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(54) **Title:** DEVELOPMENT OF OPTICAL METHOD FOR GAS ISOTOPOLOGUE MEASUREMENT AND PALEOTHERMOMETRY BASED ON CONCENTRATION OF METHANE ISOTOPOLOQUE ($^{13}CDH_3$)

(57) **Abstract:** The present invention is directed to the methods of (1) determining natural gas paleotemperature, origin, and maturity by measuring $^{13}CDH_3$ methane double isotopologues, and (2) optical methods to determine both $^{13}CDH_3$ and $^{13}C^{18}O^{16}O$ double isotopologues. In addition, the invention is also disclosed a method to determine carbon and hydrogen isotopes in methane, ethane and propane by using a gas chromatography followed by a combustion and optical methods.

Development of Optical Method for Gas Isotopologue Measurement and Paleothermometry Based on Concentration of Methane Isotopologue ($^{13}CDH_3$)

RELATED APPLICATION

[0001] This application claims the benefit of U.S. Provisional Applications No.60/698,100, filed July 11, 2005, No. 60/700,888, filed July 19, 2005 and No. 60/790,016 filed April 7, 2006 which are hereby incorporated by reference in their entireties including drawings as fully set forth herein.

FIELD OF THE INVENTION

[0002] The present invention relates to the field of gas isotopologue applications and measurements for both oil and gas exploration and production allocation. It is also related to broad geochemical applications for environmental, gas hydrate, and paleo climate studies.

BACKGROUND OF THE INVENTION

[0003] Because natural gases are dominated by a few simple, low molecular weight hydrocarbons, important genetic information is commonly obtained from stable carbon and hydrogen isotope ratios. Stable isotope measurements on the C1–C5 (C1, C2, C3, C4 and C5 are methane, ethane, propane, butane, and pentane respectively) hydrocarbons provide a kind of "fingerprint" which can be used to assess the nature and thermal maturity of potential source beds, the pathways by which gas migration occurred, the presence of mixed-source gases and, more controversially, reservoir accumulation and loss histories. Until the last decade or so, genetic models for natural gases were based primarily on field data collected for different gas types. These include shallow, low-temperature bacterial gases (e.g., Claypool and Kaplan, 1974; Schoell, 1977; Jenden and Kaplan, 1986; Coleman et al., 1988; Rice, 1992), higher temperature

"thermogenic" gases, often associated with oil (Galimov et al., 1970; Stahl and Carey, 1975; Schoell, 1980; Jenden and Kaplan, 1989), and coalbed and shale-hosted gases (Colombo et al., 1970; Smith et al., 1985; Rice, 1993, Martini et al., 1996, Rowe and Muehlenbachs, 1999). Papers attempting to synthesize this knowledge (Stahl, 1977; Bernard, 1978; Schoell, 1983; James, 1983; Whiticar et al., 1986; Chung et al., 1988; Schoell, 1988) still provide the backbone of most natural gas interpretations carried out in the oil and gas industry.

[0004] These empirical schemes are not without problems, however. Models developed for one basin often do not work for another, some schemes are contradictory (Jenden et al., 1988; Lorant et al., 1998), and a given data set may give rise to very different interpretations, particularly when post-generative processes such as diffusive fractionation are invoked (Jenden et al., 1993; Prinzhofer and Huc, 1995; Prinzhofer and Pernaton, 1997). The most important challenge is to define the gas maturity (at what temperature gas was formed). Thus, one of the important inventions in this disclosure is to use measure the concentration of methane double isotopologue ($^{13}CDH_4$) can provide a unique measures for gas formation temperature and environment. Methane isotopmer, $^{13}CDH_3$ (Mass 18) along with other isotopmers ($^{12}CH_3D$ and $^{13}CH_4$), have broad implications in revealing wide range of information regarding origin of natural gas, its formation temperature, age and instantaneous and cumulative patterns of gas reservoir. This important information can play significant role in gas exploration and discovery.

[0005] Another big challenge for gas isotope application towards exploration and production is to develop a field deployable gas isotope machine which can measure gas isotope right at the field of oil and gas production, mud gas logging and etc. Halliburton disclosed a first laser based isotope machine which can measure methane isotopologues by using laser based spectroscopy. However their technology is not able to measure higher hydrocarbons. Thus, in the scope of our invention disclosure, we have developed the first non-mass spectrometer based gas isotope machine which can measure methane, ethane and propane (or even higher molecular weight hydrocarbons).

[0006] The analysis of isotope ratios requires the technique to have two basic capabilities. First, the technique must have the sensitivity to detect the amount of pure isotopologues in the sample. For example, in the case of methane stable isotope analysis, in order to get 1/1,000th change of $^{13}CDH_3$ isotopologue change, because the natural abundance of $^{13}CDH_3$ is already only 5 millionth of the natural methane gas, the technique must be able to detect 1ppbV of methane $^{13}CDH_3$ isotopologue. Many modern day techniques, such as mass spectrometers (MS) and several laser based spectrometers, already have such sensitivities.

[0007] Secondly, the technique must be able to distinguish between the isotopologues of interest and the rest isotopologues and other impurities, often at much higher concentration. For example, MS could distinguish different isotopologues through their differences in masses, and laser based spectrometers could distinguish different isotopologues through their differences in their optical spectra. However, nearly all of these techniques have their limitations.

[0008] MS could only distinguish isotopologues with different masses, e.g. MS could easily distinguish between $^{12}CH_4$ (mass 16) and $^{13}CH_4$ (mass 17), based on their mass, but it could not distinguish between $^{13}CH_4$ (mass 17) and $^{12}CDH_3$ (mass 17) because they have the same mass. Also, MS has huge problems when the isotopologue of interest has the same mass as the back ground molecule mass, e.g. $^{13}CDH_3$ (mass 18) has the same mass as H_2O (mass 18) and the accurate measurement of $^{13}CDH_3$ (mass 18) is always plagued by the prevalence of H_2O in the MS instrument.

[0009] Laser based techniques distinguish individual isotopologues based on the detailed differences of each isotopologues optical spectroscopic peaks. Since each isotopologue must have its uniquely different peak positions, in principle, it is easy for laser based techniques to distinguish any pure isotopologues. However, when the technique is used to analyze one particular isotopologue that makes a rare tiny proportion of the major abundant isotopologues, it must find spectroscopic features that are not only unique to that rare isotopologue of interest, but also free of the interferences from the

major abundant isotopologues. For example, although many laser based techniques could detect 1ppbV level of pure methane isotopologue, $^{13}CDH_3$, if the pure sample is not mixed with other methane isotopologues. But, because the natural abundance of $^{13}CDH_3$ is already only 1 millionth of the natural methane gases, the absorption of other abundant methane isotopologues are often 6 orders of magnitude stronger, and are severely interfering the accurate measurement of $^{13}CDH_3$ at the unique spectroscopic features of $^{13}CDH_3$.

[0010] Such sensitive laser based sensing techniques include Frequency Modulation and Wavelength modulation (WM) that have superior signal to noise ratio, and more recently cavity enhanced techniques, such as cavity ring down spectroscopy and integrated cavity output spectroscopy that have ultra long absorption lengths. US Patents #5,528,040 (by Lehmann 6/1996) and US patent #5,912,740(by Zare et al. 6/1999) and US patent #6,795,190 (by Paul et al. 5/2004) along with many published references listed in this patent filing, detailed the various cavity enhanced absorption measurement techniques. But they did not mention or publish results about measuring the much less abundant methane isotopologues, i.e. $^{12}CDH_3$ and $^{13}CDH_3$ when they are mixed in the majority isotopologue $^{12}CH_4$. The existence of more abundant isotopologues at orders of magnitudes higher concentrations could easily make the measurement of rare isotopologue of interest almost impossible. US Patent # 7,054,008 disclosed about using cavity enhanced technique, i.e. cavity-ring-down spectroscopy, to analyze elemental atomic isotopes when the samples are atomized with microwave induced plasma. This method, although using the latest sensitive cavity enhanced absorption measurement technology, is only measuring elemental or atomic isotopes not isotopologues of molecules.

[0011] Besides using cavity to enhance absorption path length, it is also possible to use long hollow waveguide to entrain very tiny volume of sample gas and conduct absorption measurement over a long optical path length, thus increasing the absorption sensitivity while minimizing the total sample volume. US patent # 5,497,440 described about the making and property of such hollow waveguide, and published results have

demonstrated conducting FTIR measurement inside such hollow waveguide. But, no disclosures have been documented that use such hollow waveguide after GC line and analyze the isotopologues of each effluent peak after the GC line.

SUMMARY OF THE INVENTION

[0012] One aspect of the present invention is directed to the use of methane double isotopologue for new geochemistry applications, such as origin, maturity and gas generation temperature. The double isotopologue is defined as the concentration of $^{13}CDH_3$ for methane.

[0013] Another aspect of the present invention is directed to a method of using methane double isotopologue with methane traditional carbon and hydrogen isotope to determine gas generation temperature based on the theoretical calculations.

[0014] Another aspect of the present invention is directed to a method of using laser optical method to measure isotopologues such as $^{13}CDH_3$ and $^{12}CDH_3$; $H_2{}^{32}S$ and $H_2{}^{34}S$, $^{13}C^{18}O^{16}O$ and $^{13}C^{16}O_2$ in different methane gases with an accuracy reaching the sub part per billion level (ppb).

[0015] Another aspect of the present invention is directed to a method of using Gas Chromatograph (GC) and laser optical method to measure the isotopologues of methane, ethane and propane (also possible higher hydrocarbons).

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] Figure 1 shows the Infrared (IR) Spectroscopy of $^{12}CH_4$, $^{13}CH_4$, $^{12}CDH_3$, and $^{13}CDH_3$. The detail of this spectroscopy will lead to the most significant part of this invention disclosure for the measurements of double isotopologue of methane and its related isotopologues.

[0017] Figure 2. Unique absorption bands for $^{13}CDH_3$ and $^{12}CDH_3$ isotopologues, the bottom spectra is the absorption spectra of refinery gas, while the top spectra is the absorption spectra of pure $^{13}CDH_3$ isotopologue synthesized by us. The unique band at $6400cm^{-1}$ is clearly interference free from other absorptions.

[0018] Figure 3. Spectra of $^{12}CH_4$ (top), $^{12}CDH_3$ (middle) and $^{13}CDH_3$ (bottom). The unique bands for $^{13}CDH_3$ and $^{12}CDH_3$ are located at 2200cm-1 and 3400cm-1. We also discovered the overtone bands at 6300cm-1, i.e. telecom band, for these two isotopologues.

[0019] Figure 4. ICOS spectra showing M18 peaks in refinery gas recorded at 1554nm. The red line is pure M18 absorption spectra. With ICOS, the M18 of concentration could be measured without interferences from other abundant hydrocarbons to an accuracy of sub ppbV level.

[0020] Figure 5. M17 single pass spectra (red) v.s. refinery gas ICOS spectra (black).

[0021] Figure 6. In schematic 1, the process of detecting isotopologue ratios in hydrocarbons is illustrated. The hydrocarbon mixture is injected (via a sampling loop) into the GC column and separated into C1, C2, C3, and higher molecular weight species. After going through a combustion converter (it may be based on a flame-ionization detector, or using gas oxidant or solid oxidant such as CuO/NiO), all the hydrocarbon species are converted to CO_2 and H_2O and flow into the IR absorption detector. The IR absorption detector, with the laser wavelengths tuned to isotopic-specific lines, then measures the isotopologue concentrations of that species through their respective losses.

[0022] Figure 7. In Schematic 2, the details of one of the IR absorption detectors, e.g. CRDS, are illustrated. It consists of a sealed, high-finesse resonant cavity that has a small volume to minimize peak broadening. It also has inlet and outlet holes to allow the

GC effluent to enter and exit the detection cavity cell. It is temperature regulated to avoid condensation. The narrow-bandwidth lasers are combined and delivered into the resonant cavity either through commercial fiber optics (e.g., DWDM wavelength combiners) or free space optics (beam splitter with special coatings to do the same). On the output side the single detector could be used, and the data collected will be synchronized with external laser wavelengths.

[0023] Figure 8. In Schematic 3, the details of the detector using laser as the light source are illustrated. Here, hollow fiber loop is used as the beam path for both IR laser and GC effluent, it has a volume of much less than 1mL even when the single round beam path is quite long, e.g. 1m. The hollow tube is coated with special coating inside that provides a low loss pathway for IR light from 2μm to 10μm. The IR light is focused into the hollow tube from the entrance port, and the transmitted IR light coming out of the hollow tube is directed toward a detector.

[0024] Figure 9. GC effluent peaks for Methane (C1), Ethane (C2) and Propane (C3) mixture before (top figure) and after (bottom figure) the hollow tube assembly. The peaks still maintain their shape and sharpness.

DETAILED DESCRIPTION OF THE INVENTION

[0025] *THEORETICAL VALIDATION OF $^{13}CDH_3$ CAN BE USED AS PALEO THERMOMERS*

[0026] The fundamental concept for our approach to quantifying the abundance ^{13}C-D and ^{13}C-^{18}O molecules in methane and CO_2 is based on the temperature dependence of the following equilibrium expressions for isotopic fractionation (Equations 6 and 7). Thus the change in the relative abundance of the individual isotopologues in Equations (6) and (7) might provide us with unique information about the temperature or environment of gas formation.

Methane (CH_4): $$^{13}CH_4 + CDH_3 = CH_4 + ^{13}CDH_3 \quad (6)$$

Carbon Dioxide (CO_2): $$^{13}CO_2 + C^{18}O^{16}O = CO_2 + ^{13}C^{18}O^{16}O \quad (7)$$

[0027] For given ^{13}C and D concentrations of N_1 and N_2, the stastistical abundance of $^{13}CDH_3$ is simply N_1*N_2. However, thermal equilibrium governed by Eq. (6) could substantially alter this number. Assuming an additional X amount of $^{13}CDH_3$ is formed, we have:

$$K_{sp} = \frac{(1-X)X}{(N_1 - X)(N_2 - X)} \quad (8)$$

where K_{sp} is the thermal equilibrium constant of Equation (6). Since $1 >> N_1, N_2 >> X$, we have:

$$X = K_{sp} N_1 N_2 \quad (9)$$

[0028] Therefore, the actual $^{13}CDH_3$ concentration, combining the statistical and thermal equilibrium effects, becomes $(1+K_{sp})*N_1*N_2$.

K_{sp} at temperature T is related to the Gibb's Free Energy difference ($\Delta\Delta G$).

$$K_{sp} = \exp(\frac{-\Delta\Delta G}{RT}) \quad (10)$$

[0029] From first-principles calculations, $\Delta\Delta G$ can be determined by calculating the Gibb's Free Energy changes (ΔG) of each component in Equation (6).

$$\Delta G = E_0 + ZPE + \delta H(T) - T * \delta S(T) \quad (11)$$

where E_0 is total electronic energy, ZPE is the zero-point energy correction, $\delta H(T)$ and $\delta S(T)$ are the enthalpy and entropy changes from T=0 to T, and:

$$\Delta\Delta G = \Delta G(CH_4) + \Delta G(^{13}CH_3D) - \Delta G(^{13}CH_4) - \Delta G(CH_3D) \quad (12)$$

[0030] Molecular modeling based on Quantum Mechanics Density Functional Theory (DFT) can be applied to determine the Gibbs' Free Energy of each isotopic compound. Using the DFT/B3LYP/cc-pVDZ(-d)+ calculations, we have quantified the temperature effect on the equilibrium constant for the equilibrium reaction described in Equation 6, and the results of these calculations are shown in Figure 5. From these

calculations, we can see that thermal equilibrium of the Equation 6 favors the double-isotopologue $^{13}CDH_3$ formation, while increasing temperature decreases its concentration. Furthermore, the calculation also predicts the detection resolution of the $^{13}CDH_3$ concentration change per 50 ^0C is on the order of $\sim 10^{-9}$. It is not clear at present time whether the natural gas will be randomly populated or if it might follow equilibrium conditions. The relative concentration change in $^{13}CDH_3$ will provide us with valuable information about gas formation temperature (paleothermometer). For example, if we choose a gas with a carbon isotopic composition of -30‰ and a deuterium isotopic composition of -120‰, then this gas could potentially be generated by one of three different sources. One possibility might be from a mixture of biogenic and shale gases. Secondly, it is possible to generate such isotopic compositions from early shale gases. Lastly, this could also be generated from secondary cracking of oil. However, if we can measure the concentration of $^{13}CDH_3$, we then can determine the gas formation temperature, and when integrated with other geologic data determine other information about the origin of the gas.

[0031] *Infrared (IR) Measurement of Methane Isotopologue Spectra* – In order to calibrate our CRD system, one needs to have IR spectra for $^{13}CDH_3$. However, there is no database available. In the past year, we have combined our theoretical and experimental efforts to determine the spectral changes in IR intensity related to isotopic methane elements. Methane (CH_4), consisting of 5 atoms, has a total of 15 degree of freedom. Among them, there are 3 translational, 3 rotational and 9 vibrational degrees of freedom. Both CH_4 and $^{13}CH_4$ have T_d symmetry, and when one of the H-atom is replaced by D, the symmetry is lowered to C_{3v} for both $^{13}CH_4$ and $^{13}CDH_3$. Totally 9 fundamental vibrational frequencies and their IR-intensities are calculated and listed in Table 1. For CH_4 and $^{13}CH_4$ with the T_d symmetry, these frequencies are grouped as $T_1 + E_0 + A_0 + T_2$ (A: singlet, E: doublet, T: triplet) and only T_1 and T_2 are IR-sensitive. By lowering the symmetry to C_{3v}, the triplet splits to a singlet plus a doublet, such that both $^{13}CH_4$ and $^{13}CDH_3$ have the $E_1+A_1 + E_0+A_0 + E_2+A_2$ combination. The most significant change is for the A_0 mode (the breathing mode) with a $\sim$ 650 cm^{-1} frequency shift from CH_4 to $^{13}CDH_3$. And more importantly, it has changed from IR-invisible for CH_4 to the IR-

detectable for $^{13}CDH_3$. Such a change not only creates an additional IR-peak in the fundamental region around 2200 cm^{-1}, but also generates more overtone combinations. For instance, a sum of the E_1 and A_0 yields the lower overtone at the ~3400 cm^{-1} range.

Table 1 Calculated vibrational frequencies and their IR-intensities.

CH_4		$^{13}CH_4$		CH_3D		$^{13}CDH_3$	
Frequency (cm-1)	IR-intensity (km/mol)	Frequency (cm-1)	IR-intensity (km/mol)	Frequency (cm-1)	IR-intensity (km/mol)	Frequency (cm-1)	IR-intensity (km/mol)
1365.10	10.24	1356.58	10.02	1200.34	6.77	1192.36	6.67
1365.20	10.22	1356.68	10.00	1200.37	6.75	1192.39	6.65
1365.21	10.22	1356.70	10.01	1359.76	10.99	1352.38	10.70
1547.83	0.00	1547.83	0.00	1492.96	1.90	1491.67	1.79
1547.84	0.00	1547.84	0.00	1492.99	1.91	1491.69	1.80
2991.55	**0.00**	**2991.55**	**0.00**	**2263.30**	**12.02**	**2252.37**	**12.42**
3135.31	39.58	3124.24	39.77	3034.15	11.87	3030.34	11.72
3135.31	39.66	3124.24	39.85	3135.00	39.45	3123.89	39.62
3135.45	39.67	3124.37	39.85	3135.11	39.45	3123.99	39.62

Note: Calculations are using Quantum Mechanics Density Functional Theory (DFT) at the B3LYP level with the cc-pVDZ(-d)+ basis set.

[0032] Experimentally, we have synthesized methane with a high concentration (80%) of the $^{13}CDH_3$ double isotopologue. This enables us to first measure its FTIR spectrum, and to identify the unique features that are free of interferences from other methane isotopologues by comparing with FTIR spectra from other isotopologues. This is a crucial step since the $^{13}CDH_3$ is 100 times to even 1 million times smaller in concentration than other isotopologues. Figure 1 depicts the IR-spectrum for $^{13}CDH_3$ compared to those of CH_4, $^{13}CH_4$, CDH_3. This is, to our best of knowledge, the first ever complete IR-measurement for methane double isotopologue. For the CO_2 double isotopologue ($^{13}C^{18}O^{16}O$, mass47), there are already databases of IR spectrum from 6,000cm^{-1} to 1,000cm^{-1} in HITRAN. We will use the band at 4.3 microns for CO_2 mass 47 detection. This is described in the example section below where we use hollow waveguide for the $^{13}C^{18}O^{16}O$ (mass 47) detection.

[0033] EXAMPLES

[0034] Example 1. Measurement for a refinery gas isotopologue for their generation temperature.

[0035] Detection of CH4 isotopologues and use the ratios as a paleometer for gas/oil exploration. These isotopologues include 12CH4 with Mass 16, 13CH4 with Mass 17, 12CDH3 also with Mass 17, and 13CDH3 with mass 18, The exact determination of the relative ratios of these four isotopologues will give the exact temperature at which the methane gas are formed. Measurement of CH4 isotopologues with cavity enhanced absorption techniques at unique spectra bands of CH4 isotopologues. Till now, the traditional band for detecting methane, CH4, is at 1640nm or 6100cm^{-1}, where $^{13}CDH_3$ and $^{12}CDH_3$ all have absorption bands there. However, since $^{12}CH4$ and $^{13}CH_4$ are dominant in the natural gas sample, the natural abundance of the two isotopologues, $^{12}CDH_3$ and $^{13}CDH_3$ are only ½000th to 50ppm of the regular $^{12}CH_4$ (mass 16) isotopologues, the bands there at 1640nm are all saturated with regular CH4 absorptions. Other hydrocarbons, e.g. C2H4 and C2H6 all have weak and broad absorption there as well. Such saturated absorption bands for CH4 that coexist with absoprtion bands of $^{13}CDH_3$ and $^{12}CDH_3$ prevent the accurate measurement of the much less abundant isotopologue species.

[0036] The overtone vibration bands of $^{12}CDH_3$ centered at 1558nm has never been documented before, not to mention the double isotopologue $^{13}CDH_3$'s overtone vibration band centered at 1563nm. We are the first to identify the overtone vibration bands of CDH_3 centered at 1558nm and $^{13}CDH_3$ centered at 1563nm. This band provides a unique band for measuring the much less abundant isotopologues of methane, $^{13}CDH_3$ and $^{12}CDH_3$. The absorption strength at this band is also quite strong, and provides sub-ppbV level sensitivity when measuring $^{13}CDH_3$ and $^{12}CDH_3$ isotopologues.

[0037] Similar unique bands exist for $^{13}CDH_3$ and $^{12}CDH_3$ isotopologues at 3micron or 3,200cm-1 and 4.3 micron or 2200cm-1, because they have the symmetry broken when compared to CH4 and 13CH4 isotopologues. We are the first to record

complete IR spectra of pure $^{13}CDH_3$ and $^{12}CDH_3$ isotopologues, and identify these unique bands that are free from interferences from other abundant isotopologues (see figure 3).

[0038] These unique interference free bands for $^{13}CDH_3$ and $^{12}CDH_3$ enable sensitive absorption techniques, such as cavity ring-down spectroscopy (CRDS) and integrated cavity output spectroscopy (ICOS), to directly and accurately measure the concentrations of these two much less abundant isotopologues without interferences from other abundant hydrocarbons in the natural gas sample.

[0039] Detection of $H_2{}^{32}S$ and $H_2{}^{34}S$ isotopologues

[0040] Ratio of $H_2{}^{32}S$ and $H_2{}^{34}S$ isotopologues is extremely important for both petroleum exploration and production issues. Using the S isotope ratio, one can determine if the H_2S is from organic or bacteria sulfur reduction (BSR) or thermal sulfate reduction (TSR). Traditional method for measuring the ratio of $H_2{}^{32}S$ and $H_2{}^{34}S$ isotopologues in natural gas is to use GC system first to separate pure H2S from natural gas. Then, the H_2S is converted into SO_2 and the ratios of $H_2{}^{32}S$ and $H_2{}^{34}S$ isotopologues is measured with MS detector that is tuned to measure corresponding converted SO_2 isotopologues. Now, because natural gas has a relatively absorption background free band in the 1560nm to 1610nm region, and H_2S also has relatively strong absorption at this band, it is possible to measure the H_2S isotopologues now directly without separation from natural gas.

[0041] Example 2, Measurement for C1, C2, C3 gas isotopes.

[0042] Detection of carbon and hydrogen isotopes in natural gases, or more specifically, the deviations of Carbon and Hydrogen isotope distribution in small hydrocarbon molecules, i.e. Methane (C1), Ethane (C2), and Propane (C3), could aid the determination of maturity, age and origin of natural gases. In particular, developing a field deployable isotope machine so one can measure the gas isotope on site will help for production location, well logging and etc. Currently the technology of measure gas isotope is mainly using isotope mass spectrometer. Halliburton disclosed a first laser based isotope machine which can measure methane isotopologues by using laser based spectroscopy. However their technology is not able to measure higher hydrocarbons. We need to accurately measure the isotopes of carbon and hydrogen in these hydrocarbons. The working horse of detection of the isotope deviations up to now is the mature GC/MS system. For example, CO_2 has several different effluent, such as $^{13}CO_2$, $^{12}C^{18}O^{16}O$ and $^{13}C^{18}O^{16}O$ isotopologues. These isotopologues all appear after GC separation and combustion as a single peak. Traditionally, only Mass Spectrcopy (MS) detector could measure each isotopologue's mass provided that they have different mass. However, in a GC/MS system, special vacuum system for MS detector prevents the field application of such instrument.

[0043] Now, with online GC IR absorption detectors described below, we could measure the isotopologues' concentrations without MS detection system. This provides a field deployable system for such analysis.

[0044] In the online GC IR detectors, by tuning the IR light to the absorption band of the GC effluent, the absorption loss measured inside the hollow tube or the cavity could be used to quantitatively detect the concentration of GC effluent. Because the absorption bands for different isotopologues are different, such detector combination could not only detect total concentration of single effluent by measuring the absorption

peak total area, but could also measure the concentrations of each isotopologue within an effluent peak accurately.

[0045] In schematic 1, the process of detecting isotope ratios in hydrocarbons is illustrated. The hydrocarbon mixture is injected (via a sampling loop) into the GC column and separated into C1, C2, C3, and higher molecular weight species. After going through a combustion converter (it may be based on a flame-ionization detector, or using gas oxidant or solid oxidant such as CuO/NiO), all the hydrocarbon species are converted to CO_2 and H_2O and flow into the IR absorption detector. The IR absorption detector, with the laser wavelengths tuned to isotopic-specific lines, then measures the isotope concentrations of that species through their respective losses. Take CH_4 for an example, it will be the first major peak eluded from the GC column. After its complete conversion into CO_2 and H_2O in the combustion converter, it flows into the IR absorption detector while maintaining its peak shape. With laser wavelengths tuned to $^{12}CO_2$ and $^{13}CO_2$, i.e. the band at 4.3μm, the detector measures the concentrations of each and the ratio is obtained. The same applies to C_2H_6, C_3H_8, and other species, *without* the need to switch laser wavelengths, since they are all converted to CO_2 and H_2O. Thus here lies a major advantage of this approach versus a direct spectroscopic method. In that method, every species would require a pair of laser wavelengths, the number of lasers quickly multiplies, not to mention spectral congestions in hydrocarbon species beyond C2 would render this approach useless since it would be impossible to find isolated spectral lines free from overlapping lines from the other isotope species. *In our approach, one pair of laser wavelengths can measure the isotope ratios of all hydrocarbon species.* However, it is not our intention to preclude the direct spectroscopic method where it may be feasible. For example, discreet and well-isolated peaks can be easily located for C1 and C2 species. Thus it might be more advantageous to use the IR absorption methods directly without GC separation to measure the isotope ratios in C1 and C2 species.

[0046] In Schematic 2, the details of one of the IR absorption detectors, e.g. Cavity Ring-Down Spectroscopy (CRDS), are illustrated. It consists of a sealed, high-

finesse resonant cavity that has a small volume to minimize peak broadening. It also has inlet and outlet holes to allow the GC effluent to enter and exit the detection cavity cell. It is temperature regulated to avoid condensation. The narrow-bandwidth lasers are combined and delivered into the resonant cavity either through commercial fiber optics (e.g., DWDM wavelength combiners) or free space optics (beam splitter with special coatings to do the same). On the output side the single detector could be used, and the data collected will be synchronized with external laser wavelengths. Since the laser wavelengths of interest in general fall into those for optical telecommunications, the components can be obtained off the shelf. In this band, isotopologues of some species could be detected accurately, and H_2O has strong absorption band at 1.3μm or 7300cm-1, and could be detected with this method. This detector when coupled with GC system could be used to measure H/D isotopes in the C1, C2 and C3 accurately. It has been demonstrated the H_2O concentration could be detected at 100ppt level, and this translate into H/D ratio could be measured with an accuracy of 0.1‰.

[0047] Furthermore, the optical design is easily scalable, so that more than 2 wavelengths can be combined and separated. With this scalability, more than one pair of isotope species can be measured simultaneously with our instrument, demonstrating again the power and versatility of our approach. For example, in the case of H_2S isotope detection, tunable telecommunication lasers at H_2S bands could be combined with lasers at CH_4 isotope bands with provide simultaneous measurement of different isotopes.

[0048] A second example for GC inline IR absorption detection is the use of long hollow tubes and tunable lasers for GC effluent detection. In Schematic 3, the details of the detector using laser as the light source are illustrated. Here, hollow fiber loop is used as the beam path for both IR laser and GC effluent, it has a volume of much less than 1mL even when the single round beam path is quite long, e.g. 1m. The hollow tube is coated with special coating inside that provides a low loss pathway for IR light from 2μm to 10μm. The IR light is focused into the hollow tube from the entrance port, and the transmitted IR light coming out of the hollow tube is directed toward a detector. Such IR transmitting hollow tube product is commercially available from Polymicro LLC. It also

has inlet and outlet holes to allow the GC effluent to enter and exit the detection tube. It is temperature regulated to avoid condensation. Specially designed connectors at the entrance and exit of the hollow tube have inside diameter and other parameters matching that of the GC line, so that the GC effluents still maintain their peak shape. The results of our hollow tube in maintaining GC effluent peaks are shown in figure 4. In the detection of ^{13}C in methane, ethane and propane, tunable wavelength laser at 4.3 μm is focused into the hollow waveguide, and the laser wavelength is tuned to detect CO_2 isotopologues $^{13}CO_2$ and $^{12}CO_2$. Such lasers is now commercially available, e.g. quantum cascade laser from Alps Lasers, Switzerland, and could be deployed in the field for long term operation with minimal maintenances. In this way, carbon isotope ratios could be measured in methane, ethane and propane from natural gas samples with great accuracy in the field.

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What is claimed is:

1. A method of measuring methane double isotopologue ($^{13}CDH_3$) comprising the steps of a) measuring the presence and absorption of a first methane isotopologue and a second methane isotopologue at unique and interference-free absorption bands for the isotopologues; and

b) determining the ratio between the two methane isotopologues.

2. The method of claim 1 wherein the first methane isotopologue is $^{12}CDH_3$..

3. The method of claim 1 wherein the second methane isotopologue is $^{13}CDH_3$.

4. The method of claim 1 wherein the first methane isotopologue is $^{12}CDH_3$, and the second methane isotopologue is $^{13}CDH_3$.

5. The method of claim 4 wherein the first set of unique and interference-free absorption bands for $^{12}CDH_3$ and $^{13}CDH_3$.occurs at a wavelength region ranging from 1520nm to 1590nm.

6. The method of claim 4 wherein the second set of unique and interference-free absorption bands for $^{12}CDH_3$ and $^{13}CDH_3$.occurs at a wavelength region ranging from 3000nm to 4300nm.

7. The method of claim 2 wherein the unique and interference-free absorption band for $^{12}CDH_3$ occurs at the wavelength of 1558nm or 4300nm.

8. The method of claim 3 wherein the unique and interference-free absorption band for $^{13}CDH_3$.occurs at the wavelength of 1563nm or 3000nm.

9. The method of claim 1 wherein the absorption of the methane isotopologues can be measured through an optical method.

10. The method of claim 9 wherein the optical method is selected from the group consisting of infrared spectroscopy, frequency module technique, wavelength module technique, cavity enhanced technique, multipass cell absorption technique, and single pass absorption technique.

11. The method of claim 10 wherein the cavity enhanced technique is cavity ring-down spectroscopy (CRDS) or integrated cavity output spectroscopy (ICOS).

12. The method of claim 1 wherein the methane double isotopologue is measured to determine natural gas origin, maturity or generation paleo temperatures.

13. A method of measuring H_2S isotopologues comprising the steps of

a) measuring the presence and absorption of a first isotopologue $H_2{}^{32}S$ and a second isotopologue $H_2{}^{34}S$ at unique and interference-free absorption bands for the isotopologues, and

b) determining the ratio between the two isotopologues.

14. The method of claim 13 wherein unique and interference-free absorption bands occurs at a wavelength region ranging from 1560nm to 1610nm.

15. The method of claim 13 wherein H_2S isotopologues are measured and used as an indication for gas exploration.

16. The method of claim 13 wherein H_2S isotopologues are measured without separating H_2S from natural gas.

17. A method of measuring carbon isotope ratio and/or hydron isotope ratio in each gasterous hydrocarbon among a mixture of gasterous hydrocarbons comprising the steps of:

a) separating each gasterous hydrocarbon from the mixture using gas chromatography;

b) determining carbon isotope and/or hydrogen isotope using an optical measurement technique.

18. The method of claim 17 further comprising a step of converting each gasterous hydrocarbon effluent after being separated through the gas chromatography into CO_2 and H_2O in a combustion column.

19. The method of claim 18 wherein the CO_2 isotopologues and H_2O isotopologues are measured using an absorption detector.

20. The method of claim 19 further comprising a step of transmitting infrared light through a hollow waveguide, wherein the inlet of the hollow waveguide connects to the outlet of the combustion column and the outlet of the hollow waveguide connects to the absorption detector.

21. The method of claim 20 further comprising a step of coupling the infrared light into and out of the hollow waveguide in synchronization with each gasterous hydrocarbon effluent.

22. The method of claim 18 wherein the carbon isotopologue is selected from the group consisting of $^{12}CO_2$, $^{13}CO_2$, $^{12}C^{18}O^{16}O$, $^{13}C^{18}O^{16}O$ and any combination thereof.

23. The method of claim 18 wherein the hydrogen isotopologue is selected from the group consisting of H_2O, HDO, $H_2{}^{18}O$, $HD^{18}O$, and any combination thereof.

22. The method of claim 17 wherein the mixture of gasterous hydrocarbons include methane (C1), ethane (C2) and propane (C3).

23. The method of claim 22 wherein the carbon isotopologue for methane include methane double isotope ($^{13}CDH_3$) and the double isotopologue is measured according to methods in claims 1-12.

24. The method of claim 17 wherein the optical measurement technique is cavity enhanced spectroscopy detector, such as cavity ring-down spectroscopy (CRDS) and integrated cavity output spectroscopy (ICOS) detector, or hollow tube infrared detector.

25. The method of claim 24 wherein the cavity enhanced detector includes high fitness resonant cavity.

26. A device for measuring carbon isotope ratio and/or hydron isotope ratio in each gasterous hydrocarbon among a mixture of gasterous hydrocarbons comprising:

a) a gas chromatography column, wherein the column is used for separating each gasterous hydrocarbon from the mixture into each separate hydrocarbon effluent;

b) a combustion converter, wherein the converter converts each separate hydrocarbon effluent into CO_2 and H_2O;

c) an absorption detector, wherein the detector detects the carbon isotopologue of CO_2 and the hydrogen isotopologue of H_2O.

27. The device of claim 26 further comprising a hollow waveguide that connects the combustion column and the detector.

28 The device of claim 27 further comprising a connector that connects the combustion column and the hollow waveguide, wherein the connector synchronizes a infrared light with the hydrocarbon effluent.

29. The device of claim 26 wherein the absorption detector is cavity enhanced spectroscopy detector, such as cavity ring-down spectroscopy (CRDS) and integrated cavity output spectroscopy (ICOS) detector, or hollow tube infrared detector.

30. The device of claim 29 wherein the CRDS detector includes high fitness resonant cavity.

31. The device of claim 26 wherein the mixture of gasterous hydrocarbons include methane (C1), ethane (C2) and propane (C3).

32. The device of claim 31 wherein the separated hydrocarbon effluent is methane (C1), ethane (C2), or propane (C3).

33. The device of claim 26 wherein the carbon isotopologue is selected from the group consisting of $^{12}CO_2$, $^{13}CO_2$, $^{12}C^{18}O^{16}O$, $^{13}C^{18}O^{16}O$ and any combination thereof.

34. The device of claim 26 wherein the hydrogen isotopologue is selected from the group consisting of H_2O, HDO, $H_2{}^{18}O$, $HD^{18}O$, and any combination thereof.

35. .A method of determining natural gas origin, maturity and generation paleo temperatures comprising a step of measuring methane double isotopologue ($^{13}CDH_3$)

36. A method of measuring methane double isotopologue ($^{13}C^{18}O^{16}O$) comprising the steps of a) measuring the presence and absorption of a first CO_2 isotopologue and a second CO_2 isotopologue at unique and interference-free absorption bands for the isotopologues; and

b) determining the ratio between the two CO_2 isotopologues.

37. The method of claim 36 wherein the first CO_2 isotopologue is $^{12}C^{18}O^{16}O$.

38 The method of claim 36 wherein the second CO_2 isotopologue is $^{13}C^{18}O^{16}O$.

39 The method of claim 36 wherein the first CO_2 isotopologue is $^{12}C^{18}O^{16}O$, and the second CO_2 isotopologue is $^{13}C^{18}O^{16}O$.

40. The method of claim 39 wherein the first set of unique and interference-free absorption bands for $^{12}C^{18}O^{16}O$ and $^{13}C^{18}O^{16}O$ occurs at a wavelength region ranging from 4100nm to 4500nm.

41. The method of claim 37 wherein the unique and interference-free absorption band for $^{12}C^{18}O^{16}O$ occurs at the wavelength of 4100nm or 45300nm.

42. The method of claim 38 wherein the unique and interference-free absorption band for $^{13}C^{18}O^{16}O$ occurs at the wavelength of 4100nm or 45300nm.

43. The method of claim 36 wherein the absorption of the CO_2 isotopologues can be measured through an optical method.

44. The method of claim 43 wherein the optical method is selected from the group consisting of infrared spectroscopy, frequency module technique, wavelength module technique, cavity enhanced technique, multipass cell absorption technique, and single pass absorption technique.

45. The method of claim 44 wherein the cavity enhanced technique is cavity ring-down spectroscopy (CRDS) or integrated cavity output spectroscopy (ICOS).

46. The method of claim 36 wherein the methane double isotopologue is measured to determine natural gas origin, maturity or generation paleo temperatures.

FIGURE 1

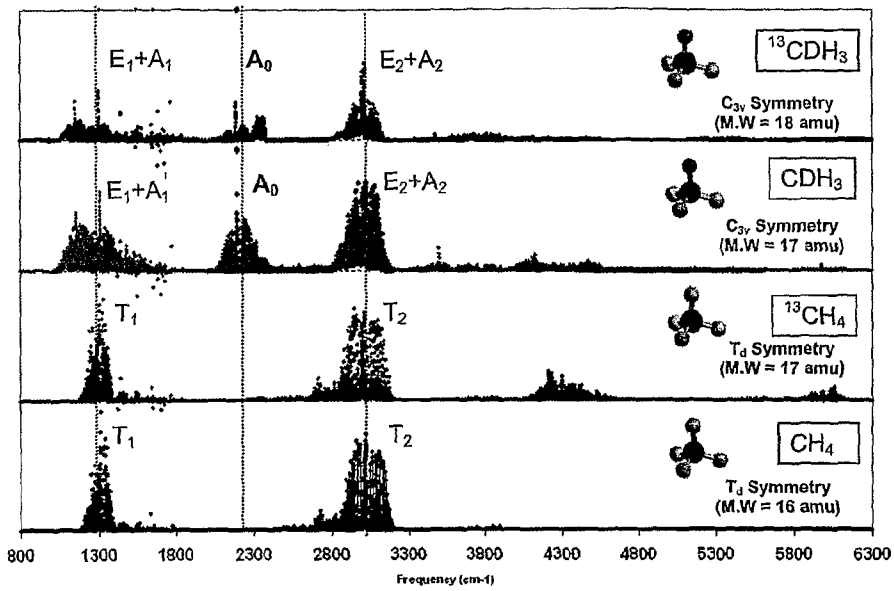


Figure 2

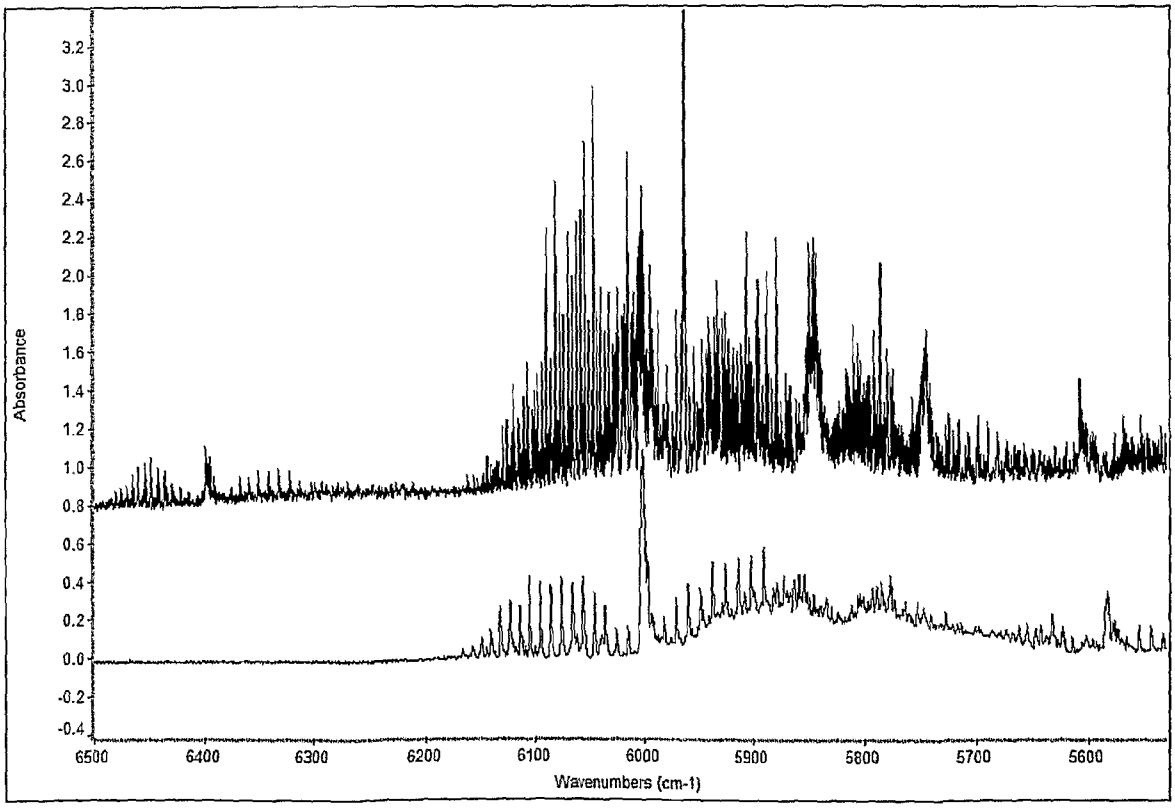


Figure 3

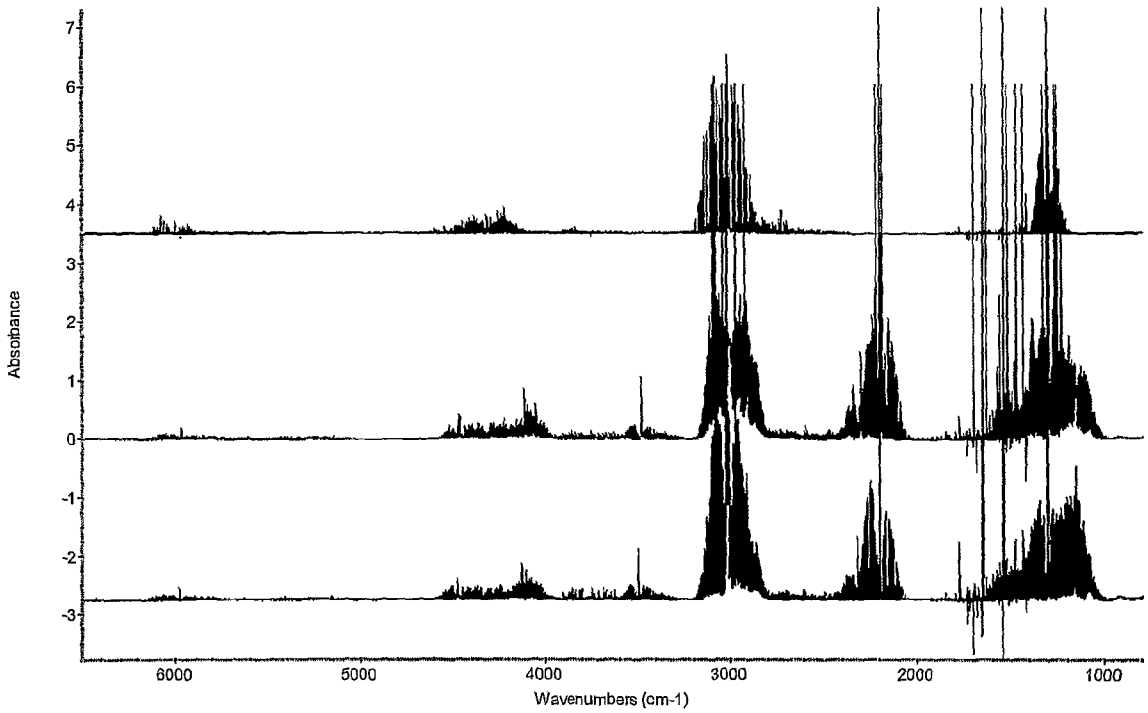

Absorbance
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3000
2000
1000
Wavenumbers (cm-1)

Figure 4.

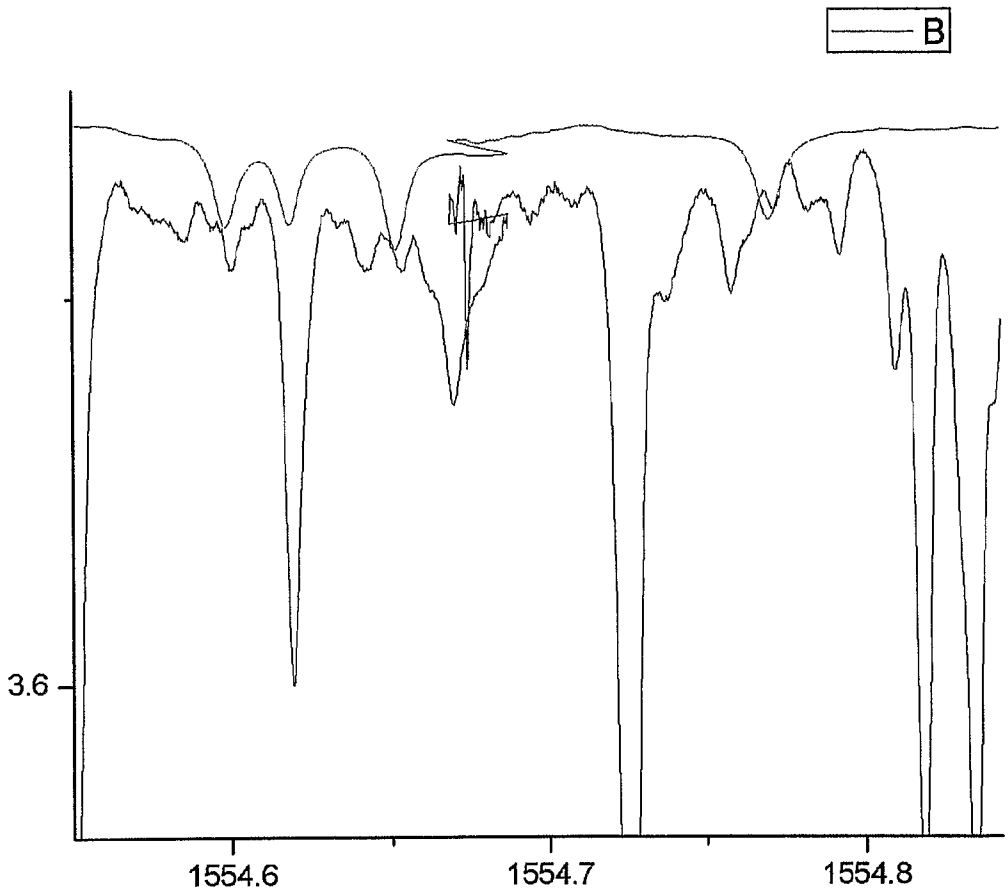


Figure 5

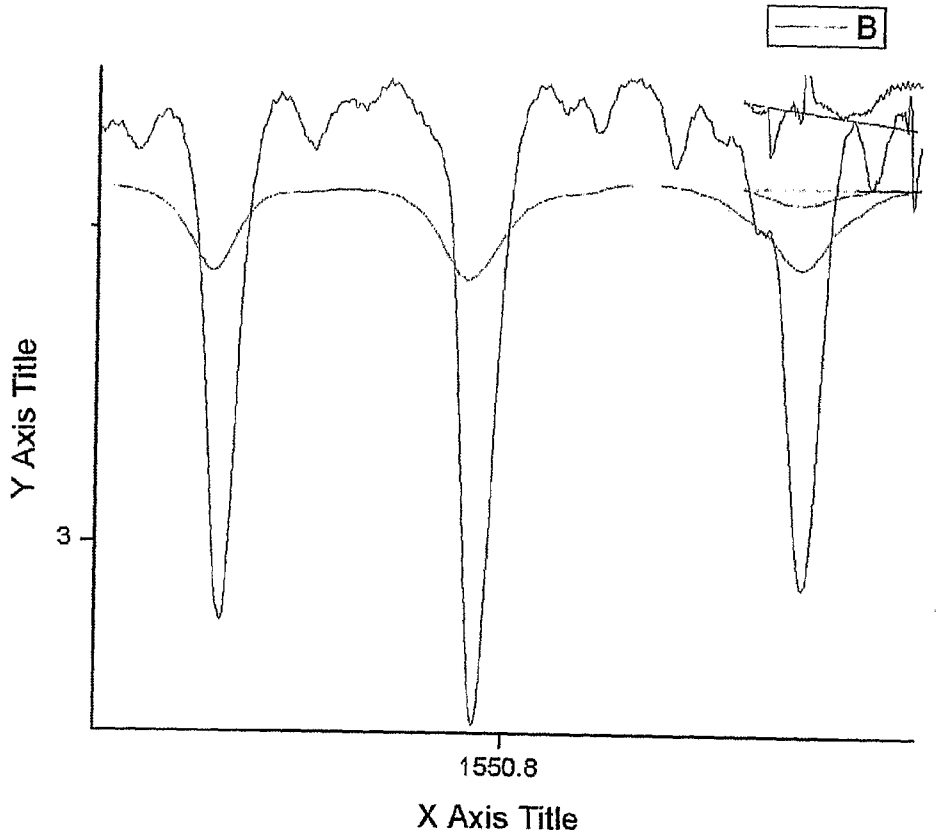
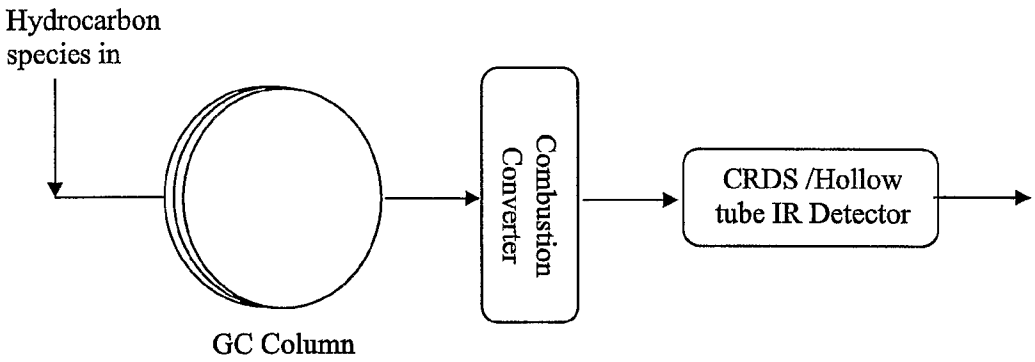
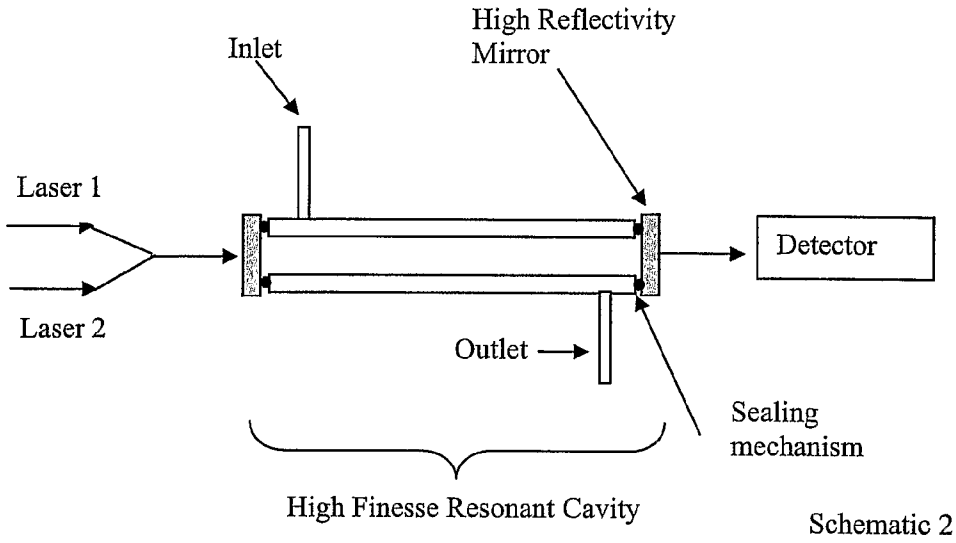


Figure 6



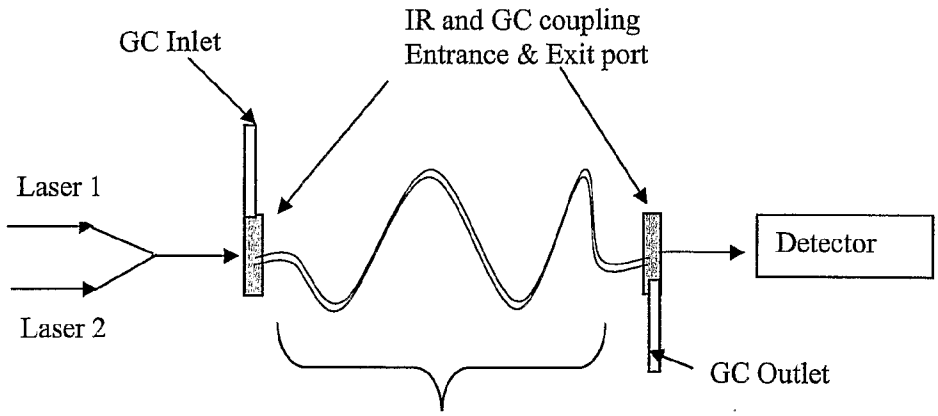
Schematic 1

Figure 7.



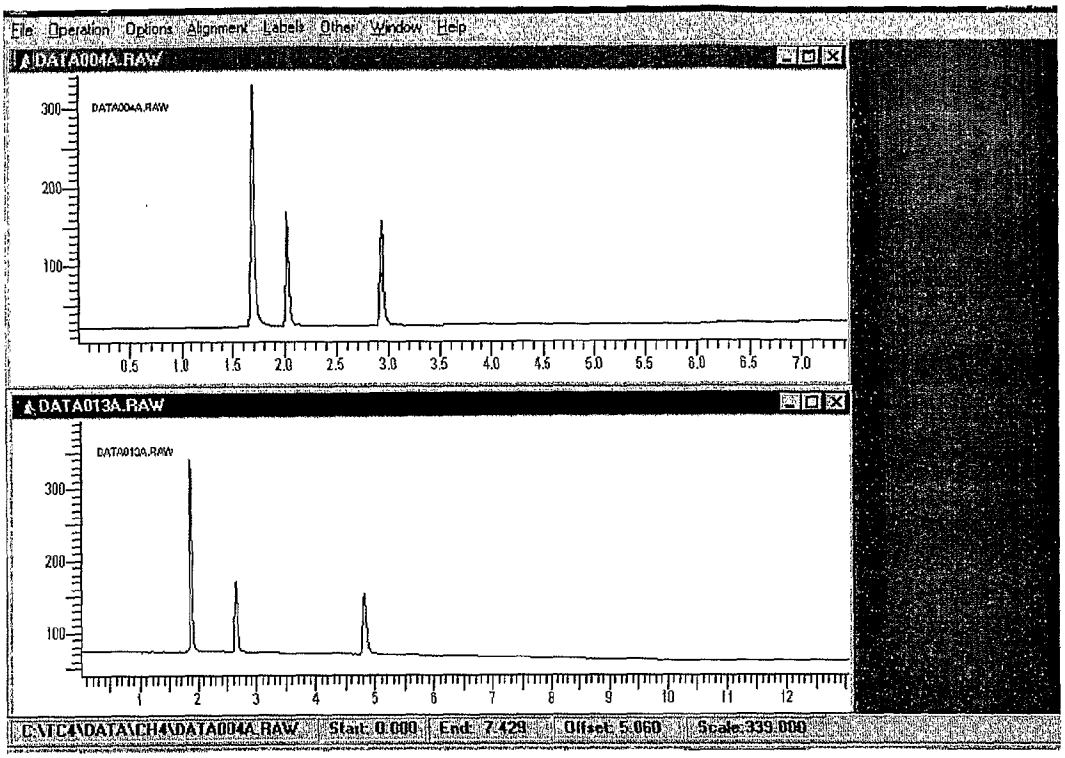
Schematic 2

Figure 8



Schematic 3

Figure 9


File Operation Options Alignment Labels Other Window Help
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DATA013A.RAW
DATA013A.RAW
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200
100
1 2 3 4 5 6 7 8 9 10 11 12
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