Bureau of Mineral Resources, Geology & Geophysics

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BMR Record 1990/75

Australian Petty Patent: An Underwater Operable Dissolved Gas Analyser.

Project 121.20

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1990/75
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Division of Marine Geosciences and Petroleum Geology, Bureau of Mineral Resources, P.O. Box 378 Canberra, Australia.

Executive Summary.

This Record describes Australian Petty Patent No. 597230: Underwater Operable Dissolved Gas Analyser. The BMR, as part of the Continental Margins Program, conducts geochemical surveys to search for hydrocarbon vents and seeps, from sub-seafloor hydrocarbon accumulations, to the overlying seawater. The existing technology for these types of surveys includes; a towed fish with submersible pump, a relatively large winch and A-frame with about 400m of hollow 'faired' cable, a gas extractor and gas chromatographs to measure hydrocarbons extracted from seawater, these latter installed in a laboratory aboard ship. A relatively large ship is required to accomodate this equipment. The Underwater Operable Dissolved Gas Analyser was conceived in an attempt to simplify dissolved gas measurements in seawater by making those measurements 'in-situ', hence eliminating the need for a hollow 'faired' cable and shipboard analysis equipment. The main components of the design herein include: i. a chamber to extract gases from seawater, ii. a second chamber that houses neon-helium lasers for the measurement of methane by differential absorption, iii. these chambers are housed in a submersible 'fish' towed behind a ship, iv. methane concentrations are relayed to the ship, and power provided to the submersible 'fish' via a co-axial cable. The equipment is estimated to measure methane in seawater 'in-situ' with a sensitivity comparable to gas chromatographic techniques. The equipment described herein has potential application for; hydrocarbon exploration on the continental margin and in lakes, surveys of gas pipelines, surveys of pollution such as that which occurs at ocean outfalls, the monitoring of a greenhouse gas (methane) in aquatic locations. The equipment may be installed on small vessels for continuous underway measurements of methane, or be operated in a fixed but remote location. Published with the permission of the Executive Director, BMR.

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Attention: Dr. Simon Kravis

Dear Sir(s),

Re: Australian Petty Patent Application No. 51211/90
Your Ref: 88/332

We have pleasure in enclosing the Deed of Letters Patent (Petty Patent) for the case identified below. If the printed specification is not attached to the Deed it will be forwarded when received from the Patent Office.

Yours faithfully
DAVIES & COLLISON

Patentee	The Commonwealth of Australia
Application No.	51211/90
Petty Patent No.	597230
Title	Underwater Operable Dissolved Gas Analyser
Initial term of Petty Patent	17 April 1991
Extension due date	17 March 1991
Extended term, if granted	12 March 1996

Commonwealth of Australia

Letters patent

Patents Act 1952

No. 597230

PETTY PATENT

ELIZABETH THE SECOND, by the Grace of God Queen of Australia and Her other Realms and Territories, Head of the Commonwealth.

To all to whom these presents shall come Greeting:

WE DO, by these Letters Patent, give and grant to the person whose name is specified hereunder Our Special Licence and the exclusive right, subject to the laws in force from time to time in Australia or a part of Australia, by that person, that person's agents and licensees, at all times during the term of these Letters Patent, to make, use, exercise and vend throughout Australia the invention the title of which is specified hereunder and being the invention that is fully defined in the claim of the petty patent specification accepted in accordance with the **Patents Act 1952** in such manner as that person thinks fit, so that that person shall have and enjoy the whole profit and advantage accruing by reason of the invention during that term.

Name and Address of Patentee:
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Names of Actual Inventors: Simon Philip Kravis and David Thomas Heggie

Title of Invention: Underwater operable dissolved gas analyser

Application Number: 51211/90

Term of Letters Patent: Twelve months commencing on 17 April 1990

IN WITNESS whereof our Commissioner of Patents has caused these Our Letters Patent to be made and to be sealed with the seal of the Patent Office on 17 April 1990

P.A.SMITH
COMMISSIONER OF PATENTS

SPECIFICATION OF PETTY PATENT APPLICATION

APPLICANT:	COMMONWEALTH OF AUSTRALIA
TITLE OF INVENTION:	"UNDERWATER OPERABLE DISSOLVED GAS ANALYSER"
COUNTRY:	AUSTRALIA
APPLICATION DATE:	12 March 1990
APPLICATION NO:	51211/90
PRIORITY DATE:	15 March 1989 (Australian Patent Application No PJ 3228)

FORM 10 A
Sub-Regulation 13(3)

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

PETTY PATENT SPECIFICATION

(Original)

FOR OFFICE USE:

Class Int. Class

Application Number:
Lodged:

Priority:

Related Art:

Name of Applicant: COMMONWEALTH OF AUSTRALIA
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Petty Patent Specification for the invention entitled:

"UNDERWATER OPERABLE DISSOLVED GAS ANALYSER"

The following statement is a full description of this invention, including the best method of performing it known to us:-

Technical Field

This invention concerns the analysis of gases dissolved in water. More particularly, it concerns the monitoring of the concentration of specific gases in a sample of water, in situ, using the differential absorption of light by the gas at different wavelengths.

Background to the Invention

It is known that anomalous concentrations of C1 to C4 hydrocarbons in lake water or sea water may be associated with the natural seepage of gas from the floor of the lake or the ocean or anthropogenic inputs. Hence measurements of the concentration of C1 to C4 hydrocarbons in sea water has become, over the last few years, an auxiliary tool in offshore petroleum exploration, to complement the data obtained using seismic and geomagnetic surveys. In addition, the monitoring of light hydrocarbons in inland waterways and the ocean is important in documenting pollution and the concentrations of "greenhouse" gases.

The current "underwater sniffing" technique involves pumping water from the depth being sampled on to a ship and analysing the gases dissolved in the sample, using a gas chromatograph. One particular (and typical) system for such analysis is marketed by InterOcean Systems Inc, of San Diego, California, USA. That system measures the total hydrocarbon content of a water sample every 30 seconds, at a ship

speed of 5 knots, with a sensitivity of about 50 microlitres of gas per litre of water. The C1 to C4 hydrocarbon concentrations are measured every 3 minutes with a sensitivity of about 5 microlitres of gas per litre of water.

To perform this analysis, substantial equipment is required. The pumping of water from depth to a ship carrying the gas chromatograph requires a large winch, with a special cable. For example, a winch measuring approximately 3 metres by 2 metres is required to accommodate the cable and fairings (plastic fittings that reduce the frictional drag of the cable through the water) for sampling from depths down to about 400 metres. Existing technology is limited to water depths of about 450 metres. The on-board gas analysis equipment is also large; and it is complex. Furthermore, a specialist operator is required to perform the analysis using this equipment.

An in situ gas analysis system, which could be towed by a ship in a manner similar to towing a magnetometer, would be a substantial improvement on the current dissolved gas analysis system.

The use of a gas chomatograph underwater is not a practical answer to this need because:

(a) The equipment is simply too bulky and cumbersome for in-situ operation; and

(b) Maintaining a burning flame of a hydrogen/air mixture in a submerged unit would be extremely difficult.

Disclosure of the Present Invention

It is an object of the present invention to provide underwater gas analysis equipment which (a) can be used to measure the concentration of dissolved gas in situ, at short sampling intervals, (b) can be used without significant depth limitation, (c) can be towed by a ship, and (d) does not require a specialist operator when in use.

This objective is achieved by a twin chamber unit. One of the chambers, which may be termed an optical equipment chamber, contains a pair of lasers, producing beams at wavelengths which are different from, but close to, each other. One of the wavelengths is selected so that it is absorbed by the gas to be detected while the other wavelength suffers no (or substantially less) absorption when passed through the gas to be detected. The second chamber is a gas sampling chamber equipped with (a) at least one pump to substantially evacuate it, and (b) inlets for water and a purge gas. The water inlet, when activated, allows water from the exterior of the second chamber to enter as a spray, which releases the gas dissolved in the water. The second chamber also has an optical path region, separated by a gas-permeable membrane from the region of the second chamber which communicates with the pumping system

and the water and purge gas inlets. The optical path region of the second chamber is connected to the optical equipment chamber by a transparent window. The beams from the lasers are arranged to enter the optical path region of the second chamber through the window, traverse that optical path region twice (being reflected by a mirror after one traversal), and leave it through the window. The beams are then sampled by a detector and the differential absorption during the double traverse of the optical path region is measured to provide an indication of the concentration, in the second chamber, of the gas to be detected.

Typically, the volume of the second chamber of such equipment will be about 5 litres, and samples of about 1 litre of sea water or lake water will be released into the second chamber through its water inlet. With optical equipment having a signal-to-noise ratio of 1000, 1 micromole of gas in one litre of water can be detected. If a signal-to-noise ratio of 1 is acceptable, 1 nanomole of gas per litre of water can be measured.

Thus, according to the present invention, there is provided apparatus for the in situ measurement of a hydrocarbon or other gas dissolved in water, said apparatus comprising:

(a) a first chamber, containing a first laser and a second laser, said lasers producing beams of radiation which have respective wavelengths

close to each other, one of said wavelengths being within an absorption band of the hydrocarbon or other gas, the other wavelength being outside or substantially outside the absorption band, said beams being presented alternately to a window of the first chamber which is transparent to each of the wavelengths;

(b) a second chamber having a first region thereof which is adjacent to said window, said first region having a mirror mounted therein remote from said window and positioned to reflect the beams of radiation from the lasers which enter the second chamber through said window back to the first chamber through said window; said second chamber having a second region thereof adapted to receive and discharge samples of the water, said second region being separated from said first region by a gas-permeable membrane;

(c) optical detector means within said first chamber to receive the beams of radiation reflected by said mirror, and means associated with said optical detector means to analyse the differential absorption of the respective beams from the lasers during their traversal of said first region of said second chamber;

(d) pumping means connected to the second region of the second chamber and adapted to substantially evacuate the second chamber;

(e) purge gas inlet means connected to the second region of the second chamber to allow a controlled quantity of a purge gas to enter said second chamber; and

(f) a water inlet valve connected to the second region of the second chamber and adapted to allow a predetermined volume of the water to enter the second chamber.

Preferably the pumping means connected to the second region of the second chamber comprises two pumps, one adapted to pump gases (including water vapour) and the other adapted to pump water from the second chamber.

An output signal from the means to analyse the differential absorption of the beams from the lasers may be transmitted to ship-board equipment to enable the hydrocarbon or gas concentration in a sample of sea water or lake water to be evaluated, or to be stored by any suitable means for further analysis later.

An embodiment of the present invention will now be described, by way of example, with reference to the accompanying drawing, which is a schematic representation of an underwater operable, dissolved gas analyser constructed in accordance with the present invention.

Description of the Illustrated Embodiment

In the embodiment illustrated in the drawing, a first chamber 10 contains lasers 11 and 12, which generate, respectively, beams of radiation 13 and 14. The beam 13 is periodically interrupted by a rotating disc chopper 15, powered by an electric motor 16. That portion of the beam 13 which passes the chopper 15 is divided by a beam splitter 17. The intensity of that portion of the beam which is deflected by the beam splitter is monitored by a detector 18. The portion of the beam which is not deflected by the beam splitter 17 is passed through a window 19 which separates the first chamber 10 from a second chamber 20.

The beam 14 from the laser 12 is reflected by a mirror 21 and then by the reflecting surface of the "underside" of the chopper disc 15, to be aligned with the beam 13. Thus, when the beam 13 is not incident upon the beam splitter 17, the beam 14 impinges upon the beam splitter 17 and is partly reflected into the detector 18 and partly transmitted through the window 19. A second detector 22 receives light, though the chopper disc 15 from a light source 23 and provides a reference signal to a phase detector and modulator 24, which also receives the output from the first detector 18. The reference signal from the second detector 22 is used to provide information regarding which of beams 13 and 14 is being monitored, at any given time, by the first

detector 18. The chopping frequency should be chosen to minimise noise, and thus will normally be between 1 KHz and 2 KHz.

When this equipment is used to detect methane in a gas sample, the lasers 11 and 12 will normally be helium-neon lasers which produce beams of radiation in the mid-infrared region. Methane has a strong absorption band around 3391 nanometres (nm) and one of the lines in the absorption band coincides with a strong helium-neon laser line at 3392.2 nm. A nearby helium-neon laser line at 3391.1 nm is only weakly absorbed by methane. Thus arranging for the beam 13 to have a wavelength of 3392.2 nm and for the beam 14 to have a wavelength of 3391.1 nm ensures that the system in the chamber 10 in Figure 1 is capable of measuring the differential absorption of light from the laser beams while they perform their double traverse of the chamber 20, which is described below.

A sample of the gas that has been dissolved in a sample of sea water, lake water or the like, is contained in an arm 30 which constitutes a first region of the second chamber 20. The radiation passing through the window 19 travels the length of the arm 30 and is then reflected by a mirror 31 to perform a second traverse of the arm 30 and leave the arm 30 through the window 19, to re-enter the first chamber 10. The radiation reflected by the mirror 31 is received by a third detector 25, the output of which is input to a lock in amplifier 27. The output

28 of the amplifier 27 is a stream of signals which provide data about the differential absorption by the gas in the arm 30.

The optical differential absorption technique is not new. It has been developed and used in the remote sensing of methane in coal mines, over landfill sites and near natural gas pipelines. As methane is the most abundant light hydrocarbon in sea water, the inclusion of equipment to perform differential absorption measurements in the apparatus of the present invention substantially enhances the commercial potential of the present invention.

Reverting again to the embodiment of the invention that is illustrated in the drawings, the first region or arm 30 of the second chamber 20 is separated from the second region 34 of the second chamber 20 by a gas-permeable membrane 33. Two pumps, 35 and 36, are connected to the second region 34 and are used to evacuate the second chamber 20. The pump 35 is designed to pump out gases. The pump 36 is used to pump out the water which collects at the lowest point of the second chamber when a sample of sea water has been admitted during the analysis cycle.

A sample of water is admitted to the evacuated second chamber 20 through a solenoid controlled valve 38, mounted on the wall of the second region 34. In a typical analysis unit, the volume of the second

chamber 20 will be about 5 litres and a controlled sample of about 1 litre of sea water will be admitted through the valve 38.

When the sample of water enters the second chamber 20 through the valve 38, it does so as a fine spray. The water boils off until saturation vapour pressure is reached. All the dissolved gas is released during this boiling off period. Once liquid water is present in the chamber 20 (in the second region 34), dissolved gas is still released efficiently from the incoming spray of sea water due to the relatively large surface area of the water droplets of the spray. The liquid water collects as a small pool 37 at the bottom of the second region 34; the gas above the pool 37 permeates through the membrane 33, until the gas pressure in the arm 30 is the same as the gas pressure in the second region 34.

After the differential absorption of light by the gas sample in the arm 30 has been monitored using the equipment in the first chamber, the pumps 35 and 36 empty the second chamber 20. Before pumping out the chamber 20, however, a purge gas - for example, nitrogen - is admitted to the chamber 20 via inlet valve 39 from a cylinder 40, until the pressure within the chamber 20 is about 0.5 atmosphere. This procedure greatly simplifies the pumping of water vapour and dissolved gases from the chamber 20. A gas cylinder 40 containing 8 cubic metres of purge gas at 1 atmosphere can supply enough gas to purge

the second chamber 20 about 3000 times. If a water sample is analysed every 30 seconds and the volume of the second chamber is 5 litres, an 8 cubic metres cylinder of purge gas will last for about 40 hours.

The sensitivity of the differential absorption method depends upon the difference in absorption coefficient of the two beams, the optical path length through the absorbing gas, the intensity noise of the lasers, the noise of the optical detectors, and the time over which the differential absorption signal is analysed. Using published figures of noise levels of the lasers and the detectors, assuming an absorption path length of 1 metre and an integration time of 1 second, the absorption due to a partial pressure of 1.3×10^{-9} atmosphere of methane can be detected with a signal to noise ratio of 1.

Power for the operation of the apparatus illustrated in the drawing is supplied through an umbilical cable from the ship towing the apparatus. The lasers consume a few hundred watts; the pumps have a power requirement of several kilowatts; the remaining equipment consumes relatively little power. The equipment can be conveniently operated under microprocessor control. The signals 28 from the amplifier 27 can be transferred to the ship via the cable for analysis and/or storage.

Those skilled in gas analysis and electronic equipment will appreciate that although a specific embodiment of the present invention has been illustrated and described in this specification, variations to and modifications of this equipment can be made without departing from the present inventive concept.

The claim defining the invention is as follows:

1. Apparatus for the *in situ* measurement of a hydrocarbon or other gas dissolved in water, said apparatus comprising:

(a) a first chamber, containing a first laser and a second laser, said lasers producing beams of radiation which have respective wavelengths close to each other, one of said wavelengths being within an absorption band of the hydrocarbon or other gas, the other wavelength being outside or substantially outside the absorption band, said beams being presented alternately to a window of the first chamber which is transparent to each of the wavelengths;

(b) a second chamber having a first region thereof which is adjacent to said window, said first region having a mirror mounted therein remote from said window and positioned to reflect the beams of radiation from the lasers which enter the second chamber through said window back to the first chamber through said window; said second chamber having a second region thereof adapted to receive and discharge samples of the water, said second region being separated from said first region by a gas-permeable membrane;

(c) optical detector means within said first chamber to receive the beams of radiation reflected by said mirror, and means associated with said optical detector means to analyse the

differential absorption of the respective beams from the lasers during their traversal of said first region of said second chamber;

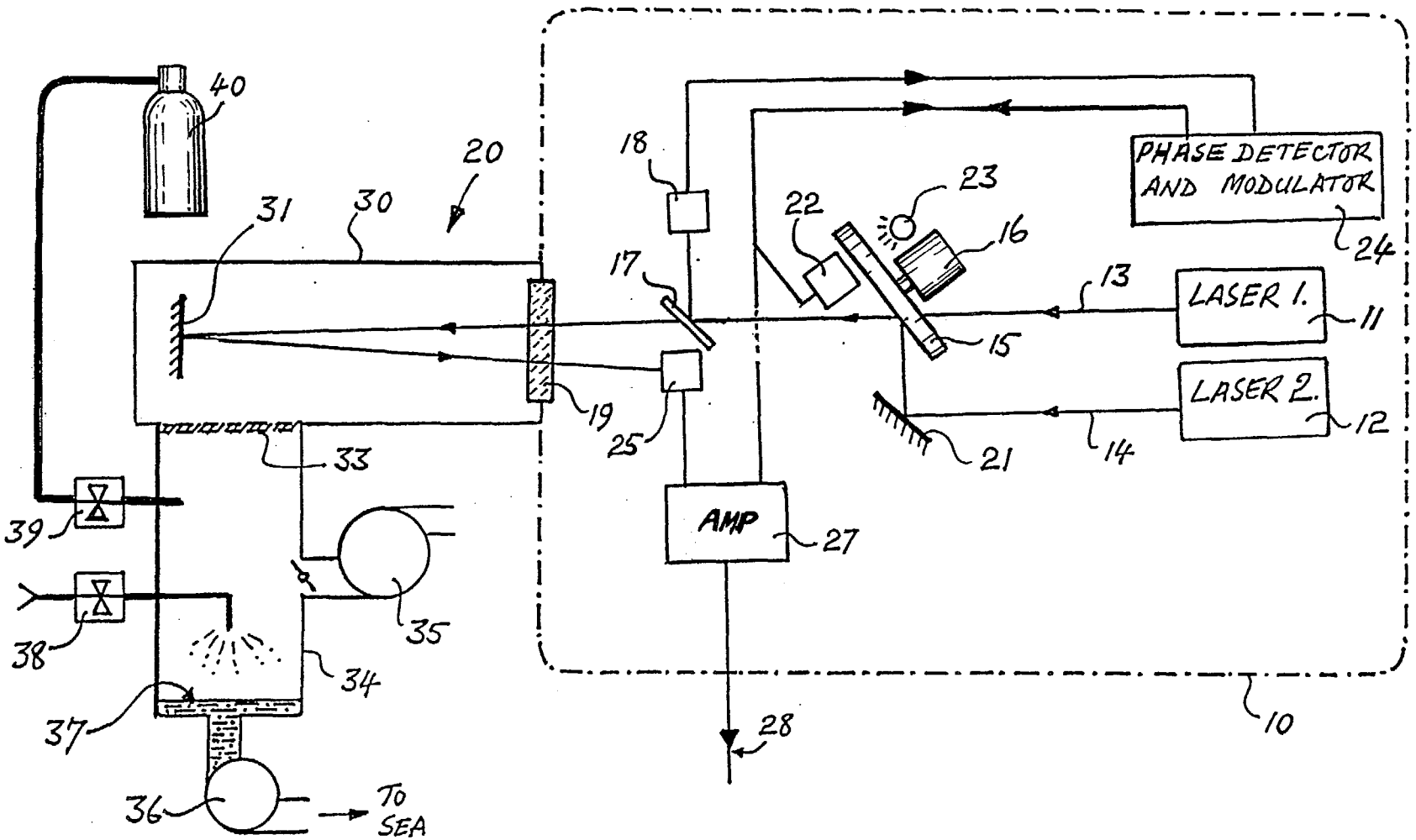
(d) pumping means connected to the second region of the second chamber and adapted to substantially evacuate the second chamber;

(e) purge gas inlet means connected to the second region of the second chamber to allow a controlled quantity of a purge gas to enter said second chamber; and

(f) a water inlet valve connected to the second region of the second chamber and adapted to allow a predetermined volume of the water to enter the second chamber.

DATED this twelfth day of March 1990
COMMONWEALTH OF AUSTRALIA

by its Patent Attorneys
DAVIES & COLLISON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