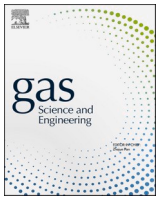
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Quantitative composition analysis of natural gas by high-pressure proton low-field NMR spectroscopy: Development of an improved experimental methodology

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ABSTRACT

Natural gas (NG) has been proposed as a bridging fuel between fossil and renewable energy sources, playing a significant role in the decarbonization of the energy sector. Its commercial value and the integrity of the NG infrastructure depend on the NG physical properties, which are strongly related to its composition. Thus, the development of low-cost and reliable analytical methods for composition analysis of NG can enable a more efficient operation. Recently, we showed that high-pressure (HP) benchtop ^{1}H NMR spectroscopy combined with indirect hard modelling (IHM) is an efficient and low-cost method for composition quantification of NG. The current work extends this methodology by introducing and testing novel experimental strategies for increasing the reliability and accuracy of the method. This new approach includes the use of a recently published high-pressure tube design and single-scan acquisition combined with novel quality control parameters to obtain highly reproducible peak shape ^{1}H NMR spectra over long periods. The proposed methodology tested on binary, ternary, and more complex mixtures at 200 bar and 160 bar gives compositions in excellent agreement with the vendor certificates.

1. Introduction

During the last few decades, the energy sector has been going through a long-term transformation process to meet the society energy demands while fulfilling the international agreements that aim at the reduction of carbon dioxide (CO_2) emissions (Mac Kinnon et al., 2018). The derived mitigation policies have lead natural gas (NG) to occupy a unique role around the globe in the transition process from the traditional CO_2-emitting fossil fuels to cleaner energy options (Gürsan and de Gooyert, 2021). The role of NG in this transition is expected to be even more important in less developed countries, where an immediate implementation of clean and renewable energy is not feasible due to the associated high costs and lack of infrastructure for its generation (Mohammad et al., 2021; Bistline and Young, 2022). Another critical aspect in the value chain is the transport of NG through expensive infrastructure, such as storage facilities, compressor units, and extensive pipelines whose designs are based on the physical properties of NG including gas compressibility and specific gravity (Fredheim et al., 2016; Faramawy et al., 2016; Ríos-Mercado and Borraz-Sánchez, 2015; Lim et al., 2013). With increasing global diversification of NG supply sources, concerns regarding equipment operation and possible safety risks linked to the resilience of the existing NG network need to be considered (Denys and de Vries, 2013).

The NG and oil prices have traditionally been linked as both were considered mutual substitutes within various processes, but with the new global energy conditions, NG has continuously been developing its own market, which makes its price largely dependent on its own offer and demand dynamics (Hulshof et al., 2016; Uribe et al., 2022; Guan et al., 2023). This price is given in energy content units (e.g., MWh, MBTU) which depends on the physical properties derived from the

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specific composition of the NG (Zhao et al., 2019). Therefore, accurate quantitative composition analysis is necessary to characterize physical properties such as calorific value, density or mean molar mass, which can be used for both trading and technical purposes.

Gas Chromatography (GC) is usually the method of choice to perform accurate NG composition analysis with steadily reported upgrades aiming to enhance its robustness (Karpash et al., 2010; Rhoderick, 2003; Brown et al., 2004; Veerakumar et al., 2018). For instance, gas chromatographs are normally found in custody transfer locations for the quality control of NG required by contractual obligations during its commercialization (Koulinas et al., 2022; Veerakumar et al., 2019). Such measurements are conducted at a working pressure of 1 atm. The method has high analytical performance considering constant replacement of the chromatographic column and regular calibration efforts. Moreover, GC has to be operated by highly trained personnel and usually under controlled conditions.

Therefore, various alternatives to GC are currently under development. Among them, spectroscopic methods, such as Infrared (IR) and Raman spectroscopy, show already at the current development stage a high potential for composition analysis of NG (Li et al., 2012; Marteau et al., 1996; Bai et al., 2009; Kiefer et al., 2008). For this purpose, IR is usually complemented with chemometric methods such as principal component analysis, principal component regression or partial least-squares (Van Agthoven et al., 2002; Haghi et al., 2017). For these intensive data-driven analytical solutions, a calibration spectra data set covering the concentration ranges of interest of the different gas species in the mixture, the pressure and temperature ranges to be used, and the presence of water or any other contaminant, needs to be populated to build a calibration model able to correlate spectral variations with the various component's concentration (Van Agthoven et al., 2002; Alsmeyer et al., 2004; Zientek et al., 2014). Being another promising option, Raman spectroscopy was successfully applied for the composition analysis of gaseous fuels of a gas turbine power plant (Kiefer et al., 2008). With all components present in NG detectable with Raman spectroscopy (Petrov and Matrosov, 2016; Knebl et al., 2021; Gao et al., 2019), the pressure and temperature dependence of the methane signal (Tanichev and Petrov, 2022) and the high noise levels caused by laser beam dispersion on liquid droplets and overlapped contaminant peaks with the fingerprint peaks increase the complexity in the analysis of Raman spectra (Dąbrowski et al., 2019). These issues have been recently addressed by the development of high-power small-sized lasers and more sensitive sensors to improve the detection limits (Petrov et al., 2021; Sieburg et al., 2019). Nevertheless, the development of a robust analytical method for the quantitative composition analysis of NG suited also for in-field and remote applications is still in high demand.

NMR spectroscopy is another method that shows high potential as an alternative to GC. Using high-field ^{13}C NMR spectroscopy and a dedicated high-pressure setup, quantitative analysis was conducted on representative complex gas mixtures at 44 bar and in excellent agreement with the GC values (Meyer et al., 2017). The major issue of this approach was the low natural abundance of ^{13}C which led to several days of spectra acquisition for a single sample. Such long measuring times and the associated drawbacks of the high-field NMR devices (including high costs, large size, intensive maintenance, and the need for specialized personnel) hamper the use of this approach as an economically feasible alternative to GC for fast and low-cost composition analysis screening. We could recently show that these issues could be circumvented by a combination of proton low-field high-pressure NMR spectroscopy and IHM (Duchowny et al., 2022a).

For this, a newly introduced high-pressure setup for benchtop NMR allowed the measurement of gaseous samples up to 200 bar (Duchowny et al., 2021). The application of IHM enabled the extraction of quantitative information from ^{1}H NMR spectra of various NG samples pressurized at 200 bar in a short period of time, without the need of calibration and in excellent agreement with the GC data (Duchowny et al., 2022a). Yet, despite successful proof-of-concept shown on four ternary mixtures containing methane, ethane, and propane and a more complex sample, further improvements were required to enhance the applicability and reliability of the proposed approach also towards an online monitoring scenario. Thus, within the current work, novel strategies are proposed to improve: 1) the quantification of the methane signal, as even small errors for the integral of this component leads to large errors for the composition of the other components; 2) the spectral resolution, which is of fundamental importance for methane to have a signal well separated from the other components, but also for improved differentiation of the higher-order hydrocarbons (HC); 3) the quality of spectra of higher-order HC using a higher number of scans for a better signal-to-noise ratio (SNR); and 4) the reproducibility of spectra with passing of time. In addition, a higher number of gaseous mixtures were included to assess the proposed concept. Finally, it will be demonstrated how the implementation of these strategies helps to build a robust and refined methodology for the composition analysis of complex NG mixtures by ^{1}H NMR spectroscopy at 200 bar and 160 bar in excellent agreement with the vendor certificates.

Given the advantages of modern benchtop NMR devices in terms of affordable prices, compact size, user-friendly interfaces, reduced maintenance, versatility, and the quantitative nature of the NMR experiments without the need of calibration (Castaing-Cordier et al., 2021; Meyer et al., 2016; Rudszuck et al., 2021; Giraudeau, 2017, 2023; Simmler et al., 2014; Holzgrabe et al., 2005), we expect that the proposed experimental approach will open new avenues for this analytical method for a broader range of gaseous mixtures. In addition, the whole methodology is amenable to automatization, which is of key importance for online composition monitoring.

2. Experimental section

2.1. Gas samples

Methane 4.5 (99.995%) was purchased from Westfalen AG (Münster, Germany). A binary mixture with a content of 92.43% methane and 7.57% ethane was purchased from Praxair (Ratingen, Germany). Two different batches of gas mixtures were purchased from Linde AG (Leuna, Germany): 1) a set of gaseous samples of various HC diluted in argon, supplied with a DIN EN ISO 6141 certificate (Table SI1) and 2) gaseous mixtures containing three and four components (Table SI2). The 11-component mixture (11D) (Table SI3) previously used (Duchowny et al., 2022a), was supplied by Gassco AS (Haugesund, Norway) with a DIN EN ISO 6141 certificate. All used mixtures in this study contained concentrations comparable to those typically encountered in real NG applications.

2.2. Refined high-pressure setup for benchtop NMR

The high-pressure setup used in this study (Fig. 1) is designed and built at the Institut für Technische und Makromolekulare Chemie (ITMC), RWTH Aachen University and is capable of operating up to 200 bar. Excepting the HP tube and its connecting PEEK capillary to the HP setup, all the other components were the ones employed in our previous work for the composition quantification of NG (Duchowny et al., 2022a). While a detailed description of the HP setup and of the new HP tube and their working principle can be found in refs. (Duchowny et al., 2021, 2022a, 2022b), some main features are still given in Supporting Information for the sake of clarity. A key component of the HP setup that largely contributed to boost the HP NMR's robustness, is the refined sapphire HP tube design recently published (Duchowny et al., 2022b). This novel tube has according to ref. (Duchowny et al., 2022b) following improvements as compared to the old design presented in ref. (Duchowny et al., 2021): 1) a polyether ether ketone (PEEK) capillary tube with a 1/16″ outer diameter instead of the previously used steel capillary that connects the NMR tube to the connection attached on the HP metal panel, 2) a small PEEK attachment rather than a bulky metal attachment,

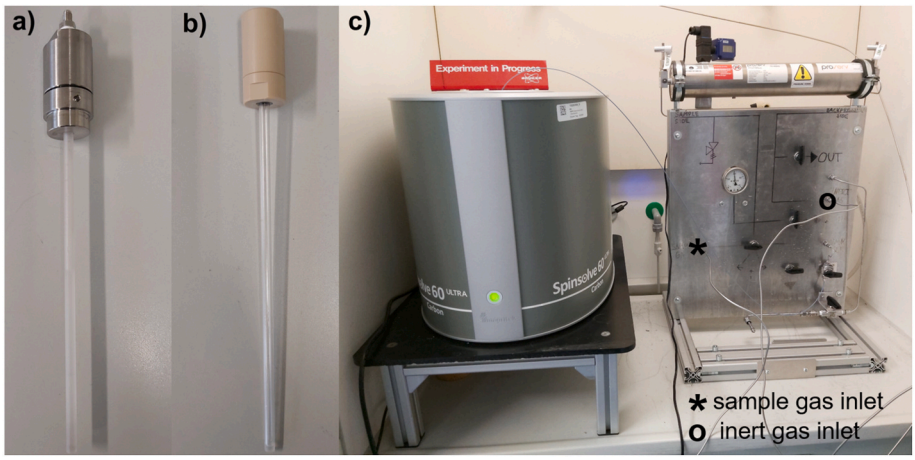


Fig. 1. Photograph of a) the old high-pressure sapphire tube using a titanium attachment employed in ref. (Duchowny et al., 2021), b) refined high-pressure sapphire tube with a polyether ether ketone attachment (Duchowny et al., 2022b), and c) high-pressure setup and the employed low-field NMR device placed together inside a fume-hood. Please note the difference in the optical transparence of the two sapphire tubes which is due to the use of different abrasive materials during the polishing procedure.

and 3) a better sapphire quality tube due to an improved manufacturing process. More specifically, standard abrasive tools containing magnetic particles used to manufacture the sapphire tube having a flange and used in our previous work (Duchowny et al., 2021, 2022a), were replaced by non-magnetic abrasive tools. The dimensions of the tube are similar to the older sapphire tube: 5 mm outer diameter, 3.2 mm inner diameter, and a length of 178 mm.

2.3. Sample preparation

Although the steps for preparing the samples are similar to those presented in (Duchowny et al., 2021, 2022a), the considerably reduced inner diameter of the newly implemented PEEK capillary attachment (Duchowny et al., 2022b) connecting the sapphire tube with the HP setup slightly increased the time for reaching stable pressure along the whole setup. Moreover, an even more rigorous vacuum-flushing process to ensure the removal of traces of previously measured samples was implemented during this work. Hence, the two sample preparation procedures required in this work were adapted accordingly prior to conducting the NMR measurements (see Supporting Information).

2.4. NMR experiments

The proton NMR spectra of samples pressurized at 160 bar and 200 bar were recorded with a Spinsolve 60 ULTRA NMR spectrometer from Magritek (Aachen, Germany) working at a ^{1}H frequency of 60 MHz and at a temperature of 26.5 °C. The spectrum of each sample was obtained by using a new experimental procedure which is described in the results section. It includes the use of single-scan acquisition, the selection of high-quality spectra with the help of an implemented quality control (QC) algorithm in MATLAB (Version 9.9.0.1570001 (R2020b) Update 4), spectra alignment using the methane signal (the predominant specie in NG) which was referenced to 0 ppm, and finally their averaging. The referencing is done in order to be able to compare the spectra recorded at different pressures and at different magnetic fields. The spectra were acquired using 16 k data points and a dwell time of 200 μs. A waiting time of 2 min was set between two scans to ensure quantitative data. As demonstrated in our previous work (Duchowny et al., 2022a), this waiting time is longer than 5 times the spin-lattice relaxation time T_1 of the slowest relaxing HC. For the implemented quality control assessment of the recorded spectra (see section 3.1.3), each file containing the raw FID was zero-filled to 256 k data points and subsequently Fourier Transformed with MATLAB. To conduct the IHM analysis of the spectra that met the quality control criteria, the corresponding FIDs were zero-filled (256 k) and Fourier Transformed and the spectra aligned and averaged using the software package PEAXACT version 5.0 (S.PACT GmbH, Aachen, Germany). The spectra were recorded by the Spinsolve software with the proper phase and baseline; therefore, no further corrections were necessary.

2.5. Indirect hard modeling methodology

The IHM concept was originally developed to model vibrational spectra from Raman or mid-IR spectroscopy (Duchowny et al., 2022a). With the passing of time, the application of IHM was extended also for NMR spectroscopy (Zientek et al., 2014, 2016a; Duchowny et al., 2022a, 2022c; Sagmeister et al., 2021). An indirect hard model consists of a set of parameterized peak-shaped signals that are based on the “pure component” spectra of individual substances. The peak-shaped signals themselves are linear combinations of several Pseudo-Voigt functions, which are linear combinations of a Gaussian and a Lorentz function. Each Pseudo-Voigt function is defined by the position of the abscissas, the maximum intensity of the signal, the full-width at half maximum height, and the Gaussian fraction ranging from 0 to 1. Once the model is fit to a spectrum, the areas can be extracted to analyze the contribution of the different components.

The key for the robustness of IHM relies on its fit algorithm that allows several degrees of freedom. Depending on the selected “interaction mode”, the position of the components of an IHM may be fixed or shifted along the abscissa axis (chemical shift axis in NMR). In addition, individual peaks may change their positions inside of a component, as well as their intensities and peak shapes. Besides, tolerance ranges for the parameter variations can be set for achieving the optimal performance of the prediction. Thus, an IHM component can be fitted in spite of linear and nonlinear variations of the mentioned spectral parameters (Alsmeyer et al., 2004). Moreover, IHM is able to overcome spectral distortions induced by various external factors, including those produced by the HP tube (Duchowny et al., 2022a).

To build an IHM, it is necessary to choose the appropriate samples for each individual pure component to capture their characteristic spectral signatures. Furthermore, a set of test samples with known concentrations are used to validate and assess the IHM performance. These samples should be chosen such that their concentrations and chemical environment are similar to the conditions found in the intended application. This helps to minimize the error by minimizing algorithm iterations. If the fit of the IHM becomes troublesome and produces large errors due to the complexity of the model, its robustness can be enhanced by a set of training samples with known concentrations

(Duchowny et al., 2022c). The IHM was built and assessed using the commercially available software package PEAXACT.

3. Results and discussions

3.1. Novel strategies to improve the proton HP NMR spectra quality

As recently shown (Meyer et al., 2017; Duchowny et al., 2022a, 2022b), the proton spectra of NG samples are very complex. Methane (C1), which is the predominant component and always present in any NG sample, gives a single signal relatively far away from the signals of the other species present in the gas mixture (Fig. 2). The signals of the higher-order HC which include ethane (C2), propane (C3), butane (C4), iso-butane (C4i), pentane (C5), iso-pentane (C5i), neo-pentane (C5o), and n-hexane (C6n) show up in the same spectral region and thus strongly overlap (Fig. 2b). The reduced magnetic field strength of benchtop NMR devices compared with the high-field spectrometers lead not only to lower SNR but also to lower spectral resolution. In addition, the proton low-field NMR spectra are usually broader than at high-field due to the lower magnetic field homogeneity and in many cases due to signal splitting because of second-order effects as the values of the *J*-couplings are in the range of the chemical shift differences (Meyer et al., 2017; Rhee et al., 2023; Keller and Maly, 2021). These effects hinder the quantification of the components with the help of simple integration or line shape analysis of the corresponding signals. It was recently demonstrated that this issue can be overcome with the use of IHM (Duchowny et al., 2022a). However, further improvements in terms of spectral reproducibility, stability, and quality would further boost the accuracy and precision of the IHM. Furthermore, we aimed also for a robust methodology to ensure high-quality spectra obtained at different acquisition moments over longer periods of time. This is a need for the implementation of the proposed approach in a real-life application for online composition monitoring, where variations in external conditions may affect the quality of the recorded spectra. An overview of the proposed strategy for composition quantification of NG and in comparison, with the approach used in ref. 42 is depicted in Fig. 3 while the details of all implemented steps can be found in the next sections.

3.1.1. Effect of the novel sapphire tube design on the spectra quality

Fig. 2 depicts the achieved spectral improvements using the recently published refined sapphire tube design (Duchowny et al., 2022b) as compared with the old sapphire tube used in our previous work for the composition quantification of NG (Duchowny et al., 2022a). For both mixtures, a simple visual inspection indicates that much narrower and more symmetric peaks were obtained. In addition, an improved signal separation between methane and the higher-order HC is achieved.

The effect of the improved spectral quality could be observed even better in the case of more complex gaseous mixtures. Fig. 2b illustrates the considerably increase in the peak intensity and the resolution enhancement for the complex 11D mixture. With the new tube, the fine structure due to the higher-order HCs could be clearly observed, while being hardly visible with the older tube (Fig. 2b). Moreover, the decrease in the Full Width at Half Maximum (FWHM) led to a large increase in the SNR. These improvements were attributed to the improved manufacturing process of the sapphire tube, which gave a surface free of paramagnetic particles. Please note that the spectra depicted in Fig. 2 are acquired for both tubes with the standard multi-scan way and do not make use of the methodology described in the next sections.

In addition to the signal improvement, as demonstrated in our recent work (Duchowny et al., 2022b), the stabilization time after filling the sample inside the NMR tube displayed a dramatic reduction from about 5 h to about 30 min. Furthermore, the long-term stability of the experiments was improved. These enhancements are attributed to the PEEK cap attached to the new sapphire tube, which minimizes the influence of external thermal variations on the sample.

3.1.2. Implemented procedure to acquire the spectra

The main condition to guarantee reliable results in quantitative NMR (qNMR) is the collection of data with the highest possible quality. For this, sample preparation and experimental methods need to be carefully considered to minimize errors (Bharti and Roy, 2012). The SNR is a key experimental parameter commonly used to describe the quality of NMR spectra. The SNR is largely impacted by both the concentration of the analyte and the performance of the instrument. Additionally, the limit of detection and the limit of quantification of an analyte are determined by SNRs of 3:1 and 10:1 of the signal of interest (Bharti and Roy, 2012; Sun et al., 2017). Thus, to extract quantitative information with IHM, for low amounts of an analyte a high number of scans has to be considered while recording the NMR spectrum. With a large number of scans, a longer

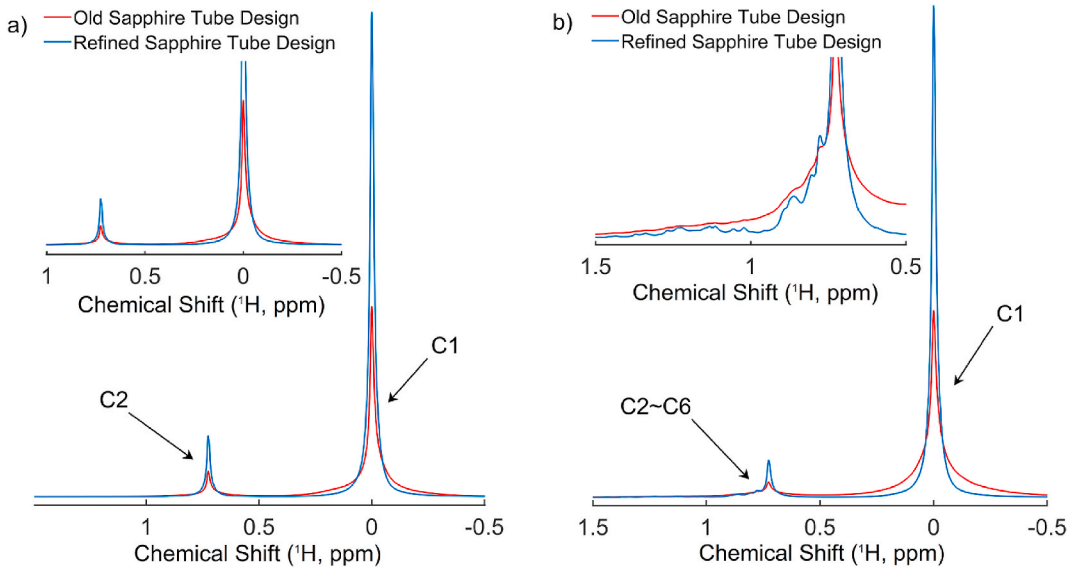


Fig. 2. ^{1}H low-field NMR spectra of two gas mixtures measured with the old and the new tube design at 200 bar: (a) binary methane/ethane mixture (*Reproduced from Ref.* (Duchowny et al., 2022b) *with permission from the Royal Society of Chemistry*) and (b) 11D as a representative 9-component gaseous mixture. The spectral region between ca. 0.6 ppm up to ca. 1.6 ppm is the region where the higher-order HCs have their proton NMR signals.

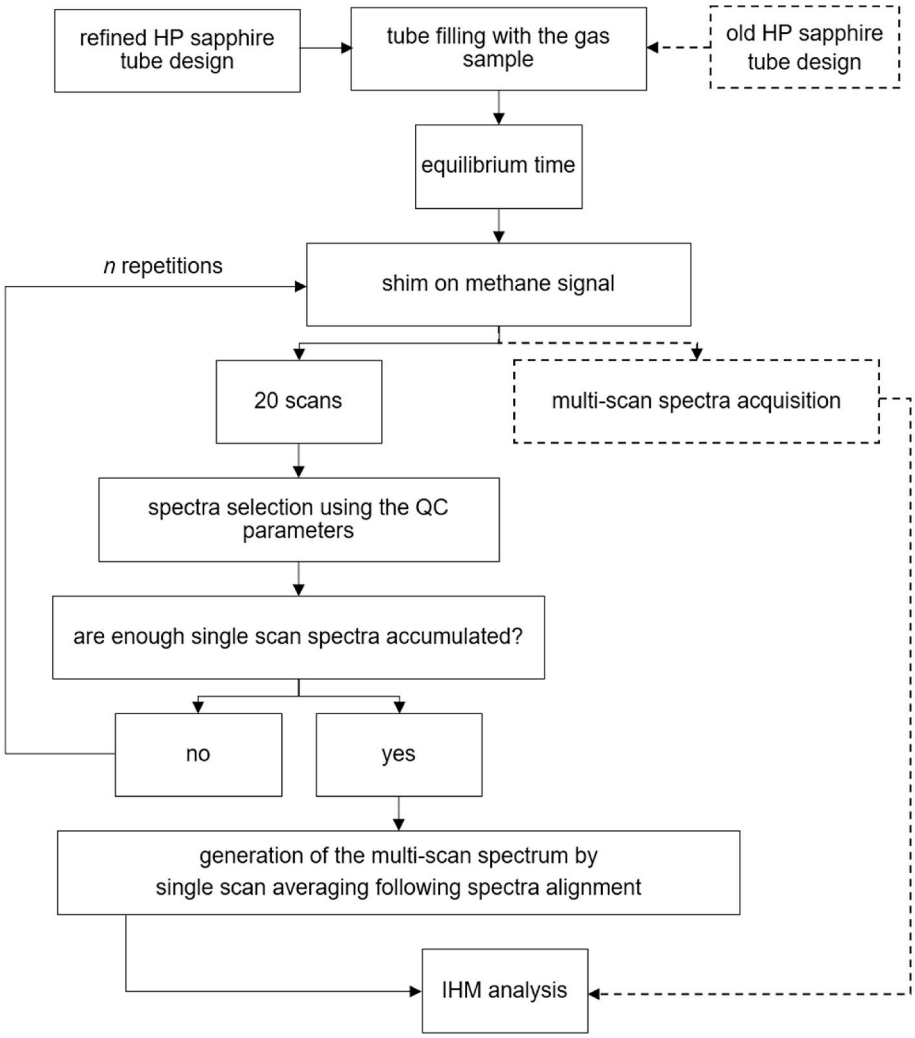


Fig. 3. Schema of the proposed methodology for the composition analysis of natural gas samples with proton benchtop high-pressure NMR spectroscopy. The variable *n* is defined by the user according to the required number of single scan spectra. The boxes and the arrows in dot lines indicate the method followed in our previous work (Duchowny et al., 2022a). The depicted working flow using methane for shimming the magnetic field was employed in the current paper for measuring the higher-order hydrocarbons and the mixtures while in the previous paper was used only for measuring the mixtures.

acquisition time is required, which can lead to long-term magnetic field instabilities contributing to signal distortions. These distortions can result in poor resolution and a lower SNR in the resulting spectrum (Duchowny et al., 2022a; Keller and Maly, 2021; Bharti and Roy, 2012; Římal et al., 2022; Minkler et al., 2020). To overcome these issues, various approaches have been implemented by NMR spectroscopists. For example, for liquid-state NMR experiments conducted in high-field, the magnetic field instabilities are compensated with hardware-based methods using a reference signal (e.g., deuterium) to lock the field-frequency of the magnet and to minimize linear drifts as a function of time (Keller and Maly, 2021; Římal et al., 2022). Alternatively, software-based methods such as data correction after acquisition or by considering spectra of reference samples, have been implemented to compensate for magnetic field drifts (Římal et al., 2022). In gas phase measurements, the inherent absence of a signal of a deuterated sample to establish the field-frequency lock strongly compromises the magnetic field stability over time (Meyer et al., 2017). Alternatives such as liquid deuterated solvents, separated from the gas phase sample by a suitable glass capillary in the active region of the spectrometer, are inconvenient due to a considerably reduction of the gas phase amount (Meyer et al., 2017). In this case, an alignment of multiple spectra recorded each with a well-defined number of scans was shown to be a viable way to correct signal shifts for measurements (Meyer et al., 2017). This art of multiple spectra accumulation and subsequent alignment based on a software approach is an appropriate option to increase the SNR accounting for magnetic field drifts when reliable frequency lock shifts alternatives are not available (Zientek et al., 2016b). In the case of modern low-field NMR spectrometers, most of them have an external lock based on advanced software algorithms which makes possible the analysis of samples in the absence of deuterated solvents (Minkler et al., 2020). Yet, our previous work (Duchowny et al., 2022a) showed that despite of the implemented external lock, a change in the spectra occurred over time. Such issues are inherent to the technological design of benchtop NMR which is based on rare earth permanent magnets. These magnets are optimally stable at temperatures between 20 and 30 °C, whereby variations outside this range result in magnetic field instability (Keller and Maly, 2021; Giraudeau and Felpin, 2018; Bornemann-pfeiffer et al., 2023). Therefore, coping with magnetic field disturbances remain challenging in environments without controlled temperature (Bornemann-pfeiffer et al., 2023). Such magnetic field disturbances will impact the peak shape and its reproducibility and thus the quantitative composition results by IHM.

To resolve the above-mentioned limitations and to ensure acquisition of spectra of reproducible shape independent of the recording times, while using a high number of scans to achieve better SNR even for the lower concentrated higher-order HC, a novel procedure for acquiring the

spectra was implemented. Specifically, the following steps were introduced for acquiring series of single-scan spectra over longer periods: 1) after filling the sample in the HP tube, a waiting time of at least 30 min was necessary to achieve stability in terms of temperature and lock frequency, as every pressurization comes along with a heating of the sample and thus of the magnet; 2) before starting the measurements, the magnetic field was shimmed based on the methane signal (considering its intrinsic presence in NG) by optimizing its FWHM and as a result its peak intensity; 3) to maintain the quality of the recorded spectra and to correct any external disturbance on the homogeneity of the magnetic field over time, a shim was conducted every 20 scans.

To get a multi-scan spectrum, the following approach was implemented: the best-acquired single-scan spectra were identified according to the QC parameters (as explained in the next section). Then, the selected spectra were aligned with the methane peak to 0 ppm and subsequently averaged. This novel approach allowed us to boost the SNR and to achieve the best possible steady and reproducible FWHM by correcting possible peak shifts.

3.1.3. Implementation of quality control parameters

Reproducibility of high-quality data is the fundamental condition to ensure accuracy of an analytical method. This implies close agreement between series of test results and the accepted true value from the same sample (Giraudeau, 2023). Thus, NMR spectroscopists put effort into software strategies to ensure repeatable high-quality spectra. For instance, the optimal shim settings were defined manually depending on the sample pressure prior to recording quantitative spectra of gaseous samples (Suiter et al., 2019). After each shim, the peak shapes were checked with an automated peak fitting routine. It was found that even small mismatches of the phase and baseline corrections were important sources of quantification error (Suiter et al., 2019; Hall et al., 2016). Furthermore, it was demonstarted that a constant signal quality (i.e. symmetry and peak shape) over the time was required for good performance of various data analysis methods (Zientek et al., 2016a). For maintaining the peak shape quality and a high degree of field homogeneity, the magnetic field can be shimmed using automatic and periodic fine-tuning shimming routines (Hall et al., 2016). However, within the context of various applications, such as, for example, reaction monitoring experiments or online composition analysis of NG, manual data processing and analysis becomes impractical for assuring the quality of the generated data, especially when dealing with large amounts of spectra. Therefore, in this case, an automatic data analysis would be the proper option, but this approach can be challenging as the spectra quality may change over time (Giraudeau and Felpin, 2018; Norwegian Petroleum Directorate Stavanger, 2023).

Within the frame of the current work, the reproducibility and quality of the spectra had to be ensured to achieve accuracy in the IHM composition analysis. Therefore, the accumulation of single-scan spectra (in the order of hundreds) following the procedure described in the previous section, was complemented with two quality control strategies (Fig. 4). For this, a MATLAB script was written to assess a huge number of spectra in an automatic way using QC criteria developed as follows. All spectra, independent of the values of the two QC parameters, were displayed. This enabled to examine all the single-scan spectra by visual inspection, and only the high-quality spectra were selected to be assessed and to identify the values of reference.

The first QC parameter is the integral of the whole frequency domain with the integration limits fixed between −0.5 and 1.8 ppm. The reference value is sample dependent and it was defined as the normalized averaged integral value of all recorded spectra for each sample under steady thermal conditions. This QC parameter was used to detect possible leakages of a pressurized sample over time. Even for small leakages, where the pressure on the manometer remained constant due to pressure compensation by the inert gas chamber, leakages with rates leading to sample residence times within the coil region lower than 5 times the T_1 relaxation time of any of the various species in the sample,

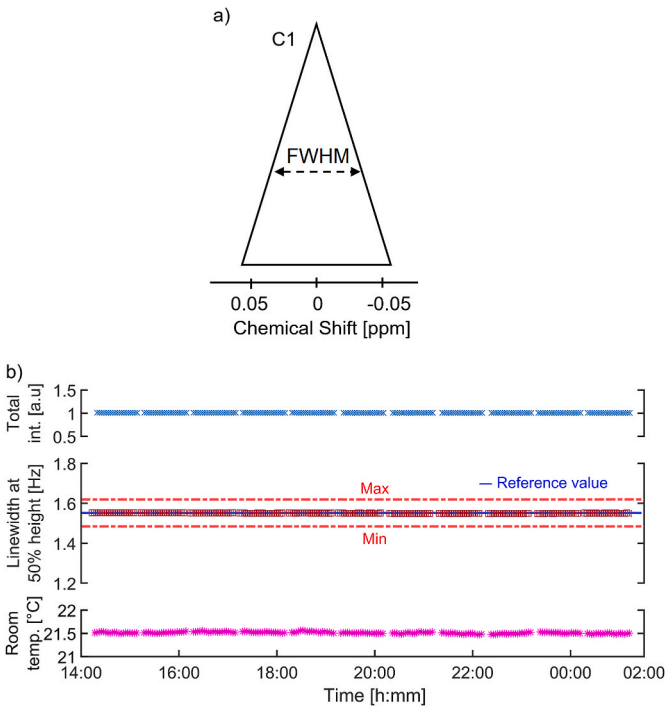


Fig. 4. Illustration of the proposed QC assessment: a) Schematic illustration of a C1 signal and the Full Width at Half Maximum (FWHM) QC as reference for each recorded single-scan spectrum. b) QC assessment on the long-term acquisition of single-scan spectra as for example shown for sample No. 5 (Table SI2). The blanks between the data are the shim periods. The red dashed lines Min and Max denote the threshold values of the QC parameter.

were expected to be detected.

The second QC parameter is the FWHM of the methane signal. To determine its acceptable minimum and maximum thresholds, from the set of selected spectra, the spectra with the most homogeneous and repeated peak shapes covering all the various compositions were chosen. For this selection, the average FWHMs of the methane signal at 200 bar and 160 bar were found to be 1.51 ± 0.06 Hz and 1.66 ± 0.06 Hz respectively. During the data processing and analysis conducted in this study, no appreciable variations of the FWHM of the methane signal was detected due to the different chemical composition of the various samples considered.

For both QC parameters a tolerance of ±10 % on the values of reference was found to be sufficient to select reproducible spectra over time and it was included in the MATLAB script to do an automatic selection of the spectra that meet these values. During this work, the HP setup was properly sealed, hence the integral values remained constant with negligible variations. Correlating the room temperature with the QC parameters showed that degradation of the magnetic field due to thermal fluctuations of the surroundings was reflected in unstable and non-reproducible FWHM over time (Fig. SI1). The possibility to continuously monitor the spectrum quality also showed that the inclusion of the shim protocol after each 20 measurements helps to maintain and recover the magnetic field homogeneity despite the unpredictable room temperature fluctuations (Fig. 4b and Fig. SI1).

Finally, after each batch of measurements, only the spectra with values within the acceptance range for both QCs were classified as high-quality data. An important advantage of this approach is that various multi-scan spectra can be obtained by summing up different numbers of single-scan spectra from the same data set. With the conventional method of measuring spectra containing e.g. 16, 32 and 64 scans, their acquisition is done independently and sequentially. Therefore, the total acquisition time of obtaining the three spectra with the three different number of scans is much longer as compared with the case when 64

single-scans are acquired and then used to obtain the spectra with different number of scans (16, 32, or 64) by averaging the necessary number of single-scan spectra.

3.2. Building an improved IHM database

For the development of the IHM presented in this work, a library with higher quality hard models of the individual components was created, as compared to those from ref. (Duchowny et al., 2022a). Methane was measured as pure component and ethane was recorded using the certificate binary mixture containing 92.43% methane and 7.57% ethane. In our previous work (Duchowny et al., 2022a) the ^{1}H NMR spectra of each higher-order HC were recorded using an argon-HC mixture at 200 bar and by employing a lower number of scans. In addition, the shim was done prior to conducting the measurements using a pure methane sample. Due to the lower amount of higher-order HC in the samples with argon and thus very low signal intensity, the shim could not be conducted directly on these samples. In the current work, each diluted HC in argon was prepared as ternary mixture with methane (Table SI4) such that the higher signal of methane could be used for a successful shim. This step was of key importance as it also allowed to apply the newly implemented recording method proposed in 3.1.2 to obtain the final spectrum. In this way, a much larger number of single-scan spectra, characterized by high and stable quality in terms of peak shape and FWHM, could be accumulated over time. As a result, multi-scan spectra with improved SNR could be produced. The used mixing pressures to record the ^{1}H NMR spectra of the different individual components are listed in Table SI4 and the final multi-scan spectra of the individual components are depicted in Fig. 5a.

To construct the hard model for each individual HC component, we utilized the available high-quality multi-scan spectra of each ternary sample listed in Table SI4 recorded at 200 bar. The spectra were resampled to 64 k data points to reduce the computational time of the IHM without compromising spectral resolution. The active frequency domain of all ternary spectra was set between −0.1 ppm and 4 ppm, since all the proton signals fall within this range and any signal overlapping between methane and the higher-order HC could be accounted for by considering only the left flank of the methane peak. Subsequently, in the case of pure methane several Pseudo-Voigt functions were adapted to the active left-flank spectrum and saved as the corresponding single-component left-flank-methane hard model. For each ternary mixture spectrum, the methane hard model was imported, and new Pseudo-Voigt peaks were added to cover the higher-order HC region. During the fitting process, the methane hard model and the newly added Pseudo-Voigt functions were fit simultaneously, ensuring that peaks with negligible area contribution or very broad functions that reduce model flexibility were avoided. In contrast to our previous work (Duchowny et al., 2022a) where the methane-left-flank-related peaks were retained, in this study, they were deleted. The remaining set of peaks was then assigned to the pure component hard model of the higher-order HC e.g., C4i, as depicted in Fig. 5b. Finally, all individual peaks within each pure component model were grouped to maintain a constant sum of the area for the pure component and to simultaneously adjust parameters during the fitting process.

The final IHM was obtained by compiling all the individual pure component hard models into a unique 9-component mixture model (Fig. 6). Similar to the previous work (Duchowny et al., 2022a), the Peaxact fitting mode “maximal interaction” was chosen to provide the highest flexibility by adjusting all global and peak model parameters simultaneously. Additionally, a tolerance of ±0.02 ppm was given for the whole model and for the individual peaks. Since the methane hard model was skipped in the new model, errors attributed to misfits of the IHM on the left flank of the overwhelming methane signal cannot be generated (Fig. 6). Here, the methane integral was determined by subtracting the summed areas of all IHM fitted C2–C6n components from the total integral of the whole frequency domain set between −2 ppm and 4 ppm. Therefore, the methane accumulates the misfits attributed to higher-order components, which has only a small effect due to the low amount of these components and at the same time the overestimation or underestimation of the methane peak itself is reduced. This new IHM model made possible a more straightforward composition analysis of the recorded spectra.

3.3. Composition analysis of gas mixtures

The reliability of the refined IHM based on spectra recorded at 200 bar was investigated by analyzing ^{1}H NMR spectra of 15 test certificate mixtures (Table SI2 and Table SI3) recorded also at 200 bar. Moreover, its pressure transferability was tested on spectra of 11 selected mixtures measured at 160 bar. Different to the approach we used in ref. (Duchowny et al., 2022a), the IHM analysis was done in the current paper using the 9-component IHM for all investigated mixtures. In ref. (Duchowny et al., 2022a), the 9-component IHM was applied only for 11D while for the ternary mixtures the IHM consisting only of the three components (C1, C2, and C3) was employed. The use of the 9-component IHM is important as in real applications no information about the composition of the mixtures is available in advance. As an example, Fig. 7a and b illustrate the IHM results obtained from sample no. 7

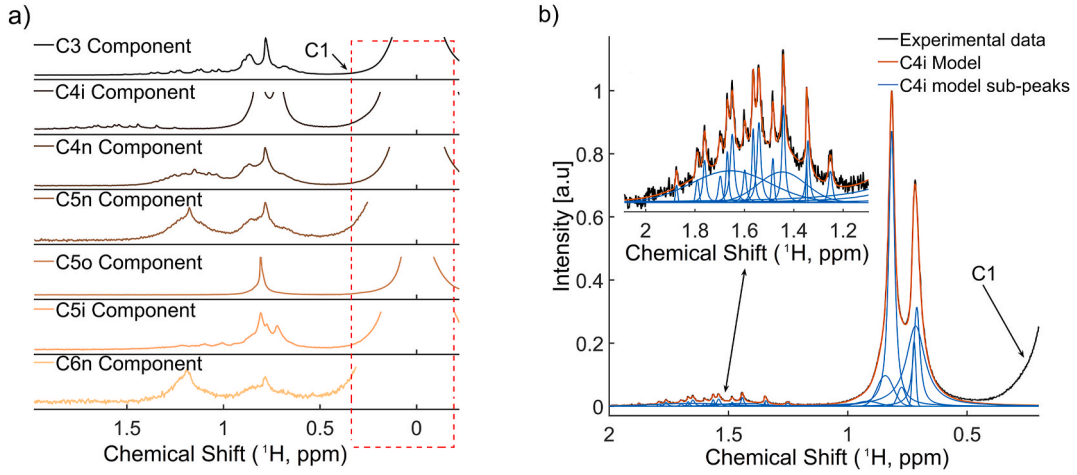


Fig. 5. Development of hard-models for each individual component. a) Experimental proton multi-scan NMR spectra of the individual components recorded at 200 bar. The spectra are zoomed for a better view of the spectral signatures of the higher-order HCs. The dotted red square marks the region of the methane signal. b) Hard model of iso-butane (C4i).

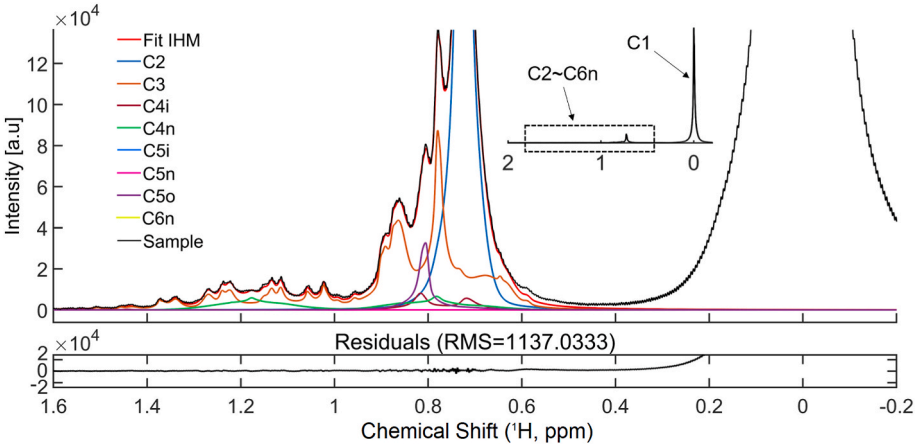


Fig. 6. Illustration of the new IHM and the contribution of individual hard model components fit on a ^{1}H NMR spectra of the complex 11D sample (Table SI3) measured at 200 bar along with the fit residual. For a better view of the C2–C6n region, the vertical axis has been magnified. The complete spectrum is shown in the inset.

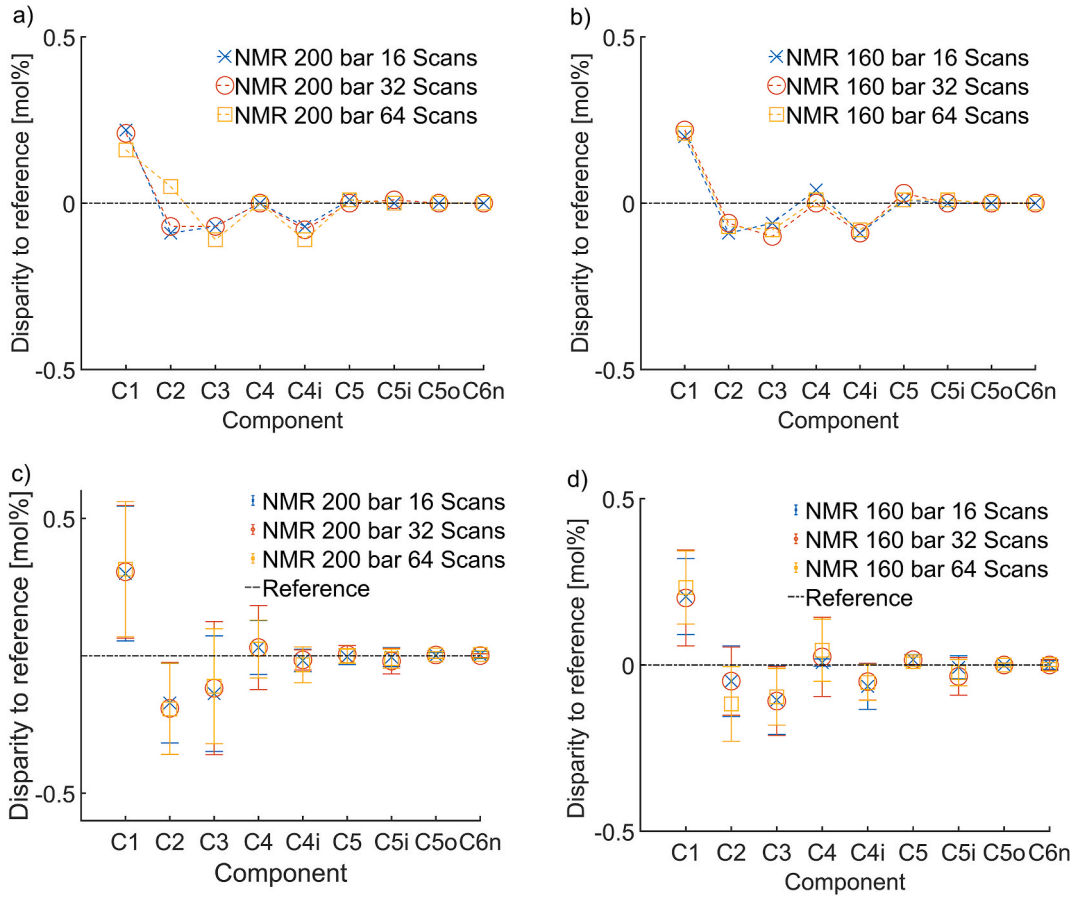


Fig. 7. Degrees of equivalence between the vendor certificates and the IHM results of ^{1}H NMR spectra with 16, 32, and 64 scans of: Sample no. 7 (Table SI2) at 200 bar (a) and at 160 bar (b), c) 15 mixtures (Table SI2 and Table SI3) at measured at 200 bar and d) 11 mixtures (Table SI2) recorded at 160 bar.

(Table SI2) in comparison with the vendor certificate. One observes that the 9-component IHM model was able to successfully identify all components present in the mixture and quantify them. For an easier and more thorough comparison, for each HC and for each pressure, an average of the differences between their concentrations obtained from the IHM analysis and the vendor certificates across all investigated samples was determined. These results are displayed in Fig. 7c and d, along with their standard deviations. Furthermore, for implementing the proposed procedure for online monitoring, it is also important to investigate the impact of the number of scans on the determined composition. Thus, spectra with 16, 32, and 64 scans were produced for each test sample. For all components and independent of the number of used number of scans (here 16, 32, or 64), an excellent agreement between the NMR results and the vendor certificate was achieved with a disparity lower than 0.5 mol% (Fig. 7). As a result of repeated and homogeneously selected peak shape quality, and minimum chemical shift

differences between the IHM and the test sample spectra recorded at the same 200 bar, reproducibility of the predicted results from different multi-scan spectra can be observed. We believe that this is also because changes in peak position and its shape remained largely constant over the time and thus the IHM algorithm did not have to account for them, reducing the number of parameters to be varied during the fit. These findings indicate that recording spectra with 16 scans was sufficient for achieving very good results. Contrary to our expectations, a higher number of scans was not needed to obtain a close agreement with the GC or the vendor certificates (Duchowny et al., 2022a).

Furthermore, it could be demonstrated that the 9-components IHM developed using the samples measured at 200 bar could be applied to the composition analysis of the samples measured at 160 bar without the need of generating a new IHM model. In this way, the number of samples to be measured for generating the IHM model was only 9 and not 18, as it would be if an IHM would have to be generated also for 160 bar. Also, in this case, the NMR and vendor certificate values were in an excellent agreement as for instance shown for the 11 selected mixtures in Fig. 7d with degree of equivalences even lower than 0.25 mol%. It was observed that in average the accuracy of primarily methane and ethane was improved compared with the results obtained at 200 bar. This enhancement in accuracy can potentially be attributed to a better separation between the methane and ethane peaks, and also between them and the other HC peaks, as a consequence of the lower pressure (Duchowny et al., 2022a). Nevertheless, lowering the pressure seems to affect some of the higher HC, most probably due to the lower SNR and slightly increased FWHMs. This led to different degrees of species recognition, which triggered position adjustments during the spectral fit process. Compared to the compositions achieved at 200 bar, the results obtained at 160 bar exhibited slightly more scattered results, especially for higher HC between the spectra containing different number of scans (Fig. 7c and d). Even so, the differences from the vendor values were very small. Most probably, including additional QC parameters may further reduce the scattering. Work along this line is currently under progress.

For the final comparison of the quantification accuracy at 160 bar and 200 bar, the derived physical properties of all investigated mixtures are depicted in Fig. 8. The predicted IHM molecular weight and calorific values were in general in excellent agreement with the reference values for both pressures. Samples no. 1, no. 4, no. 6 (Table SI2) and the complex 11D mixture (Table SI3) exhibited the largest differences to the vendor certificate. This is because they had the poorest quality stability when accumulating the single-scan spectra over time according to the QC control procedure, but they were still included for the purpose of the robustness assessment. We attributed the lower quality of the spectra of samples 1, 4, and 6 to temperature issues in the laboratory during the measurements. The lower quality of the 11D was possibly due to a change in the sample quality over time, as this gas sample was an older sample used for the last couple of years and thus a possible contamination could not be excluded. For the derived physical properties (Fig. 8), according to the Norwegian Petroleum Directorate, the relative measurement uncertainty should not exceed 0.3% for calorific value and

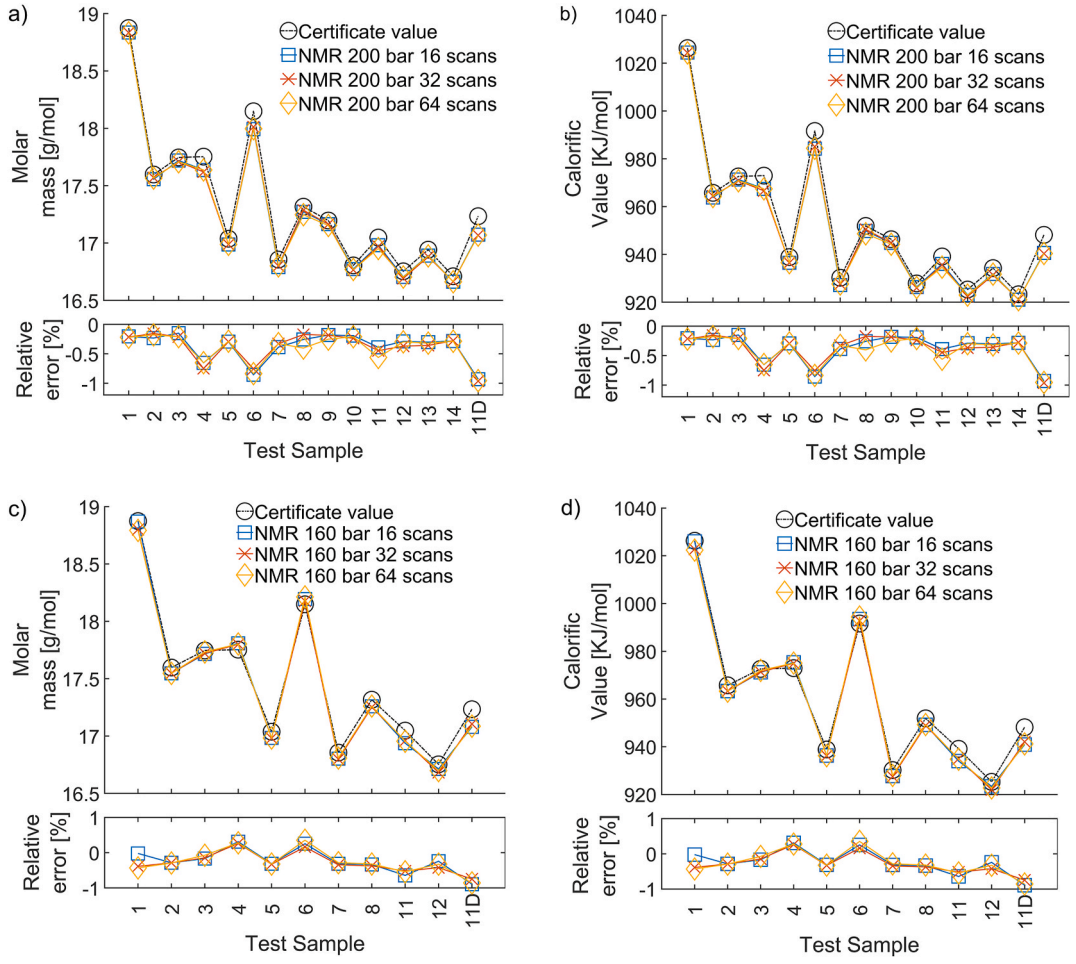


Fig. 8. Derived molar mass (a) and total superior calorific values (b) with IHM on NMR spectra of 15 mixtures with 16, 32, and 64 scans recorded at 200 bar, and derived molar mass (c) and total superior calorific values (d) of 11 selected mixtures with 16, 32, and 64 scans recorded at 160 bar in comparison with the corresponding vendor certificates.

1% for molar mass (Norwegian Petroleum Directorate Stavanger, 2023). Just the samples 4, 6, and 11D exceeded the calorific value thresholds at 200 and 160 bar (Fig. 8), which could be explained as a result of the identified lower quality of the spectra. However, for the molar mass, all the components were identified within the required tolerances.

4. Conclusion

A methodology to enhance the accuracy and the reproducibility of the quantitative composition analysis of natural gas samples with high-pressure low-field proton NMR spectroscopy and IHM was presented for the first time. This was made possible due to various hardware and software developments. In particular, the FWHM and the symmetry of all signals were remarkably improved with the implementation of a novel high-pressure sapphire tube. This has led to a larger separation of the methane signal from the signals of the other HC, which in turn was used to design a procedure to acquire their spectra with higher number of scans. This was then very useful for building a higher quality 9-component IHM. Furthermore, a strategy including single-scan acquisition, the use of a shim after a certain number of scans, the automatic selection of spectra having a quality within the tolerances given by the QC parameters, and spectra alignment was implemented to accumulate ^{1}H NMR spectra of higher quality over time.

The robustness of the introduced methodology was tested on up to 15 gaseous mixtures containing three, four, and nine different HC species with typical industrial concentrations measured with different number of scans at 200 bar and 160 bar. The disparity of equivalence between the NMR results and the certificates achieved in all cases was not larger than 0.5 mol%. The derived properties are under 0.3% for the high-quality spectra and lower than 1% for the spectra with suboptimal quality as compared with the vendor values and within accuracies demanded by industrial applications. Moreover, it could be proved that the IHM developed at 200 bar can be applied for the data recorded at 160 bar without the need of generating another IHM model. This is an important advantage over other chemometric methods such as PLS which require the build of an extensive calibration data set while in our case only the measurements of the 9 components (from C1 to C6) at 200 bar were needed. In addition, it was found that a number of scans as low as 16 is enough for excellent results.

The results of this study demonstrate that low-field HP ^{1}H NMR spectroscopy is an efficient method for the fast analysis of complex gaseous mixtures and has high potential for routine online composition analysis under real conditions. Moreover, we expect that some of the proposed concepts could be of importance for other fields of activities where it is necessary to deal with the acquisition of a large number of spectra over longer periods.

CRediT authorship contribution statement

S.A. Ortiz Restrepo: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **A. Swiatek:** Software, Formal analysis, Data curation. **A. Ohligschläger:** Writing – review & editing, Methodology, Investigation, Formal analysis, Data curation. **O. Mohnke:** Software, Resources, Methodology, Data curation. **H. Thern:** Validation, Methodology. **H.C. Widerøe:** Writing – review & editing, Validation, Resources, Methodology. **P.M. Dupuy:** Writing – review & editing, Validation, Resources, Methodology. **Ø. Leknes:** Validation, Resources. **A. Adams:** Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jgsce.2024.205377.

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