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Analysis of hydrogen and methane in seawater by "Headspace" method: Determination at trace level with an automatic headspace sampler

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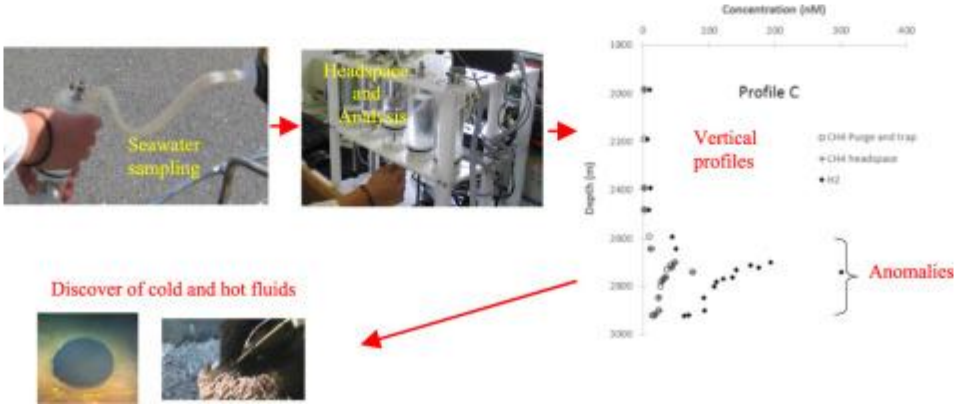
Abstract :

"Headspace" technique is one of the methods for the onboard measurement of hydrogen (H2) and methane (CH4) in deep seawater. Based on the principle of an automatic headspace commercial sampler, a specific device has been developed to automatically inject gas samples from 300 ml syringes (gas phase in equilibrium with seawater). As valves, micro pump, oven and detector are independent, a gas chromatograph is not necessary allowing a reduction of the weight and dimensions of the analytical system. The different steps from seawater sampling to gas injection are described. Accuracy of the method is checked by a comparison with the "purge and trap" technique. The detection limit is estimated to 0.3 nM for hydrogen and 0.1 nM for methane which is close to the background value in deep seawater. It is also shown that this system can be used to analyze other gases such as Nitrogen (N2), carbon monoxide (CO), carbon dioxide (CO2) and light hydrocarbons.

Graphical abstract



Highlights

► Comparison of two methods to analyze hydrogen and methane in seawater. ► Description of a compact device for onboard analysis. ► Demonstration of possible application to the analysis of other gases.

Keywords : Gas, Seawater, Headspace method

1. Introduction

Gas data are very important for localizing fluid emissions on the seafloor. For example, methane-rich plumes in deep ocean waters are known to be linked to both subseafloor hydrothermal circulation along the mid-oceanic ridges [1,2,3] and the presence of cold seeps or gas hydrate fields on continental margins [4,5]. In particular, the detection of hydrogen (H2) in plumes near the bottom show the proximity of active hydrothermal fields [6,7] and is of significant interest in the detection of highly enriched H2 fluids discovered along the oceanic ridges.

During oceanographic cruises, gas analysis of seawater from both CTD (acronym for Conductivity, Temperature, and Depth)-rosette devices equipped with 12 up to 36 bottles is a key parameter in detecting plumes. Furthermore, analysis of discrete water samples is a necessary step towards obtaining valid data when chemical sensors are used. Generally, two methods are commonly utilized to extract H2 and CH4 from seawater: the purge and trap technique [8, 9, 10] and the headspace technique with different variants [11, 12, 13, 14, 15]. In the "purge and trap" method, seawater is transferred into a stripping chamber and CH4 and H2 are completely extracted and concentrated on a cooled trap by helium (He) purging: at –80°C (activated charcoal) for CH4 trapping and at –196°C (molecular sieve) for both H2 and CH4 trapping. In a second step, by increasing the temperature, CH4 or H2 are desorbed from the trap and injected into a gas chromatograph for quantitative analysis.

The headspace method consists of putting a seawater volume in a sealed vial, a syringe or a bulb and keeping it in equilibrium with a gaseous phase (Figure 1). Using a gas-tight syringe or a headspace sampler, an aliquot of this gas phase is injected into a gas chromatographic system for separation and quantification of each component. The sensitivity can be improved by modifying the aqueous sample matrix or the ratio of headspace volume (gas phase) to sample volume (liquid phase), reducing the pressure in the headspace or heating the sample.

Due to the total extraction of gases, the first method is more sensitive but is less suitable than the headspace method for onboard measurement because it is necessary to have liquid nitrogen for H2 trapping or a cryocooler for trapping only CH4. On the other hand, it is difficult to automate it and as trapping is selective in the purge and trap technique, the headspace method offers a potential solution in the detection of different gases present in the gaseous phase. For the headspace method, in order to inject an aliquot of gas phase, an automatic sampler instead of a manual injection is preferred as it guarantees a better repeatability and is time saving. In a commercial automatic headspace sampler, the vial's volume does not exceed 20ml, which is insufficient to reach background value or CH4 and H2 in deep seawater, even with a highly sensitive detection.

This paper describes an analytical device for quantifying H2 and CH4 in seawater at trace level. Based on the use of 300 ml syringes, Valco valves, sealed solenoid valves and HID (Helium Ionization Detector), the analytical system is controlled by software with an UCI (Universal Chromatography Interface). The procedure is detailed and a comparison with a total extraction method (purge and trap) is performed. It is important to note that a particular attention has been paid to simplifying the system to obtain a lightweight and quickly operational device on an oceanographic vessel.

2. Material and methodology

2.1. Material

.Syringe for seawater sampling

Hydrocasts are performed using a rosette equipped with 16 Niskin bottles and coupled to a CTD (Conductivity-Temperature-Depth) for the acquisition of physical data. On board seawater samples are collected using a 300ml custom-made syringe (Fig. 1). The choice of syringe instead of glass vial or bulb was preferred to make the headspace with inert gas easier to carry out. These syringes have two threaded ports:

-One to allow screwing of a stainless steel plug with hole equipped of a septum. For seawater sampling, the plug is taken out and a tygon tube is connected. Once headspace is done, the hole allows an injection of a solution to prevent microbial activity. On the other hand it offers the possibility to take a sampling of gas through this septum to perform further on shore analyses for instance stable carbon isotope measurements which give information about the origin of gas.

- Another one to adapt a gas-tight valve to connect the analytical system: carrying out the gas phase and the filling of the injection loop.

The phase ratio (5: 50ml gas phase and 250ml sample phase) and total volume of syringe was chosen according to the following criteria:

. Preliminary calculation taking into account the CH4/H2 limit of detection of the HID (Helium Ionization Detector) and background values of deep seawater.

. Sufficient gas pressure and volume to fill every gas lines of the system for several injections and subsampling for onshore measurements.

. *Analytical system*

The analytical system is pictured in Fig. 2 and can be split in three parts:

. Part A: Sample selection with a 1/16”, 11 ports, ten positions valve (Valco, Houston, TX) named *Vs*.

V*s* is operated with a microelectric actuator. Syringes are placed vertically (plunger down) on an adapted plastic support to let the gas phase on top. A filter has been added between each syringe and the valve *Vs* to prevent liquid migration that could damage it.

. Part B: Injection of gas aliquots with a Valco 1/16”, 8 ports, two positions valve named *Vi*. They are injected on a packed column by means of a 2ml loop and a micro pump ensuring the purge of the injection line. The second loop, 50µl, is used for calibration and in case for highly enriched gas samples. Injection pressure is controlled by a sensor (P1).

The role of the stainless steel flask (96ml) is to bring accurately the necessary quantity of inert gas to complete the headspace.

. Part C: Separation of gases on a packed column and detection with a HID.

H2 and CH4 were separated on a 2m x 1/8” column. The choice of packing material will be discussed below. HID (Valco Pulse discharge helium ionization detector model PD-D2-I for packed columns) was chosen because it is a universal detector for the determination of both H2 and CH4. It is a non-destructive detector, with a 0.01-0.1 % ionization and it allows a connection to another detector if necessary. Furthermore, due to its high sensitivity, over one order magnitude comparatively to a Flame Ionization Detector [16, 17, 18], it is suitable for trace detection in the low ppb range. HID also has significant advantages in terms of sensitivity, ruggedness and simplicity of gas supply.

No gas chromatograph was used in our setup. As the objective is to have a compact and portable instrument, the Valco and solenoid valves, the small oven (25x12x12cm), micro pump (weight 195g) and detector are independent and integrated into the syringe support.

The technical details of the analytical system and sampling syringe are given in the supplementary content.

2.2. Methodology

Experimental procedure

For the most precise and accurate measurements, water samples, subsampled from Niskin bottles (8l) and collected into 300ml syringe, are allowed to overflow at least two volumes of seawater. A particular care is taken to exclude air bubbles during sampling to prevent contamination. Syringes containing air bubbles are resampled. 0.1ml of mercuric chloride solution (70g/l) is then injected immediately across the septum to inhibit any biological activity. Then, each syringe is connected to the analytical device in order to achieve gas phase (headspace). Firstly, the pressure in the stainless steel flask is adjusted with an electronic pressure controller. Secondly, using a specific computer program (action on Vp1, Vp3, Vp2 and micro pump), the gas line is purged with purified inert gas. Thirdly, after connecting the syringe to the valve selector *Vs*, headspace phase is created by slow displacement of the syringe plunger (Vp1 and Vp2 are opened) until atmospheric pressure is reached. Pressure is checked by P_1 sensor (+/- 0.1% full scale output; Combined Non-Linearity, Hysteresis and Repeatability). The stopcock of the syringe is closed. Then the syringe is disconnected from Vs, shaken by hand vigorously and placed during one hour on a rotary shaker at ambient temperature to achieve the equilibrium of gases between the liquid and gas phases. Note that one hour was sufficient to adjust the syringe temperature to the temperature of the laboratory. Once equilibrium is reached, all syringes are reconnected to *Vs*. Now all samples can be analyzed with a specific program according to the following steps for each sample:

.Switch on micro pump and simultaneous open Vp2 and Vp3 so that headspace can expand into the gas sampling loop.

. Close Vp2 and Vp3 during the time assigned to the loop equilibration.

. Finally, the sample is injected into the column by switching the eight-port valve *Vi* to connect the loop, still filled with sample, with the carrier gas flow and column.
The pressure reading by P1 during injection is acquired and stored on computer.

. At the end of the chromatogram *Vi* is switched to its initial position after a purge of the injection line and Vs is switched to the next position.
Moreover a standard is injected at the beginning and at the end of the sample sequence. In this way, the detector response is included in a statistical process control.

H2 and CH4 concentration determination

Once equilibrium has been established in precise conditions, the initial concentration of gas in seawater can be determined. This latter can be obtained by two methods. The first method uses a simple calibration performed by seawater enriched in given amount of gas.

The second method is based on calculations of equilibrium. Indeed, the dissolution of H2 or CH4 in seawater is governed by Henry's Law:

$$C = \alpha . p$$

Where C is the concentration of H2 in water, α is the solubility coefficient and p is the partial pressure of H2 or CH4 in the gas phase in equilibrium with the water phase.
α is called the Bunsen solubility coefficient when the partial pressure of gas (gas volume corrected to STP, 0°C and 1 atm) above the water is 1 atm. It is expressed as cm3 of gas STP per cm3 of water at the temperature of measurement.
Weiss [19] has shown that the Bunsen solubility coefficient can be expressed as a function of temperature (T) and salinity (S).
Wiesenburg and Guinasso [20] proposes a general form taking into consideration variation of atmospheric trace gases.

The constants of Yamamoto [21] for CH4 and of Crozier [22] for H2 are used to calculate the gas solubility in nM.
Schmidt [23] demonstrates experimentally that these latter constants can be used at partial pressures of about 10^{-5} atm.
They are both applicable to a salinity range of 27-40°/∞ and a temperature range of 0-30°C.
This method requires the sample salinity and temperature determination. The salinity is evaluated by the CTD data and the temperature is measured by using a constant temperature bath (± 0.1°C). Alternatively the sample can be placed in a controlled area (≤ ±1°C). This

information can be omitted if MHE (Multiple Headspace Extraction) is performed [24]. This point will be discussed in the following section.

In order to describe the different steps of calculation to have the final concentration, tables, based on three samples of widely different concentration (CH4), are included in the supplemental section. For hydrogen, the evaluation is the same except for the calculation of the Bunsen coefficient.

The second approach based on the analysis of seawater enriched in gas can be employed only if the range of salinity is not too large to avoid calibration with solutions of different salinity.

3. Results and discussion

3.1 Headspace phase

The choice of gas to make Headspace phase is important for two reasons:

. It is necessary to have on board another gas cylinder (or gas generator) in case the carrier gas is different from the headspace gas.

. Depending on the separation column, a problem of chromatographic separation of N2 and CH4 peaks may occur due to possible coelution of these two peaks if N2 is in high concentration. As in the case of seawater, it is even more critical when N2 is the headspace gas. This requires an additional detector/valve or even a second oven to remove it [25].

Considering these arguments and the fact that helium is compulsory for our detector, the latter was chosen as headspace gas.

Secondly the headspace volume must be done as accurately as possible and exempt from any contamination from the air. For this purpose, an original protocol, as presented previously was considered. The 96ml stainless steel flask was filled up with purified helium at a pressure of 1567 mbar. Helium was then drawn to the syringe by slow displacement of the plunger until atmospheric pressure was reached. According to the total volume of the syringe, the relative error on headspace volume is better than 0.5%. On the other hand, purified helium was injected to perform a blank GC analysis to identify the presence of any impurities.

In routine use, no H2 or CH4 peak was detected in the blanks.

Due to possible contamination by air during headspace carrying out, this step is very critical in any case when the CH4 or H2 concentrations in seawater are very low.

3.2 Chromatographic separation of H2 and CH4

Conditions of chromatographic separation were based on the choice of isothermal mode for two reasons:

. HID has an excessive baseline drift in temperature programming mode and a maximum temperature rating of 100°C which means that the column connected to the detector must not exceed this temperature.

. Temperature programming mode requires a specific oven with efficient temperature control. Therefore, in isothermal mode, two columns were tested: 2m length, 1/8” diameter with a molecular sieve 13X and 2mx 1/8” with Shincarbon. The molecular Sieve 13X was preferred to 5A. Indeed the molecular sieve 13X column separates permanent gases in half the time, compared to an identical column filled with a molecular sieve 5A (equal particle sizes). Note that 13X appears to have greater capacity than 5A for H2O or CO2 before its performance is affected.

Compounds are eluted consecutively as follows: H2, O2, N2, CH4.

To optimize H2, O2, N2 and CH4 separation on these two columns, a design of experiments was applied. The objective was to reduce analysis time while maintaining a sufficient resolution between the different peaks and maximizing the signal to noise ratio for H2 and CH4 to reach the lowest detection limit. Optimization was conducted with two factors, carrier gas flow and column temperature, and modeled with a Doehlert experimental design [25, 26]. Finally, optimal separation conditions were 77°C and 38.3ml/mn for Shincarbon and 35° et 39.6ml for Molecular Sieve 13X. The final choice was Shincarbon due to its highest efficiency for CH4 peak and its fast return to baseline after N2 peak. With this column it is possible to analyse CH4 at trace level combined with N2 high concentration. It is a good alternative to avoid a second oven [27]. On the other hand, if H2O does condense inside the column, 30 minutes at 250°C will dry a Shincarbon unlike the 5A & 13X which needs 300°C for 3 hours. In this case, H2 and CH4 retention time are respectively 0.7min and 2.8 min (Fig. 3).

3.3 Calibration

External calibration is automatically carried out with two standard gas mixtures:

.Standard 1 CH4 10.81 ± 0.5 ppmv and H2 8.25 ± 0.4 ppmv; confidence level 95% (Helium balance).

.Standard 2 CH4 101 ± 2 ppmv and H2 100 ± 5ppmv; confidence level 95% (Helium balance).

The HID response was explored on a range from 0.001 nmol to 15 nmol by 50µl and 2ml loops injection of standard at appropriate pressure and constant temperature. Different levels of injection pressure were obtained by changing the pumping time.

The calibration curves of H2 and CH4 (section supplementary content) are all straight lines passing through the origin with a linear dynamic range of 10^4. Concentrations in seawater up to 2µM can be thus obtained which is suitable for hydrothermal field exploration and cold seep studies. For the low peak area, the determination of the account was carried out according to plot B (range 0-1nmol) to have an accurate estimation of the gas quantity in the loop.

Equally important, noise level and signal responses were both measured under the operating conditions to evaluate the limit of detection. A noise level of 0.03mV is usually obtained and is used to calculate the limit of detection. If the detection limit is considered to be the concentration of component providing a peak height of three times the baseline noise, 0.04 ppm of H2 and 0.01 ppm of CH4 are detectable in the equilibrated headspace. Equivalence in gas concentrations in seawater are 0.3nM for H2 and 0.1nM for CH4.

From these values, the limits of quantification (3.3 x limit of detection) can be evaluated: 1nM for H2 and 0.3nM for CH4. These limits were checked experimentally by injection of 10 samples with these concentrations. For their validation two criteria were taken into account:

. Criteria of trueness: $\left|\frac{LQ-\bar{u}_{LQ}}{\frac{s_{LQ}}{\sqrt{n}}}\right|$ with LQ limit of quantification; $\bar{u}_{LQ}$ mean concentration and s_{LQ} standard deviation. The estimated value was 8 for H2 and 6 for CH4 and it is less than 10, the critical value. It means the chosen LQ are true.

. Criteria of precision: R.S.D.= s_{LQ} / LQ in % . The estimated value are 11% for H2and 8% for CH4 less than 20% (limit: 5 s_{LQ}< LQ). According these two criteria the LQ are acceptable.

Analytical precision of chromatographic measurements, established from replicate analyses (n=10) of standard 1 and 2 at 1013mbar and 22°C with 2ml loop is better than +/-0.5% (R.S.D.: Relative Standard Deviation 100σ/m).

3.4 Automation of the headspace sampler

This work was presented at the Chromeleon International Users Symposium 2009 [28]. Briefly, the analytical system is electrically connected to an UCI (Universal Chromatography Interface). UCI is controlled by Chromeleon software.

The combination of flexibility and advantage of both UCI and Chromeleon software were essential for:

- Manual and automatic control of two valco valves *Vs* and *Vi*: in server configuration of Chromeleon, two devices were added to timebase. With adequate instruction in the program file, automatic control of these valves was ensured. Furthermore, the addition of a script button in the control panel authorizes manual switching of valves. These valves were controlled by a serial port of UCI.

- Manual and automatic control of three solenoid valves Vp1, Vp2, Vp3. Using three relays of UCI, power was upon order to either open or close those valves.
- Manual and automatic control of pump, performed by using a relay of UCI.
- The integration of an analytical diagram in the control windows of Chromeleon. Thus, the user was able to have a precise idea of the analytical system at anytime.
- Data acquisition of a detector via analog input of UCI and monitoring of signal in Chromeleon.

The Chromeleon software has a layout mode to add, delete and modify different controls, devices and functions in the control panel. Its appearance and functionality can be changed as desired. Fig. 4 illustrates the customization of the control panel in order to command different elements of the analytical system and display the detector signal.

Three programs have been created to control devices automatically by running predefined sets of commands that specify the function each instrument in the system should perform at a specific time. The first program controls the calibration, the second the purge of the line to achieve the headspace gas and the third the automatic injection of samples including the option “Mutiple Headspace Extraction“ mode.

3.5 Comparison of results between the headspace and purge and trap method

To check the accuracy of the headspace method, seawater bottles were analyzed by the two methods. This study was conducted offshore on natural samples (not enriched in gas) but also onshore to explore a large range of concentrations and to use nitrogen liquid for analysis of H2 by purge and trap method. For this purpose, seawater bottles (rosette bottles) were doped in H2 and CH4 to obtain low, medium and high concentrations of these two gases in seawater. The protocol to enrich seawater in H2 and CH4 was closed to the one described by Donval [5; protocol 2]. Niskin bottle was degassed with an inert gas. In addition, an aliquot of 250 ml of seawater was flushed by CH4 or H2 until saturation. Finally a fraction of this solution, according the chosen concentration, was transferred in the Niskin bottle. From this bottle, seawater was transferred into a 300ml syringe for analysis by Headspace and into a 125ml glass bulb for analysis by purge and trap. The purge and trap method used here is based on Swinnerton et al. procedure [8] and modified by Charlou et al.[2]. For conducting this study, especially for H2, a molecular sieve trap placed in liquid nitrogen was added. After 8mn of degassing, gases from the trap are desorbed at 96°C on the analytical column and quantified.

All data have been compiled in Fig. 5 which plot purge and trap versus headspace results. The cross symbol indicate natural samples and the circle symbol on shore samples. The slopes are very close to 1, showing that there is a good agreement between H2 and CH4 measurements using the two methods. It proves that the equilibrium of gases between the two phases was reached and computations corroborate their initial concentration in seawater.

Global analytical precision based on five replicates from the same rosette bottle (0.6µM H2 and 1.5µM CH4) is about +/- 2% with purge and trap technique and +/- 5 % with headspace equilibrium technique. These results are in agreement with previous work on the two techniques and demonstrates that a suitable precision is possible and is largely sufficient when the objective is plume detection in seawater.

Fig. 6 illustrates examples of CH4 and H2 profiles versus depth in different geochemical environments. Seawater samples were collected during oceanographic cruises and immediately analyzed onboard by the two methods for CH4 and only by the headspace method for H2. The three CH4 profiles show a large range of concentrations in the seawater column.

. Profile A is located above mud volcanoes of the eastern Mediterranean Sea. This profile suggests an evidence of high turbid fluid seepage associated with high methane degassing at mud volcanoes.

. Profile B is a characteristic profile on the Black Sea which is a classic marine anoxic basin. Methane can reach relatively high levels, up to 12µM. This profile shows the location of the methane concentration increase at the top of the anoxic zone.

.Profile C is an example of the use of gases as tracer of hydrothermal activity. On this profile, H2 anomalies are linked to very close presence of a hydrothermal field along the Mid Atlantic Ridge. This hydrogen anomaly can be variable especially when H2 production in the source is likely to be associated with the serpentinization process [29].

3.6 Analysis of other gases

To consider the analysis of other gases three elements must be taken into account:

. The choice of detector regarding its specificity and sensitivity.

. The level of concentration.

. The chromatographic separation of gases.

The first condition is the choice of detector which must be in accordance with the compounds to detect. In our system the choice of detector, the HID, is ideal for both trace analysis of fixed gases and light hydrocarbons. Its response is linear over five orders of magnitude with minimum detectable quantities (MDQs) in the low or subpicogram range. However, in the

case of injections of high concentration the detector signal can saturate. One solution is to inject two different loops. In our system, this is achieved by the presence of an 8-port valve which includes two loops: 50µL and 2ml. The 2ml loop, corresponding to the first injection, is used for the determination of low gas concentration, typically H2 and CH4 (except in the case of high concentration as profile B cited above). A second injection with the 50µl loop can be performed to quantify high concentration compounds such as N2, O2 or CO2. Furthermore, the pressure in the loop can be adjusted by means of the micro pump. The chromatographic separation is also a major challenge in determining the different compounds. Figure 7 is an example of chromatograms of mixed gases on a Shincarbon column. On this column, an injection of two different loops allows to H2, N2, CO, CH4 and CO2 quantification (Fig. 7; chromatogram A). If the quantification of light hydrocarbons is reached, the temperature of the column must be increased (Fig. 7; chromatogram B).
In conclusion headspace method enables to analyze a large range of gases. We recommend adopting, as soon as possible, to have methodology using a reference method in order to validate the gas data. For example, Kampbell [30] uses the headspace technique (bottle instead of syringe) to determine oxygen in water and compares the results with Winkler titration. In the other hand, for CO2 analysis, specific precautions are required from the sampling to the analysis. The use of a constant temperature bath is needed to have accurate measurement of CO2. Dickson [31] describes exactly recommended standard operating procedures for ocean CO2 measurements.

3.7 Approach by MHE

Multiple Headspace Extraction (MHE) is a quantitative method used in static headspace-GC. The MHE consists of continuous gas extraction conducted stepwise with established equilibrium conditions in each step. The concentration ”c” of the analyte in the headspace decreases exponentially during the series of extraction steps according to the following equation: $\frac{-dc}{dt}=q.c$

At time t, the concentration c_i is linked to the concentration c_1 (first extraction t=0, n=1): $c_i=c_1.e^{-qt}$

Assuming that concentration and area are directly linked by a linear regression, we can replace c_i and c_1 by their corresponding area A_i et A_1, we have $A_i=A_1.e^{-qt}$

with $A_i=A_1+A_2+...+A_n=A_1[1+e^{-q}+e^{-2q}+...+e^{-(n-1)q}]$

Finally, we obtain the geometric sum : $\sum_{i=1}^{n} A_i = \frac{A_1}{1 - e^{-q}}$ (1)

To reach q in the equation (1), it is necessary to solve the linear calibration function $\ln A_i = -q.(i-1) + \ln A_1$ where q is the slope of a linear regression y=ax+b

To achieve a good estimation of q, three extractions are needed. Once A_1, A_2 and A_3 are measured and q calculated, the sum of the peak area values can be deduced. Then the total concentration is obtained using the calibration curve. This approach has been tested both for H2 and CH4.

After injecting known amounts of H2 and CH4 into four seawater samples, analyses have been performed by means of the MHE procedure (three extractions). Table 1 compares the gas concentration results obtained by MHE procedure with the gas quantity added to the flask. On all four points the final concentrations are similar in the two methods with a global R.S.D. of 3%. The advantage of this method is that knowledge of certain parameters as salinity or equilibrium temperature is not necessary. However, if the gas concentration is very low, this approach is not relevant because no peak detection can occur.

4. Conclusion

In the present paper, we describe an analytical device specifically designed for the quantification of hydrogen and methane in seawater at trace levels. By means of valves (selection, sampling, open/close) and a controlled micro pump in a time program via an electronic interface, the system is automated and so offers many advantages. It includes a pressure sensor and an 8 port valve to inject different amounts of gas taking into account the type of gas, the chromatographic separation and detector sensitivity into consideration. It shows that this device based on headspace method, can be an interesting alternative to the purge and trap method due to its simplicity, reliability and adaptability for routine analysis. To obtain a good level of precision and accuracy, the sample collection and headspace preparation phase must be conducted with particular care to avoid significant uncertainties with regard to gas quantification. The use of a highly sensitive detector such as a pulse discharge helium ionization detector and a volume of 300ml seawater is a good compromise for determining low concentrations of hydrogen and methane in seawater. Finally, this device which targets the detection of methane and hydrogen could be applied to other gases after optimization following a similar protocol and validation by a reference method.

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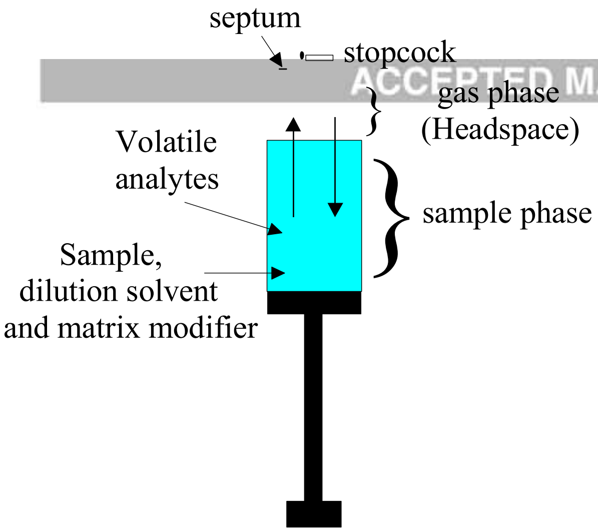


Figure 1: The two phases of a Headspace syringe

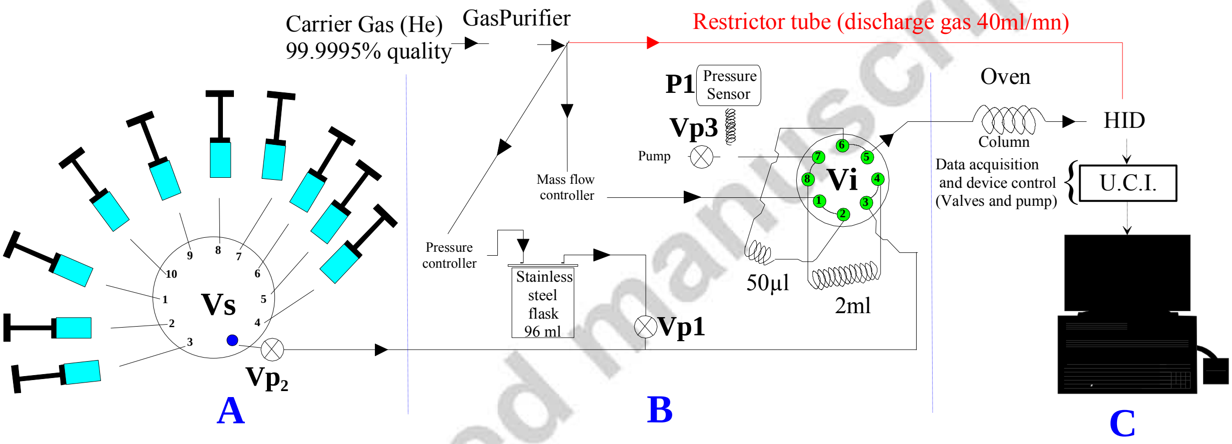


Figure 2: Schematic diagram of the analytical system

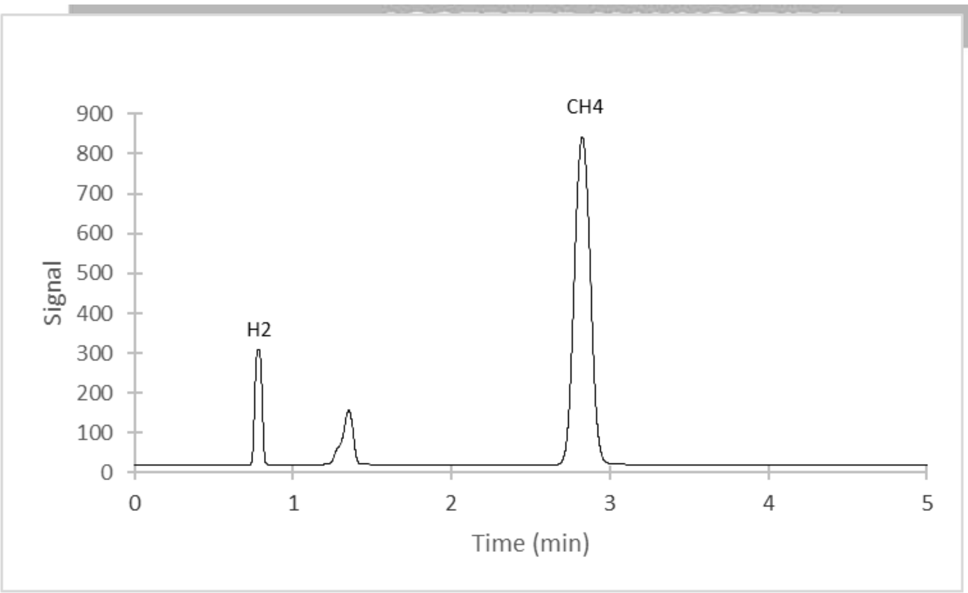
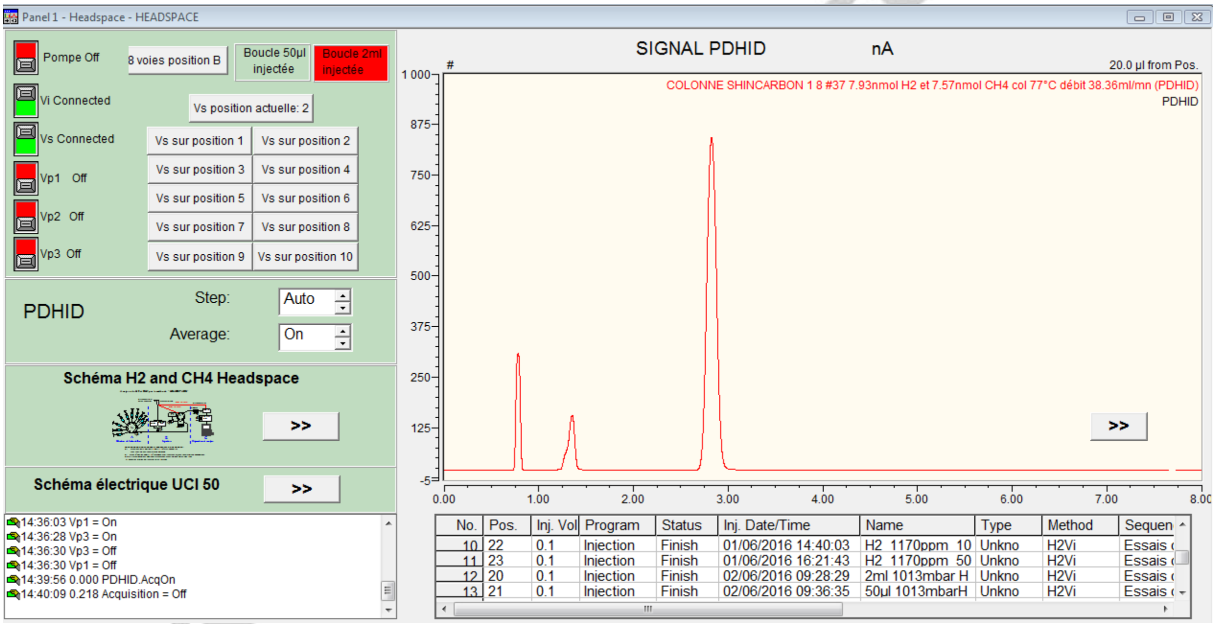


Figure 3: Chromatogram of the standard 2 on the shincarbon column in optimal conditions: 77°C and 38.3ml/mn



Step: Auto
Average: On

COLONNE SHINCARBON 1 8 #37 7.93nmol H2 et 7.57nmol CH4 col 77°C débit 38.36ml/mn (PDHID)

```
14:36:03 Vp1 = On
14:36:28 Vp3 = On
14:36:30 Vp3 = Off
14:36:30 Vp1 = Off
14:39:56 0.000 PDHID.AcqOn
14:40:09 0.218 Acquisition = Off
```

No.	Pos.	Inj. Vol	Program	Status	Inj. Date/Time	Name	Type	Method	Sequen
10	22	0.1	Injection	Finish	01/06/2016 14:40:03	H2 1170ppm 10	Unkno	H2Vi	Essais (
11	23	0.1	Injection	Finish	01/06/2016 16:21:43	H2 1170ppm 50	Unkno	H2Vi	Essais (
12	20	0.1	Injection	Finish	02/06/2016 09:28:29	2ml 1013mbar H	Unkno	H2Vi	Essais (
13	21	0.1	Injection	Finish	02/06/2016 09:36:35	50µl 1013mbarH	Unkno	H2Vi	Essais (

Figure 4: Control panel of the analytical system

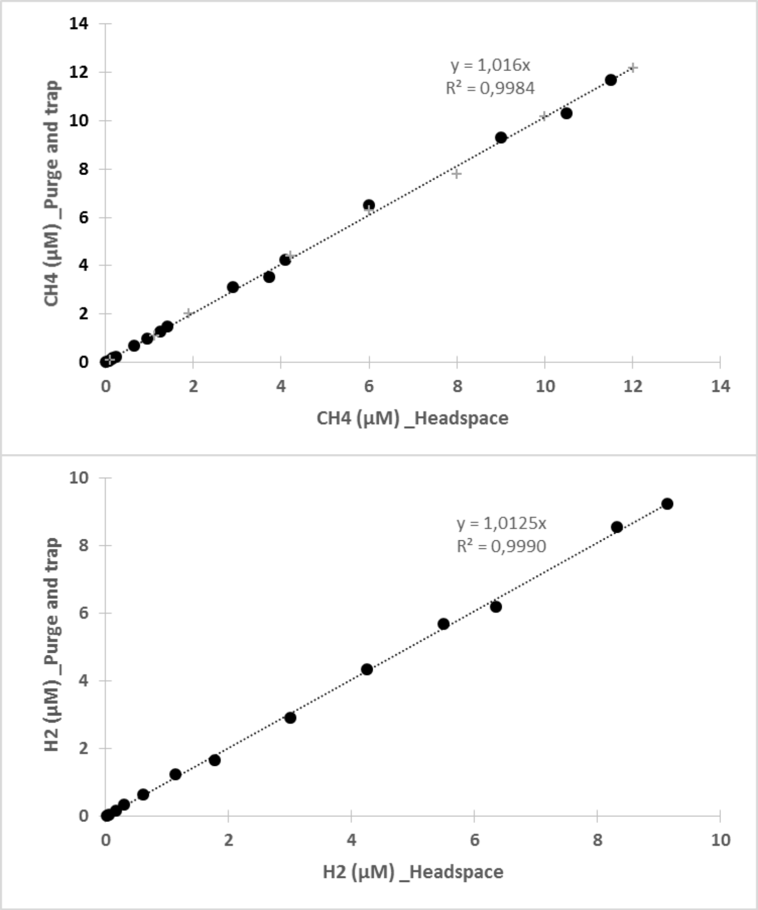


Figure 5: Comparison of results obtained by purge and trap and headspace methods

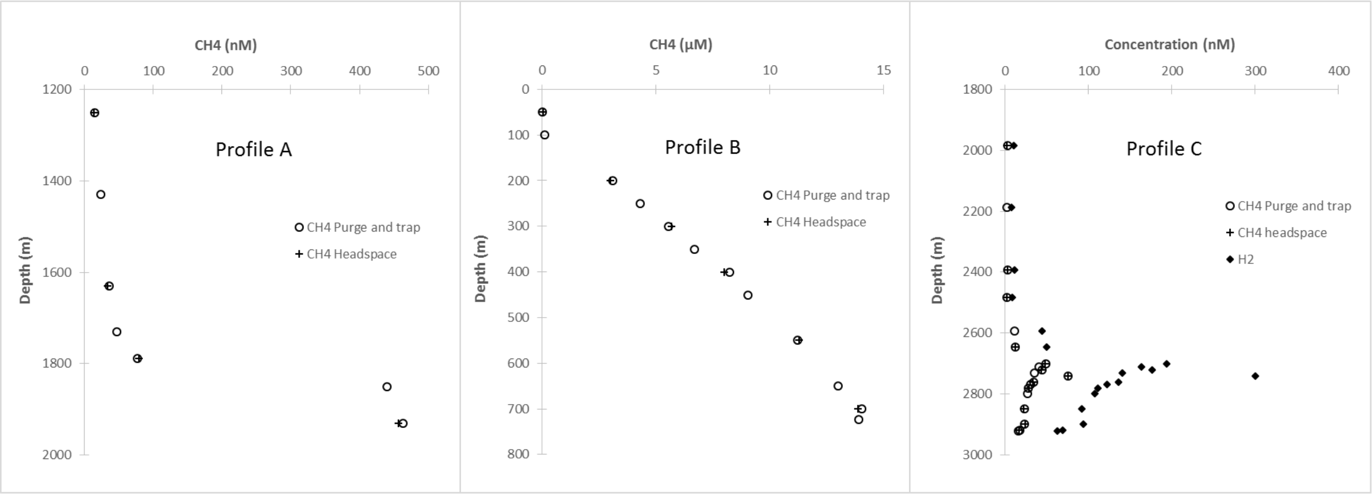


Figure 6: Examples of CH4/H2 profiles: Mediterranean (A), Black sea (B) and Atlantic (C)

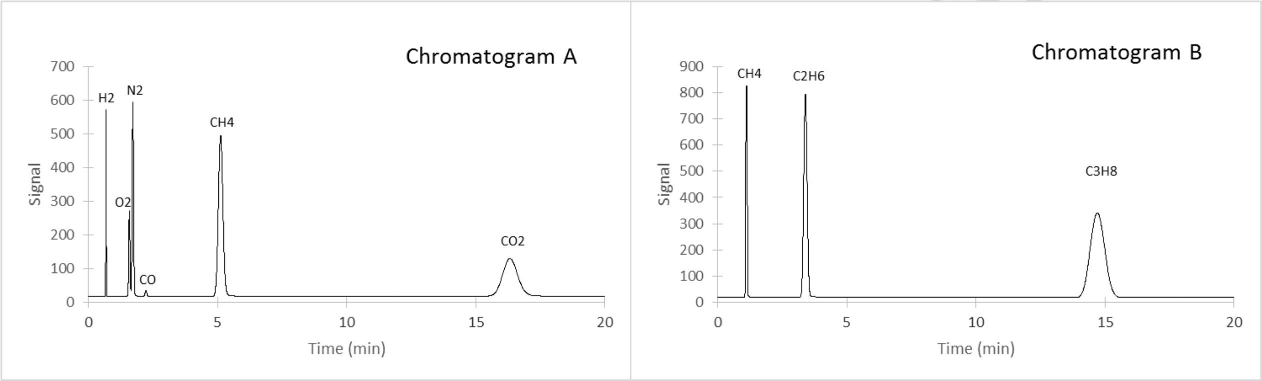


Figure 7: Chromatograms of gas mixtures using the shincarbon column: Chromatogram A 38°C and 36ml/mn, Chromatogram B 200°C and 32ml/mn

Table 1: comparison of results with an approach using Mutiple Headspace Extraction.

	CH4 concentration (µM) calculated with known quantity of CH4	CH4 concentration (µM) with MHE procedure
Vial 1	0,023	0,025 ± 0,002
Vial 2	0,038	0,327 ± 0,017
Vial 3	0,66	0,688 ± 0,03
Vial 4	1,40	1,38 ± 0,05

Graphical abstract