

On-line full Molecular Characterization of Flashed Gases with a new Generation of NGD Detectors for Micro-GC

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Introduction

Context of the molecular characterization in PVT laboratories

PVT experiments are conducted to calibrate equation of state (EOS) parameters, used for reservoir modeling simulations. The EOS is adjusted based on PVT data (volumetric properties, density, viscosity) and compositions (reservoir fluid, liberated gases during a process, atmospheric liquid). As a result, the accuracy of a fluid model relies on the molecular characterizations and their consistency. The separation step of fluids (gas and liquid) realized in our PVT laboratories is carefully monitored and controlled throughout the entire process. However, on the molecular characterization side, uncertainties regarding the gas composition in some certain fluids may be significant due to two factors: sampling and analytical methods.

Firstly, gases from the processes are sent to a cylinder and then analyzed using a delocalized analytical system. The pressure in these cylinders is reduced to maintain the gas phase. However, in fluids with a high gas-to-oil (GOR) ratio, a pressure reduction can cause the sample to enter the phase envelope. Phase diagrams of fluids with a low GOR compared to the one with a high GOR (and fluid with exotic separation conditions as light oils) are represented on **Erreur ! Source du renvoi introuvable.** The phase envelope is represented in blue, and the orange dot represents the separation conditions of the fluid into gas and liquid phases. On the one hand, in the case of a "standard" gas (a), decreasing the pressure moves the sample state further away from the two-phase zone, ensuring it remains in the gas phase. On the other hand, for a condensate gas (b), reducing the pressure brings the sample conditions back into the phase envelope (two-phase zone), thereby posing a risk of losing the heavy gases.

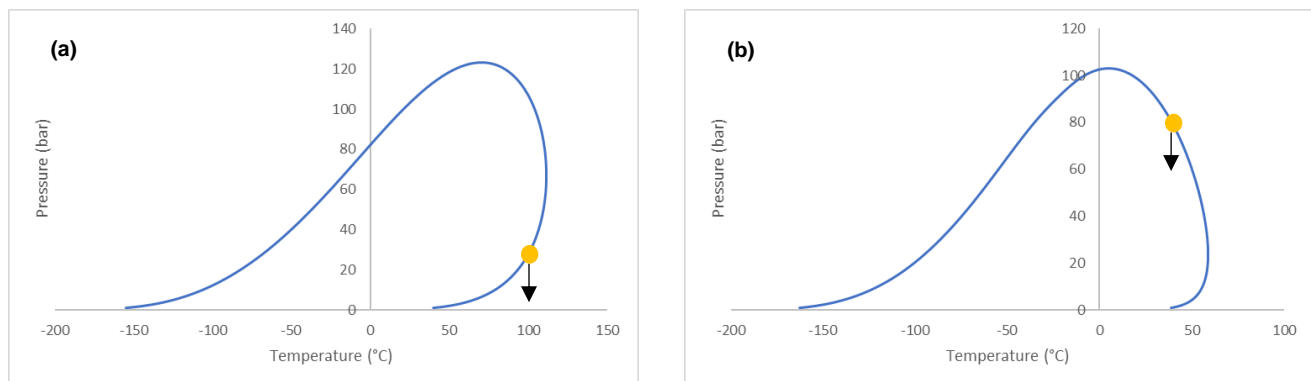


Figure 1. Phase envelope diagrams in blue and the orange dot corresponds to the separation conditions. From left (a) to right (b): diagram of a "standard" gas (low GOR) and a second for a condensate gas (high GOR).

Therefore, bypassing the sampling step through an on-line analysis can effectively reduce these uncertainties. On-line analysis ensures that the entire process from phase separation to analysis is conducted at constant pressure and temperature without any cold spots or pressure losses. The presence of cold spots or a pressure loss increases the risk of gas condensation and subsequent loss of heavy gas compounds which can impact the accuracy of the modeling.

Secondly, in fluids with a low gas oil ratio (GOR) <500, as oil sample, the proportion of hydrocarbons from C₅ to C₁₂ are negligible in the gas phase compared to the oil phase. Nevertheless, in condensate gas with a GOR >500, the proportion of hydrocarbons from C₅ to C₁₂ in the gas phase can be very significant. The current detectors used for gas composition analysis from C₅ to C₁₂ in the gas chromatography (flame ionization detector, FID, and thermal conductivity detector, TCD) operate near their detection limits due to similar response coefficients. Even slight variations can have a significant impact on the state equations and reservoir modeling. Moreover, FID detectors are prohibited for on-site, on-line analysis in ATEX (explosive atmosphere) zone.

To mitigate these uncertainties, a detector with a higher sensibility is required. This detector should also be ATEX-compliant to ensure compatibility with on-site, online analysis.

On-line analysis

In a context of continuous improvement in industrial performance, maintaining optimal process conditions is crucial. A significant industrial challenge lies in the measurement and quantification of essential parameters for process monitoring. These parameters cover physical aspects such as pressure and temperature, as well as physicochemical factors including molecular and elemental composition. Understanding the variations of these influential parameters facilitates the comprehension and design of installations during the R&D phases. Ultimately, it enables effective control and monitoring of industrial processes. The development and application of new analytical technologies in industry enhance process control, ensuring sample representativeness, increased productivity, improved safety and environmental aspects, and accelerated research.

Industrials continue to hold high expectations in terms of innovation (R&D) and implementation for industrial process control:

- To be able to analyze and characterize complex mixtures on-line and, if possible, "in situ", as close as possible to the reactor (analysis at the heart of the process), to gain better insights into phenomena and propose optimizations. Analytical systems compatible with extreme industrial conditions (temperature, pressure, corrosive environment, etc.) are also required.
- Real-time" measurements integrated into advanced control loops to react as quickly as possible in the event of process drift (economic gain, safety aspect in the event of drift that could trigger risks, etc.).
- An "adapted" cost system: with a return on investment that can be justified on each production line (payback concept).
- High-performance miniaturized systems that can be easily adapted to processes and conditions of micro-sampling or "in situ" analysis.
- Miniaturization of systems results in reducing costs associated with online analysis, obtaining rapid analyzes and compatibility with industrial processes such as micro-pilots.

Miniaturized gas chromatography [1]

Micro-chromatographs have been around since the late 70s. The first micro-GC was developed as part of the international space program, thanks to the development of MEMS (micro-electromechanical system) technology [2]. Micro-GCs consist of gas injection valve, a capillary column and silicon TCD, all integrated in very compact unit. They are well adapted to analyze light gaseous samples, up to C₈.

Micro-GC technology is used for detailed and rapid analysis of ambient air, as well as for field and industrial applications. Instruments can be used for quality control of a gaseous effluent (rapid response on material quality) or for environmental monitoring of gaseous emissions from a factory (methane, carbon dioxide, sulfur dioxide, hydrogen sulfide).

Micro-GC, a compact gas chromatography system, is a reliable and robust tool known for its good instrumental performance. However, certain precautions need to be taken when utilizing it. Proper sample treatment is essential and should be adapted according to specific requirements, which may include filtration, traps, heating, and other appropriate techniques.

The micro-GCs dedicated to process control feature a modular, compact, and flexible composition, capable of integrating up to four separate systems. This modular configuration on a single system is a real advantage in terms of versatility; it can perform parallel analyses on several modules to provide much information in a short time. Each analytical compartment or module is heated and incorporates a pressure regulator, a MEMS injector, an analytical column, a reference column, and a detector (micro-TCD). The columns used in these analytical modules have internal diameters of the order of 0.20 mm, and these instruments have detection limits of the order of ten ppm.

Currently, micro-GCs encounter several technological challenges in analyzing “heavy” gases. The implementation of ramp temperature programming on micro-GC represented a notable technological advancement. However, none of the commercially available micro-GCs are currently equipped with a universal detector capable of quantifying gases up to of C₁₂ effectively. This limitation restricts the application of micro-GC for gas quantification in petroleum products. A non-exhaustive literature review on micro-GCs currently on the market, and their technical characteristics has been compiled in Table 1.

Manufacturer	Model	Ramp temperature	Detector	Portable	Modular	ATEX
Agilent Technologies (exVarian)	490 micro-GC		μTCD		X	X
Alpha MOS	Micro GC		μTCD			
Cbana Labs	Portable micro-GC		μFID	X		
Defiant Technology	Frog 4000 Canary-0-3	X	PID ¹	X		
Elster GmbH	Encal 3000		μTCD			X
Falcon Analytical	Calidus	X	μTCD + μFID	X	X	
Global Analyser Solutions	Compact GC 4.0		TCD/PED ² /PID/PFPD ³ /MS ⁴		X	
HNU PID Analyzers	312 Portable GC		PID/TCD/FID	X		
INRAG AG	I-GraphX		μTCD	X		X
Qmicro	Qmicro GC cartridge	X	μTCD			
Seacost	SeaPort		MCCD ⁵	X		
Torion	Tridion-9 GC-MS	X	Trap MS	X		
Siemens	Micro SAM		μTCD			X
INFICON	Inficon modules		μTCD	X	X	X

Table 1. Non-exhaustive literature review on micro-GCs currently on the market, and their technical characteristics

Due to the existing limitations, there is a clear need for the development of a highly universal and sensitive detector that is compatible with micro-GCs for analyzing C₈⁺ cuts. Such a detector would enable accurate and efficient analysis of heavier gases in petroleum products. Additionally, it is essential for the system to have temperature programming capabilities, allowing for optimized separation and analysis.

Furthermore, the complete system should be ATEX certified, ensuring its safe operation in potentially explosive atmospheres. Transportability and portability are also desirable features, allowing for flexibility in various settings and applications. By fulfilling these requirements, the development of such a comprehensive micro-GC system would significantly enhance the capabilities of gas analysis in petroleum products and facilitate broader industrial applications.

¹ PhotoIonization Detector

² Plasma Emission Detector

³ Pulsed Flame Photometric Detector

⁴ Mass Spectrometer

⁵ Multi-core Continuous Collision Detection

Nano-gravimetric detector (NGD) [2]

The Nano-gravimetric detector (NGD), based on nano-electromechanical systems (NEMS) technology, has recently emerged as a miniaturized gas chromatography detector. The NGD detector offers numerous advantages for gas detection:

- **Small Size:** The NGD is compact, allowing for easy integration into miniaturized gas chromatography systems.
- **Low Power Consumption:** The NGD operates on low power, contributing to energy efficiency and prolonged battery life in portable applications.
- **Ultra-Sensitive:** The NGD exhibits exceptional sensitivity, enabling the detection of trace levels of analytes in gas samples.
- **Universal Detection:** The NGD has the capability to detect a wide range of compounds, making it versatile for various analytical applications.
- **Compatible with High-Speed Analysis:** The NGD is suitable for high-speed analysis in gas chromatography, facilitating rapid separation and detection of analytes.
- **Reliability:** The NGD demonstrates consistent and reliable performance over time, ensuring accurate and dependable results.
- **Cost-Effective:** The NGD offers cost-effectiveness due to its long lifespan and minimized maintenance requirements.
- **Non-Destructive:** The NGD operates in a non-destructive manner, allowing for repeated use in multiple analyses.
- **Performance Independent of Carrier Gas:** The NGD's performance remains unaffected by the choice of carrier gas, providing flexibility in gas chromatography setups.
- **Low Environmental Impact:** The NGD has a minimal impact on the environment, aligning with sustainability goals in analytical instrumentation.

The NGD detector consists of two independent arrays of 25 identical silicon resonators (5 μm long, 300 nm wide and 160 nm thick) covered with a 180 nm thick, porous oxide layer and connected electrically in parallel. This coating allows the adsorption-desorption of gaseous compounds at the NEMS surface. The arrays have two different resonance frequencies (75 and 70 MHz) and they can be measured using phase-locked loop electronic circuitry combined with a demodulation technique. Two independent fluidic channels are graved and a silicon cap. The cap is sealed using a glass frit technique on top of the NEMS resonator silicon chip so each array is encapsulated in an independent fluidic channel. The NEMS chip is mounted on a ceramic substrate that can stand a maximum temperature of 250°C. The 75 MHz NEMS array named as analysis channel is connected to the analytical column. A mass shift (m_{ads}) caused by the adsorption-desorption of molecules on the NEMS surface leads to a proportional shift of the resonance frequency. So, the detector response, $R(t)$, is a measurement of the resonance frequency variation in the time ($\Delta f(t)$) and is described with Eq 1:

$$R(t) = \Delta f(t) = \left(\frac{f_0}{2M_{\text{eff}}} \right) m_{\text{ads}}(t) \quad \text{Equation 1}$$

Where M_{eff} is the masse of each resonator and f_0 is the specific resonance frequency for each of them. The 70 MHz NEMS array named as reference channel is connected to the carrier gas through a deactivated capillary. This array is used to reduce the influence of the temperature fluctuation (15 KHz °C⁻¹) on the NGD response. Since two sets of NEMS array are integrated on the same silicon chip, they are submitted to the same temperature. So, the resonance frequency variation, $\Delta f(t)$, can be expressed as follow:

$$\Delta f(t) = f_{\text{analysis}}(t) - f_{\text{reference}}(t) \frac{f_{\text{analysis}}(0)}{f_{\text{reference}}(0)} \quad \text{Equation 2}$$

Where $f_{\text{analysis}}(t)$ is the frequency of the NEMS array connected to the GC column, $f_{\text{reference}}(t)$ is the frequency of the NEMS array used to track temperature fluctuation of the chip and $f_{\text{analysis}}(0)$ and $f_{\text{reference}}(0)$ are respectively the frequencies measured at the injection time $t=0$.

The NGD detention principle is based on an adsorption-desorption mechanism and its sensitivity is directly related to the partition equilibrium of the compound between the concentration in the gaseous phase and the amount adsorbed of the resonator surface. Since the NGD response is not linear for high analyte concentrations, these quantities are related according to the following Langmuir adsorption isotherm relationship:

$$K_T = \frac{n(t)}{M_m C_m(t) \left(1 - \frac{n(t)}{M_m}\right)} \quad \text{Equation 3}$$

Where C_m is the analyte concentration in the mobile phase, n is the adsorbed quantity of matter of analyte in the beam, M_m is the adsorption surface of each beam of the NGD and K_T is the equilibrium constant for the temperature T . For low analyte concentrations, it can be assumed that adsorbed quantity of matter of analyte relative to the adsorption surface of beam is negligible and the following linear relationship is obtained:

$$K_T = \frac{n(t)}{M_m C_m(t)} \quad \text{Equation 4}$$

As a function of chromatographic time t , the absorbed mass, $m_{ads}(t)$, is related to the adsorbed quantity of matter of analyte:

$$m_{ads}(t) = M_w n(t) \quad \text{Equation 5}$$

Where M_w is the molecular weight of the analyte. By combining equations 1, 4 and 5, the NGD linear response as a function de la concentration is obtained:

$$R(t) = \left(\frac{f_0}{2M_{eff}}\right) M_m M_w K_T C_m(t) = S C_m(t) \quad \text{Equation 6}$$

The NGD sensitivity (S) is dependent on NGD geometry, $f_0(0) M_m/(2 M_{eff})$, M_w that is analyte dependent and K_T that is a function of the analyte affinity with the NGD chemical layer for a given temperature. For a chromatographic Gaussian peak with a concentration-dependent detector, such as NGD, the peak area A_p can be calculated by integration of equation 6.

The isotherms for each analyte can be thus obtained through representation of analyte peak area versus analyte injected concentration. The equation 6 is only used at low analyte concentrations in the linear concentration range. For high analyte concentrations, the response NGD is related to concentration through a hyperbolic equation obtained by combining equations 1, 3 and 5:

$$R(t) = \left(\frac{f_0}{2M_{eff}}\right) M_m M_w \left(\frac{K_T C_m}{K_T C_m + 1}\right) = \frac{a C_m}{b + C_m} \quad \text{Equation 7}$$

Where a is dependent on NGD geometry and analyte M_w , and $b(1/K_T)$ is a function of the analyte affinity with the NGD chemical layer for a given temperature. This affinity is also strongly related to the NGD temperature, so the sensitivity can be optimized through temperature detector control. Previous studies have shown that the adsorbed amount of analyte decrease at higher NGD temperature for a fixed gas phase concentration. This is related to the partition coefficient K_T which is only dependent on temperature. Indeed, K_T is related to the standard enthalpy ΔH° and to the standard entropy ΔS° of adsorption for a given solute according to equation 8:

$$\ln(K_T) = -\frac{\Delta H^\circ}{R} \frac{1}{T} + \frac{\Delta S^\circ}{R} \quad \text{Equation 8}$$

Where R is the gas constant and T is the NGD absolute temperature. According to Ellingham approximation, ΔH° and ΔS° are assumed to be constant in the applied temperature range for a given analyte. Previous studies have shown that the logarithm of the NGD sensitivity for different n-alkanes is a function of the reciprocal of the NGD temperature and a linear correlation was obtained between these two factors. It has also been demonstrated that the slope increases linearly as a function of the number of carbon atoms in the alkyl chain of the same family of compounds. It is then possible to predict the NGD sensitivity for molecules belonging to the same family at any given temperature. However, for the same number of carbon atoms of compounds of different families, at a constant NGD temperature, different NGD sensitivities are obtained.

The affinity of the compounds with the silicon porous oxide covering the resonator beam is consistent with the polar nature of the compounds, enabling stronger interactions with the beam. To facilitate the quantification of volatile organic compounds, a linear relationship between NGD sensitivity and the number of carbon atoms is utilized. In order to compare the sensitivity of different compounds from various families to n-alkanes, a relative response factor has been introduced. Similar to how the Kovats index

compares the retention time of a specific compound to n-alkanes on a GC column with a specific stationary phase, the NGD relative response index compares the NGD sensitivity to the n-alkanes.

To calculate the NGD relative response Index, the NGD sensitivity of a compound is interpolated between the sensitivity for adjacent n-alkanes according to the following equation:

$$I_R = 100 \left(n + \frac{R_x - R_n}{R_{n+1} - R_n} \right) \quad \text{Equation 9}$$

Where R_x is the logarithm of the NGD sensitivity to the specific compound and R_n , $R_{(n+1)}$ are the logarithm of the NGD sensitivity to the adjacent n-alkanes.

The objective of the present study is to quantify hydrocarbons in gas samples ranging from C_3 to C_{10}^+ using the NGD detector. Typically, this range of hydrocarbons is analyzed offline using GC-FID, while lighter gases such as N_2 , O_2 , H_2 , He, CH_4 , and C_2H_6 are analyzed using GC-TCD with specific analytical columns. However, the main limitation of conducting online analysis of gas samples in PVT units is primarily due to the non-ATEX compliant nature of the FID detector. By replacing the FID detector with an NGD detector that provides accurate and precise quantification, it becomes feasible to perform online analysis.

The isotherms of different compounds (n-alkanes C_3 - C_{10} , iso-alkanes i- C_4 and i- C_5 and BTEX) from different families were determined by plotting the NGD area as a function of concentration. A linear relationship was observed for all compounds in the concentration range studied. The isotherms obtained allowed quantification of the hydrocarbons studied with errors < 10% and with an accuracy < 5%. As expected, a linear relationship was obtained between the logarithm of the NGD sensitivity and the number of carbon atoms for the same family of compounds. This relationship, specific for each family, allowed the quantification of the hydrocarbons studied with similar errors to the previous method. To simplify the quantification process, the relative response factors for each hydrocarbon studied to the n-alkanes were calculated and quantitative errors < 5% were obtained. The Kovats indices for each hydrocarbon studied were finally calculated to further simplify the quantification, obtaining the NGD sensitivity of each hydrocarbon as a function of retention time. This approach allowed the accurate quantification of iso-alkanes with respect to n-alkanes with an error of 3%. However, the Kovats indices calculated for BTEX resulted in quantitative errors of the order of 30-50%. It appears that this approach cannot be used for hydrocarbons with a polarity very different from that of n-alkanes and further studies are necessary.

Since gaseous standards are not accessible for all hydrocarbons found in the gas samples, the NGD response factor for hydrocarbons without available gaseous standards was estimated by utilizing the linear relationship between NGD sensitivity and the number of carbon atoms within the same family. Finally, relative response factors were calculated for each of the hydrocarbons present in the gas samples, except for cycloalkanes for which no standard was available. The quantitative data obtained were compared with those obtained by GC-FID and a discrepancy of less than 10% was obtained between the two detectors. This discrepancy can be considered acceptable for the on-line analysis of gas samples in PVT units.

Material and methods

Standards and samples

Different gas standards of n-alkanes, iso-alkanes and BTEX in nitrogen were supplied from Air Products (France): a gas cylinder at 200 bar containing the alkanes n- C_3 (29700 ppm-mol), i- C_4 (9770 ppm-mol), n- C_4 (11690 ppm-mol), i- C_5 (1895 ppm-mol) and n- C_5 (10110 ppm-mol); a gas cylinder at 200 bar containing the n-alkanes n- C_6 (663 ppm-mol), n- C_7 (204 ppm-mol) and n- C_8 (64 ppm-mol); a gas cylinder at 90 bar containing the n-alkanes n- C_9 (22.5 ppm-mol) and n- C_{10} (9.4 ppm-mol); and a gas cylinder at 30 bar containing benzene (281.4 ppm-mol), toluene (31.25 ppm-mol), ethylbenzene (30.35 ppm-mol), m-xylene (29.77 ppm-mol), p-xylene (29.7 ppm-mol) and o-xylene (30.49 ppm-mol).

Two real gas samples were injected for identification and quantification purposes.

μ GC-NGD Instrument

A modular multi gas analyzer ChromPix 2 (4 channels) and a plug&play analytical module specially developed for analysis of complex gas mixtures from C_3 to C_{12}^+ were supplied from APIX Analytics SA (Grenoble, France). This module embeds a whole analytical GC chain: i) a 6-way 2-position injection valve thermally controlled to introduce the sample into the chromatographic system, ii) an oven with ramp temperature control (up to 100°C/min) for ultrafast separation and detection and a maximum temperature at 280°C, iii) a GC capillary column, and iv) a NGD detector with a fast temperature control up to 200°C.

Separations of different mixtures were performed on a GC-column HP-PONA (50 m length, 0.20 mm internal diameter, and 0.50 μ m film thickness: Agilent, France). Helium was used as carrier gas with a constant pressure of 3 bar. The injector temperature was

set at 60°C. The injection loop volume was 25 µl. The sampling pressure was 1 bar. The GC temperature was programmed with an initial temperature of 35°C and a hold time of 15 min, a ramp rate of 1.5°C/min until 70°C and a second ramp rate of 3°C/min until a final temperature of 170°C and a final hold time of 11 min. A constant temperature of 40°C was used in the NGD detector. In order to eliminate drift, regeneration of the NGD detector was systematically carried out between analysis by maintaining NGD temperature at 180°C for 5 min.

An Aiolos II Gas Mix (Alytech, France) was used to dilute standard gases and perform a multi-point calibration. Nitrogen was used as dilution gas.

GC-FID Instrument

A 6850 Gas Chromatograph (Agilent Technologies, France) with a 6-way 2-position valve, a split/splitless injector, and a flame ionization detector with a HP-PONA capillary column (50 m length, 0.20 mm internal diameter, and 0.50 µm film thickness; Agilent, France) was used. Hydrogen was used as carrier gas with a constant pressure of 1.23 bar. The injector temperature was 200°C. The injection loop volume was 25 µl. The sampling pressure was between 0.9 and 1 bar. The GC temperature was programmed with an initial temperature of 35°C and a hold time of 6.6 min, a ramp rate of 1.4°C/min until 114°C and a second ramp rate of 2.6°C/min until a final temperature of 160°C and a final hold time of 30 min. The FID was set with a constant air flow of 300 ml/min and 30 ml/min for hydrogen and a constant temperature of 300°C.

Results and discussion

Separation of hydrocarbons standard gas Mixtures at a constant NGD temperature

Standard gas mixtures containing different concentrations of n-alkanes (C6-C10) and BTEX (benzene, toluene, ethylbenzene, m-xylene, p-xylene, and o-xylene) in nitrogen were analyzed. To make sure that the NGD temperature set at 40°C did not affect the efficiency, this separation was also previously performed with a GC-FID Instrument. The observed separation efficiency ($N = t_r/\sigma$)², where t_r is the retention time and σ is the peak standard deviation, was 10715 and 9225 for the n-alkane C6 and 36199 and 39361 for o-xylene by GC-FID et GC-NGD, respectively, ensuring the chromatographic resolution required for the analysis of gas samples. Figure 2 shows the chromatograms obtained with the GC-NGD (2a) and GC-FID (2b) for the standards gas mixtures. Complete chromatographic resolution of the meta- and para-xylene isomers is not possible with the HP-PONA column, independently of the detector. Integration of the chromatographic peaks for these isomers was performed as a single compound. As expected, the FID peak height and peak area varied according to injected carbon amount of each hydrocarbon. On the other side, because the NGD sensitivity is strongly dependent on the solute, the response factor varied according to the amount of hydrocarbon injected, its molecular weight, and affinity of the compound with the silicon porous oxide covering the resonator beam.

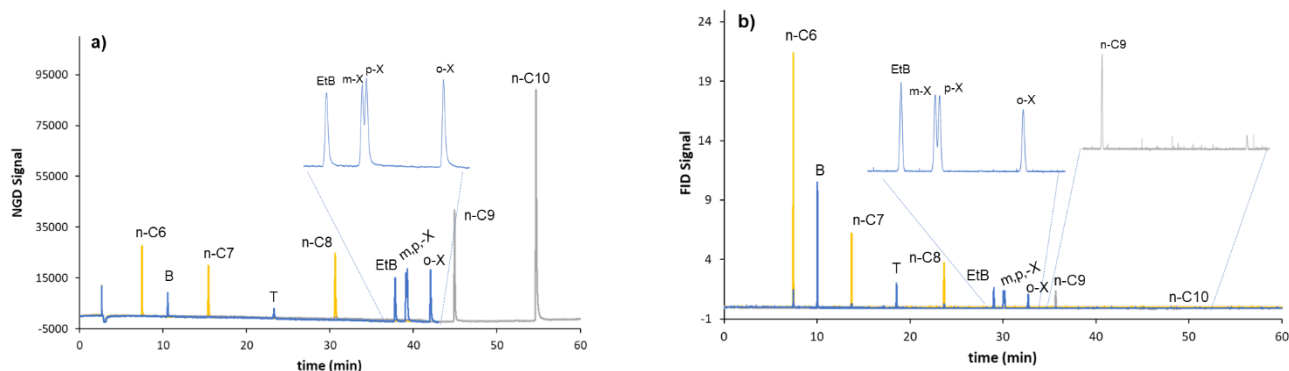


Figure 2. From left to right : chromatograms obtained of standard gas mixtures of n-alkanes C6-C10 and BTEX with the NGD (Fig. 1a) and FID (Fig. 1b) detector (each color corresponds to a single run with different standard mixture)

The limit of detection for the different analytes, defined by the minimal concentration injected in the column required to produce a signal greater than three times the standard deviation of the noise level, by GC-NGD and GC-FID is given on Table 2. LODs obtained from n-C6 to n-C8 were higher using the NGD detection. A decrease of the detector temperature could improve NGD sensitivity. However, the temperature used in NGD detector of 40°C is at the lower limit of the instrument. In contrast, NGD detection limits decreased for hydrocarbons eluted after n-C8, reaching a 30-fold lower for n-alkane C10.

compound	NGD LOD (ppm-mol)	FID LOD (ppm-mol)
nC6	2.42	0.36
Benzene	2.41	0.30
nC7	1.00	0.40
Toluene	0.62	0.23
nC8	0.31	0.19
EtB	0.22	0.35
m-X	0.21	0.33
p-X	0.20	0.33
o-X	0.20	0.35
nC9	0.06	0.18
nC10	0.01	0.51

Table 2. Limits of Detection (ppm-mol) for the standard gas mixtures of n-alkanes C6-C10 and BTEX obtained with NGD and FID detector.

Isotherm Construction

Different standard gas mixtures: i) n-alkanes C3-C5, iso-C4 and iso-C5, ii) n-alkanes C6-C8, iii) n-alkanes C9-C10 and iv) BTEX, were analyzed by GC-NGD under the same conditions. Firstly, the gas standards were analyzed by direct connection to ChromPix analyzer. To obtain the isotherms for each hydrocarbon, different dilutions of gas standards were carried out with the Gas Mix diluter. Repeatability of the peak area for $n=5$ at the highest concentration was found to be below 2% for all hydrocarbons, whereas it was approximately 5% for BTEX compounds due to the lower signal obtained by the NGD. Plotting the analyte peak area against analyte concentrations exhibited a linear relationship for all compounds within the studied concentration range. The obtained isotherms for each hydrocarbon were utilized for quantification through external calibration. Figure 3 illustrates the percentage quantitative errors calculated as the deviation between the calculated concentration and the actual concentration of each compound across all analyzed concentrations. For most hydrocarbons, errors lower than 10% were observed across the range of concentrations analyzed. However, aromatic hydrocarbons, namely toluene and m,p-xylene, exhibited a larger error of 20% at the lowest concentration due to the low intensity of the NGD signal obtained. Overall, the GC-NGD analysis demonstrated reliable performance, with quantification errors below 10% for most hydrocarbons and concentrations analyzed.

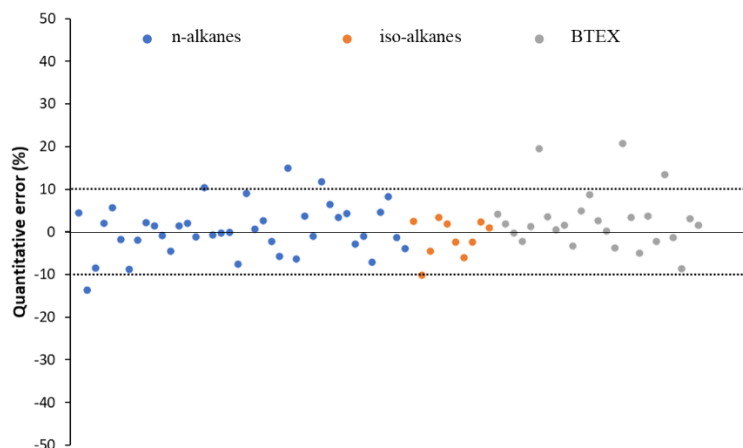


Figure 3. Quantitative errors (%), expressed as deviation between the calculated concentrated and the real concentration of each compound for all concentrations analyzed, obtained from the quantification using different isotherms.

Carbon number effect

The sensitivity of the NGD for each hydrocarbon was determined by calculating the slope at the origin of the isotherms obtained (eq. 6). This sensitivity value is a measure of the NGD's response to each hydrocarbon and is reported in Table 3. It was observed that the NGD sensitivity increased in accordance with the order of elution of the hydrocarbons.

compound	NGD Sensitivity (Peak area/ppm-mol)
nC3	0.9
i-C4	3.3
nC4	5.4
i-C5	17.3
nC5	22.6
nC6	142
Benzene	161
nC7	646
Toluene	904
nC8	3061
EtB	4405
m,p-X	4491
o-X	4557
nC9	14691
nC10	86760

Table 3. NGD sensitivity calculated from slope at the origin of the isotherms for each hydrocarbon of different families studied

Different quantification methods were evaluated making use of this increased sensitivity of the NGD detector in order to simplify the quantification process and to calibrate hydrocarbons for which specific standards are not available.

The logarithm of NGD sensitivity can be related to the number of carbon atoms of compounds of the same family. Figure 4 shows the response (logarithm of NGD sensitivity) for the different families of hydrocarbons analyzed as a function of the number of carbon atoms in the molecular structure at a NGD temperature of 40°C. A linear relation was obtained for hydrocarbons of the same family.

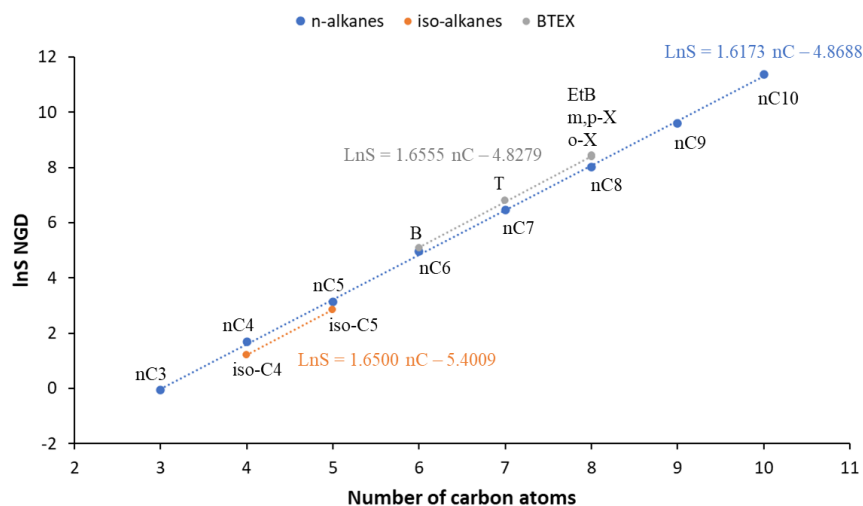


Figure 4. Logarithm of NGD sensitivity obtained from the isotherms of hydrocarbons gas mixtures versus the number of carbon atoms for each family of compounds

The quantification of hydrocarbons at all analyzed concentrations was conducted using the linear relationship established for each family of hydrocarbons. Quantitative errors were calculated as the deviation between the calculated concentrations and the actual concentrations (as shown in Figure 5). For most hydrocarbons and concentrations, errors lower than 15% were obtained. However, larger errors above 20% were observed for n-alkanes C3, C6, and C7, as well as for the aromatic hydrocarbons toluene and m,p-

xylene, particularly at the lowest concentration. This approach offers a satisfactory quantification method that simplifies the quantification process. Working within the linear range of the detector, a single analysis of each standard is sufficient for quantifying the studied compounds. Furthermore, it is possible to predict the sensitivity of intermediate compounds present in gas samples based on the number of carbon atoms. This enables the quantification of hydrocarbons for which specific standards are not available. This methodology will be implemented for quantifying all hydrocarbons present in gas samples, ranging from C3 to C10, once they have been identified. Overall, this quantification approach provides accurate results with acceptable errors and offers the potential for predicting the sensitivity of uncharacterized hydrocarbons based on their carbon atom count, enabling broader quantification capabilities.

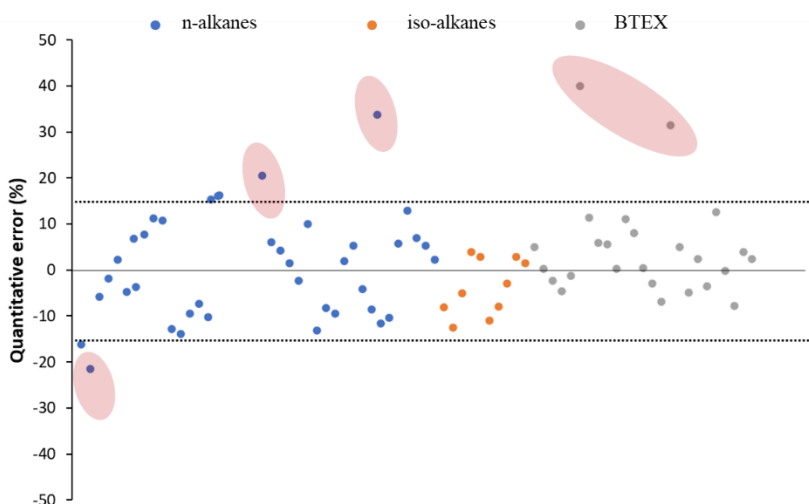


Figure 5. Quantitative errors (%), expressed as deviation between the calculated concentrated and the real concentration for each hydrocarbon for all concentrations analyzed, obtained from the quantification using the linear relation of the logarithm of NGD sensitivity as a function of the number of carbon atoms for each family compounds

The response of the NGD is influenced by the compound's affinity for the silicon porous oxide layer that covers the resonator beam. A higher response indicates a greater affinity of the compound with the silicon porous oxide. In the studied compound families, aromatic hydrocarbons exhibited a higher affinity compared to n-alkanes, while n-alkanes had a higher affinity than iso-alkanes. This trend aligns with the polar nature of the compounds, as polar compounds tend to have stronger interactions with the silicon porous oxide layer. To explore this further, the hypothetical number of carbon atoms was calculated for iso-alkanes and BTEX (benzene, toluene, ethylbenzene, and xylene) using *equation 9* without multiplying by 100 (Figure 6). The logarithm of the NGD sensitivity was plotted against the number of hypothetical carbon atoms calculated for iso-alkanes and BTEX. Remarkably, a linear relationship was observed irrespective of the polarity of the compounds. Hydrocarbon quantification for all analyzed concentrations was conducted using the linear relationship established for linear alkanes. The quantitative errors obtained using this approach were similar to those obtained in the previous method. However, while the Kovats index only requires the retention time of the compounds, the hypothetical carbon number necessitates the analysis of each specific compound to obtain the NGD response. A prediction of the hypothetical number of carbon atoms will be made for the hydrocarbons present in the real samples. The quantitative results obtained using this prediction will be compared with those obtained by GC-FID for further validation and assessment.

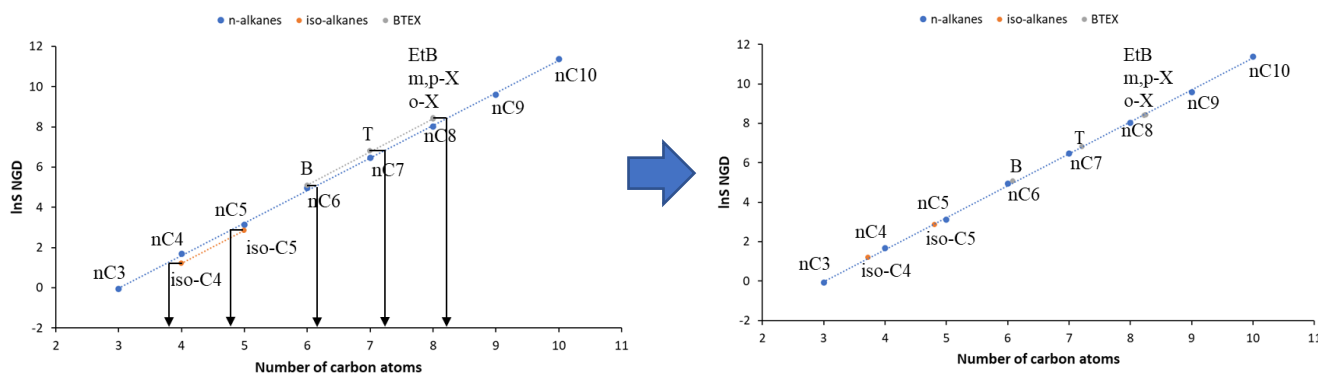


Figure 6. NGD Calibration methodology to obtain the hypothetical number of carbon atoms in relation to the n-alkanes

Conclusion

In conclusion, the Nano-gravimetric detector (NGD) covering a hydrocarbon range from C_1 to C_{40}^+ represents a significant advancement in miniaturized gas chromatography (GC) detection. The NGD offers multiple advantages including small size, low power consumption, ultra-sensitivity, universality, compatibility with high-speed analysis, reliability, cost-effectiveness, long lifespan, non-destructive operation, independence from carrier gas, and minimal environmental impact.

The NGD demonstrates excellent performance in quantifying hydrocarbons, with errors below 15% for most compounds and concentrations analyzed. Although aromatic hydrocarbons and certain n-alkanes displayed small quantification errors at lower concentration, overall quantification results were satisfactory. The NGD's linear response to the number of carbon atoms allows for the prediction of compound sensitivity, facilitating quantification even for compounds without specific standards.

This innovative detection technology simplifies the quantification process and requires a single analysis of each standard, reducing analysis time and resource requirements. The NGD's potential for quantifying a wide range of hydrocarbons opens possibilities for analyzing complex mixtures in various applications, such as the characterization of petroleum products.

Further validation and comparison with GC methods, such as GC with flame ionization detection (GC-FID), will enhance the credibility and accuracy of NGD quantification results.

In a context of reducing greenhouse gas emissions (CO_2) and the use of natural gas in the energy transition, gas condensate will be more and more present on our activities and portfolio. Moreover, in the context of swelling, a NGD would be able to characterize gases after the separator to monitor them before reinjection in the oil reservoir.

In summary, the NGD offers a promising solution for miniaturized gas chromatography detection, enabling sensitive and reliable quantification of hydrocarbons. Its small form factor, energy efficiency, and broad applicability make it a valuable tool for gas analysis in diverse fields including environmental monitoring, petrochemical industry, and process control.

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