

An Alternative Gas Chromatography Setting for Geochemical Analysis

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Abstract

Gas chromatography is one of the most important techniques used to characterize gas composition of geochemical samples. This work presents a new gas chromatography setting to characterize gaseous composition using three detectors: a Flame Ionization Detector (FID), a Thermal Conductivity Detector (TCD) and a Flame Photometric Detector (FPD). The new gas chromatography setting developed is able to quantify hydrocarbons gases (C₁-C₅) and non-hydrocarbons (H₂S, CO, CO₂, N₂, O₂ and H₂) in only one injection and in the same analysis. This alternative gas chromatography is able to reduce time of analysis and save sample that can be used for other kind of analyses.

Keywords: Gas chromatography; Geochemical analysis; Gases detections

Introduction

Gas Chromatography (GC) technique is widely used in geochemical studies [1-3]. One of its extensive applications is the determination of gaseous hydrocarbons (C₁-C₅) and non-hydrocarbons gases (N₂, CO₂, H₂, O₂) in marine sediments. The knowledge of composition and concentration of these gaseous is used to constrain the origin of gases [4].

Gas chromatography is applied to conventional petroleum exploration to determine the quantity of light hydrocarbon gases (methane, ethane, ethylene, propylene, propane, butane, iso-butane, butylene, and pentane) in marine sediments which are proxies for deeper petroleum reservoirs. Differences in concentration of the gases above may reflect origin of hydrocarbons and their upward migration to seabed [5]. The gas composition in combination with stable isotopic composition ($\delta^{13}\text{C-CH}_4$) can be used to distinguish thermogenic from biogenic gases [6].

Other GC application is for the exploration of unconventional gas reservoir such as gas shale as gas hydrates [7]. Thermal maturity provides an indication of the maximum palaeo temperature reached by a source rock, which determines the type and quantity of the hydrocarbon product from kerogen. Therefore, gas shale is characterized by widespread hydrocarbons gases purity content. Furthermore, it is possible to distinguish thermogenic, biogenic or combined biogenic/thermogenic origin using gas composition and additional geochemical parameters [8,9].

Composition of trapped gas in gas hydrate can also be determined using gas chromatography techniques [10]. Methane is the most common gas in gas hydrate, but others gases like CO₂ and H₂S also occur [11,12]. The gas composition of hydrates will determine its crystalline structure and stability [13].

This work presents an alternative gas chromatography setting to characterize gaseous composition using an innovative device containing three detectors: (1) Flame Ionization Detector (FID), (2) Thermal Conductivity Detector (TCD) and (3) Flame Photometric Detector (FPD). In this paper we will present the results of standard gases used to methodology development of the new gas chromatography setting which is able to quantify hydrocarbons gases (C₁-C₅) and non-hydrocarbons (H₂S, CO, CO₂, N₂, O₂ and H₂) in only one injection and in the same analysis.

Equipment descriptions

The analytical methodology was developed using a Shimadzu Gas Chromatograph Model GC-2014. Helium was used as carrier gas at a 30 ml/min flow rate. This device is equipped with FID detector use to quantify principally light hydrocarbons (C₁-C₅), CO and CO₂. Hydrogen and air, both with 30 ml/min flow rate, are used as combustion gas in the FID detector at 200°C. The methanation reaction of CO and CO₂ occur using methanator (MTN-1) with excess of hydrogen. The methane produced is detected in the FID. For CO, CH₄, CO₂, N₂, O₂ and H₂ detection it is used a TCD detector at 200°C. The reference gas and the capillary makeup flow rates are 30 ml/min. A FPD detector at 200°C is used to detect H₂S. Hydrogen and air were used as detector gases at 30 ml/min flow rate.

The gas chromatograph is equipped with a Carboxen capillary column (30 m length, 0.53 mm ID), two Hayesep Q columns (2 m length, 3.0 mm ID) and a Molecular Sieve column (3 m length, 3.0 mm ID). The GC conditions are as follows: starting temperature of the oven of 80°C (hold for 3.5 min) ramp of 8°C min⁻¹ to 170°C (hold 10.2 min).

The injection system is equipped with three different loops. In a single injection, the gas sample is distributed in the loops and to the specific detectors. The FID detector has a 100 μL loop, while the TCD and FPD detectors have loop volumes of 500 and 250 μL , respectively. The properties of the columns and volumes of loops used in the development of the methodology can be seen in table 1.

The gases required for operation of the equipment are helium (99.999% purity), hydrogen (99.999% purity) and nitrogen (99.999% purity). Mixture of helium and methane (C₁), ethane, ethylene, propane, propylene, butane, butylenes and pentane (C₂-C₅) is used as standards. The methane concentration is 1,000 ppm (v/v) while C₂-

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Detector	Loop (μL)	Column	Length (m)	Inside diameter (mm)
FPD	250	Haysep Q	2	3
TCD	500	Haysep Q	2	3
		Molecular Sieve	3	3
FID	100	Carboxen 1006	30	0.53

Table 1: Properties of the columns and loops used in the development of the methodology.

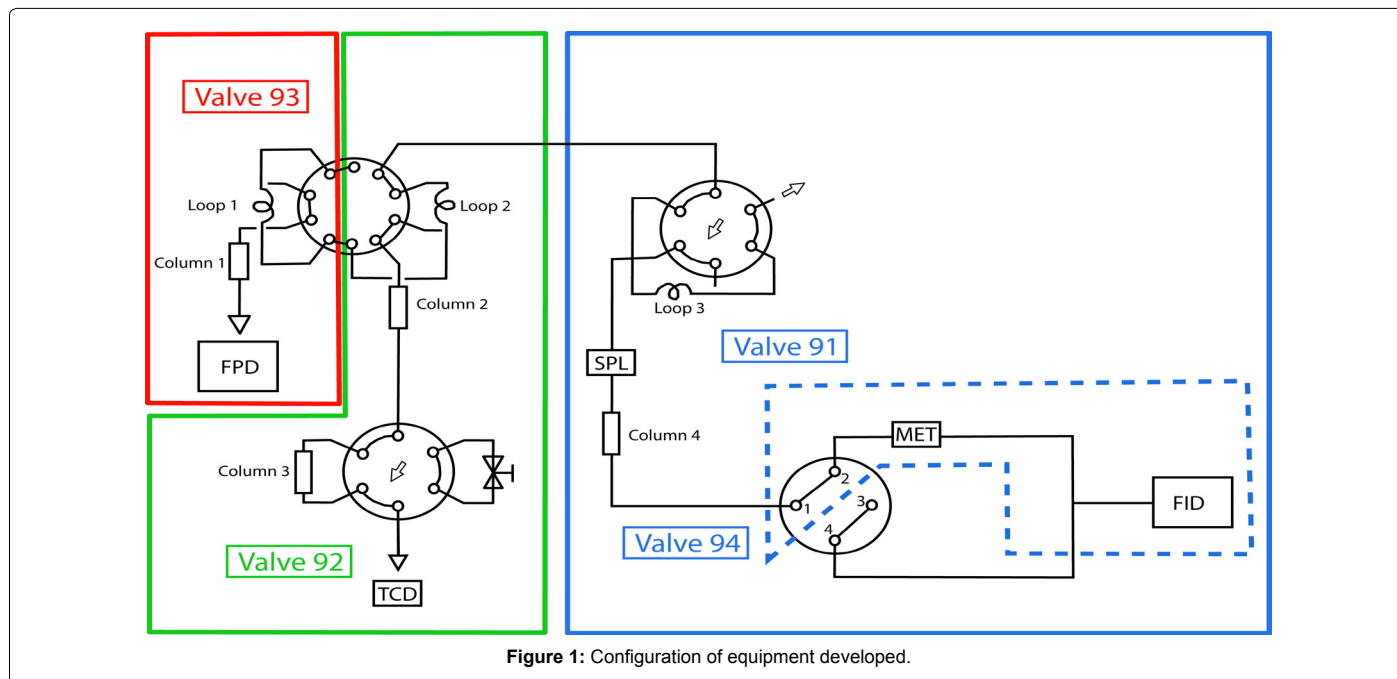


Figure 1: Configuration of equipment developed.

Flow Rate (mL min ⁻¹)	Heating Rate (°C min ⁻¹)	Temperature (°C)	Time (min)
30	-	80	3.5
	8	170	10.2

Table 2: Gas chromatography temperature program.

C₅ concentrations are 250 ppm (v/v). Other standard gases used are a mixture of helium and CO, CO₂, O₂, N₂ and H₂ with 2,500 ppm (v/v) of concentration. Finally, 10 ppm of H₂S in helium also was used in this work. All gas standards were provided by White Martins Company.

The gas chromatograph configuration was designed to detect C₁-C₅, CO, CO₂, O₂, N₂ and H₂ in only one injection. Injection of gases is made using syringes of BD PrecisionGlide™ coupled of three-way tap rotation and BD PrecisionGlide™ hypodermic needle.

Figure 1 shows four rectangles with different colors. Each color represents a possible pathway which the gas sample will be directed until its detection. The load position is shown in figure 1, where the gases are filling the sampling loops.

After injection (A), the gas sample is divided in three loops (B, C and D) with different volumes. The gas sample will fill the loop B with 250 μL, loop C with 500 μL and loop D with 100 μL and will be carried to the FPD, TCD and FID detectors, respectively, by helium. The gases pathway after injection is described below:

Way 1 - Red rectangle

After starting time, the valve 93 allows 250 μL of the sample to be carried until the Haysep Q (column 1). After gases separation the H₂S is detected in the FPD (Figure 1).

Way 2 - Green rectangle

The valve 93 also allows the sample to the loop with 500 μL and, therefore, the gas helium carries the sample to Q Haysep column (column 2) and after that to the molecular sieve packed column (column 3). After gas detection in TCD the valve 92 allows a back flush flux to discard the undesirable compounds. These CO, CO₂, O₂, N₂ and H₂ will not be detected in TCD (Figure 1).

Way 3 - Blue rectangle

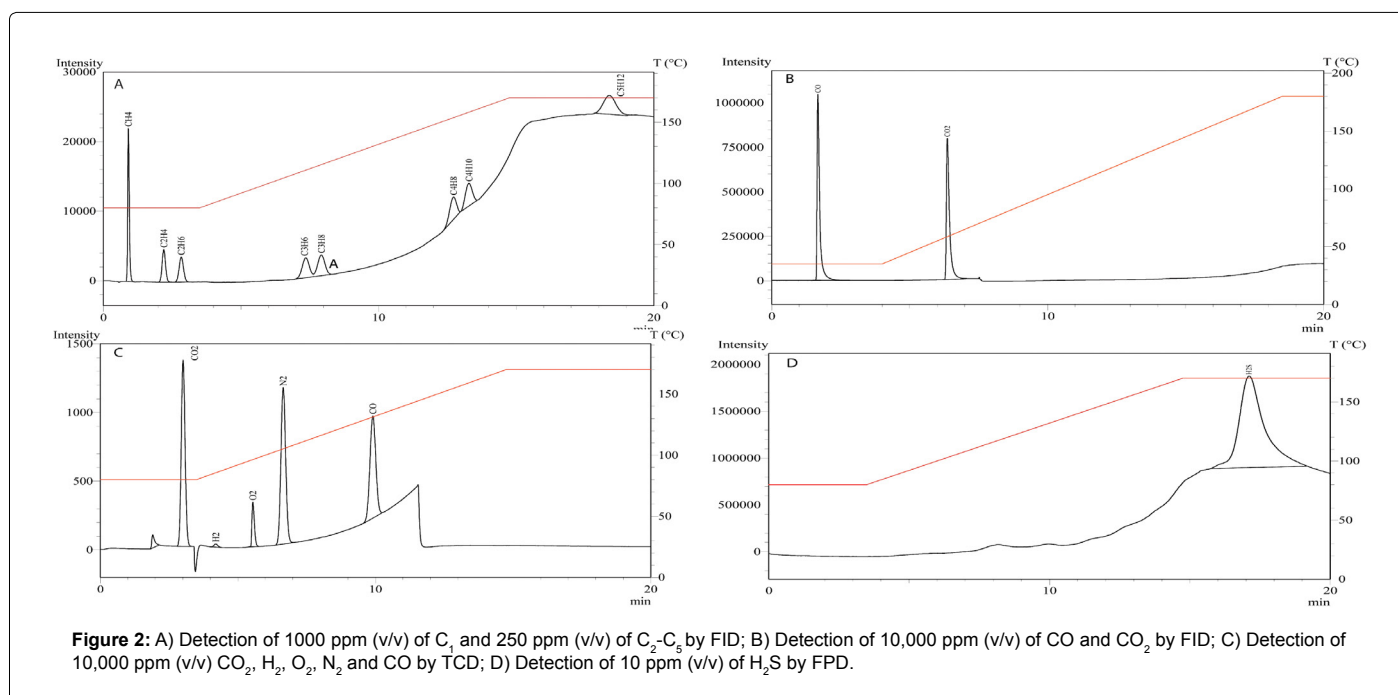
After starting time, the valve 91 allows 100 μL of the sample to be carried to the Carboxen 1006 (column 4). There are two main directions controlled by valve 94: to the FID detector (where C₁-C₅ will be detected by FID detector) or to the methanator (dashed blue rectangle) (where after methanation, CO and CO₂ will be detected by FID detector).

Results and Discussions

Detection of C₁-C₅, CO₂ and CO by FID detector

The oven's temperature was maintained constant during the other optimization. Table 2 shows the gas chromatography temperature program during this work.

Initially, it was injected the standard containing a mixture of hydrocarbon (C₁-C₅) to adjust their signal behavior and retention time. The separation and identification of hydrocarbons is made with the capillary column (Carboxen 1006) and the FID detector. For this purpose, the valve 91 is allows the injection of 100 μL in the column, and the valve 94 avoids deviation of the sample to the methanator. In the beginning, it was chosen an isotherm temperature (100°C) but in



this temperature, butane, butylene and pentane had their retention time above 50 min therefore, the time of analysis would stay infeasible. It was chosen a temperature program with two ramps to reduce the retention time for these compounds. The initial temperature was fixed at 35°C for three minutes and after methane (0.9 min), ethylene (2.2 min) and ethane (2.8 min) separation, the temperature is increased to 100°C using a heating rate of 50°C min⁻¹. The temperature must remain at 100°C for 10 min and during this period, propane and propylene were separated in 7.4 and 7.9 min, respectively. Finally, using a heating rate of 25°C min⁻¹, the temperature is increased until 250°C, hold for 12 min to separate butylene (12.7 min), butane (13.3 min) and pentane (18.4 min). The chromatogram for C_1 - C_5 is shown in Figure 2A.

After the C_1 - C_5 analysis, CO and CO_2 are analysed with the injection of 100 µL of standard containing 25,000 ppm (v/v) of CO and CO_2 . The separation and identification of these gases is made with a capillary column (Carboxen 1006) and the FID detector, respectively. Carbon dioxide and carbon monoxide CO and CO_2 must be reduced to methane in the methanator before their detection by FID detector. This procedure is achieved by closing the valve 94, allowing the CO and CO_2 passing through the methanator.

The main purpose of this optimization is to analyse hydrocarbon (C_1 - C_5), CO_2 and CO in the same run. Methane will be first detect in the FID detector and after its signal integration, CO is the next compound (retention time in 1.7 min). Because ethylene has the retention time (2.2 min) similar to CO (1.7 min), the valve 94 must be kept closed. This valve will be kept closed until CO_2 is detected by the FID detector. This procedure will allow ethylene and ethane with 2.2 min and 2.8 min respectively, get in the methanator because CO_2 has a retention time of 5.3 min. After CO_2 signal integration, the valve 94 will actuate again and C_3 - C_5 will go direct to the FID detector. Figure 2B shows the chromatogram of CO (1.7 min) and CO_2 (6.4 min).

Detection of CO, CO_2 , N_2 , O_2 and H_2 by TCD detector

For detection of CO, CO_2 , N_2 , O_2 and H_2 in TCD detector it was used a standard containing 25,000 ppm (v/v) of CO, CO_2 , N_2 , O_2 and

H_2 . The valve 93 directs the sample to the loop with 500 µL and helium carries the sample to Q Haysep column (column 2). In this column occurs the first separation of the compounds. While the hydrocarbons C_2 - C_5 have a high affinity with the stationary phase, the compounds with Low Molecular Weight (LMW) such as CO, CH_4 , CO_2 , N_2 , O_2 , H_2 do not have great affinity and cross the column earlier than C_2 - C_5 . The purpose of this column is only to separate the hydrocarbons C_2 - C_5 to the LMW. After the last LMW compound detection in TCD, the valve 92 is closed. This valve will act as a back flush flux in order to discard the retained fraction (C_2 - C_5) in column 2 and therefore, only CO, CO_2 , N_2 , O_2 and H_2 will reach the TCD detector. Figure 2C shows the results of LMW gases detection in the TCD: CO_2 (3.0 min) is the first compound that is detected in TCD followed by H_2 (4.2 min), O_2 (5.4 min), N_2 (6.7 min) and CO (9.9 min). Although it is possible to detect C_2 - C_5 in TCD it was chosen to discard these compounds because their detection take more than 50. Furthermore, C_2 - C_5 are in low concentration, therefore, it is necessary to use one specific detector for this purpose.

Detection of H_2S by FPD detector

When the valve 93 is open, 250 µL of the sample is also carried to the Haysep Q (column 1). A standard containing 10 ppm (v/v) of H_2S is injected. In our first trial, no signal after followed injections was observed. How the H_2S is a reactive gas, probably it reacted with the tubing material (stainless steel). Therefore, it was changed the tubing and loop to sulfonert material to avoid some possible reaction. After that, it was possible to detect H_2S how can be viewed on the retention time 17.05 min (Figure 2D).

Limits of Detections (LODs)

Limits of Detection (LODs) of each gas are shown in Table 3. Methane, carbon dioxide and carbon monoxide can be analyzed using TCD and FID detectors. This is advantage because if the samples have low concentration, it will be necessary to use FID detector due its lower LODs and higher sensitivity. Carbon dioxide and carbon monoxide are determined by FID only due the methanator actuation. Even TCD is known as universal detector, in this gas chromatography there are no

Compounds	Limit of Detection (ppm _{v/v})		
	FID	TCD	FPD
Methane	3.0	250	ns
Ethene	0.5	n.a.	ns
Ethane	0.5	n.a.	ns
Propene	0.5	n.a.	ns
Propane	0.5	n.a.	ns
Butene	0.5	n.a.	ns
Buthane	0.5	n.a.	ns
Pentane	0.5	n.a.	ns
Carbon dioxide	3.0	290	ns
Carbon monoxide	1.0	670	ns
Hydrogen	ns	3000	ns
Oxygene	ns	800	ns
Nitrogen	ns	700	ns
Sulfur dioxide	ns	n.a.	0.001

ns - nonspecific detector
n.a. - not applicable for this methodology

Table 3: Limits of detection of gases.

values of LODs for C₂-C₅ in TCD detector because the configuration was performed to detect these gases only in FID detector. Sulfur dioxide is only detected in the selective FPD detector and the LOD was 0.001 ppm_{v/v}. FID detector is nonspecific for H₂S compound and there is no value of LOD for H₂S in TCD detector because our standard gas contained 10 ppm_{v/v} which is insufficient concentration to get some signal in this detector.

Conclusion

The alternative gas chromatograph developed and presented here was able to quantify hydrocarbons (C₁-C₅) and non-hydrocarbons (H₂S, CO, CO₂, N₂, O₂ and H₂) gases in only one injection in the same equipment. Our methodology is very useful in situations where gas samples are scarce for multiple injections such as in head space mud samples from marine sediments.

Our work demonstrated that it is possible to detect low gas content (ppm_{v/v}) and high concentration (%_{v/v}) using FID detector for light hydrocarbons (C₁-C₅). Samples contain high concentration (%_{v/v}) of CO₂ and CO can be detected by the TCD detector, whereas samples containing low concentrations (ppm_{v/v}), need to be directed to the methanator redirected to FID detector.

Other advantage of this device is the H₂S detection by FPD at the same time with other gases, which normally has to be done in separate equipment. Finally, our new equipment setting will extend the gases characterization reducing the time analysis and saving samples that can be used in other analyses such as stable isotopes. Using this alternative

gas chromatography, many types of geochemical samples can be characterized with this device.

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References

- Galimov EM, Kodina LA, Stepanets OV, Korobeinik GS (2006) Biogeochemistry of the Russian Arctic. Kara Sea: Research results under the SIRRO project, 1995–2003. *Geochemistry International* 11: 1053-1104.
- Nemirovskaya IA, Brekhovskikh VF, Kazmiruk TN (2009) Origin of hydrocarbons in bottom sediments of the Ivankovo Reservoir. *Water Resources* 36: 337-344.
- Korobeinik GS, Tokarev VG, Waisman TI (2002) Geochemistry of Hydrocarbon Gases in the Kara Sea Sediments. *Polar and Marine Research* 419: 158-164.
- Safronova NS, Grishantseva ES, Korobeinik GS (2013) Hydrocarbon gases (C₁-C₅) and organic matter in bottom sediments of the Ivankovo Reservoir on the Volga River. *Water Resources* 40: 285-296.
- Vice DH, Halleck PM (1999) The effects of soil environment on the ability of surface geochemical surveys to detect underlying hydrocarbon traps. *Journal of Geochemical Exploration* 66: 457-468.
- Whitcar MJ (1996) Stable isotope geochemistry of coals, humic kerogens and related natural gases. *International Journal of Coal Geology* 32: 191-215.
- Curtis JB (2002) Fractured shale-gas systems. *AAPG Bulletin* 86: 1921-1938.
- Jarvie DM, Hill RJ, Ruble TE, Pollastro RM (2007) Unconventional shale-gas systems: The Mississippian Barnett Shale of north-central Texas as one model for thermogenic shale-gas assessment. *American Association of Petroleum Geologists Bulletin* 91: 475-499.
- Jenkins CD, Boyer CM (2008) Coal-bed and shale-gas reservoirs. *Journal of Petroleum Technology* 60: 92-99.
- Schicks JM, Ziemann MA, Lu H, Ripmeester JA (2010) Raman spectroscopic investigations on natural samples from the Integrated Ocean Drilling Program (IODP) Expedition 311: indications for heterogeneous compositions in hydrate crystals. *Spectrochim Acta A Mol Biomol Spectrosc* 77: 973-977.
- Lu H, Seo YT, Lee JW, Moudrakovski I, Ripmeester JA, et al. (2007) Complex gas hydrate from the Cascadia margin. *Nature* 445: 303-306.
- Bourry C, Chazallon B, Charlou JL, Donval JP, Ruffine L, et al. (2009) Free gas and gas hydrates from the Sea of Marmara, Turkey: Chemical and structural characterization. *Chemical Geology* 264: 197-206.
- Kida M, Hachikubo A, Sakagami H, Minami H, Krylov A, et al. (2009) Natural gas hydrates with locally different cage occupancies and hydration numbers in Lake Baikal. *Geochemistry, Geophysics, Geosystems* 10: 1-8.

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