapted to detect leaks of two or more petroleum-derived VOCs by interrogating the distant target **32** with two or more excitation wavelengths, each of the two or more excitation wavelengths corresponding to a resonance Raman excitation wavelength of respective ones of the two or more petroleum-derived VOCs.

Use of the device **10** to detect spills of petroleum-derived VOC along the pipeline path **28** of a given pipeline can thus be made remotely, without disrupting the normal operation of the given pipeline, and at any desired frequency (e.g., once per day, once per month, once per year).

FIG. **2** shows a graph of an example of a first absorption spectrum **50** of a benzene molecule, in accordance with an embodiment.

As depicted, the benzene molecule has a plurality of resonance Raman excitation wavelengths. More specifically, the first absorption spectrum **50** shows that the benzene molecule has a first resonance Raman excitation wavelength λben,**1** at about 241.60 nm, a second resonance Raman excitation wavelength λben,**2** at about 247.60 nm, a third resonance Raman excitation wavelength λben,**3** at about 252.87 nm and a fourth resonance Raman excitation wavelength λben,**4** at about 258.92 nm.

In this way, the UV radiation generator **30** can be adapted to generate a UV radiation beam **34** having an excitation wavelength λe tuned to at least one of the first, second, third, fourth resonance Raman excitation wavelengths λben,**1**, λben,**2**, λben,**3** and λben,**4** of the benzene molecule in order to cause the desired resonance Raman interaction. As can be understood, the benzene molecule may have other resonance Raman excitation wavelengths which are not shown in FIG. **2**.

FIG. **3** shows experimental results of a specific experiment conducted on a sample containing molecules of benzene at a concentration of 10 ppm in air. As shown, an experimental return signal **52** was obtained upon illumination of the sample with a UV radiation beam **34** having an excitation wavelength λe tuned to the fourth resonance Raman excitation wavelength λben,**4** of the benzene molecule (i.e. λe≈259.8 nm). In this example, the UV radiation beam **34** is a UV pulsed laser beam having an emission band Δλe of about 0.03 nm and a pulse width of 10 ns. The excitation wavelength λe was added to the experimental return signal **52** for ease of understanding.

As can be seen in this specific example, the experimental return signal **52** includes a Raman scattering **54** including a first intensity peak P**1** at a wavelength of about 268 nm, a second intensity peak P**2** at a wavelength of about 275 nm, a third intensity peak P**3** at a wavelength of about 283 nm and a fourth intensity peak P**4** at a wavelength of about 291 nm. In this example, as can be understood, some of the intensity peaks P**1**, P**2**, P**3** and P**4** can be associated with Raman interaction between the UV radiation beam and nitrogen molecules or oxygen molecules in the air.

In this experiment, it was found convenient to use a radiation beam in the UV region of the electromagnetic spectrum to illuminate the distant target **32** in order to reduce the impact of noise associated with sunlight in the return signal **36**, as there is no sunlight shining on the earth's surface below 300 nm. Also, fluorescence generated by the UV radiation beam **34** hitting the earth surface, e.g. grass, is generated at wavelengths usually higher than 260 or 270 nm as shown at **56** in FIG. **3**. Fluorescence of rock, sand and earth is not likely to be present below 310 nm.

Indeed, since the Raman scattering **54** is distributed in a given spectral region in the solar blind region of the electromagnetic spectrum, the given spectral portion of the return signal **36** is not likely to be blurred with the noise associated with sunlight.

As can be seen, most of the energy of the Raman scattering **54** is distributed where the noise due to fluorescence of grass such as shown at **56** is relatively low.

FIG. **4** shows a graph of an example of a superposition of the first absorption spectrum **50** for the benzene molecule and a second absorption spectrum **58** for a toluene molecule, in accordance with another embodiment. Data for the benzene molecule and the toluene molecule can be found in the publication "Fally, S., M. Carleer, and A. C. Vandaele, UV Fourier transform absorption cross sections of benzene, toluene, meta-, ortho-, and para-xylene. Journal of Quantitative Spectroscopy and Radiative Transfer, 2009. 110 (9-10): p. 766-782.". Data for the ethylbenzene molecule can be found in the publication "Etzkorn, T., et al., Gas-phase absorption cross sections of 24 monocyclic aromatic hydrocarbons in the UV and IR spectral ranges. Atmospheric Environment, 1999. 33 (4): p. 525-540." The spectrums shown in this graph may have been acquired in different measurement environments and with different measurement systems.

As depicted, the benzene molecule has the first, second, third and fourth resonance Raman excitation wavelengths λben,**1**, λben,**2**, λben,**3** and λben,**4** described above. Additionally, the toluene molecule has a first resonance Raman excitation wavelength λtol,**1** at about 260.28 nm, a second resonance Raman excitation wavelength λtol,**2** at about 263.04 nm and a third resonance Raman excitation wavelength λtol,**3** at about 266.76 nm.

As can be understood, the toluene molecule and the ethylbenzene molecule may have other resonance Raman excitation wavelengths which are not shown in FIG. **4**.

In some embodiments, the UV radiation generator **30** can be adapted to generate a UV radiation beam **34** having an excitation wavelength λe tuned to at least one of any one of the resonance Raman excitation wavelengths of the benzene molecule. In some other embodiments, the UV radiation generator **30** can be adapted to generate a UV radiation beam **34** having an excitation wavelength λe tuned to any one of the resonance Raman excitation wavelengths of the toluene molecule. In alternate embodiments, the UV radiation generator **30** can be adapted to generate a UV radiation beam **34** having an excitation wavelength λe tuned to any one of the resonance Raman excitation wavelengths of the ethylbenzene molecule.

FIG. **5** shows a graph of an example of a superposition of a fourth absorption spectrum **62** for a m-xylene molecule, a fifth absorption spectrum **64** for an o-xylene molecule and a sixth absorption spectrum **66** for a p-xylene molecule, in accordance with another embodiment.

As depicted, the m-xylene molecule has a first absorption wavelength that can be a resonance Raman excitation wavelength λm-xyl,**1** at about 258.47 nm, a second absorption wavelength that can be a resonance Raman excitation wavelength λm-xyl,**2** at about 263.75 nm and a third absorption wavelength that can be a resonance Raman excitation wavelength λm-xyl,**3** at about 272.22 nm.

In some embodiments, the UV radiation generator **30** can be adapted to generate a UV radiation beam **34** having an excitation wavelength λe tuned to at least one of any one of the resonance Raman excitation wavelengths of the m-xylene molecule. In some other embodiments, the UV radiation generator **30** can be adapted to generate a UV radiation beam **34** having an excitation wavelength λe tuned to any one of the resonance Raman excitation wavelengths of the o-xylene molecule. In alternate embodiments, the UV radiation generator **30** can be adapted to generate a UV radiation beam **34** having an excitation wavelength λe tuned to any one of the resonance Raman excitation wavelengths of the p-xylene molecule or any other petroleum-derived VOC.

As can be understood, the m-, o- and p-xylene molecules may have other absorption peaks that can be resonance Raman excitation wavelengths which are not shown in FIG. **5**.

FIG. **6** shows an example of the device **10** for determining the presence of a remote spill of petroleum-derived VOC, in accordance with an embodiment.

As depicted in this illustrated example, the UV radiation generator **30** includes a UV laser source **70** optically coupled with a beam forming element **72** and routing reflective elements **74***a* and **74***b*. In this embodiment, the UV laser source **70** is a pulsed UV laser source and, accordingly, the UV radiation beam **34** is a UV pulsed laser beam. The beam forming element **72** can be a diverging element, a collimating element or a focusing element depending on the embodiment.

As shown, the beam forming element **72** is adapted to receive a first laser beam **72***a* from the UV laser source **70** and to collimate it to provide a second laser beam **72***b*, generally referred to as the UV radiation beam **34**. In the illustrated embodiment, the first laser beam **72***a* is a diverging beam whereas the second laser beam **72***b* is a collimated beam. However, in other embodiments, the first and second laser beams **72***a* and **72***b* can differ from the illustrated embodiment.

As can be seen, the routing reflective elements **74***a* and **74***b* receive the second laser beam **72***b* and redirect it towards the scene **26** as desired. The number of routing reflective elements may differ from an embodiment to another. For instance, in some embodiments, a UV radiation generator can have no reflective element whereas, in some other embodiments, a UV radiation generator can have either a single one reflective element or more than two routing reflective elements. The routing reflective elements can be provided in the form of scanning heads which are controllable by the computer **40**. Scanning heads can be useful in scanning the pipeline path and areas surrounding the pipeline path.

In this example, the UV radiation generator **30** has a first filter element **76** to filter out undesired spectral portions of the spectrum of the UV laser source **70** in order to provide the excitation wavelength λe with a suitably narrow wavelength band Δλe.

Still referring to FIG. **6**, the receiver assembly **38** includes a photomultiplier (PM) tube **80**, a second filter element **82** and a telescope **84** optically coupled with one another to receive and monitor the return signal **36**. In these embodiments, the photomultiplier tube **80** is adapted to measure an intensity of the filtered return signal. The measured intensity can be indicative of the total (or integrated) amount of energy that reaches the photomultiplier tube **80** and which is within the Raman scattering band of the second filter element **82**. As will be understood, a grating spectrometer can be used instead of the filter element **82** or a camera can also be used instead of the PM tube **80** in other embodiments.

As shown in this example, the reflective element **74***b* is provided in the form of a dichroic element which reflects the excitation wavelength λe towards the scene **26** and that is optically transparent to wavelengths of the Raman scattering higher in wavelength than the excitation wavelength λe such that the return signal **36** can reach the PM tube **80** without letting the excitation wavelength λe reach it.

In this embodiment, the telescope **84** is used to collect as much as possible of the return light **36** and to produce a reduced diameter beam of the return signal **36** to fit the detector or pass through a second filter element **82**, and which can be used to filter out undesired spectral portions of the return signal **36**. For instance, wavelengths higher than any expected Raman scattering (e.g., >300 nm) may be filtered out using the second filter element **82**. Example of filtered wavelengths can include wavelengths associated with the UV radiation beam or noise due to fluorescence of grass for instance.

As shown in this embodiment, the UV laser source **70** includes an Ytterbium-doped fiber laser **86** adapted to generate a fundamental laser beam **88** (e.g., having a fundamental wavelength **λ1** between 1000 nm and 1100 nm), and a fourth harmonic generator **90** optically coupled with the Ytterbium-doped fiber laser **86** in a manner to generate a fourth harmonic laser beam **92**. In these embodiment, the fourth harmonic laser beam **92** corresponds to the UV radiation beam **34** and has a fourth harmonic wavelength **λ4** corresponding to the fundamental wavelength **λ1** divided by the number 4.

For instance, when the petroleum-derived VOC is benzene, the fundamental laser beam **88** can have a fundamental wavelength of 1035.6 nm whereas the fourth harmonic laser beam **92** can have a fourth harmonic wavelength of 258.9 nm which corresponds with a resonance Raman excitation wavelength of the benzene molecule, as described above.

UV laser beams having other wavelengths can be generated in any other suitable ways depending on the petroleum-derived VOC under examination and on which resonance Raman excitation wavelength is interrogated.

For instance, still in the case of benzene, using a Nd:YAG laser source or any suitable equivalent may be used to produce a UV laser beam having an excitation wavelength of 258.9 nm.

More specifically, in an embodiment, generating a third harmonic laser beam (e.g., having a third harmonic wavelength of 355 nm or equivalent) from a fundamental laser beam of a Nd:YAG laser source (e.g., having a fundamental wavelength of 1064 nm), pumping an optical parametric oscillator (OPO) with the third harmonic laser beam to generate a green laser beam having a wavelength of about 517.8 nm, and then generating the second harmonic laser beam from the green laser beam to produce a UV laser beam having 258.9 nm may be possible.

However, it will be understood that other suitable UV radiation generator may be used. For instance, short-wave UV lamps, gas discharge lamps, UV light-emitting diodes (LEDs) may be used in some embodiments.

For instance, FIG. **7** is a graph showing an integrated Raman intensity measured by the photomultiplier tube **80** when a sample containing benzene molecules is excited with a UV radiation beam having an excitation wavelength tunable between 0.25885 μm and 0.25905 μm and a spectral spread at half intensity of approximately 0.00003 μm.

More specifically, it can be seen that when the UV radiation beam having an excitation wavelength of 0.25885 μm excites the sample, the total amount of energy that reaches the photomultiplier tube **80**, or the intensity measured by the photomultiplier tube **80**, is relatively low (e.g., about 0.1×100000 counts) as compared with when the UV radiation beam has an excitation wavelength of 0.25893 μm. Indeed, when the UV radiation beam has an excitation wavelength tuned to a resonance Raman excitation wavelength of the benzene molecule, the intensity measured by the photomultiplier tube **80** is about 1.2×100000 counts.

In these embodiments, the computer **40** may be configured to determine the presence of a spill of petroleum-derived VOC when the measured intensity is indicative of a resonance Raman interaction between the UV radiation beam and the molecules of the petroleum-derived VOC. The computer **40** can be configured to determine the presence of a spill of petroleum-derived VOC when the measured intensity is above a threshold. For instance, the threshold can be set to about 0.8×100000 counts in the specific embodiment shown in FIG. **7**.

FIG. **8** shows a schematic representation of the computer **40**, as a combination of software and hardware components. The computer **40** may be part of the device **10** or be provided externally. In this example, the computer **40** is illustrated with one or more processing units (referred to as "the processing unit **94**") and one or more computer-readable memories (referred to as "the memory **96**") having stored thereon program instructions **98** configured to cause the processing unit **94** to generate one or more outputs based on one or more inputs. The inputs may comprise one or more signals representative of the instructions to generate the UV radiation beam, the threshold, the excitation wavelength λe, the petroleum-derived VOC under examination, any expected form of Raman scattering, and the like. The outputs may comprise one or more signals representative of the presence or absence of a spill of petroleum-derived VOC at the distant target, a concentration, a mapping indicating the presence or the absence of a spill of petroleum-derived VOC, and/or a concentration thereof, at any suitable spatial location of the scene **26**, a warning and the like.

The processing unit **94** may comprise any suitable devices configured to cause a series of steps to be performed so as to implement computer-implemented methods such that the instructions **98**, when executed by the computer **40** or other programmable apparatuses, may cause the functions/acts/steps specified in the methods described herein to be executed. The processing unit **94** may comprise, for example, any type of general-purpose microprocessor or microcontroller, a digital signal processing (DSP) processor, a central processing unit (CPU), an integrated circuit, a field programmable gate array (FPGA), a reconfigurable processor, other suitably programmed or programmable logic circuits, or any combination thereof.

The memory **96** may comprise any suitable known or other machine readable storage medium. The memory **96** may comprise non-transitory computer readable storage medium such as, for example, but not limited to, an electronic, magnetic, optical, electromagnetic, infrared, or semiconductor system, apparatus, or device, or any suitable combination of the foregoing. The memory **96** may include a suitable combination of any type of computer memory that is located either internally or externally to device such as, for example, random-access memory (RAM), read-only memory (ROM), compact disc read-only memory (CDROM), electro optical memory, magneto-optical memory, erasable programmable read-only memory (EPROM), and electrically-erasable programmable read-only memory (EEPROM), ferroelectric RAM (FRAM) or the like. The memory **96** may comprise any storage means (e.g., devices) suitable for retrievably storing machine-readable instructions executable by the processing unit **94**.

Each computer program described herein may be implemented in a high level procedural or object oriented programming or scripting language, or a combination thereof, to communicate with an engine computer. Alternatively, the programs may be implemented in assembly or machine language. The language may be a compiled or an interpreted language. Computer-executable instructions may be in many forms, including program modules, executed by one or more computers or other devices. Generally, program modules include routines, programs, objects, components, data structures, etc., that perform particular tasks or implement particular abstract data types. Typically the functionality of the program modules may be combined or distributed as desired in various embodiments.

In some embodiments, the computer **40** identifies Raman scattering in the received return signal **36** in a manner that a presence of the spill **12** of petroleum-derived VOC at the distant target **32** can be determined. In some other embodiments, the computer **40** identifies no Raman scattering in the received return signal **36**. In this case, the computer **40** can determine an absence of the spill **12** of petroleum-derived VOC at the distant target **32**.

In some embodiments, the computer **40** compares an intensity of the received return signal **36** with a threshold and then identifies Raman scattering in the received return signal **36** when the intensity is above the threshold. In these embodiments, the computer **40** can be configured to signal an alert. In some embodiments, the alert is signalled in real time, in some other embodiments, the alert is stored on a computer-readable memory for latter consultation.

In alternate embodiments, the computer **40** compares the intensity of the Raman scattering with calibration data stored on a computer-readable memory. Indeed, the intensity of the Raman scattering from a vapor plume is generally proportional to the concentration-length product, therefore, calibration data can be obtained. In these embodiments, the computer may generate an output indicative of a concentration-length product of the petroleum-derived VOC in the plume **13**. The output can be stored on a computer-readable memory, transmitted to an external computer, or displayed on a user interface.

It is envisaged that the computer **40** can determine a distance, along the UV radiation beam **34**, between the receiver assembly **38** (or any reference point relative the aircraft **24** or the ground) and the spill **12** of petroleum-derived VOC or distant target based on a time delay between the generation of the UV radiation beam **34** towards the distant target **32** and the reception of the return signal **36** from the distant target **32**.

As it will be understood, in this disclosure, the word "processor" is used broadly so as to encompass one or more processors and other synonyms (such as one or more computers, one or more processing units and the like). Moreover, the expression "computer-implemented" is meant to be implementable by a processor. Accordingly, computer-implemented steps can be executed by a processor.

It will be understood that the expression "computer" as used herein is not to be interpreted in a limiting manner. It is rather used in a broad sense to generally refer to the combination of some form of one or more processing units and some form of memory system accessible by the processing unit(s). A computer can be a personal computer, a smart phone, an appliance computer, etc.

It will be understood that the various functions of the computer, or more specifically of the processing unit or of the memory controller, can be performed by hardware, by software, or by a combination of both. For example, hardware can include logic gates included as part of a silicon chip of the processor. Software can be in the form of data such as computer-readable instructions stored in the memory system. With respect to a computer, a processing unit, a memory controller, or a processor chip, the expression "configured to" relates to the presence of hardware, software, or a combination of hardware and software which is operable to perform the associated functions.

Conventional Raman spectroscopy detection devices when operated in a LIDAR configuration can have a high optical resolution spectrometer as part of their receiver assembly. Such spectrometers may be provided in the form of a grating spectrometer, and often in the form of double or triple monochromators or spectrographs. The spectrometers are used to filter out, as much as possible, Rayleigh scattering associated with the pulsed laser beam by molecules in the air or from scattering by liquid or solid targets in the case of returns from liquid or solid surfaces. In addition, spectrometers may allow for a reduction in interference from other molecules and thus may provide an increase in effective sensitivity when coupled with a very low optical linewidth laser system. In some embodiments, these detection devices have gated imagers in the detection plane of the spectrometers, in the form of intensified charge coupled device cameras (ICCDs). Such conventional Raman spectroscopy detection devices can thus be bulky.

In the case of a molecule having a Raman resonance, the combination of spectrometers and gated imagers may be replaced with a filter element and an intensity detector such as a photomultiplier tube, as described above. Since the resonance Raman excitation wavelengths are associated with gas phase absorption peaks (electronic transitions), methods developed for the absorption approaches to detection can be modified for use in the resonance Raman approach described herein.

FIG. **9** shows a schematic view of an example of a device **110** for determining the presence of a petroleum-derived VOC having a Raman resonance in a sample. The sample can be a distant target such as described above, depending on the embodiment. Examples of petroleum-derived VOC having a Raman resonance can include any aromatic compounds (e.g., benzene, toluene). Similar elements bear similar reference numbers, but in the 100 series.

More specifically, the device **110** can be used to illuminate the sample with a radiation beam **134**, wherein the radiation beam **134** has an excitation wavelength tuned to a resonance Raman excitation wavelength of the petroleum-derived VOC under examination.

The device **110** can be used to receive a return signal **136** from the sample following said illumination with the radiation beam **134**. A filter element **182** is used to filter out, from the return signal **136**, wavelengths other than wavelengths of a Raman scattering band of the petroleum-derived VOC for the radiation beam. In other words, when illuminating the sample with the radiation beam **134**, Raman light is expected to be found, if the petroleum-derived VOC is present in the sample, in a given Raman scattering band. For instance, if the excitation wavelength of the radiation beam **134** is λe, then the Raman scattering band can span between λe±λλ1 and λe±λ2, wherein the plus sign is used in case of Stokes waves and the minus sign is used in case of anti-Stokes waves. In the case of Stokes waves, for instance, the filter element **182** is used to filter out wavelengths lower than λe+λ1 and wavelengths higher than λe+λ2.

The device **110** can be used to measure an intensity of the filtered return signal using an intensity detector such as a photomultiplier tube or a photodiode, for instance, and to determine the presence of the petroleum-derived VOC in the sample when the intensity is indicative of a resonance Raman interaction between the radiation beam and the petroleum-derived VOC.

In this example, the laser source **170** is used in a LIDAR configuration. As can be understood, the pulsed laser beam **134** is shaped so as to have a suitable footprint when it reaches the ground. In this embodiment, the laser beam is routed to beam shaping optics and transmitted along an optical axis. Close to the ground, or on the ground, the pulsed laser beam **134** interacts with the selected petroleum-derived VOC, if any.

With the correct excitation wavelength λe, a return signal **136** having an enhanced, more intense Raman scattering can be generated from the interaction of the pulsed laser beam **134** with vapors in the air, liquids or solids on the ground. The return signal **136** travels back to the device **110**. A receiver assembly **138**, including a telescope **184**, collects the return signal **136**. The collection telescope **184** and associated optics shape the return signal **136** for further optical processing. A high pass optical interference filter **182** may be provided to reject the scattered laser light and let pass the Raman light of the return signal **136** and any other light at wavelengths above the excitation wavelength λe. The return signal **136** can be further optically filtered to let pass light at selected Raman emission wavelengths of the petroleum-derived VOC of interest, rejecting most of the unwanted collected light. This can be done again with band pass interference filters or with a specially designed grating monochromator or polychromator. Finally, the filtered Raman light or any other light in the band pass of the optical filtering elements of the return signal **136** falls onto an optical detector, usually in the form of a photomultiplier tube **180**. A camera can also be used in the case of an imaging configuration.

The computer **140** is used to operate the device **110** in a LIDAR configuration, which helps reducing unwanted long lived fluorescence. As shown, the computer **140** has a synchronization unit, a signal acquisition unit and a control unit in this example. Raman light is generated within a few picoseconds. The Raman scattering signal can thus have a temporal shape similar to that of the laser excitation pulse. If the laser excitation pulse is short, say a few hundreds of picoseconds or a few nanoseconds, synchronizing and rapidly gating the detection may allow removal of fluorescence generated at later times. The LI DAR configuration can also allow for spatially resolved standoff detection, enabling the rejection of any return signal generated at distances not of interest and allowing for a better signal to noise ratio for detection of vapors close to the ground (where petroleum-derived VOC can be present since the petroleum-derived VOC may be heavier than air) or for the detection of liquids or solids (e.g., spills) on the ground.

The resonance Raman LIDAR may allow detection, from an altitude of about 100 m, and flying at up to 100 km/h, of amounts of benzene vapor as low as a few hundreds of ppb-m (concentration times distance parameter proportional to total amount of benzene to be detected) above a pipeline path. This may be done in as little as 0.3 second with the device **110** installed in a pod attached to an aircraft. The device **110** may allow low resolution imaging of a selected molecule having a resonance Raman in a terrain such as a pipeline path while scanning the field of view of the device **110** along the terrain.

FIG. **10** shows a schematic view of an example of a device **210** for determining the presence of a petroleum-derived VOC having a resonance Raman in a sample. Similar elements bear similar reference numbers, but in the 200 series.

In this embodiment, the device **210** can be used to illuminate the sample with a first radiation beam, the first radiation beam having a first excitation wavelength being tuned to a resonance Raman excitation wavelength of the petroleum-derived VOC under examination. The device **210** can be used to receive a first return signal from the sample and to measure a first intensity of the first return signal using an intensity detector **280**. In this embodiment, the device **210** has a tunable radiation beam generator **270** which can be tuned to any one of the resonance Raman excitation wavelengths of the petroleum-derived VOC under examination.

In this approach, the laser's optical frequency that is on the resonance Raman excitation peak may be stabilized using a laser optical frequency stabilization subsystem **235**.

It can be understood that in these embodiments, the filter element **282** is adapted to filter out wavelengths that are not in the Raman scattering band, which is, in this case, selected to cover the Raman light that can be emitted following excitation with the first radiation beam.

As can be understood, the examples described above and illustrated are intended to be exemplary only. The scope is indicated by the appended claims.

What is claimed is:

1. A method of determining the presence of a spill of a petroleum product by the detection of a petroleum-derived volatile organic compound (VOC), the method comprising:

providing an ultraviolet (UV) radiation generator and a receiver assembly aimed at a scene;

the UV radiation generator illuminating a distant target in the scene with a UV radiation beam, the UV radiation beam having an excitation wavelength being tuned to a resonance Raman excitation wavelength of the petroleum-derived VOC;

the receiver assembly receiving a return signal from the distant target; and

determining the presence of the spill of the petroleum product upon detecting a Raman scattering in the received return signal, the Raman scattering being indicative of a resonance Raman interaction between the UV radiation beam and molecules of the petroleum-derived VOC.

2. The method of claim **1** wherein said receiving includes filtering out, from the return signal, wavelengths other than a Raman scattering band of the petroleum-derived VOC for the UV radiation beam and wherein said detecting includes measuring an intensity of the filtered return signal.

3. The method of claim **1** wherein the petroleum-derived VOC is an aromatic compound.

4. The method of claim **3** wherein the petroleum-derived VOC is benzene having Raman resonances at at least 241.6 nm, 247.6 nm, 252.9 nm and 258.9 nm, the excitation wavelength of the UV radiation beam being tuned to at least one of the Raman resonances of benzene.

5. The method of claim **3** wherein the petroleum-derived VOC is toluene having Raman resonances at at least 260.3 nm, 263 nm and 266.8 nm, the excitation wavelength of the UV radiation beam being tuned to at least one of the Raman resonances of toluene.

6. The method of claim **3** wherein the petroleum-derived VOC is ethylbenzene having Raman resonances at at least 260.2 nm, 263 nm and 266.6 nm, the excitation wavelength of the UV radiation beam being tuned to at least one of the Raman resonances of ethylbenzene.

7. The method of claim **3** wherein the petroleum-derived VOC is m-xylene having Raman resonances at at least 258.5 nm, 263.7 nm and 272.2 nm, the excitation wavelength of the UV radiation beam being tuned to at least one of the Raman resonances of m-xylene.

8. The method of claim **1** wherein said determining includes operating the UV radiation generator and the receiver assembly in a synchronized manner allowing to determine a range-resolved concentration of the petroleum-derived VOC.

9. The method of claim **1** wherein said providing includes flying the UV radiation generator and the receiver assembly over the scene using an aircraft.

10. A device for determining the presence of a spill of petroleum product by the detection of a petroleum-derived volatile organic compound (VOC), the device comprising:

a housing;

an ultraviolet (UV) radiation generator mounted to the housing and adapted to illuminate a distant target in a scene with a UV radiation beam, the UV radiation emitter being adapted to generate the UV radiation beam at an emission wavelength tuned to a resonance Raman wavelength of the petroleum-derived VOC;

a receiver assembly mounted to the housing and adapted to receive a return signal from the distant target; and

a computer configured to operate the UV radiation emitter and the receiver to determine the presence of the spill of petroleum product upon identifying a Raman scattering in the received return signal, the Raman scattering being indicative of a resonance Raman interaction between the UV radiation beam and molecules of the petroleum-derived VOC.

11. The device of claim **10** wherein the receiver assembly includes an intensity detector adapted to measure an intensity of the received return signal.

12. The device of claim **10** wherein the UV radiation generator and the receiver assembly are operated in a synchronized manner allowing to determine the petroleum-derived VOC at a predetermined range.

13. The device of claim **10** wherein the housing is mountable to a vehicle.

14. The device of claim **13** wherein the vehicle is an aircraft.

15. The device of claim **14** wherein the aircraft is an unmanned aircraft.

16. An aircraft comprising a frame to which is secured the housing of the device of claim **10**.

17. A method for determining the presence of a spill of a petroleum product by the detection of a petroleum-derived volatile organic compound (VOC), the method comprising utilizing the device of claim **10**.

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