

METHOD FOR PREDICTING HYDROCARBON POTENTIAL OF
AN EARTH FORMATION UNDERLYING A BODY OF WATER

This invention relates to a method for providing for isotopic chemical analysis of carbonaceous fluids from a hydrocarbon pool or other source of organic matter associated with an earth formation underlying a body of water, and is concerned with providing for on-site capture of such fluids whereby indications of their biogenic and/or thermogenic origin can be accurately forecasted.

While marine exploration systems are presently available for continuously sampling water seeps so as to analyze for presence of carbonaceous fluids such as methane, none have the capability of providing a compositional parameter that is uniquely diagnostic of seep origin, and hence allowing the user/operator to distinguish the biogenically derived sample from a sample associated with a thermogenic source. The reason for this is that other interpretative tests were thought to be sufficient from a cost/result standpoint. Also, the lengthy and complexed nature of the steps involved in collecting, isolating and tagging sufficient amounts of the samples for such analysis were thought to be beyond the capability of present on-site collection and analytical systems.

In accordance with the present invention, a quick, convenient and highly accurate technique for the acquisition of sufficient amounts of one or more carbonaceous constituents dissolved in seep water is provided. Thus indications of the carbon isotopic character in the collected samples _____

1 and their biogenically- and/or thermogenically-derived origin can be easily and surprisingly accurately determined.

According to the invention, there is provided a method of on-site collection and examination of
5 small concentrations of a carbonaceous gas dissolved in a body of water under which there is an earth formation so as to predict hydrocarbon potential of the earth formation underlying said body of water, said formation being a source of said carbonaceous gas, said method comprising:

10 (i) at a known geographic location continuously sampling said water at a selected flow rate and at a selected depth;

(ii) continuously vacuum separating said water into liquid and gas phases;

15 (iii) quantitatively separating a selected carbonaceous gas from interfering gas species in the presence of an air carrier vented to atmosphere at a known flow rate; and

(iv) quantitatively oxidizing said selected gas and
20 then cryogenically trapping an oxidation product thereof in the presence of said air carrier so as to provide for accurate isotopic examination.

According to a preferred embodiment of the invention, there is provided a method of on-site collection and
25 examination of small concentrations of methane dissolved in sea water so as to predict hydrocarbon potential of an earth formation associated with generation of said methane, said method comprising

(i) at known geographic locations continuously
30 sampling said sea water at depth;

(ii) continuously vacuum separating said collected sea water into liquid and gas phases;

(iii) continuously monitoring said gas phase of said separated water for the presence of hydrocarbons;

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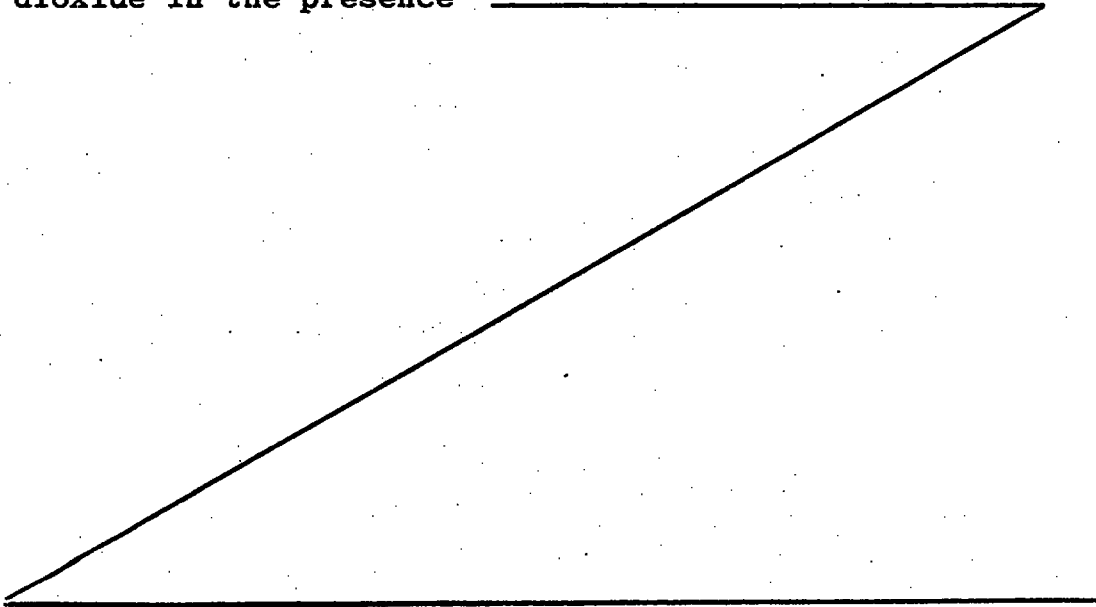
- 1 (iv) if hydrocarbons are present, quantitatively separating out all interfering gas species to the detection of methane and its oxidation product, carbon dioxide;
- 5 (v) quantitatively oxidizing said methane to carbon dioxide and then cryogenically trapping the resulting carbon dioxide in the presence of an air mixture flowing at a rate of about 20 to 120 millilitres per minute; and
- 10 (vi) isotopically examining the carbon distribution of said trapped carbon dioxide, so as to determine biological and/or thermogenic origin of said methane.

The present invention provides for the acquisition of highly accurate data related to the isotopic chemistry - and the biogenic and/or thermogenic origin -
15 of extremely small concentrations of carbonaceous gases and oils, say 100 to 1000 microliter per litre of the sea water, being constantly collected at depth.

Dissolved carbonaceous fluids including natural
20 gases and oils are collectable in sufficient amounts utilizing vacuum separation and selective capture of natural gases utilizing an air carrier mixture. The sequence of steps includes: The fluids are first separated from the water collected at depth; then the
25 methane present is quantitatively converted to carbon dioxide in the presence

30

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of a continuous air carrier vented to the atmosphere. Basis of later analysis is the isotopic composition of the ^{14}C or ^{13}C of the collected sample. Further, since the normalized variation of ^{13}C to ^{12}C (i.e., the delta ^{13}C measurement) requires less amounts of methane to be collected, such analytical method is preferred. The delta ^{13}C measurement is defined in Petroleum Formation and Occurrence, B. P. Tissot, D. H. Welte, Springer-Verlag, N.Y., (1978) at p. 88 as: $^{13}\text{C}^0/00 =$

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$$\frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}} - (^{13}\text{C}/^{12}\text{C})_{\text{standard}}}{(^{13}\text{C}/^{12}\text{C})_{\text{standard}}} \times 1000.$$

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In more detail, sea water is first collected via an electro-hydraulic cable, at depth by a drone trailing from a sea-going vessel, the water being pumped at a substantially constant flow rate in a range from about 3

15 to 7 litres/minute up to a vacuum chamber aboard the vessel where the water is broken into droplets under a slight vacuum (27-28 inches of mercury) and the carbonaceous gaseous constituents, liberated. These constituents are carried via an air stream to a continuous

20 hydrocarbon flame monitor where, if the flame monitor response is positive, more complexed analytical equipment is brought into play; e.g., a multi-port valve can be energized so as to allow the dissolved gases to be analyzed chromatographically. Or still another of the

25 ports of the valve can be activated to allow the same constituents to flow into and through an isotopic trapping network where collection in microliter amounts occurs. Within the isotopic network, use is made of the flowing air stream (flow rate being preferably about 30 milliliters

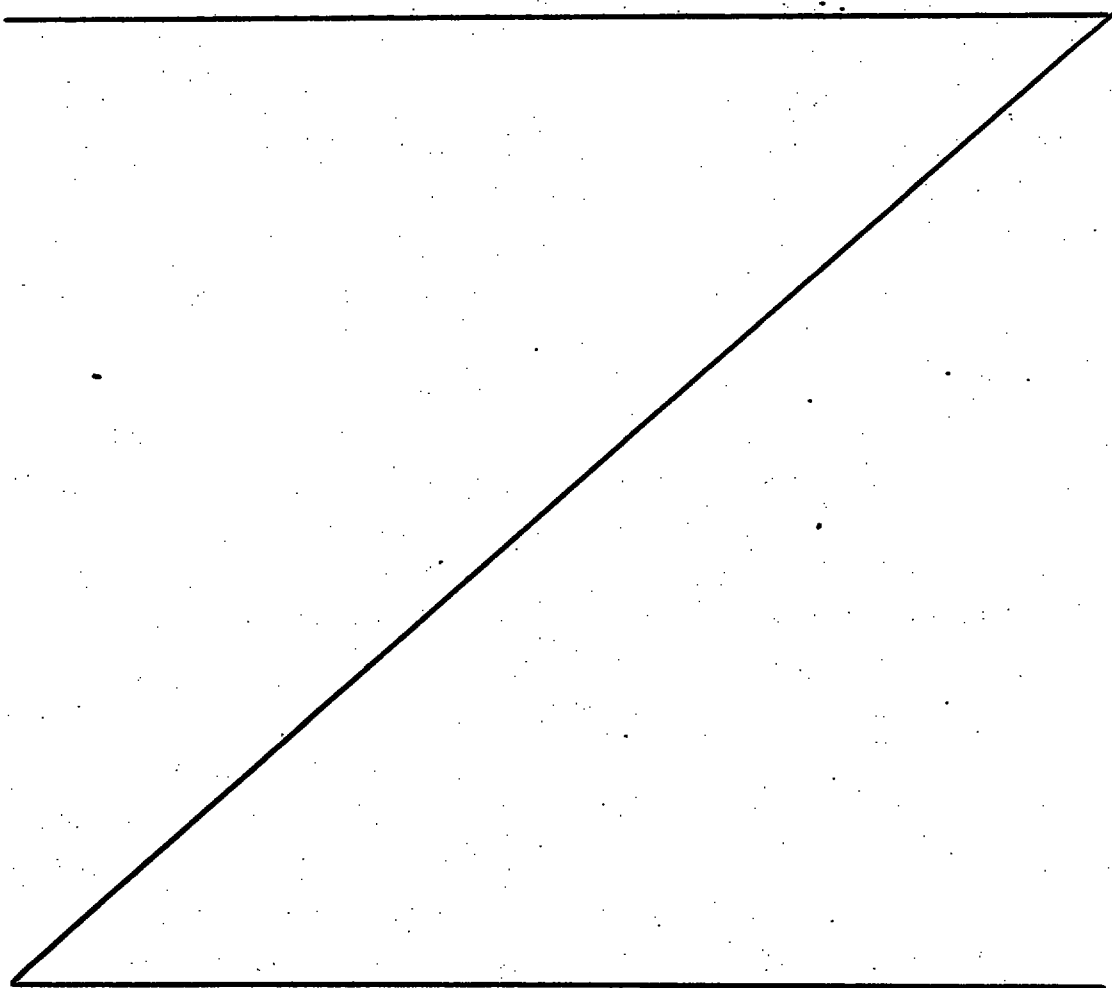
30 per minute in a range of 20-120 milliliters per minute). Gases of interest pass, in seriate, from station-to-station: Methane is isolated (by removing all interfering species), and finally converted to carbon dioxide (in a catalytically-aided oxidation reaction) and cryogenically

35 trapped in a U-shaped trapping chamber. Next, the ends of the trapping chamber are heated and collapsed, sealing them from the atmosphere.

After being transported to a mass spectrometer, the chamber is re-opened so that isotopic analysis can occur. Using the latter results (along with geographic address data) allows for accurate biogenically- and thermogenically-associated predictions to be made, based on the delta ^{13}C values of each collected sample as a function of location.

For a better understanding of the invention and to show how the same may be carried into effect, reference will now be made, by way of example, to the accompanying drawings in which:

Fig. 1 illustrates operation of the present invention, utilizing a vessel positioned on a body of water overlying an earth formation that collects and analyzes, continuously, samples of water at depth;



01 FIG. 2 is a schematic diagram of collection and analytical operations attendant on-site collection of water samples by the vessel of FIG. 1; and

05 FIGS. 3-5 are detailed drawings of an isotopic capture network of the associated on-site collection and analytical operations of FIG. 2.

Referring to Fig. 1; a drone 10 is positioned at a depth Z_0 below a vessel 11 floating at the surface 12 of the body of water 13. Within the drone 10, is a pump (not shown).
10 The purpose of the pump is to draw water samples ^{into the} interior of the drone 10 and pump them upcable (via electro-hydraulic cable 14) to a diagnostic system 15 aboard the vessel 11.

In addition to pumping equipment, the drone 10
15 is fitted with various oceanographic devices, including a depth sensor; a current monitor is also provided that includes a bottom-oriented sonar device in combination with an electromagnetic sensor for measuring the speed and direction of the ocean currents relative to the bottom.
20 Signals from these devices pass via conductors in the side walls of the cable 14 so as to provide annotation (both visual and on tape), associated with geographic position (of the drone and/or the vessel), depth of the drone, etc., as shown. In that way, accurate geographic
25 addresses for the samples as a function of drone and/or vessel location, is assured.

Diagnostic system 15 also provides for a series of geochemical tests, and includes vacuum separation system 16 and a gas phase analysis network 17. Key to
30 diagnostic results using network 17: determination that hydrocarbon gases are present and what types (using

1 hydrocarbon analyzer system 18) in combination with a
gas chromatograph 19, and then isotopic examination via
isotopic capture network 20.

5 FIG. 2 illustrates operation of diagnostic system 15
in still more detail.

As shown, vacuum separation system 16 includes an
air-tight chamber 21 for separating the water into
liquid and gas phases. Entry and egress from the chamber
21 via a series of inlets and outlets 21A-21C. Inlet 21A
10 receives the water samples via cable 14 and associated
manifold 22. A nozzle 24 breaks water into droplets.
Note that even though the flow rate of the water can
be as high as 7 liters per minute, usual flow rate is
usually about 3.7 liters per minute. The separated liquid
15 phase is discharged from the chamber via outlet 21B and
pump 25. The separated gas phase exits the chamber via
outlet 21C through vacuum pump 26 and then passes through
outlet 27 for eventual testing by isotopic capture system
20.

20 Also of importance in the operation of diagnostic
system 15 is the storage and display of all annotation
data via the electrical network/display 34 to allow
for determination of geographic addresses of all samples
taken by the drone, as previously explained.

25 Manifold 27 includes an arm 28 which terminates in
a continuously operating hydrogen flame ionization
analyzer 18. Remaining arm 29 of the manifold 27 termin-
ates at multi-port valve 30.

One port 31 of the valve 30 is open to the atmosphere.
30 Another port 32 is disconnectably connected to gas
chromatograph 19 which, when operating, providing gas
chromatograms. Yet another port 33 of the valve 30 is
disconnectably connected to isotopic capture system 20
of the present invention.

01 Since the gas chromatograph 19 as used in asso-
 ciation with operations of the present invention is usual,
 that is, the gas chromatograph 19 provides chromatograms of
 hydrocarbon components in the water, emphasis of descrip-
05 tion is placed on isotopic analysis system 20 of the
 present invention.

 FIG. 3 illustrates how easily isotopic capture
 system 20 can be transported aboard a vessel 11 in either
 an assembled or unassembled state and be effectively oper-
10 ated in any type of environment. And since all functions
 associated with the isotopic capture system 20 occur
 aboard a sea-going vessel often in a hostile environment,
 constructional aspects related to portability, reliability
 and ruggedness are of some importance.

15 As shown, the capture system 20 includes a
 series of trapping and stripping stations 35-40 mounted to
 upright front panel 50 of carry-on capture box 51. The
 box 51 includes side, top and back panels 52, which form
 an enclosure interior thereof, wherein equipment associa-
20 ted with operations can be stowed either temporarily as
 during transport (or permanently as required). Carry
 handle 53 facilitates hand-transport of the box 51 to and
 from the vessel. Note also that the front panel 50
 intersects bottom panel 58 near its center. Hence, not
25 only can the operator use bottom panel 55 as a floor for
 equipment associated with stations 35-40, but also he can
 place a separate cover 54 (shown in phantom line) in
 attachment with the panels 52, 58 as when transport of
30 the box is required. In that way, the equipment compris-
 ing the stations 35-40 can be protected against breakage
 during transport. Note that the cover 54 has extending
 side and top panels 55 of reverse orientation with respect

01 to the shape provided the side, top and bottom panels.
Result: Disconnectably connecting hinges 56 can be
aligned with mounts 57 to releasably attach the cover 54
with respect to the panels 50, 52 and 58.

05 FIG. 4 illustrates operation of stages 35-40 of
system 20 in more detail.

Assume the operator has allowed dissolved gases
to enter the system 20 via valve 60 to station 35 to begin
operations.

10 The key to isotopic operation of system 20 lies
in quantitative oxidation of the dissolved gases as within
oxidation station 39 and subsequent collection at station
40. These operations occur after sinusoidal travel of the
dissolved gases via the intermediate stations 35-38 as set
15 forth below. The usual flow rate of the dissolved gases
within system 20 is about 30 microliters per minute.
The amount of collection at station 40 is dependent on the
methane concentration in the sample sea water, the flow
rate of the air carrier system, and the separation effi-
20 ciency of the vacuum separation system aboard the vessel.
If the normal methane concentration is 100 microliters per
liter of water, and the extraction rate of the drone is 7
liters per minute at depth, then 40 minutes will be needed
to collect 20 microliters of the gas of interest at
25 station 40, assuming extraction efficiency at the vacuum
system of 75%. In the vicinity of modest gas seeps, the
concentration of methane can easily approach 1000 micro-
liters per liter of water (STP) particularly in deep
water.

30 Briefly with reference to FIG. 4, the wet air
carrier and the dissolved gases from the vacuum separation
center enters station 35 at inlet 61. At the station 35,
the gases percolate downwardly through the series of
absorbent materials 62 supported in upright tube 63.

35

01 Materials 62 remove both water vapor and molecular carbon
dioxide. Next, the carbon monoxide which also occurs in
variable abundance in water, is removed at station 36 by
oxidation to carbon dioxide; the latter is subsequently
05 removed from the carrier system after passing via valve 64
to station 37. The carrier gas stream containing both air
gases and low molecular weight alkanes is then directed to
stage 38 after passage through valve 65.

At the station 38, the lower, mid- and higher-
10 range molecular weight hydrocarbons are removed, that is,
all hydrocarbons above C₁. The remaining methane then
enters station 39 where it is oxidized to carbon dioxide.
After passage through valve 66 the latter is subsequently
retained at station 40. The details of operation of
15 stages 35-40 will now be presented in more detail below.

STATION 35.

Purpose: To trap water vapor and molecular
carbon dioxide in the gas phase of the separated sample.
The station 35 is constructed of the tube 62 attached to
20 the front panel 50 of capture box 51 upright position, see
FIG. 3, the tube 63 usually being constructed of standard
wall Pyrex (registered Trade Mark) tubing. A bed of absorbent materials 62 is
held in place by small wads of glass wool 67 placed at the
ends of the tube 63. The absorbent materials 62 are con-
25 ventional and are available in the industry for removing
water vapor (viz calcium chloride, CaCl₂) and for absorb-
ing molecular carbon dioxide (namely, sodium hydroxide,
Na(OH)). Mixture ratio 1:1.

STATION 36.

30 Purpose: To remove carbon monoxide which occurs
in variable amounts in sea water using a flow-through
furnace system 70.

As shown in detail FIG. 5, furnace 70 consists
of a helix 71 wound about a quartz tube 72, the tube being
35 previously wrapped with a single layer of asbestos tape

01 73. The helix 71 is then covered with additional asbestos
tape 74 as well as with a glass wool matting 75 forming a
sidewall into which a thermocouple (not shown) can be
05 inserted. The ends of the helix 71 and the thermocouple
are electrically connected to thermal controller 76 of
FIG. 4. The controller 76 supplies regulated power to the
furnace as a function of temperature. At the remaining
annular space between the sidewall of the wool matting 75
and the glass wall of the tube 70 are positioned cupric
10 oxide wire 77 along with platinized alumina pellets 78.
The pellets 78 are placed at the downstream end of the
tube 70, and held by quartz wool, not shown. The furnace
operates about 125°C whereby the carbon monoxide is
oxidized to carbon dioxide.

15 STATION 37.

Purpose: To remove carbon dioxide previously
generated at station 36. Station 37 is constructed of a
glass tube 80 filled with an absorbent material 81 such as
sodium hydroxide, NaOH, held in place with glass wads
20 82, and is similar in construction to station 35 previ-
ously described.

STATION 38.

Purpose: To remove lower-, mid- and high-range
molecular weight hydrocarbons. Station 38 is constructed
25 of a metallic tube 83 filled with inert chromatographic
glass beads 84 in a size range of 60-80 mesh held in place
by glass wool wads (not shown). When removal of low- mid-
and high-range hydrocarbons is desired (removal of all
hydrocarbons above C₁) a bath 85 consisting of liquid
30 argon (-180°C) or isopentane-liquid nitrogen slush
(-160°C) is placed circumferentially about the bed of
beads 84.

If desired, station 38 can be by-passed via
valve 65. Hence, clean-up of the tube 83 can be facili-
35 tated, i.e., a clean gas can be passed via valve 65

01 through the tube 83 while the bed of beads 84 is heated to
a temperature of about 200-300°C for several minutes.
Note that at temperatures above 400°C however, the beads
84 will soften.

05 STATION 39.

Purpose: To oxidize the methane of interest to
carbon dioxide. The station 39 includes a furnace 86. It
is similar in design and construction to the furnace 70 of
station 36 shown in detail in FIG. 5, except that furnace
10 86 operates at temperatures in excess 600°C in a catalyti-
cally aided reaction. The temperature preferred is about
650°C. Result: methane is quantitatively converted to
carbon dioxide at a lower operating temperature than would
be normal, due in part to the effect of the cupric oxide
15 helix and platinized alumina beads used as catalysts
within the furnace 86. In this regard, it should be noted
the combustion efficiency of the furnace 86 at different
ranges and temperatures has been tested. A standard
hydrocarbon mixture consisting of say 66 parts per million
20 methane, 10 parts per million C_2H_6 , 10 parts per million
 C_3H_8 , and 10 parts per million C_4H_{10} in a helium carrier,
was passed through furnace 86 at 30 milliliters per min-
ute. The test was repeated at 20 milliliters per minute.
The vent of the furnace 86 was connected to a gas chromat-
25 ograph equipped with a flame ionization detector. At the
maximum sensitivity of the detector (approximately .5
parts per million CH_4 equivalent) with the above mixture
flowing through the furnace 86 at the above rates, no
methane was detected at the detector. The condition con-
30 tinued as long as combustion furnace 86 was above 600°C,
say preferably 650°C. Larger amounts of methane were
syringe-injected (say up to 400 microliters of methane)
into the furnace with similar results. Thus, it is
concluded that furnace 86 will quantitatively oxidize

01 all methane concentrations that are likely to be obtained
in the field.

STATION 40.

05 Purpose: To trap microliter quantities of
carbon dioxide oxidized at station 39.

Station 40 is constructed of a glass tube 87 bent into a U-shape. Its arms connect to transfer tubes 88 (and its inlet and outlet, respectively) which facilitate gas passage through the tube 87. The tube 87 is also filled with inert chromatographic grade glass beads 89 of average size, say 60-80 mesh forming a trapping bed. Beads 89 are held in place by wads of glass wool (not shown). Collection of the carbon dioxide is effected by immersing the tube 87 and beads 89 in a bath 90 of either liquid argon at -180°C or an isopentane-liquid nitrogen slush at -160°C . Note that at the outlet of the station 40, the transfer tube 88 connects via valve 91 to either (i) flow meter 92 and vent 93 or (ii) to a vacuum pump (not shown). During collection, item (i), above, is connected to the tube 87. After the collection is complete, the valve 91 is operated to connect the interior of the tube 87 to the vacuum pump and the latter is turned on. The transfer tubes 88 are then sealed by heating them with a small oxy-propane torch. At a mass spectrometer site, the contents of the tube 87 (carbon dioxide) and impurities, if they exist, (air gases, water vapor primarily) are introduced into a vacuum line where the carbon dioxide is purified prior to isotopic analysis. Prior to reusing the tube 87 and beads 89, both are heated to $200-300^{\circ}\text{C}$ in the stream of clean air to remove organic contaminants. Note that cryogenic trapping by bath 90 can present some problems if the bath temperatures are not maintained within a range of -160 to -180°C . For example, it has been found that at higher temperatures (say -125°C) using an isopentane-liquid nitrogen slush, the carbon dioxide

1 can break through the tube 87 to vent 93 at modest flow
rates, say 16 milliliters per minute. At lower temp-
eratures, say -196°C , oxygen can condense on the beads
89 interrupting the carrier flow. Carbon dioxide has been
5 found quantitatively to be retained on the beads 89 at
 -160°C using an isopentane-liquid nitrogen slush, for 25
minutes at flow rates of about 100 milliliters per
minute.

Thus, at air carrier flow rates of 20-30 milliliters
10 per minute, the carbon dioxide will be retained for
periods of two hours or more. Moreover, at -180°C , the
retention time of carbon dioxide will undoubtedly increase
if liquid argon (-180°C) is used.

EXPERIMENTAL DATA

15 An investigation of isotopic fractionation associat-
ed with system 20 of FIG. 4, has been undertaken, such
investigation utilizing standard 5% methane-argon and 10%
methane-nitrogen mixtures. Results of isotopic exam-
ination are as set forth below in Table I.

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-14-
TABLE I

Sample No.	Std	Vol. Inj.	Recovery %	Delta ¹³ C (PDB) o/oo
HC-11	5% CH ₄ /Ar	50	100	-39.31
HC-12	5% CH ₄ /Ar	50	100	-39.27
HC-13	5% CH ₄ /Ar	100	100	-36.36
HC-14	5% CH ₄ /Ar	100	100	-39.57
HC-23	10% CH ₄ /N ₂	100	100	-26.07
HC-24	10% CH ₄ /N ₂	100	100	-25.45
HC-25	10% CH ₄ /N ₂	100	100	-25.53
HC-26	10% CH ₄ /N ₂	100	100	-26.73
Ref-1	10% CH ₄ /N ₂	-	100	-30.50
Ref-2	10% CH ₄ /N ₂	-	100	-28.11
Ref-3	10% CH ₄ /N ₂	-	100	-29.13

1 Samples HC-11 through HC-14 show good agreement
and demonstrate a high level of precision at two concen-
tration levels of 50 microliters and 100 microliters of
the carbon dioxide (STP). Mean and standard deviations of
5 the delta ^{13}C composition were $-39.38 \pm .13$. Reference
samples have not yet been analyzed.

 Samples HC-23 through HC-26 and reference
samples 1-3, provide similar results except the delta ^{13}C
distributions were systematically "lighter" by a value of
10 $-3.57 \text{ }^{\circ}/\text{ }^{\circ}$. There is, at present, no explanation for the
systematic bias noted above.

 In a parallel study, sea water saturated with a
methane/argon mixture at two temperatures (18°C and 2°C)
was stripped of its dissolved methane. The dissolved
15 methane was then condensed to carbon dioxide at an air
carrier flow rate of 30 milliliters per minute. Approxi-
mately 30% of the methane was removed from solution in 10
minutes. Results of isotopic examination are set forth
below with reference to Table II.

20

TABLE II

Sample No.	Std	Vol. Inj.	Recovery %	Delta $^{13}\text{C(PDB)}$ $^{\circ}/\text{ }^{\circ}$
25 HC-15	5% CH_4/Ar	1495 ^a	32	-40.16
HC-19	5% CH_4/Ar	2180 ^a	30	-39.17

a = saturation concentrations in 1 liter sea water at 18°
30 and 2°C .

 Note that samples HC-15 and HC-19 represent
partially stripped sea water previously equilibrated with
the 5% methane/argon mixture, the same mixture used to
obtain the results in Table I. But also note that the
35 results of Table II are not significantly different than
those obtained for samples HC-11 through HC-14 of Table I

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01 which were achieved using the same source tank of methane/
argon. Of particular interest in Tables I and II, is the
fact that the fractionation associated with incomplete
stripping of the samples HC-15 and HC-19 in Table II is
05 less than 1‰. This is expected since the fractionation
factor is about 1.03 (or the square root of 17/16). That
is to say, for small methane stripping efficiencies (less
than 1%), the resulting carbon dioxide will be 3‰
lighter than the parent methane. At 30% recoveries, the
10 fractionation is within experimental error.

Isotopic fractionation is dependent on vapor
pressures of $C_{12}H_4$ and $C_{13}H_4$, each of which being temper-
ature dependent. At temperature extremes likely to be
encountered at the surface of the earth (-2°C to 45°C),
15 isotopic fractionation associated with gas extraction
should be within experimental error. It is also worth
noting that success of the present invention does not
depend on the absolute delta C^{13} values provided for
either the biogenic or thermogenic methane fractions.
20 Relative changes in a local region are the focus of
interest.

1 CLAIMS:

1. A method of on-site collection and examination of small concentrations of a carbonaceous gas dissolved in a body of water under which there is an earth formation so as to predict hydrocarbon potential of the earth formation underlying said body of water, said formation being a source of said carbonaceous gas, said method comprising:

5 (i) at a known geographic location continuously sampling said water at a selected flow rate and at a
10 selected depth;

 (ii) continuously vacuum separating said water into liquid and gas phases;

 (iii) quantitatively separating a selected carbonaceous gas from interfering gas species in the presence of
15 an air carrier vented to atmosphere at a known flow rate; and

 (iv) quantitatively oxidizing said selected gas and then cryogenically trapping an oxidation product thereof in the presence of said air carrier so as to provide for
20 accurate isotopic examination.

2. A method according to Claim 1, wherein said carbonaceous gas of step (iii) is methane and said oxidation product is carbon dioxide.

3. A method according to Claim 1 or 2, wherein
25 the flow rate of said air carrier of steps (iii) and (iv) is from 20-30 millilitres per minute and a cryogenic capture period for trapping said oxidation product is sufficient to trap at least 10 microlitres thereof.

4. A method according to Claim 1, 2 or 3, wherein
30 said cryogenic trapping in step (iv) is effected at a temperature of from -160°C to -180°C at air carrier flow rates of from 20 to 30 millilitres per minute.

5. A method according to Claim 1, 2, 3 or 4, wherein step (ii) includes the sub-step of continuously
35 monitoring said gas phase in the presence of a continuously flowing air carrier at a flow rate of 20 to 30 millilitres



per minute for the presence of hydrocarbons using an ionization flame detector, step (iii) only occurring if hydrocarbons are detected by said flame detector.

6. A method according to Claim 5, wherein said monitored gas at said flame detector is methane.

7. A method according to Claim 5, wherein said monitored gas is any hydrocarbon and said selected gas is methane.

8. A method according to Claim 7, wherein said separation of gas species that might interfere with accurate trapping of said methane includes the sub-steps of:

(i) removing water vapour and molecular carbon dioxide from passing gas in the presence of said air carrier;

(ii) oxidizing said carbon monoxide to carbon dioxide;

(iii) trapping the carbon dioxide of step (ii);
and

(iv) cryogenically trapping out all low-, mid-, and high-range molecular weight hydrocarbons above C_1 .

9. A method according to Claim 7, wherein oxidation of said methane is catalytically assisted.

10. A method according to Claim 7, wherein cryogenic trapping of said methane so as to provide for isotopic examination includes the sub-steps of:

(a) interrupting venting of said air carrier to the atmosphere by connecting a downstream end to a vacuum pump;

(b) with said vacuum pump operating, sealing both upstream and downstream ends of the cryogenic trapped carbon dioxide; and

(c) removing said trapped carbon dioxide to a mass spectrometer for isotopic examination.

11. A method according to Claim 10, wherein said isotopic examination provides a delta ^{13}C value.

12. A method of on-site collection and examination of small concentrations of methane dissolved in sea water



so as to predict hydrocarbon potential of an earth formation associated with generation of said methane, said method comprising

- (i) at known geographic locations continuously sampling said sea water at depth;
- (ii) continuously vacuum separating said collected sea water into liquid and gas phases;
- (iii) continuously monitoring said gas phase of said separated water for the presence of hydrocarbons;
- (iv) if hydrocarbons are present, quantitatively separating out all interfering gas species to the detection of methane and its oxidation product, carbon dioxide;
- (v) quantitatively oxidizing said methane to carbon dioxide and then cryogenically trapping the resulting carbon dioxide in the presence of an air mixture flowing at a rate of about 20 to 120 millilitres per minute; and
- (vi) isotopically examining the carbon distribution of said trapped carbon dioxide, so as to determine biological and/or thermogenic origin of said methane.

13. A method according to Claim 12, wherein said isotopic examination of step (vi) provides a series of delta ^{13}C values indexed to known geographic locations associated with said sampling locations of step (i).

14. A method according to Claim 12 or 13, wherein step (iv) includes the following sub-steps performed in sequence in the presence of an air carrier having a flow rate between 20 and 120 millilitres per minute:

- (a) removing water vapour and molecular carbon dioxide from said gas phase of said separated water, by passing same through a bed of absorbent materials;
- (b) oxidizing any carbon monoxide to carbon dioxide by passing said gas phase through a catalytically-aided oxidation oven, maintained at mid-temperatures;
- (c) removing the carbon dioxide of step (b) by passing the gas phase through another bed of absorbent material; and



1 (d) cryogenically trapping out all low-, mid-, and
high-range molecular weight hydrocarbons above ^{13}C , by
passing the gas phase through an inert bed of beads
maintained at extremely low temperatures, whereby all
5 interfering gas species in said gas phase are removed
prior to oxidation of said methane.

15. A method according to Claim 14, wherein said
bed of absorbent materials of sub-step (a) is a mixture
of CaCl_2 and NaOH .

10 16. A method according to Claim 14 or 15, wherein
said bed of absorbent material of sub-step (c) is NaOH .

17. A method according to Claim 14, 15 or 16,
wherein cryogenic-trapping temperatures of sub-step (d)
for said interfering hydrocarbons is in the range from
15 -160°C to -180°C .

18. A method according to any one of Claims 12 to
17, wherein step (v) includes the sub-steps of:

(a) oxidizing said methane to carbon dioxide by
passing said methane and air mixture through a catalytic-
20 ally-aided oxidation oven maintained at a selected
temperature range, and

(b) cryogenically trapping out said carbon dioxide
of sub-step (a) by passing said carbon dioxide through an
inert bed of glass beads maintained at extremely low
25 temperatures.

19. A method according to Claim 18, wherein said
cryogenic-trapping temperatures of sub-step (b) for said
carbon dioxide are in the range between -160°C and -180°C .

20. A method of on-site collection and examination
30 of small concentrations of a carbonaceous gas, substant-
ially as hereinbefore described with reference to the
accompanying drawings.

