

Modeling the natural gas knocking behaviour using gas-phase infrared spectra and multivariate calibration

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ARTICLE INFO

Keywords:

Methane number
Liquefied natural gas
Service methane number
Infrared spectrometry

ABSTRACT

To assess the knocking properties of natural gas (NG) when it is used as fuel for vehicles is vital to optimize the design and functioning of their motors. Analytical efforts in this field are needed as the engines used to define it empirically are not available anymore, and existent mathematical algorithms yield different accuracy. The hybridization of gas-phase infrared spectrometry and partial least squares multivariate regression is presented first time to address the determination of the methane number (MN) of NG samples. It circumvents the need for the previous knowledge of the NG composition required to apply dedicated equations. The use of true NG samples to develop the models is also quite new in the field. Proof-of-concept studies were made with synthetic spectra and, then, a collection of liquefied NG samples for which MN values were computed by the National Physics Laboratory algorithm (NPL) from their sample composition were used to develop operative models. Additional validation was made with a collection of synthetic standard mixtures prepared for two European projects (EMRP LNG II and EMPIR LNG III) whose service methane numbers (SMN) were measured with an engine. The FTIR-PLS approach yielded statistically unbiased predictions with average standard errors around 0.4% MN when compared to the NPL-MN and SMN values, and standard deviations of the means ca. 1% MN. The approach is fast, cost effective as it involves standard instrumentation, and can be considered compliant with the green chemistry principles.

1. Introduction

Natural gas has been used as a fuel for decades and has gained increasing interest recently. It produces lower CO₂ emissions relative to the energy content than any other hydrocarbon because of its low C/H-ratio. Furthermore, it is available in large quantities from fossil sources but can also be produced from regenerative sources, be it biologically (biogas) or via the P2G-path (power to gas production). Natural gas is a first step to reduce greenhouse gas emissions and the utilisation of compressed natural gas (CNG) for light vehicles, and liquefied natural gas (LNG) and liquefied biogas (LBG) for heavy duty and marine

transport fuels (due to their higher energy content), is one of the pillars of the European clean fuel strategy and, in particular, the EU Directive on alternative fuels (European Commission, 2014).

The knock resistance (or antiknock property) is an important property of a fuel when used in Otto engines. The higher the knock resistance of the fuel is, the higher the compression ratio and the later the ignition timing can be set, resulting in an increase in the engine efficiency. The knocking properties of gases have been measured empirically by the Methane Number (MN), defined as the proportion of methane in a mixture of methane and hydrogen that shows the same knock resistance as the gas under investigation, in a defined test engine under defined

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<https://doi.org/10.1016/j.jngse.2021.103944>

Received 30 October 2020; Received in revised form 22 February 2021; Accepted 20 March 2021

Available online 1 April 2021

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operating conditions. The MN of hydrogen is defined to be 0, for methane it is 100 (Andersen, 1999; Giesekeing and Brown, 2016; Eilts and Klare, 2018). CNG and LNG may differ in their composition due to different production procedures. LNG normally has a higher content of heavier components (less knock resistance) as the composition changes over time and lighter components evaporate first, which is called aging.

The MN was defined first time by AVL (*Anstalt für Verbrennungskraftmaschinen List*) within a large project funded by the FVV (*Forschungsvereinigung Verbrennungskraftmaschinen*, Research Association for Combustion Engines) (Leiker et al., 1972; Cartellieri and Pfeifer, 1971). One of its outputs was a method intended to calculate the MN from the gas composition that has been further developed by MWM (*Motorenwerke Mannheim*) and adapted by Euromot (2017). Another refinement of the AVL method was developed by Giesekeing and Brown (2016) within the framework of the European 'LNG II' project (Euramet, 2017).

The experimentally-measured value of the MN depends on the test engine and its operating conditions. Disappointingly, the equipment used by AVL in the 1970's decade does not exist and is not replicable. For this reason the MN, according to the original definition, cannot be measured anymore. However, a measurement can be made on another engine and other operation conditions. To distinguish such a result from the MN measured in the phased out reference engine under reference conditions AVL introduced the designation 'Service Methane Number' (SMN) (Leiker et al., 1972; Cartellieri and Pfeifer, 1971) (defined as the vol.-% of methane in a mixture of methane and hydrogen that shows the same knock resistance as the gas which is investigated in any desired test engine under any desired operating conditions). For mixtures of methane and hydrogen the SMN is identical to the MN and although they show in general the same tendencies, in many cases the absolute values differ. Hence, they are comparable in quality but not in quantity (Eilts and Klare, 2018) (Euramet, 2017).

Several algorithms were developed to predict the SMN of the gas mixtures using the graphs deployed in the seminal studies (as a matter of example, the so-called NPL –National Physics Laboratory, UK- algorithm) (Andersen, 1999; Giesekeing and Brown, 2016; Eilts and Klare, 2018). Efforts were also made to predict the knocking properties of ternary blends using kinetic mechanisms (Gómez Montoya et al., 2016). All these efforts yield reasonably good results (Eilts and Klare, 2018) making it difficult to select the best one for trading, custody and provider-customer agreements purposes. It is worth noting that the composition of the samples must be known before applying any algorithm to ascertain their MNs. Usually this is done using gas chromatography (GC), which may be slow, ca. 4 min per analysis plus additional runs for blanks and test standards, needs frequent calibrations/recalibrations and/or verification/checks, along with a quite high expenditure (to buy the GC devices, consumables, standards, etc.). A rough estimation indicated that a chromatographic composition quantification performed by an ISO17025-accredited laboratory could amount up to €600/sample (Ferreiro et al., 2019). Accordingly, a low-cost, fast, reliable and easy-to-use analytical methodology would be welcome in the field.

The research presented here stems from efforts undergone in the petrochemical arena to accelerate the measurement of the gasoline-based Research Octane Number (RON) and Motor Octane Number (MON) (Andrade et al., 1997a, 1997b; Daly et al., 2016), and the Cetane Number (for diesel fuel) (Santos et al., 2005; Nespeca et al., 2018). This paper aims to present a novel analytical methodology to accelerate and, potentially, simplify the monitoring of the Methane Number in NG samples generated in a standard regasification LNG plant, along with NG samples from other different sources. The approach hybridizes gas-phase FTIR (Fourier transform mid-infrared) spectrometry and multivariate regression (Partial Least Squares, PLSR). Besides being fast, the intended approach can be implemented readily in an industrial environment and is intended to potentially substitute/complement the current algorithmic calculations for common routine applications. To

the best of our knowledge this is the first time the use FTIR-PLSR approach is proposed to address the Methane Number of gas-phase LNG samples.

2. Experimental part

2.1. FTIR measurements

Measurements were made with an 8400S Shimadzu FTIR spectrometer and a fixed-path gas cell (two external Viton O-rings were added to ensure tightness without compromising the optical path). The cell setup required customizing a temperature-controlled (25 °C), 10 cm path, stainless steel Harrick gas cell (Harrick Scientific, USA), equipped with 2 mm thick, 25 mm-diameter zinc selenide (ZnSe) windows (Fig. 1). All the measurements were made using 0.2 barg of the sample and 1.3 barg of argon (Ar), used as a broadening gas in order to increase the sensitivity of the measurement; more specific details can be found elsewhere (Ferreiro et al., 2019). Note that the 'g' after 'bar' stands for gauge pressure; i.e., the pressure within the system, excluded the atmospheric pressure. All references to 'bar' hereinafter should be understood as 'barg', otherwise stated.

The measurements were made in absorbance mode, with a nominal resolution of 1 cm⁻¹, 200 scans per spectrum, a Happ-Genzel apodization and in a 5500-480 cm⁻¹ range. The background was measured in the same conditions, before each sample, filling the sample cell with 0.5 bar of argon. The software used was the Shimadzu IR Solutions 1.30.

The pressurizing gas, Ar, was from Carburros Metálicos (Barcelona, Spain) with 99.9992% purity. The samples used to perform the studies were provided by Reganosa (Regasificadora del Noroeste, Mugaros, Spain) and correspond to real production batches. Fig. 2 exemplifies the spectra obtained throughout, which were digitized to 9375 spectral points, equispaced between 479.81 and 5000.14 cm⁻¹.

2.2. Gas chromatographic measurements

The GC measurements were made with an Emerson 575e gas chromatograph equipped with a thermal conductivity detector (Emerson, Scotland); four packed columns and three chromatographic switch valves (all of them into the same oven). Hexane and heavier compounds were separated in the first column OPN Porous Sil C (80/100 mesh) with a backflush system.

The backflush valve reverses the flow in the first column so that components C₆ and heavier elute first, as a single peak, to the detector. The second column 20% SF96 Chromosorb P (80/100 mesh) allows the separation of propane, butanes and pentanes. The lighter compounds are trapped on a Hayesep N (80/100 mesh) column. The last column, Silcoport P (80/100), is used mainly to enhance the resolution of the

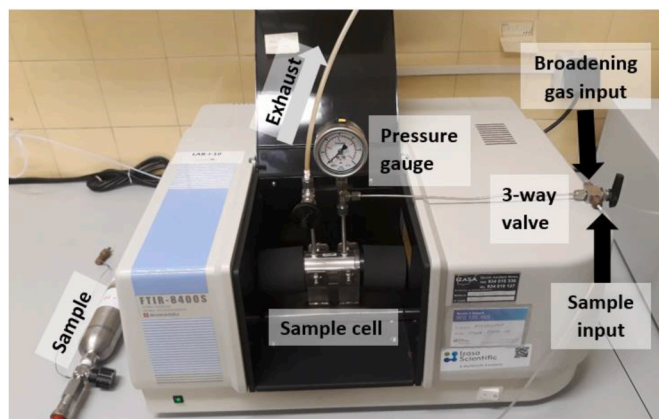


Fig. 1. FTIR spectrometer setup used to measure the LNG samples.

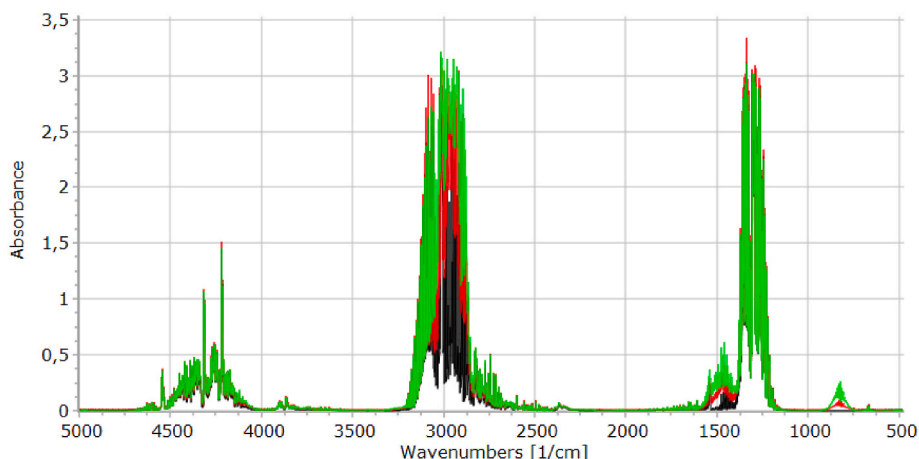


Fig. 2. FTIR spectra of three LNG samples.

chromatographic peaks. An isothermal program was used for the separation (oven temperature = 80 ± 5 °C). Helium was used as carrier gas, 99.9999% purity (Linde, Barcelona, Spain).

The samples and the standard mixtures were injected at 1.6 bar and the pressure of the carrier was 6.2 bar. The overall analysis time was 4 min and the time for purging the sampling line was 60 s between samples. All the standard gas mixtures (see Table 1) were fabricated following ISO 6142 (ISO6142-1, 2015) and ISO 6143 (ISO6143, 2001), and they were used for the multipoint calibration and further quality controls. Samples and standards were subjected to routine quality control tests under the ISO 17025 (ISO/IEC17025, 2017) accreditation scope of the Reganosa's laboratory. The analytical method was developed in-house based on ISO 6974-4 (ISO6974-4, 2000). All reported results correspond to normalized values (the sum of the concentrations of all of the measured components was set to 100%).

2.3. Methane number, reference methodologies

As introduced above, the determination of the MN of NG has been a matter of controversy and a central objective in this research field. Within the framework of the 'LNG III' European project, the so-called NPL approach (Giesekeing and Brown, 2016) was used to calculate a reference Methane Number (NPL-MN) for each commercial sample employed throughout after measuring its composition. The components to be specified are methane, ethane, propane, iso- and n-butane, iso- and n-pentane, $C_{n>6+}$ hydrocarbons, carbon dioxide and nitrogen. In this case the $C_{n>6+}$ slot is given only the n-Hexane percentage volume fraction, and the iso-pentane one is assigned the sum of iso-pentane and neopentane volume percentages. To validate the NPL-MN values a reduced set of gas mixtures developed in the framework of two European projects (EURAMET-EMRP 'LNG II' and EMPIR 'LNG III') were measured by an operational engine so that SMN values were generated for them. The experimental setup, technical details and measurement conditions of the operational engine employed to develop the SMN measurements

Table 1

Compositional range of the standard gas mixtures employed for calibration and instrumental quality control validation.

Component	Calibration range (% , mol/mol)
Methane	68.0–99.9
Propane	0.03–3.0
Ethane	0.01–12.0
i/n-butane	0.002–0.7
i/n/neo-pentane	0.002–0.1
n-hexane	0.003–0.1
Nitrogen	0.1–13.0
Carbon dioxide	0.03–2.0

are described in the [Supplementary Material](#).

The correlation between the NPL-MN and the SMN values was studied before validating the FTIR-PLS approach. As the line is very close to the diagonal (Fig. 3) it was deduced that the SMN and the MN values were very similar, despite some particular discrepancies appeared. The [Supplementary Material](#) details how the confidence intervals depicted in the figure were calculated.

2.4. Samples

The samples used in this work came from the production process of a regasification terminal (Reganosa, Spain), commercial standard gas mixtures, and mixtures provided by two European projects. They were measured by IR and GC, and the MN was calculated using the NPL algorithm (Giesekeing and Brown, 2016). Only the special mixtures from the European projects had SMN values determined by an operational engine.

2.4.1. Samples from the production process

In total, 114 samples were taken at dedicated locations of the regasification terminal. They were natural gas (NG), vaporized liquefied natural gas (LNG), and boil-off-gas (BOG) samples. The origin of the NG cargoes varied (Nigeria, Russia, USA, Trinidad and Tobago, etc.) and, so, the LNG compositions. LNG samples from tanks of the terminal port were also taken.

The BOG is the continuously evaporated (or boiled) LNG vapor that is in contact and equilibrium with the LNG inside the tanks. It is formed by the most volatile and lighter LNG compounds, mainly methane, ethane, propane (traces) and nitrogen. When samples are taken during the unloading of a vessel, the returned BOG can contain up to 9% nitrogen.

2.4.2. Standard gas mixtures

Eleven standard gas mixtures, some of them including the eleven compounds that may be present in NG -including carbon dioxide, were purchased and their composition was certified by accredited laboratories. Samples from the regasification terminal do not contain CO_2 because at LNG operating temperatures it is solid and is extracted in the liquefaction plants before shipping.

2.4.3. Samples from EURAMET projects

The SMN of 27 mixtures specially prepared by Nippon Gases (formerly Praxair) and Linde Gas Benelux B.V were measured within the framework of the EURAMET-EMRP LNG II and EURAMET-EMPIR LNG III projects at the Institute of Internal Combustion Engines (Technical University of Braunschweig). Their compositions were assessed first by

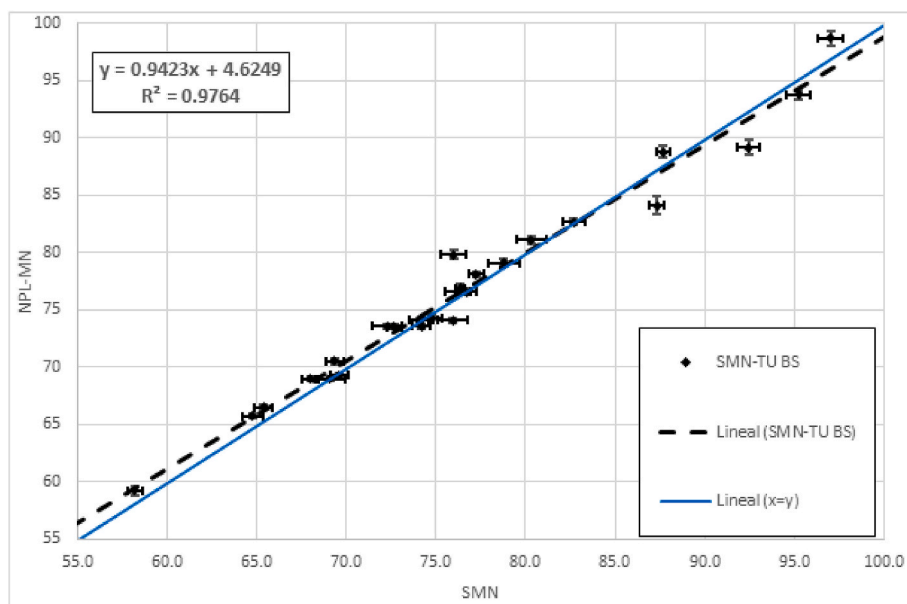


Fig. 3. Comparison of the SMN values with the NPL-MN ones plus their confidence intervals. (TUBS stands for *Technical University of Braunschweig*; the units of both axis are MN).

accurate weighing of the corresponding mass quantities required to get the standard mixtures and finally determined at Physikalisch-Technische Bundesanstalt (PTB) by gas chromatography. See [Supplementary Material](#) for details on their composition, MN and SMN, and how they were prepared, analysed and refilled. This collection is only used in the FTIR-PLS approach to study their applicability to such kind of samples and to externally validate the models. Recall that multivariate regression models, like partial least squares regression, are *ad-hoc* statistical models which depend on the calibration samples; and in this study they were true commercial samples, not synthetic ones.

2.5. Software

The freely available *PLS* package (Mevik and Wehrens, 2007) of the CRAN R project (Schmitt, 2016) has been used. Both the *HITRAN* database (High resolution Transmission Molecular Absorption Database) (Gordon et al., 2017) and the *Bytran* radiative transfer algorithm (Pliutau and Roslyakov, 2017) were used to obtain the approximate molecular absorption cross sections of the IR-active compounds needed to compute synthetic IR spectra. The GNU Octave scientific computing environment (Eaton et al., 2017) was used to run the NPL algorithm and to compute piecewise cubic interpolations. The Mnova *ELVIS* plugin for Electronic and Vibrational Spectroscopies (Mestrelab Research, 2018) was used to visualize and pre-process spectral data.

2.6. Sample sets and chemometric approach

Many branches of applied Science tackle complex problems by means of multivariate calibration models where a physical explicit formulation/equation is not required. In multivariate calibration a model is developed through training on a number of samples each comprising an input (the set of variables that can be measured ‘easily’, i. e. the mid-IR spectrum) and an output (the property under study, whose numerical qualification is derived from another measurement approach). This model then serves to generate predictions of outputs corresponding to new input data.

Among the linear models PLSR has demonstrated outstanding performance in quite different situations (Webster et al., 2017; Cheng and Sun, 2005, 2017; Jie et al., 2007), becoming a *de facto* standard method, well-documented (Wold et al., 1987; Martens, 2001), well-known and

universally accepted in academia and industry nowadays. It has three fundamental steps: model development (regression or training), validation (typically, internal) and testing (typically, external validation using a new collection of samples). Training starts once a collection of representative samples has been characterized using both a candidate, fast measurement analytical technique (e.g. IR spectrometry) and a reference procedure (typically, a standardized labour-demanding and/or slow methodology). After that, validation is required before accepting a model. The test set with totally new samples demonstrates the performance of the model in routine use.

In this work the feasibility of this approach was evaluated by considering two different datasets: (i) a collection of synthetic IR spectra, developed as detailed next, to comply with MN values set in advance (by direct calculation with the NPL algorithm); and (ii) a set of experimentally measured FTIR spectra, whose MNs were obtained applying the NPL algorithm to the gas compositions derived from GC standardized measurements of the samples. Although feasibility studies are not common in papers, they are indeed recommended as a proof of concept before going on (Broad et al., 2006), especially to address problems without previous reported assays, as it is the case here.

Hereinafter those datasets will be denoted *synthetic* and *experimental*. Both, apart from having the same spectral dimensions and experimental working ranges, are envisaged to be numerically unrelated, though from a qualitative point of view they are expected to hold the same major patterns within the models to predict the MN.

2.6.1. Synthetic data

The working scheme to get the synthetic IR spectra is detailed next. First, a set of K different 11-components (methane, ethane, propane, isobutane, n-butane, pentane (*iso* and *normal*), neopentane, n-hexane, carbon dioxide and nitrogen) gas mixtures (compositions expressed in volume percentage) are generated and stored:

$$\%vol_i^{(k)}, i = 1, \dots, 11, k = 1, \dots, K \quad (1)$$

Note that molecular nitrogen is IR inactive, though its presence in the mixture does indeed influence its methane number and has to be accounted for. Next, for each composition k , the approximate molecular absorption cross section of each pure compound i (ACS_i) is weighed by its corresponding percentage in volume $\%vol_i^{(k)}$, so that a synthetic,

approximate IR spectrum of gas mixture k is

$$S_k = \sum_{i=1}^{10} ACS_i \frac{\%vol_i^{(k)}}{100} \quad (2)$$

The molecular absorption cross section is the ability of a molecule to absorb a photon of a particular wavenumber and each compound's approximate molecular ACS_i was obtained as follows: the working range was set from 449.43 to 5501.17 cm^{-1} . Then the Hitran database (Gordon et al., 2017) was used to retrieve the molecular absorption cross sections. They were available only for some of the compounds in common natural gas, while for others only absorption line parameters (spectral lines lists) were available. To solve this problem the open-source, freely available Bytran algorithm (Pliutau and Roslyakov, 2017) was used, designed for the calculation of approximate molecular and atmospheric absorption of gas mixtures under user-defined conditions and concentrations. Bytran itself is based partially on Hitran, and relies on the data provided by its online version. This software implements a so-called *line-by-line* method to compute absorption cross sections using individual spectral line records over a specified spectral range for given temperature and pressure (288.15 K and 1 atm in our case). Then these absorption profiles are added together to yield the total absorption spectrum as a function of the wavenumbers.

The outcomes of Bytran were processed with the shape-preserving piecewise cubic Hermite interpolation (Fritsch and Carlson, 1980) in order to obtain an approximation to each molecular absorption spectra, matching the aforementioned spectral size and wavenumber bounds. Those computations were performed in the GNU Octave scientific programming environment (Eaton et al., 2017). A stacked view of the resulting absorption cross sections is depicted in Fig. 4. For the purposes of this work they can be considered as proxies of the IR spectra of the pure commercial gas mixtures.

Finally, each synthetic FTIR spectra $\{s_k, k = 1, \dots, K\}$ is processed with

the Mnova (Mestrelab Research, 2018) software. Two processing actions are applied: A normalization to standardize to zero mean and unit variance (SNV), followed by a Savitzky-Golay filter (Savitzky and Golay, 1964) with polynomial degree 3 and kernel width 5 for noise reduction.

2.6.2. Experimental data

A grand total of 114 LNG samples were obtained by Reganosa from its industrial facilities and their corresponding mid-IR spectra (see Fig. 2), GC compositions and NPL-MN were determined as detailed in sections 2.1, 2.2 and 2.3 above, respectively.

3. Results and discussions

3.1. Relating spectra to the methane number, synthetic data

Initially, a synthetic dataset comprising 250 different compositions similar to the values of those found in the collected true LNG samples was generated. The MNs were computed considering their compositions (known by design) and the NPL-MN algorithm, which also provides their associated expanded uncertainties. These were used to calculate the associated 95% confidence intervals shown in Figure SM7 (Supplementary Material). Besides, the robustness of the regression approach was evaluated by decreasing the information provided in the training set (i.e. the number of realizations comprised). To this end, reduced training sets consisting of 200, 100, 50 and 25 synthetic spectra were used.

To develop the PLS models ten latent variables (LV) were considered as a maximum value because this is the number of independent absorption cross sections weighed to create the synthetic gas mixtures compositions. However, it was expected that less factors would be needed by PLS due to the strong dependence of the NLP-MN value on the chemical composition. A LV in PLS can be explained (in simple terms) as a linear combination of spectral variables (wavenumbers) that compile as much spectral information as possible under the condition that, at the

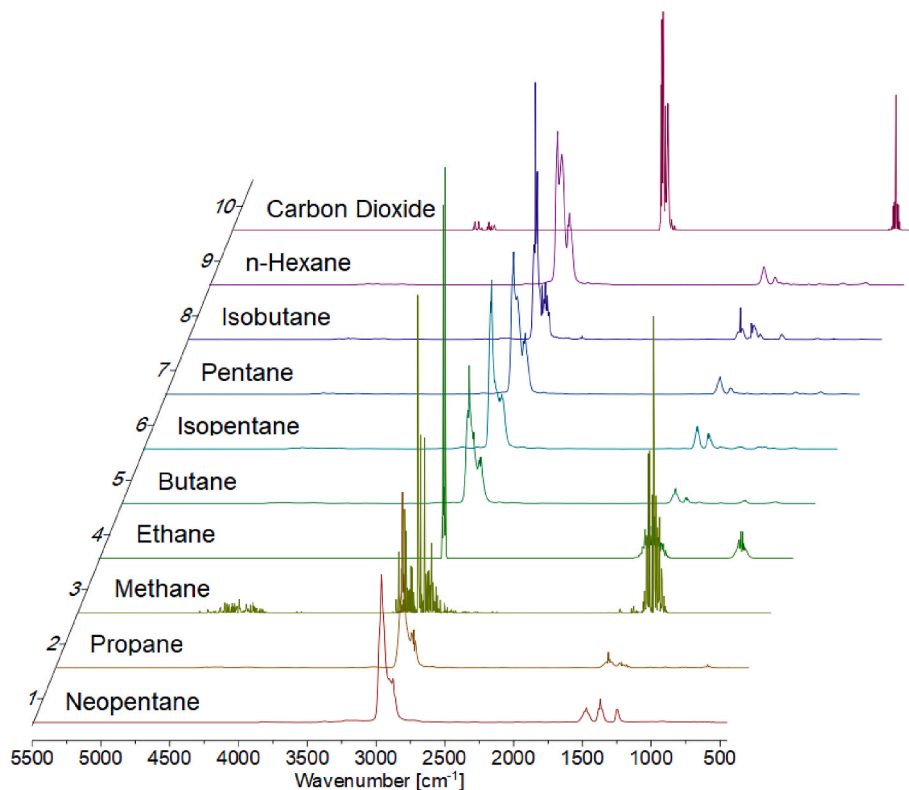


Fig. 4. Approximate, relative absorption cross sections (ACS_i) of IR-active compounds comprised in NG (see text for details). Vertical scale units are $\text{cm}^2/\text{molecule}$. Note that absolute vertical scale magnitudes (not shown) are similar except for carbon dioxide, which has larger IR absorption cross sections, so a vertical scale factor 10 has been applied to plot its graph.

same time, it is maximally correlated to the property of interest (the MN). The first LV explains the most information, the second less, and so forth. Sometimes it is also termed “factor”. That maximization property is what makes PLS so powerful. The final number of LVs to be used was determined empirically by *leave-one-out* internal cross-validation (LOO-CV). To avoid overfitting due to LOO-CV independent external validation tests of each model developed using the synthetic spectra were considered to confirm the proposed dimensionality.

Results are presented in Fig. 5. In the second column the term validation refers to internal validation using the classical LOO-CV approach. In the third column, the results for a common validation test set (the same 50 samples to simplify the comparison) are presented. It is worth noting that the original AVL studies set uncertainties around ± 2 MN (Andersen, 1999) and therefore this interval was considered as the range of values where the PLS predictions should lie. Fig. 5 reveals that, as expected, the synthetic datasets needed the same number of LV, irrespectively of their number of samples because they have the same

inherent sources of variation.

A very positive fact that can be seen in Fig. 5 is that almost all samples lie within the target acceptance interval around the NPL-MNs. Although a curved shape can be seen in the true vs actual plots for training, it was preferred not to include more LV to avoid overfitting. This behaviour was expected because the samples with the lowest MNs are infrequent in commercial relationships and they were selected, precisely, to enlarge the calibration range. In effect, the external validation test showed very good predictions and that curved shape was not observed anymore whenever the samples out of the usual working range of true NG/LNG are avoided. This is exemplified at the top rightmost subplot of Fig. 5. Only when a very small number of training samples is used (25 samples, fourth row of the figure, which will be avoided in the experimental study) the curved behaviour was not avoided with a reduced number of LVs.

All RMSECV (root mean square error of cross-validation) and RMSEP (root mean square error of prediction) average errors were similar

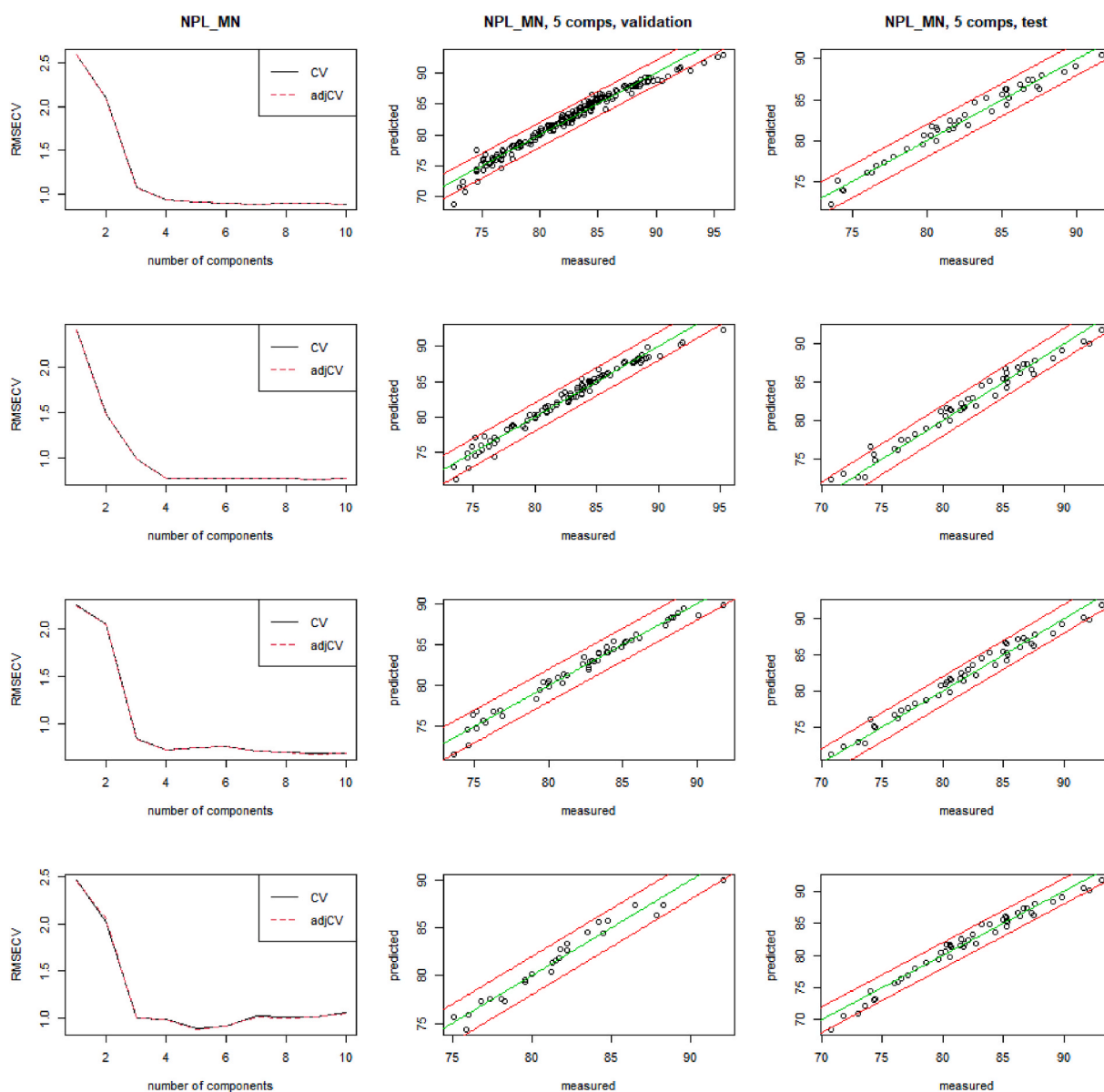


Fig. 5. PLS models for the synthetic spectra considering 200, 100, 50 and 25 training samples (top to bottom rows). For comparison, all models used 5 LV. Green lines denote perfect agreement between theoretical and predicted MNs. Red lines denote the acceptance interval for the predicted values (see text for details). ‘adjCV’ stands for adjusted error of cross-validation, which takes into account the difference between errors of the whole sample set and the mean LOO-CV error (here, a negligible correction).

between them, and along the different models, in the 0.84–0.96 MN range. This strongly suggests that overfitting did not occur.

3.2. Relating spectra to the methane number, experimental spectra

The working range expands from 74 to 100 MN. The lowest values are unusual in most common gas custody transfers and commercial uses (most current samples are between 80 and 99) and they were obtained from special samples. They were introduced into the training set only to enlarge the working range of the model. A spectrum showed a systematic outlying behaviour and was deleted from the studies.

PLSR was applied to a training set developed with 84 experimentally-measured LNG samples. As for the synthetic spectra, the maximum number of LV assayed was 10. The external validation (test set) included 29 independent samples. Two trials were devised to evaluate whether some kind of temporal trend could be present in the datasets (see **Figure SM7, Supplementary Material**): i) using the first 84 samples of the collection series to constitute the training dataset and the remaining ones for external validation, and ii) employing the last 84 samples of the collection series for training (the others for external validation). Results did not differ between them and, so, no special circumstances seemed to appear during the several months that the collection stage lasted for. **Figure SM8 (Supplementary Material)** reveals that the number of LV (as determined by LOO-CV) should be around 6 or 7 (highly similar to the synthetic data sets). The overall cross-validated error was 0.76 MN (7 LV) for trial i) and 0.86 MN (6 LV) for trial ii). **Fig. 6** exemplifies the predictive performance of each trial, considering 7 LV. The plots show that indeed no major differences on prediction capabilities can be seen (the logical minor discrepancies were attributed to the different samples in the test sets). Hence, it was decided to develop the model with the 84 first samples of the temporal series and let the others as an independent validation test set. The average error for this test set was rather good, 1.11 MN (7 LV); however, it is a bit different from the training one (ca. 32% higher) and, besides, some samples seemed not to be properly

predicted.

Further in-depth study of the model considered the scores distribution on the spectral domain, with no relevant problems; and the traditional Q-residuals and Hotelling's T^2 statistics, for which some values appeared too high (plots not shown here). Accordingly, those samples showing Q-residuals > 2 (normalized values) and/or T^2 values $> 99\%$ confidence limit were rejected (7 samples in total) and the model rebuilt.

For the new model, 7 LVs were selected by LOO-CV. The average prediction errors were 0.59 MN for LOO-CV (internal validation) and 0.96 MN for the external validation test (**Fig. 7**). There was a clear improvement on the predictions with respect to the previous model. However, the test set yielded an average error ca. 50% higher than the training one that was caused by a sample which behaved as a clear outlier for each and every model. When that sample was deleted, the average error decreased to 0.75 MN, which was considered very satisfactory (it is worth noting that even considering that outlying sample the average error was half that set initially as the target objective).

Fig. 7 illustrates that all test samples lie well within the target ± 2 MN range. The residuals of the regression had a random pattern, being the highest and lowest ones $+1.5$ and -1.3 MN. The regression equation for the external validation was $\text{PLS prediction} = 0.283 + 0.995 \cdot \text{NPL-MN}$, with a correlation coefficient of 0.9958 and its slope was statistically equal to 1 (95% confidence), which means that the overall bias was not statistically significant. Hence, the PLS model is predicting on average the same values as the NPL-MN algorithm calculated. Another proof of this important statement is to calculate the average residual (considering its sign) and test its significance by means of a Student's t -test. Here, the average residual was -0.14 and the experimental t was 1.01, which clearly was lower than $t_{\text{tab}, 95\%, 27} = 2.06$.

Fig. 8 depicts that all PLS predictions but two at the lowest range locate within the 95% confidence intervals associated to the NPL algorithmic calculation of the MN values. Such 95% confidence intervals are much smaller than the target objective (± 2 MN) as they derive uniquely from the NPL-MN algorithm computation, which considered the CG

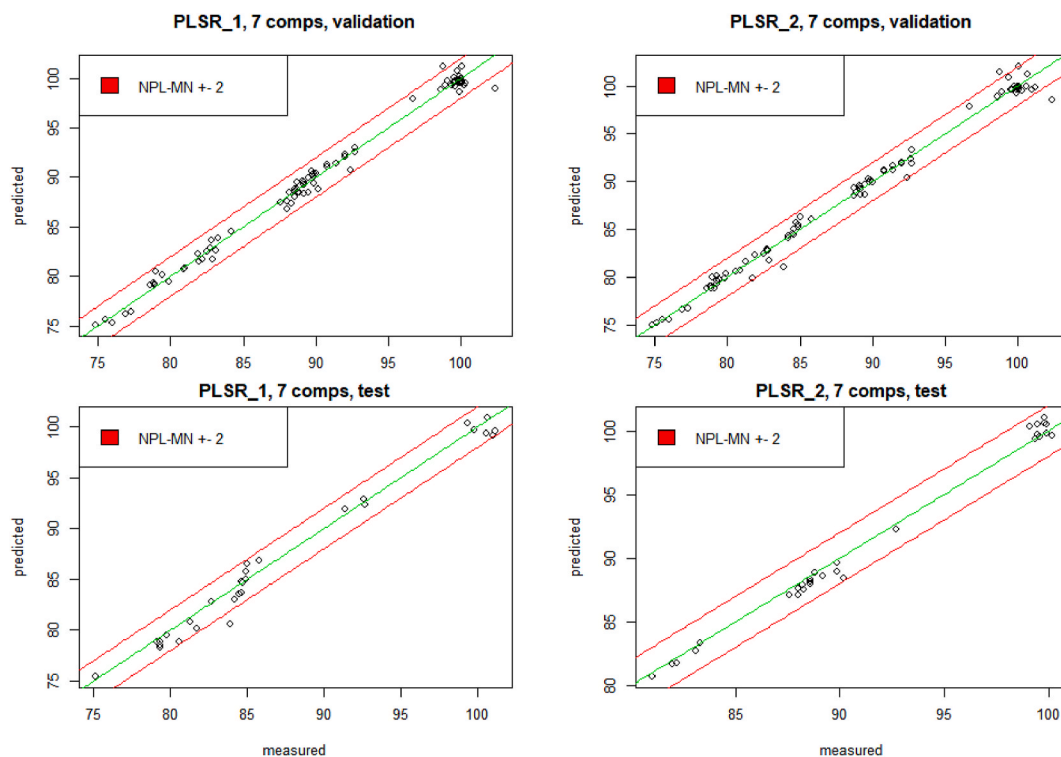


Fig. 6. Comparison of the predictive performance of PLS models considering 7 LV and either the first 84 samples (left column) or the last 84 ones (right column) for training. ('validation' = internal LOO-CV, 'test' = external validation test) Green lines denote perfect agreement between the theoretical and predicted MNs. Red lines denote the acceptance interval for the predicted values (see text for details).

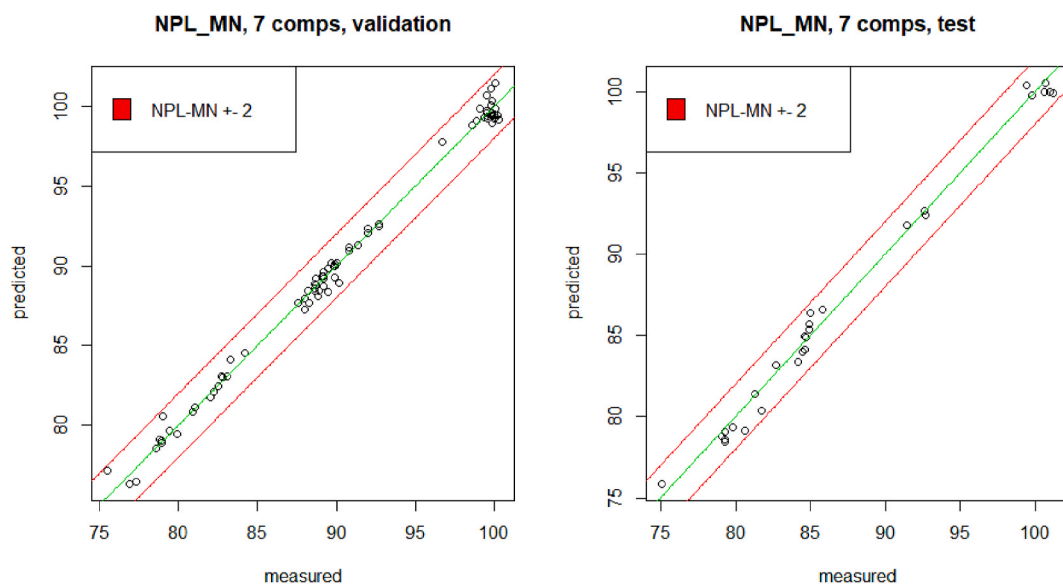


Fig. 7. Predictive capability of the refined PLS model, 7 latent variables ('validation' = internal LOO-CV, 'test' = external validation test).

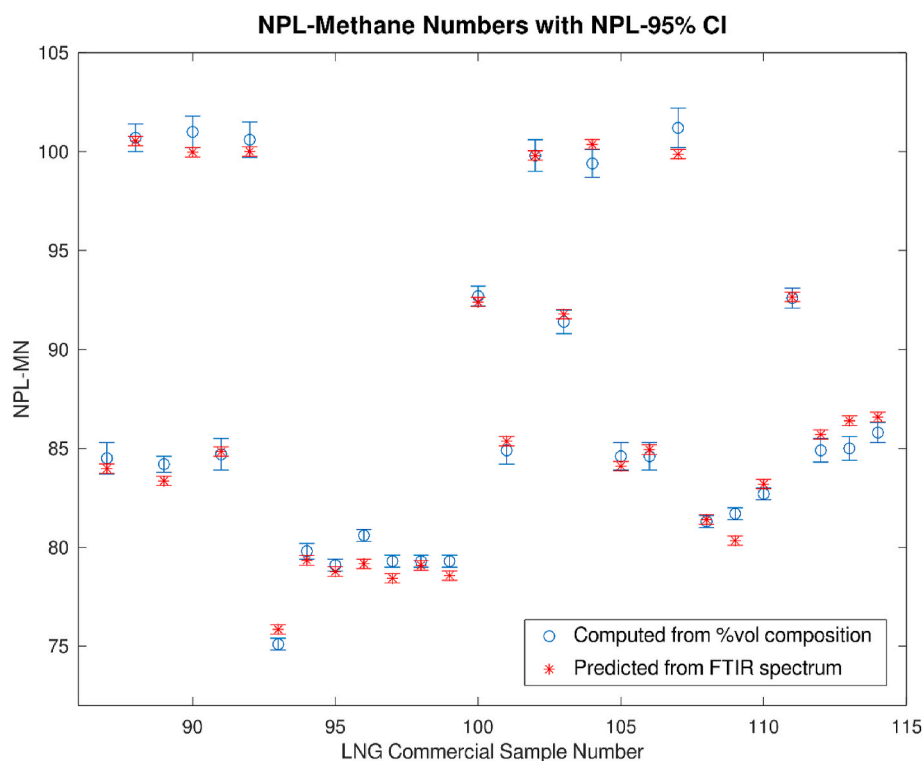


Fig. 8. Comparison of the computed NPL-MN values, along with their estimated 95% confidence intervals (CI), for the external validation test samples with the PLS predictions (red filled symbols).

uncertainty negligible when performed in metrological laboratories (Gieseking and Brown, 2016). That might not be exactly the case in CG industrial laboratories, even those being ISO 17025-accredited. Taking this into account, it is considered that even in this case the overall results are quite satisfactory.

3.3. Relating spectra to the service methane number

Despite NPL values were employed to train the PLS model it was considered interesting to study whether predictions close to the SMN of the synthetic mixtures could be obtained. Fig. 9 reveals, in general,

excellent agreements. The five samples situated at the rightmost side in Figs. 9 and 10 correspond to binary mixtures of methane and pentane and two mixtures whose compositions are clearly different from any commercial LNG or NG product (see the last five mixtures in Table SM1, Supplementary Material) and they could not be predicted properly, as expected. A similar problem has been pointed out recently in a study that considered a subset of the samples used here (Sweelssen et al., 2020).

To potentiate the robustness of the PLS model all the LNG samples used so far were joined so that an overall collection of 112 samples constituted an extended PLS model. Then, the FTIR spectra of the LNG II

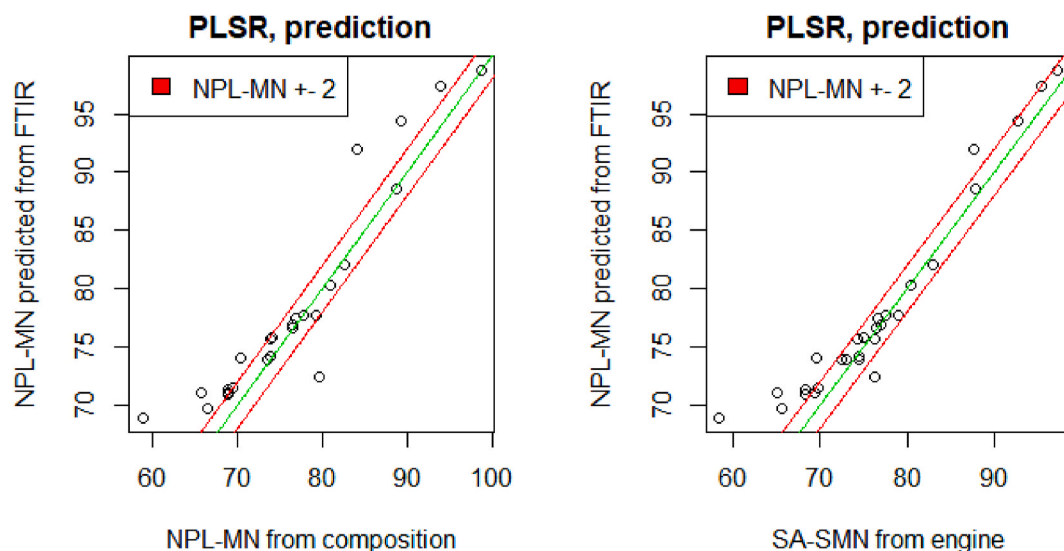


Fig. 9. Comparison between the FTIR-PLS predictions and the NPL-MN and SMN values. The ± 2 MN bands are given for visual information (see text for details).

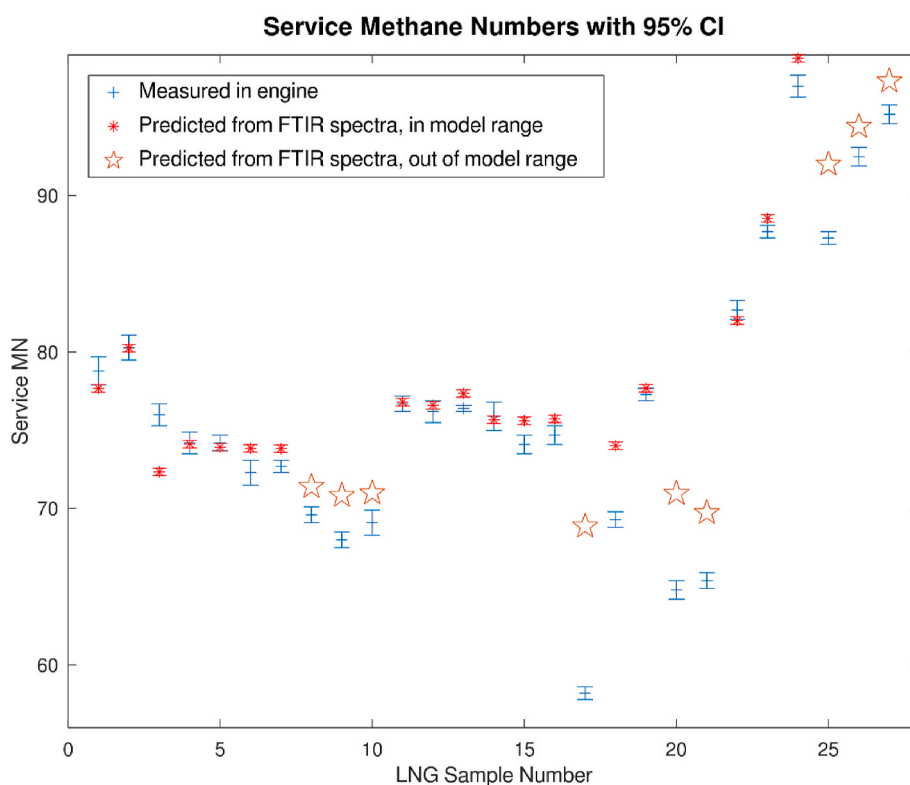


Fig. 10. Comparison of the FTIR-PLS predictions and the SMN, including their 95% confidence intervals. Note that the major errors occur for samples out of the model domain (denoted with stars) and, as such, are not considered for model validation.

and LNG III mixtures were used to yield PLS predictions (7 LVs). Positively enough, less extreme differences were observed when the PLS predictions were compared to the SMN values than to the NPL-MN ones (see Fig. 9).

Despite all mixtures are shown for completeness in Fig. 9, it is worth stressing that the PLS model should only be applied to mixtures/samples whose expected MN is higher than 70 (the lowest working limit of the PLS model) and that, in addition, some of the rightmost samples should not be considered as their composition is out of the working domain of the model. This is detailed in Fig. 10, along with the 95% confidence intervals associated to the FTIR-PLS predictions. They were estimated as

follows: Two samples, at the low and high extremes of the PLS calibration range each, were replicated in different days, their PLS predictions obtained and their ranges averaged. This was considered a proxy for the intermediate precision of the overall FTIR-PLS approach, which was 0.24 MN.

The 95% confidence intervals of the SMN values were calculated during the measurements at TU-Braunschweig (see Table SM1, Supplementary Material). It is worth noting that even for out-of-the-model samples the PLS predictions are not so bad, see Fig. 10 (excluding some extreme cases, as mentioned above).

The average prediction errors of the FTIR-PLS approach when

compared to the NPL-MN and SMN values, measured as RMSEP, were 2.2 MN and 1.6 MN, respectively. However, one of the standard mixtures (Mix3 of the LNG III mixtures; **Table SM1, Supplementary Material**) had problems to calculate the NPL value (also reported by (Sweelssen et al., 2020)) and one of the LNG II samples (Mix2) had large prediction errors, c.a. 7.3 and 3.6 MN. These obviously bias any further calculation and were therefore rejected as outliers. Then, the new RMSEPs were 0.9 MN for the PLS comparisons against both NPL-MN and SMN. Furthermore, when only the LNG III mixtures are considered in order to compare with (Sweelssen et al., 2020), the RMSEPs were ca. 1.0 MN and 0.9 MN (when predicting NPL-MN and SMN, respectively). These values are highly positive but they are not straightforwardly comparable to common error expressions and, thus, more details are provided next.

When all LNG III and LNG II samples (excluding the two outliers) were considered the average differences (PLS prediction minus NPL-MN or SMN value) and their associated standard deviations amounted ca. 0.3 & 0.9 MN and 0.5 MN & 0.8 MN for the NPL-MN and SMN comparisons, respectively. Moreover, the Student's test revealed that the average differences were not statistically significant (95% confidence level; $t_{exp} = 0.5$, $t_{tab(17,2 \text{ tails}, 95\%)} = 2.1$) and, as a consequence, the FTIR-PLS method provides accurate predictions, without bias. When the LNG III subset of standard mixtures was considered, the average differences and their standard deviations were ca. 0.5 & 1.0 MN and 0.4 MN & 0.8 MN for the NPL-MN and SMN comparisons, respectively. The average values were not statistically different from zero and, so, the predictions are again unbiased.

Noteworthy, these results are totally comparable with previous efforts to develop electronic capacitance and tuneable IR sensors (Sweelssen et al., 2020), although with slightly lower precisions here. Regarding the operative time, the FTIR-PLS requires about 45 min per sample (including a background, which is always done before sample measurement), so it is a bit slower than the electronic sensor (ca. 10–30min/sample); while the tuneable IR is clearly faster (ca. 10 s/sample).

4. Conclusions

This paper presents the use of gas-phase mid-IR spectrometry combined to PLS regression to address the MN of gaseous samples. First, a statistical study based on synthetic spectra as a proof of concept demonstrates that the approach is reasonable and that sensible and potentially useful models can only be obtained using more than 50 samples in the training set.

The selected PLS model has no bias and the average predictive error is 0.75 MN, well below the target ± 2 MN interval set initially (such an interval was the estimated expanded uncertainty of the original AVL studies develop when the MN was defined).

Finally, and in order to validate further the model, a collection of 27 synthetic standard mixtures prepared for two European projects and whose SMNs were measured with a service engine, is considered. The FTIR-PLS approach yields predictions with average differences around 0.5 MN and 0.4 MN (when compared to the NPL and SMN reference values). These differences are statistically not significant so that the FTIR-PLS approach is unbiased and shows the same tendencies than the measured SMN and therefore reflects the gas knocking resistance in an operating engine.

From an operative viewpoint the approach is cost effective as it involves standard instrumentation and requires only ca. 45 min of instrumental work per sample (if a background is made before measuring each sample; otherwise the required time is about half that); ca. 10 min dedication of personnel. A drawback of this method –as it is based on mid-IR spectrometry– is that it cannot register signals for N₂ and this gas has a participation in the MN when determined by a motor (or alternative algorithms). The methodology presented here can be considered within the green chemistry principles since it does not

require chemical reagents, uses little sample and does not generate liquid or solid residues (the exhaust gas and argon are the only gaseous residues).

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.

Acknowledgements

This work is part of the EMPIR 16ENG09 project 'Metrological support for LNG and LBG as transport fuel (LNG III)'. This project has received funding from the EMPIR programme co-financed by the Participant States and from the European Union's Horizon 2020 Research and Innovation programme. The authors from TU Braunschweig would like to thank IAV, Mahle, MAN Truck & Bus and Motortech for their support in preparing the test engine. The Group of Applied Analytical Chemistry of the University of A Coruña acknowledges Mestrelab, Reganosa and Naturgy for hiring its services for FTIR method development.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jngse.2021.103944>.

Credit author statement

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