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## Chemical and isotopic analysis of hydrocarbon gas at trace levels Methodology and results

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### ABSTRACT

Isotopic mass spectrometry coupled online with gas chromatography (GC-C-IRMS) permits measurement of relative proportions of gaseous hydrocarbon ( $\text{CH}_4$  to  $\text{C}_4\text{H}_{10}$ ) and  $\text{CO}_2$ , and determination of carbon isotope ratio of hydrocarbon molecules. Access to these parameters provides valuable information about the source and the genesis of naturally-occurring gas, as well as on post-formation physico-chemical processes which might have taken place in the geological environment. In particular, it is possible to distinguish hydrocarbon gas of bacterial origin from that of thermogenic origin based on proportion and carbon isotope ratio of methane as measured by GC-C-IRMS. However, in samples containing very low amounts of hydrocarbons (from 1 ppm to 1000 ppm), accurate measurement of isotope ratios is often impossible due to the limitations of conventional GC-C-IRMS techniques using direct sample introduction. A technique was developed to overcome this limitation. It is based on a novel approach allowing pre-concentration of hydrocarbons prior to GC-C-IRMS analysis. The pre-concentration step consists in selective trapping of hydrocarbon molecules on a cold adsorbent phase, and removal of non-adsorbed gases ( $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{Ar}$ ,...). In a second step, pre-concentrated alkanes are desorbed, and released in an inert carrier gas, focused through a capillary and introduced into the GC-C-IRMS for chromatographic separation and measurement of concentration and carbon isotope composition of each individual carbon molecule. In order to achieve sufficient accuracy, several operating conditions are of prime importance, including sufficient signal intensity, well defined peak shape and low signal/noise ratio. Accurate measurements can be performed on samples as small as  $10\text{ cm}^3$  of bulk gas in standard conditions, with concentrations as low as 1 ppm of methane, 0.5 ppm of ethane and 0.3 ppm of propane and butane. Total analytical uncertainty on  $\delta^{13}\text{C}$  measurements ranges from  $\pm 0.2\%$  to  $\pm 1.5\%$ , depending on the hydrocarbon molecule.

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### 1. Introduction

The demand for analysis of gaseous hydrocarbons at trace levels in natural samples has been increasing in the recent years. Many oil operators and companies have developed interest in surface

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geochemistry measurements during the exploration phase in order to better understand the genesis and history of hydrocarbons accumulated at depth (Pernaton et al., 1996; Prinzhofer and Pernaton, 1997). Also, during drilling, gas sampling is often done at different depths, appropriately identified by the mud logger system, in order to achieve a refined and complete description of drilling conditions. The characterization of trace hydrocarbon gas from surface and drilling samples provides useful data for unraveling the geological history of successive events in a hydrocarbon-bearing basin.

In the field of environmental protection, analyses of trace amounts of gaseous hydrocarbons in soils, surface water or underground water provides insights into the processes at work in polluted areas (abandoned or active industrial sites, gas stations, areas close to roads, oil slicks, etc). In paleoclimatology, analysis of trace methane found in air bubbles occluded in ice yields essential clues to the understanding of climatic evolutions in relation to the greenhouse effect (Chappellaz et al., 1993a,b). The characterization of hydrocarbon traces outgassed from pore water in low-permeability sedimentary rocks provides information on the degree of confinement in sites under investigation for waste repository.

These examples, among others, illustrate the importance of improving detection limits of techniques used to determine the isotopic and chemical composition of gaseous hydrocarbons in trace amounts. Except for systems dedicated to analysis of methane and CO<sub>2</sub>, current commercial spectrometers are not able to analyze trace hydrocarbons with sufficient accuracy. A pre-concentration step for the molecules of interest is therefore required. The difficulty is amplified by the fact that sampling is often done under low pressure conditions. In all cases, it

is essential to know sampling pressure with a good precision (0.1 mbar) to be able to determine the final concentrations of the different gas compounds.

At the University of Grenoble, France, in the research group of the Laboratoire de Glaciologie et de Géophysique de l'Environnement (LGGE), J. Chappelaz and co-workers (Aballain, 2002; Bernard, 2004) developed a pre-concentration system for measuring methane in trace amounts from air bubbles in ice cores. Test was performed at the LGGE in a preliminary stage of our study in order to assess the applicability of the system to the analysis of trace hydrocarbons dissolved in argillites porewater (Girard et al., 2002). The results of these tests indicated that measurement was acceptable for methane, but not for heavier hydrocarbons. This leads us to modify and adapt the technique followed at the LGGE in order to develop the ability to make measurements of all major hydrocarbons, i.e., CH<sub>4</sub> to C<sub>4</sub>H<sub>10</sub>, with sufficient accuracy (Huiban et al., 2004).

## 2. Instrumentation and analytical procedures

A detailed diagram of the analytical system used at IFP is shown in Fig. 1. It consists of a stainless steel vacuum line equipped with single or multiple path valves, traps, pressure gauges and gas-flowmeters permitting control of key parameters at each of the six steps used for the process:

– step 1: prior standard/sample injection, operating conditions require the line to be evacuated down to a pressure of at least  $5 \cdot 10^{-4}$  mbar using a pumping system with a diaphragm primary pump (1) and a

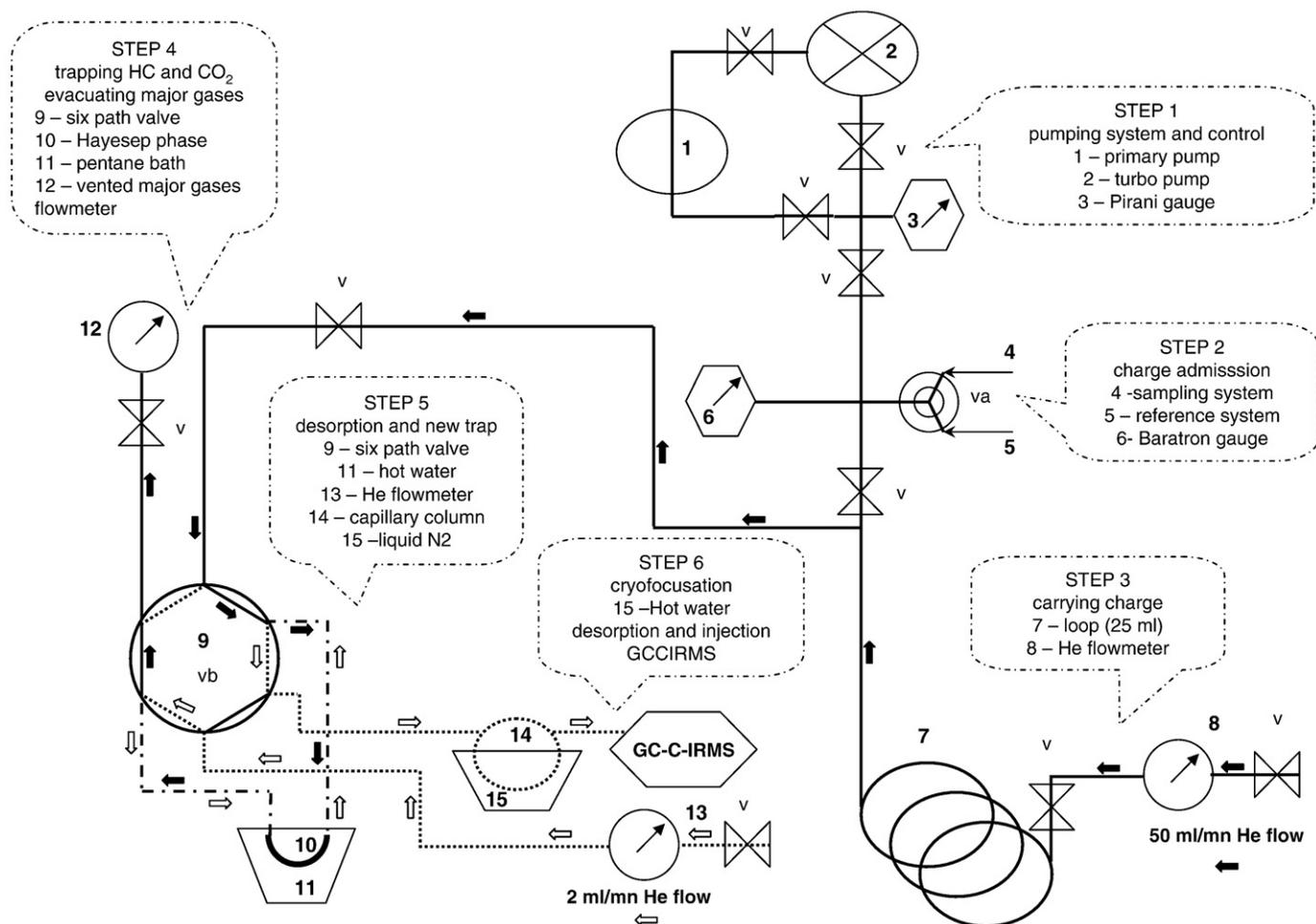


Fig. 1. Detailed diagram of the IFP pre-concentration system.

**Table 1**  
Composition and precision of the carbon components of the reference gas.

Compound	CH <sub>4</sub>	CO <sub>2</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	iC <sub>4</sub> H <sub>10</sub>	nC <sub>4</sub> H <sub>10</sub>
ppm	52.4	49.59	52.4	51.3	51.3	53.4
Precision	±2%	±2%	±2%	±2%	±2%	±2%
δ <sup>13</sup> X	−42.8	−36.5	−32.2	−27.2	−27.2	−24.2
Precision	±2‰	±2‰	±1‰	±1‰	±1‰	±1‰

turbomolecular pump (2) (speed about 50 l/s for N<sub>2</sub>). Vacuum is controlled with a Pirani gauge (3).

- step 2: the gas charge (4) (5), reference or sample, is admitted to the circuit. Its pressure is measured to a precision of 0.1 mbar using a “Baratron™ gauge” (6).

- step 3: the charge is released into a 25 ml loop of stainless steel tube (7), and a He flow, controlled and regulated by a digital flow meter, is introduced as carrier gas at 50 ml/min (8).

- step 4: using a six path valve (9), the He flow carries the gas molecules to a chromatographic column (10), a 20 cm length stainless steel tube of 1/8”, in a U form, filled with a stationary phase (Hayesep Q™ type<sup>1</sup>) and cooled in a pentane bath at −115 °C (11). This cryogenic trap is designed to selectively adsorb hydrocarbon fractions and CO<sub>2</sub>. The major gases (He, N<sub>2</sub>, O<sub>2</sub>, Ar, etc.) pass through and are vented to atmosphere. This elimination is controlled via a flowmeter (12). To avoid a loss of efficiency of the trap due to an increase of the temperature of the pentane bath, this step is limited to 10 min.

- step 5: after 10 min, the Hayesep phase is rapidly heated in hot water at 75 °C (11) to desorb the trapped gas molecules. In the same time, turning the 6-path valve (9) allows admission of a second controlled and regulated He flow at 2 ml/min (13). This second flow (which reaches the Hayesep phase in the opposite direction to the first flow) is used to desorb hydrocarbon gases and CO<sub>2</sub> which are then trapped again in a small loop of capillary column (14) (GSQ™ type<sup>2</sup>) cooled in liquid nitrogen at −196 °C (15).

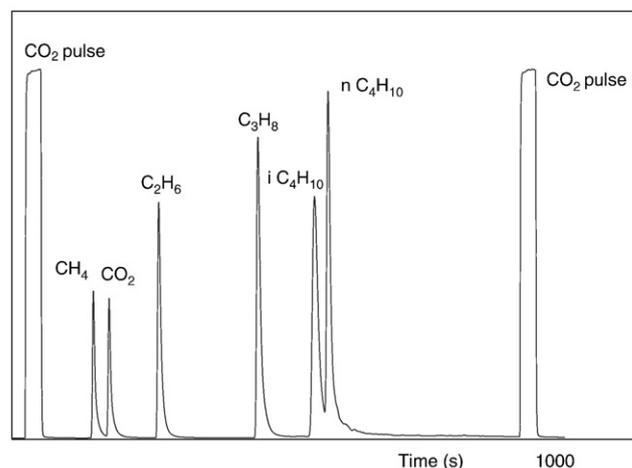
- step 6: after 5 min, the capillary column is rapidly heated in hot water at 75 °C (15) to desorb simultaneously the molecules trapped in the small loop and allow them to enter the chromatograph for separation, combustion and analysis by GC-C-IRMS. This step, called cryofocusing, allows sharp and well-separated chromatographic peaks to be obtained. Each step has been optimized and the full process now takes about 40 min.

The rest of the analytical process for the gas compounds consists in a conventional analysis by GC-C-IRMS allowing measurement of the abundance and δ<sup>13</sup>C of gas compounds. The IFP prototype uses a commercial chromatographic phase to trap hydrocarbon gas traces. The main modifications are in the design optimization, in particular the column length, which contributes to reduced operating times for the trap/desorption steps. To our knowledge, no other laboratory is currently able to analyze CH<sub>4</sub> to C<sub>4</sub>H<sub>10</sub> gaseous hydrocarbons at trace level with high accuracy.

The GC-C-IRMS instrumentation used to establish this methodology is a GVI Optima equipped with three Faraday cup detectors to measure the different proportions of masses 44, 45 and 46 on CO<sub>2</sub> ions. After injection, gases are separated in a capillary column, of GSQ™ type<sup>2</sup>, 30 m in length and of 0.32 mm inner diameter. At the outlet of the GC, hydrocarbons are heated to 950 °C in a combustion furnace and converted to CO<sub>2</sub> and H<sub>2</sub>O. Water is retained in a low temperature trap, while CO<sub>2</sub>, carrying the original C signal of the

<sup>1</sup> Hayesep phase is a large specific surface area divinyl benzene polymer with a 60/80 mesh granulometry.

<sup>2</sup> GSQ is a porous divinylbenzene homopolymer plot column.



**Fig. 2.** Chromatographic separation of the hydrocarbon traces.

hydrocarbons, is introduced in the mass spectrometer. CO<sub>2</sub> molecules are ionized, deflected by the magnet, and separated into beams of different radii corresponding to different masses. At the outlet of the flight tube, three Faraday collectors are used to detect and measure intensity of the 44, 45 and 46 ion beams.

A cylinder containing different reference carbon bearing gas compounds diluted with nitrogen is used to check the efficiency of this system.

### 3. Validation of the technique using laboratory standard gas

The pre-concentration system procedure was validated using a laboratory standard gas. Composition and concentration of the gas are certified by the manufacturer at the precision level indicated in Table 1. It is composed of about 50 ppm, diluted in nitrogen, of the following compounds: CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, iC<sub>4</sub>H<sub>10</sub>, nC<sub>4</sub>H<sub>10</sub> and CO<sub>2</sub>.

The carbon isotopic ratios of the different hydrocarbon compounds in this gas are indicated in Table 1. They are not provided by the

**Table 2**  
Isotopic results of the alkanes depending of the sampling pressure.

Runs	P (mbar)	Hydrocarbon molecules				
		CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	iC <sub>4</sub> H <sub>10</sub>	nC <sub>4</sub> H <sub>10</sub>
1	100.5	−44.2	−31.9	−26.7	−27	−23.7
2	100	−42.4	−31.2	−26.2	x	x
3	91	−45.5	−32.6	−27	−27.4	−24.2
4	88	−45.4	−33.2	−27	−27.1	−24
5	74	−46.4	−32.2	−26.9	−27.2	−23.8
6	73	−43.6	−32.3	−27	−27.2	−24
7	59	−47.5	−32.4	−27.1	−27.2	−22.4
8	59	−47.4	−32.4	−27.4	−27.4	−22.9
9	55.5	−42.3	−31.3	−26.1	x	x
10	54	−45.7	−34	−26.8	−26.9	−23.9
11	53	−47.1	−32.6	−27.2	−27.3	−23
12	53	−46.2	−31.7	−26.5	−26.7	−24.4
13	46	−48.4	−32.2	−26.9	−27	−22.8
14	43.5	−44.7	−32.5	−27.1	−27.3	−23.8
15	41	−41.7	−31.1	−26.5	x	x
16	33	−42.7	−31.6	−26.5	x	x
17	32	−47.0	−33.3	−27.5	x	x
18	23	−42.4	−31.4	−26.7	x	x
19	15	−41.9	−31.1	−26.2	x	x
20	15	−41.2	−31.1	−26.7	x	x
21	10	−45.3	−31.6	−26.1	x	x
22	7	−41.8	−31.4	−26.6	x	x
23	3.5	−43.2	−35.5	−27.9	x	x
24	2.5	−42.0	−38.7	−27.5	x	x
Average		−44.4	−32.5	−26.8	−27.1	−23.6
Standard deviation (1σ)		2.3	0.8	0.4	0.2	0.6

**Table 3**  
Chemical results of alkanes and CO<sub>2</sub> by reference at the highest pressure.

Pressure mbar	Concentration (in ppm) and corresponding intensity signal (in nA)											
	CH <sub>4</sub>	Signal	Diff (%)	CO <sub>2</sub>	Signal	Diff (%)	C <sub>2</sub> H <sub>6</sub>	Signal	Diff (%)	C <sub>3</sub> H <sub>8</sub>	Signal	Diff (%)
100	52.4	29.6	0.0	49.6	35.8	0.0	52.4	58.1	0.0	51.3	87.4	0.0
55.5	53.7	16.9	2.5	54.2	21.7	9.3	53.8	33.1	2.7	57.0	53.9	11.2
41	54.4	12.7	3.8	60.2	17.9	21.3	54.2	24.7	3.4	52.8	37.0	2.9
33	55.7	10.4	6.3	72.9	17.4	47.1	56.6	20.7	8.0	57.8	32.5	12.6
32	54.9	9.9	4.7	157.5	36.2	217.6	53.5	18.9	2.1	55.6	30.1	8.3
23	56.4	7.3	7.7	72.0	11.9	45.1	54.2	13.8	3.5	50.5	19.7	−1.5
15	58.7	4.9	12.0	94.4	10.1	90.3	56.3	9.3	7.5	52.3	13.2	2.0
15	56.8	4.8	8.4	78.7	8.5	58.7	54.1	9.0	3.3	56.6	14.5	10.4
10	64.2	3.7	22.5	275.5	20.0	455.5	57.6	6.5	9.9	60.8	10.6	18.5
7	65.8	2.5	25.5	132.4	6.5	167.0	59.2	4.5	13.1	59.2	6.9	15.4
3.5	78.6	1.6	50.0	160.2	4.2	223.0	58.8	2.4	12.3	58.2	3.6	13.4
2.5	101.2	1.3	93.0	239.6	4.0	383.1	60.2	1.5	14.8	64.4	2.5	25.5

supplier. This determination was assessed by a significant number of successive injections of hydrocarbon gas in the analytical device, in sufficient quantities, to get a high spectral quality in a very good linearity range. The statistical results on these injections allow to show the accuracy of the results (Huiban et al., 2006).

The GC-C-IRMS calibration was done using three reference gases routinely used for isotopic measurements in the IFP laboratory:

- pure commercial CO<sub>2</sub>. The  $\delta^{13}\text{C}$  value for this gas was determined as part of round robin tests involving different European laboratories. This value allows the linearity range of intensity measurements using the spectrometer to be evaluated. The isotopic value of this standard CO<sub>2</sub> is established at  $-31.6\% \pm 0.2\%$ .

- pure commercial CH<sub>4</sub>, which  $\delta^{13}\text{C}$  value was accurately determined by Pernaton (1998). This reference methane is used to control the efficiency of the combustion furnace of our GC-C-IRMS (methane is the most sensitive hydrocarbon gas for combustion). This gas also allows the linearity range of intensity measurements using the spectrometer to be evaluated. The  $\delta^{13}\text{C}$  value of this standard CH<sub>4</sub>,  $-41.3\%$  is known to  $\pm 0.2\%$ .

- a commercial mixture of hydrocarbon gases from CH<sub>4</sub> to C<sub>4</sub>H<sub>10</sub>, the isotopic composition of which was determined in our laboratory through a large number of repeated analyses. This reference gas is used to verify that all of the different critical steps of the process (elution time, separation quality, ...) do not introduce any artifact and that the linearity range for each hydrocarbon is satisfactory. The  $\delta^{13}\text{C}$  values of this reference gas have been determined with a significant number of successive injections in the GC-C-IRMS. The results obtained are the following:  $-39.6\%$  for CH<sub>4</sub>,  $-29, 1\%$  for C<sub>2</sub>H<sub>6</sub>,  $-25.3\%$  for C<sub>3</sub>H<sub>8</sub>,  $-26.6\%$  for iC<sub>4</sub>H<sub>10</sub>,  $-25.2\%$  for nC<sub>4</sub>H<sub>10</sub>. All these values are known to be  $\pm 0.2\%$ .

As shown in Fig. 2, the special design of the pre-concentration system allows good chromatographic separation of the different alkanes.

To check the system linearity, a number of gas charge admissions were carried out, at different pressures. The results are reported in Tables 2 and 3.

### 3.1. Isotopic analysis results

Data runs presented in Table 2 show the results of isotopic determination. For some of these runs the separation of the butane isomers was not successful, especially for very low pressures (from 2.5 mbar to 40 mbar). In these cases, the results for butane isomers are not reported. The isotopic values of methane, ethane and propane appear to remain relatively stable, with acceptable standard deviations, respectively 2.3%, 0.8%, and 0.4%. For pressures above

40 mbar, the results for butane isomers are very good, with very low standard deviation, 0.2% and 0.6%. Data obtained are quite close to the estimated values of Table 1.

Peak separation and linearity range for spectrometer intensities are good and allow accurate measurement of the isotopic value of alkanes. Given analytical conditions used in this work, the accuracy of  $\delta^{13}\text{C}$  determination is estimated to be  $\pm 2.5\%$ . With sufficient volume and pressure conditions (10 cm<sup>3</sup>/1 bar), the minimum quantities of hydrocarbon gases required for analysis are 1 ppm for methane, 0.5 ppm for ethane and 0.3 ppm for propane and butane.

### 3.2. Chemical analysis results

Peak area measurements were recorded to calculate the concentrations for CO<sub>2</sub> and hydrocarbon gases except butane. The separation of butane isomers was not successful, especially at very low pressures. For other alkanes, the results show good linearity.

For CO<sub>2</sub>, results are satisfactory for large gas aliquots, i.e., above 50 mbar. They are not acceptable for smaller aliquots, which yield CO<sub>2</sub> concentrations higher than expected, probably due to a slight but irreducible contamination, amplified during the process.

To check the system thresholds, the concentration measurements have been estimated using the analysis at 100 mbar as reference (Table 3). Concentrations of all other analyses have been recalculated by normalizing the reference analysis. The signal intensity (in nA) and the deviation in % are reported. The reason for choosing this analysis as reference is because it provides the highest pressure, and hence yields the largest quantity of hydrocarbon gas in the analytical device, with the best spectral quality in a very good linearity range. In addition, the proportionality between the number of carbon atoms of each chemical species and the associated relative signal intensity allows some cases of fractionation to be discarded. Results reported in

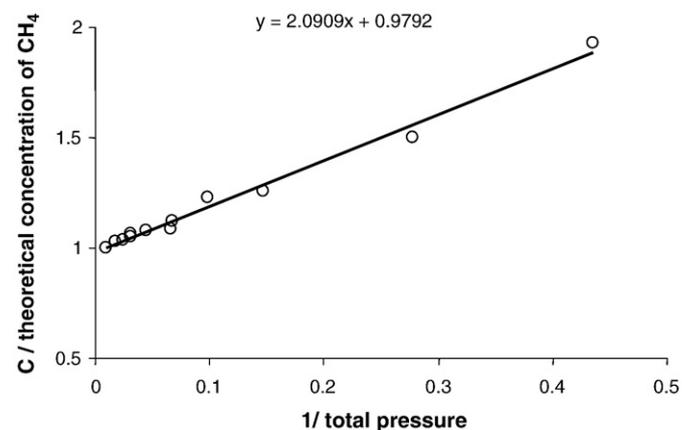


Fig. 3. Mixing diagram of methane concentration versus the inverse of total pressure.

Table 3 show higher concentrations for smaller aliquots. The signal intensity of hydrocarbon gases show that for levels under 5 nA, the recalculated concentrations give deviations above 10%. This may come from a poor linearity of the analytical process for small intensities or from a more important contamination for low pressure aliquots. The huge deviation observed for CO<sub>2</sub> with the run at 10 mbar (456%) demonstrates that there was probably a big contamination problem in this case which regarded CH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub> too. For CO<sub>2</sub> intensity all signals under 50 mbar are bad and prove a very early contamination for this gas. Fig. 3 shows the methane concentration versus the inverse of total pressure. This plot is a conventional mixing diagram, plotting parameters with a common denominator, thereby defining a straight line in the case of a two-component mixture. The mixing equation (Vollmer, 1976) is hyperbolic and has the form:  $Ax + Bxy + Cy + D = 0$  where the coefficients are dependent on the type of plot considered. Fig. 3 shows a linear correlation, suggesting contamination in the pre-concentration line. The same linear correlation exists for other gases, with a larger contamination for CO<sub>2</sub> and a very slight one for ethane and propane. The big contamination observed on some runs (for example at 10 mbar and 32 mbar) comes from unavoidable differences due to the big number of manual operations of the process: a too short time during the pumping step, a too long time during the trapping step, a too big contamination of the trap due to the previous run, a contamination by air in case of delay in closing the manual valve used to vent the major gases, a small leak when turning manually one of the numerous valves, a degradation of the tubing or capillary or their connections with a lot of manipulations with abrupt changes in temperature, ...

The quality of the reference gas being certified by the supplier, contamination with extraneous CO<sub>2</sub> can only be explained by either a "memory" effect of the pre-concentration line and/or the presence of impurities in the carrier gas. This issue has not been resolved at this stage. However, the use of high charge pressure selected for the normalization minimizes the effect of contamination due to the pre-concentration system itself or generated by impurities in the He carrier gas.

#### 4. Implications and recommendations

The results reported here show the performances but also the limitations of the newly-developed pre-concentration system. Below a sample pressure threshold, it would not be very realistic to analyze these samples in acceptable conditions of accuracy and reliability. This limitation is more restrictive for CO<sub>2</sub> and CH<sub>4</sub> than for C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub>.

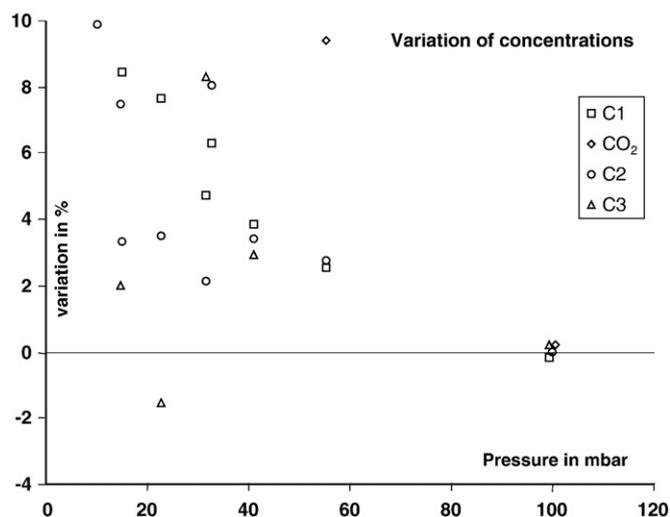


Fig. 4. Relative variation of measured concentrations after normalization versus the pressure.

To assess this threshold, the relative variation of measured concentrations recalculated after normalization has been plotted versus the pressure (Fig. 4).

Due to the low levels of concentrations and the many parameters involved that are likely to affect the results (the design system and the reference gas values), a conservative relative accuracy of 10% for results on hydrocarbon gases and CO<sub>2</sub> is admitted. We conclude from Fig. 4 that minimum pressure required for accurate analysis of gas samples using our approach is: 60 mbar for CO<sub>2</sub>, 20 mbar for CH<sub>4</sub> and between 10 and 20 mbar for C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub>.

For butane isomers, in our analytical conditions, at least 40 mbar pressure is necessary to obtain good separation and acceptable isotopic signals.

#### 5. First application study and further improvements

This methodology was developed as part of a project aiming at investigating porewater in the Callovo-Oxfordien argillites of Bure, eastern Paris Basin. GC-C-IRMS analysis was performed on gas naturally released from water-saturated argillite cores stored in specifically-designed outgassing cells shortly after drilling (Girard et al., 2005; Prinzhofner et al., 2009). It was possible to quantify the concentrations and  $\delta^{13}\text{C}$  of methane, ethane and propane. The measured concentration ranges are 12–20 ppm for methane, 28–40 ppm for ethane and 47–56 ppm for propane. Measurements of  $\delta^{13}\text{C}$  values (relative to PDB) have been carried out successfully with sufficient accuracy to provide valuable geological information. Our pre-concentration technique was a critical tool in allowing the characterization of the origin of hydrocarbons dissolved in the argillite porewater, in demonstrating the lack of bacterial degradation, and in providing insights into gas migration reconstruction.

For some special applications, it has been shown that for small CO<sub>2</sub> concentrations in the original samples, the required signal amplification was so large that it might affect the signal of CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>. To avoid this loss of information, it is recommended to trap CO<sub>2</sub> with a specific chemical product such as Ascarite™ or to evacuate this gas out of the analyzer by a special configuration of the chromatograph. Regarding the device itself, improvements could be made as to its design, by reducing volume (miniaturization) and automating all operations. Some improvements in other parameters (column specifications, replacement of the Hayesep Q trap by the Hayesep D one which is made with higher purity materials, temperature conditioning of the GC oven, carrier gas flows,...) may permit the analysis of butane under 40 mbar.

#### 6. Conclusions

We have developed and tested a pre-concentration system specifically designed for gaseous hydrocarbons which permits analysis, with good accuracy, of the chemical and carbon isotopic composition of alkanes in trace amounts under very low sampling pressure. The pre-concentration system is used online on a GC-C-IRMS. The method relies on the use of a cryogenic trap composed of Hayesep Q™ type cooled to  $-115\text{ }^\circ\text{C}$ . The analytical procedure was validated using commercial reference gas. The following analytical uncertainty on measured  $\delta^{13}\text{C}$  values were obtained:  $\pm 2.3\%$  for 1 ppm of methane,  $\pm 0.8\%$  for 0.5 ppm of ethane,  $\pm 0.4\%$  for 0.3 ppm of propane,  $\pm 0.2\%$  for 0.3 ppm of isobutane and  $\pm 0.6\%$  for 0.3 ppm of normal butane.

Considering that the results reported herein were obtained with an old generation of GC-C-IRMS coupled to a fully manual pre-concentration system, it is reasonable to expect future improvements for this technique. By using a more recent mass spectrometer, with lower limits of detection, and by optimizing volume and automation of the pre-concentration system itself, better accuracy and precision can certainly be reached. Additionally, coupling the pre-concentration

system we developed to a new generation of mass spectrometer may provide capability to perform  $\delta D$  measurements.

$\delta D$  analysis of trace hydrocarbons constitutes a real challenge for future advances, extending the field of hydrogen isotope application to samples with significantly lower amounts of alkanes than those routinely analyzed today. The combination of C and H isotopic information should provide further insight into physico-chemical processes affecting hydrocarbon gases in natural systems and in particular the nature and extent of water–gas interactions.

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