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Fast quality control of natural gas for commercial supply and transport utilities

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ABSTRACT

Quality control of natural gas frequently relies on off-line slow standardized chromatographic techniques. Previous implementations of new measurement approaches focused of synthetic mixtures without extensive industrial validation. Here, a fast alternative based on infrared spectra is presented to predict the gas constituents and a physical parameter, the Wobbe index. Commercial samples instead of synthetic mixtures were used to develop predictive models. Method performance parameters were calculated and ca. 100 % of the sample-specific confidence intervals for the predictions overlapped with those of the reference values and the approach was unbiased and precise. The limits of detection and quantification (classical and considering errors of type I and II) outperformed other approaches. Validation included commercial samples and primary mixtures. Furthermore, prediction models considering reduced sets of variables were sought for using Markov-chain Monte Carlo guided searches (uninformative variable elimination and random frog) and common (iPLS, UVE and SR) approaches. The prediction errors and limits of detection of these 'reduced' models outperformed those from other approaches. The methodology takes only minutes to analyse a sample, requires few sample and no reagents (only some argon), making this approach cost-effective and environmentally-friendly.

1. Introduction

Despite petroleum being a non-renewable resource its distillates are still critical as energetic and raw material sources. Unfortunately, their combustion lead to atmospheric pollution [1], which constitutes one of the strongest causes of global climate change. Many countries adopted policies to reduce the carbon footprint and pollution by empowering the use of greener energies. Obvious renewable energy sources (wind, sun, etc.) should be complemented with natural gas (NG) to change smoothly some energetic paradigms as its combustion leads to reduced emissions of CO₂, NO_x and SO_x [2]. Besides, massive deposits have been discovered, many of which are still under-exploited. Nowadays NG is employed mainly to generate electric power and to industrial and domestic applications. Its use in transportation is not as prevalent, mainly due to the low energy density (for liquefied NG, ca. half that of gasoline) which would require bigger fuel tanks, so that hybrid and electric engines are preferred in most cases [3]. However, the EU promoted it as a suitable fuel for heavy-duty vehicles and maritime transport [4]. The EU

objective is to change traditional diesel engines for liquefied natural gas (LNG) propellers, and it was planned to deploy the corresponding facilities on maritime ports and on land along the Trans-European Transport Networks by the end of 2025. The trend of changing traditional personal vehicles to alternative fuel vehicles (considering compressed natural gas and gas-hybrid engines) is also rising. The EU directive [5] is gaining momentum rapidly as most European capitals strongly limit the circulation of traditional vehicles through their city centers.

The growing use of NG requires reliable quality control methodologies to determine its composition and energetic properties. They depend on the geological deposit where the NG comes from. NG is composed mainly of methane (75–99 %), mixed with other light hydrocarbons, like ethane (0–20 %), propane, butanes and pentanes, plus nitrogen and/or carbon dioxide (all of them ≪ 10 %). Sometimes, hexane isomers could be present at trace levels. Hence, the composition of the NG must be known to evaluate its physical properties and combustion power. In particular:

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- i) The methane number, MN, is an analogue to the octane number in gasoline or the cetane number in diesel. Its determination is controversial [6–8] and there exist different algorithms to estimate its value once the NG composition is known. Recently an IR-based alternative without that need has been proposed [9].
- ii) The Wobbe index, WI, evaluates the combustion energy of the NG using standardized formulae and its composition and represents the volume-basis calorific value, at specified reference conditions, divided by the square root of the relative density at the same specified metering reference conditions. The WI is said to be gross or net (sometimes, lower or higher) according to whether the calorific value used is the gross or net calorific value (in common usage, the WI as employed here refers to the gross index) [10,11]. The WI is the primary gas interchangeability criterion for residential and commercial appliances as well as for some large-scale combustion equipment in industry and power generation.

Currently, the NG composition is measured by standardized gas chromatography (GC) procedures [12]. However, GC is difficult to adapt to online devices and small facilities [13], and is costly (overall, ca. 600 € per sample) [14]. Modern on-line devices are relatively rapid (ca. 4 min/sample) but they still need frequent time-consuming calibrations and verifications. GC off-line systems need ca. 150 min to get a full, validated result [14], which may delay pipeline distribution and energy custody transfer activities (shipments, storage, etc.). Thus, faster and cheaper methods are required to simplify and accelerate NG routine quality control.

Published alternatives rely mostly on IR (infrared) measurements (although molecular fluorescence was also proposed [15]), with notable reductions in costs (e.g., less than 200 € per sample, in total [14]). Note that although the IR region can reflect accurately the NG composition [16,17] gas spectra are pretty hard to interpret due to the strong overlap of the peaks and so multivariate chemometric treatments are required to get predictions, typically by partial least squares regression (PLS) [13,18].

Very scarce papers applied multivariate regression to deal with the prediction of NG properties. To the best of the authors' knowledge, the most relevant examples are reviewed herein. The two typical IR regions, near and medium (NIR and MIR) were used, although the former was more common.

Likely, one of the very first studies considered methane-ethane-propane ternary mixtures and NIR and MIR measurements combined with PLS and PCR (principal components regression) [18]. Only two pipeline NG samples were considered to test the models, with good agreements for methane and ethane and worst results for propane. The MIR models doubled the errors of the NIR ones and the latter were selected. On the contrary, another report proposed MIR to predict the concentrations of 12 light hydrocarbons (C₁-C₄) when studying the catalytic degradation of butane [19], with most errors around $\pm 10\%$ (relative standard deviation). Noteworthy, ethane and propane could not be determined individually but their sum was predicted accurately.

A fast screening NIR-based method for methane in NG was implemented considering classification by SIMCA (soft independent modelling of class analogy) instead of a regression because the interest was on ascertaining whether the samples had a minimum methane content [16]. Models were developed using synthetic gas mixtures and validated with a collection of 55 commercial NG samples. Similar to this approach, a very fast microNIR system using hollow waveguides was proposed to determine methane, ethane, propane and total butane in synthetic mixtures using PLS regression [20]. That study was amplified next considering a microNIR advanced system and an acoustic-optical tunable filter device [21]; although only synthetic mixtures were considered, not truly NG samples. In another report, the NIR spectra of 31 synthetic mixtures were used to develop PLS models that were validated using synthetic mixtures and one additional certified gas mixture [13]. The authors studied the impact of temperature and pressure

fluctuations in the models and derived some performance parameters (figures-of-merit). In these studies no commercial NG samples were analyzed.

The flue gas of a NG-fired generator was studied to determine methane, CO and CO₂ using NIR spectra, non-linear PLS regression and real samples of flue gas (reference values determined by GC) [22]. Finally, a US patent [23] was issued for a NIR-based system (coupled to a PCA-PLS computing module) to be deployed in gas fields and/or transmission infrastructures to monitor the gas composition and WI of several wells.

Very recently two different sensors comprising either six electrochemical detectors and a tunable mid-IR photometer were proposed to determine the composition of NG-like standard mixtures [7], although they are not still on the market.

With regards to the WI, to the best of our knowledge, only a handful of publications evaluated it without resorting to the composition of the gas [24] or other physical parameters [25–27]. A relevant, seminal approach predicted the energy content of NG by combining NIR and PLS [28]. There, synthetic mixtures of the NG components (including N₂ and CO₂) were used to get a model that was validated using a certified standard gas mixture. In another work, a micromachined thermoelectric sensor was proposed to measure several NG properties [29], including the WI, methane and ethane using PLS. Synthetic mixtures composed of methane, ethane, CO₂ and N₂ were used for calibration, and this involved a degradation on the performance of the Wobbe models when typical levels of propane were considered. Also, fiber-enhanced Raman spectroscopy [30] was employed to determine a partial composition of the sample (C₁-nC₄, N₂ and CO₂) used subsequently to calculate the WI in real time.

From this review it is concluded that true commercial and/or industrial NG samples have scarcely been considered into the studies. From the pragmatic viewpoint of industrial and quality control laboratories, this is a relevant drawback that should be addressed. In addition, almost no synthetic samples contained N₂ nor heavier compounds than butane (although they are indeed present in NG) and most reports did not differentiate between *i*- and *n*-butane.

The major aim of this paper is to develop and validate a methodology to determine the composition and the Wobbe index of NG samples by hybridizing their gas-phase MIR spectra with multivariate regression. Our working hypothesis was that having enough industrial samples to build a sound model, the composition of unknown samples can be predicted with remarkable accuracy and, even, complex physical parameters (the Wobbe index) can be addressed. Further, should the approach be satisfactory enough, industrial laboratories can avoid the preparation (purchase) of a huge number of synthetic gas mixtures to develop calibration models. A second objective is to reduce the time required for the analyses as much as possible and make them robust to uninformative variables. For this, a suite of spectral variable reduction methods have been applied to select the most relevant wavenumbers, although without compromising the predictions.

2. Experimental

2.1. Samples

The routine-operation NG samples used throughout correspond to a one-year-collection of ca. 120 samples in the Reganosa regasification plant (Mugardos, A Coruña, Spain) in 500 cm³ stainless steel cylinders. They were NG, vaporized liquefied NG (LNG), and boil-off-gas (BOG) samples. LNG samples from tanks at the terminal harbour were also taken. In the following only the term NG will be used for all samples for the sake of simplicity. Most samples had been employed in the European EMPIR LNGIII project [9] although it did not include the objectives addressed here.

As an additional validation set, 27 mixtures specially developed by Nippon Gases (formerly Praxair) and Linde Gas Benelux B.V. during the

European EURAMET-EMRP LNG II and EURAMET-EMPIR LNG III research projects were employed. Their compositions were determined by standardized methods [9].

2.2. Apparatus

Gas-phase IR measurements were made with an 8400S Shimadzu FTIR spectrometer. The cell setup consisted of a 10 cm path, stainless steel Harrick gas cell (Harrick Scientific, USA) with 2 mm-thick, 47 mm-diameter ZnSe windows, an input tube with a Swagelock 3 way valve, an exhaust tube and an internal pressure gauge (see Fig. 1). The resolution used was 1 cm^{-1} , with a spectral range from 5500 cm^{-1} to 480 cm^{-1} and Happ-Genzel apodization. A background was made before each sample, using 0.5 bar of the broadening gas (Argon, Carburos Metálicos (Barcelona, Spain), 99.9992 % purity). All measurements were done at $25 \pm 1\text{ }^\circ\text{C}$, mixing 0.2 bar of the selected sample (ca. 500 mL were enough to perform the studies) and 1.3 bar of argon, employed as broadening gas to enhance the intensity of the spectral features, more comprehensive details and explanations on this issue and the use of broadening gases were detailed previously [14]. The chemical composition of the samples was determined by the ISO-17025-accredited Reganosa laboratory using a protocol based on ISO 6974-4 [12] (more details can be found elsewhere [14]).

2.3. Software and chemometrics

The spectrometer was controlled by the Shimadzu IR Solutions software, v.1.30. The raw spectra were digitized to 9375 data points per spectrum (from 5000 cm^{-1} to 480 cm^{-1} , 1 datum per ca. 0.5 cm^{-1}). The spectral treatments and developments of multivariate models used the PLS Toolbox (Eigenvector Co, WA, USA). Different preprocessings were studied and the selected one consisted of an iterative baseline correction (automatic weighted least squares, using a polynomial of order 2), followed by spectral normalization (total area = 1) and mean centring. Variable selection was made using the PLS Toolbox and a collection of routines for Monte Carlo natural computation presented recently [31], the latter complemented with in-house Matlab routines.

For the purposes of this manuscript, PLS can be described conceptually as a powerful regression method where both the spectral information (X-space) and each of the properties to be predicted (Y-space) are maximally related by means of a set of abstract factors (termed latent variables or, just, factors). PLS has become a de-facto standard and, hence, it was considered here; technical details can be found elsewhere [32,33]. Roughly, PLS modelling consists of a calibration (training) and a validation stage. The latter verifies that neither underfitting (i.e., a

model with a lack of predictive capability due to a lack of information) nor overfitting (i.e., a model with a lack of predictive capability due to memorization of too particular information associated to the training samples, e.g., some minor spectral characteristics) occur. Noteworthy, the latter problem is pretty much frequent than the former [34]. See [Supplementary Material](#) for practical details. The usual practice by which a minimum in the internal validation procedure ([Supplementary Material](#)) is used to fix the number of latent variables can lead to overfitting [34] and, so, it is highly advisable to compare the average error in cross-validation (RMSECV, root mean square error of cross-validation when calibrating) and the average error in a ‘true’ external prediction set of new samples –RMSEP- (root mean square error of prediction). Sometimes, this set of samples is called the fine-tuning set, as it is used to refine the selection of the number of LV. Ideally, RMSECV and RMSEP should be of the same order, which results from a trade-off among fitting and prediction [35]. A final external validation set of samples is needed to accurately check how the model behaves (sometimes it is called testing set). Hence, two ‘validation’ steps were undergone here, both with external new samples: a first one to fine-tune the model after a number of factors was suggested by internal cross validation, and a final one to validate the model.

2.3.1. Variable reduction methods and performance parameters

A model can be refined by avoiding those spectral variables that do not contribute to the predictions. Variable selection methods, thus, play an important role in potentially improving model robustness and/or allowing for the development of dedicated instruments. In this paper we selected five strategies. The first three are applied frequently and are broadly available; the other two are based on exhaustive ‘natural computation algorithms’ (population-driven or Bayesian approaches) and constitute quite new developments [31]; however, they were not applied in quality control. A conceptual overview of each of them is presented in the [Supplementary Material](#).

After developing the models several statistical performance parameters [34] must be calculated to assess their adequacy (details are given in the [Supplementary Material](#)): the coefficient of determination (R^2), bias, the standard error of performance (SEP) (if bias is statistically negligible, the value of SEP equals the RMSEP and, so the latter is interpreted as a standard deviation), and the ratio of prediction to deviation (RPD) [34]. In addition, the modern IUPAC, EU and ISO limits of detection and quantification (i.e., including both the risks of type I –false positives- and type II -number of false negatives) [36–39,40,41] were employed.

Here, both the classical and the modern limits of detection were calculated for ethane, propane, n-butane and i-butane because they have

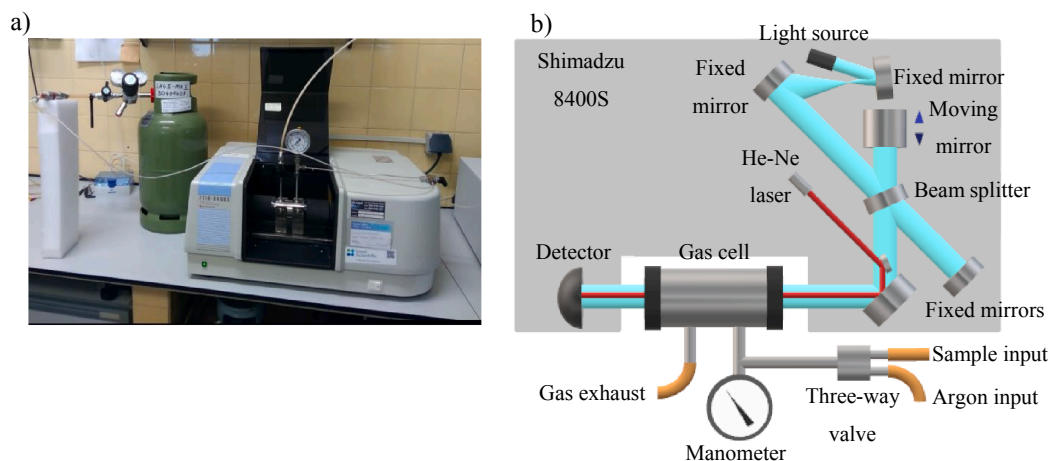


Fig. 1. a) Measurement setup, 8400S Shimadzu FTIR spectrometer and connections to a synthetic NG-like mixture container. b) Experimental setup diagram (the grey background indicates the parts of the Shimadzu 8400S spectrometer).

concentrations close to zero, whereas methane and the WI values remain far apart from the origin and, so, they would require large extrapolations which would render unreasonable figures. Noteworthy, the modern limits have not still been reported for usual NG analysis.

3. Results and discussion

3.1. Predictive model for % of methane

The model to predict the percentage molar volume concentration, vol%, of Methane was developed from a calibration set of 71 samples whose concentrations spread evenly between 89 % and 99 %. During our

sampling period (ca. one year) only 4 samples with percentages between 68 % and 85 % methane were collected and, thus, the models could not predict them reliably and they were discarded. The model selected finally considered 5 latent variables (LV), see Fig. 2, and was quite satisfactory. Note that this methodology can definitely be adequate to other ranges of values (typically, around 75 % which are common in many deposits worldwide) as long as enough samples are available to get a calibration, which was not the case here.

The external validation set to fine-tune the model consisted of 13 external samples, not included in the model at all, which confirmed its good predictive properties. It takes account of a large amount of information in the spectra and in the parameter of interest (methane), and

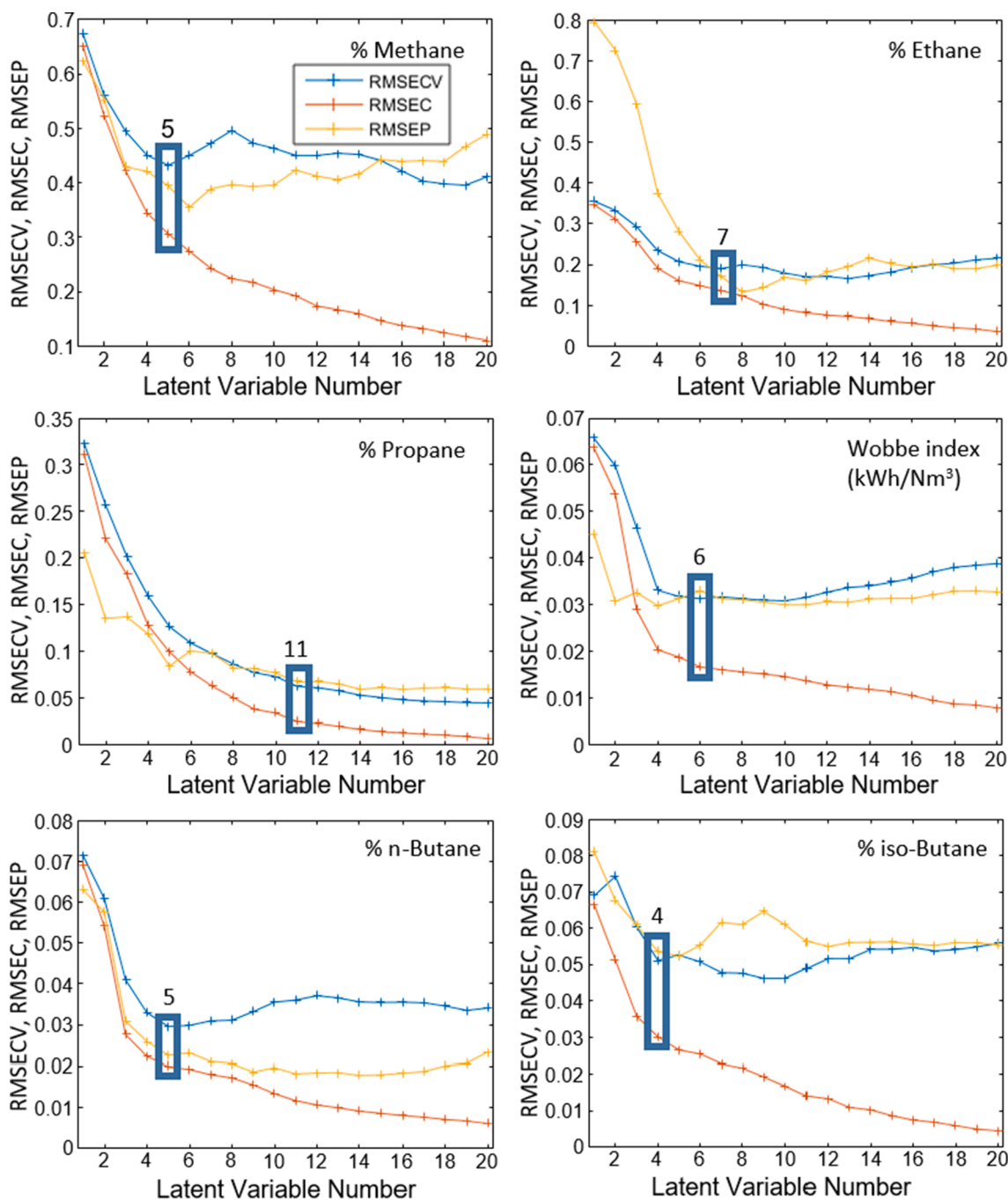


Fig. 2. Global average errors for different PLS models on calibration and validation for each studied parameter. The boxes indicate the number of latent variables selected for each model. RMSEC = root mean square error of calibration, RMSECV = root mean square error of cross-validation, RMSEP = root mean square error of prediction (fine-tuning external set), all them in vol%.

yields a high coefficient of determination, 98.5 % (Table 1), so that a huge amount of information related to methane is explained.

Fig. 3 presents the typical accuracy line ('actual vs predicted' line) for calibration, which summarizes the predictive performance of the model. The average overall error for calibration, measured as RMSEC, was ca. 0.3 vol% methane. The model has not a statistical bias (Table 1 and Fig. 3) nor relevant outliers, as seen at Figure SM1 (supplementary material), which shows two common diagnostic statistics, the Q residuals and the Hotelling T² statistics (they two yield the so-called, applicability domain) [13].

Further validation with an external test set comprising 20 NG samples distributed throughout the working range was also satisfactory. Fig. 4 presents its predictions and Table 1 resumes some relevant associated statistics. The RPD index (>3) shows that accurate predictions can be expected throughout the working range, without bias and a predictive average standard error ca. 0.4 vol% of methane. The RMSEC and RMSEP values can be compared directly with the precision of the GC method (method-reproducibility) thanks to the absence of bias. They are of the same order as the 0.37–0.39 vol% reproducibility values obtained for methane using the chromatographic method in this range (Table 2).

Indeed, 95 % of the external validation samples yield prediction differences (=predicted – reference) smaller than the maximum GC reproducibility allowed by the ISO 6975:1997 [42]. Fig. 5 depicts the reference compositional values derived from the GC measurement, along with their 95 % confidence intervals, superimposed to the MIR + PLS predicted values, also with their sample-specific 95 % PLS confidence intervals (calculated as formulated elsewhere [43]). The key idea is that to get statistically unbiased predictions both confidence intervals must overlap and this occurs for 100 % of the validation samples. A note about the interpretation of Table 2 and Fig. 5 is in order: note that the reproducibility values given in table 2 act as confidence intervals of the GC values alone. When the number of predictions that are excluded from this range are counted, a 'worst scenario' situation is considered. In effect, as the PLS predictions themselves have associated confidence intervals it may happen that even when a PLS prediction is out of the GC reproducibility range the PLS-predicted and GC-values do agree (statistically), when both confidence intervals overlap. Hence, the use of sample-specific intervals for the predictions are of most importance

(Fig. 5).

The average predictive error (RMSEP) obtained in this model compares nicely to literature, see Table 3, mostly considering that we used true NG samples whereas the other approaches considered mostly synthetic mixtures.

3.2. Predictive model for % of ethane

The model established to predict the vol% of ethane considered a calibration set with 73 industrial LNG samples in the 0 – 6 % volume molar range concentration and 7 LV (see Fig. 2). It yielded a good calibration (Fig. 3) with reasonably good statistics (Table 1). Although a slight improvement could be seen for the fine-tuning test set when 8 LV were considered (Fig. 2) it was only marginal and was not observed for the external validation set. The model explained ca. 99 % of the information in the spectral and concentration domains, and the coefficient of determination was very high (99.4 %), as well as the RPD index (>11).

No obvious suspicious samples were seen on the applicability domain plot (Figure SM1, supplementary material). No bias was observed neither for calibration (Table 1 and Fig. 3), nor for validation (Table 1 and Fig. 4) and, so, it is worth noting that the average prediction errors for the samples of the calibration, fine-tuning and external validation sets (i.e., 0.2 vol% ethane, Table 1) were comparable to the GC method-reproducibility range (Table 2). When the external validation set of samples was considered, only 37.5 % of them yielded predictions within the ISO 6975:1997 maximum GC reproducibility values. However, Fig. 5 indicates that 96 % of the 95 % confidence intervals associated to the reference and predicted values overlap. Two samples gave bad predictions although their behaviour was very good for the other parameters so we could not find a reason for that point. In addition, the average error (RMSEP) obtained when validating this model is of the same order as the best ones reported using NIR (Table 3).

Both the modern and classical limits of detection and quantification (x_d and x_q and LOD and LOQ, respectively; see Supplementary Material) were calculated (see Table 1). The classical limits were calculated following the Eurachem Guide [44] which recommends using the 10 samples with the lowest concentration values, along with blanks or samples without the analyte. As there were no industrial samples with

Table 1

Performance parameters associated to each selected model for calibration and validation; N = number of samples used in the model after removing outliers. X represents the spectra and Y represents the parameter of interest, see text for more details. The parameters specified for the selected variable reduction method are shown between brackets.

		C1	C2	C3	n-C4	i-C4	Wobbe Index
Calibration	N	71	73	65	60	50	65
	LVs (PLS)	5	7	11	5	4	9
	RMSEC (vol%)	0.3	0.1	0.03	0.02	0.03	0.02
		[SR: 0.4]	[SR: 0.2]	[SR: 0.04]	[iPLS: 0.007]	[iPLS: 0.004]	[SR: 0.05]
	RMSECV (vol%)	0.4	0.2	0.06	0.03	0.05	0.03
		[SR: 0.4]	[SR: 0.4]	[SR: 0.05]	[iPLS: 0.009]	[iPLS: 0.009]	[SR: 0.07]
	Total % info explained in X	93.40	98.86	99.44	81.58	78.83	93.42
	Total % info explained in Y	98.49	99.46	99.80	95.63	92.48	99.16
	R ²	0.985	0.994	0.998	0.956	0.894	0.992
	BIAS	0	0	0	0	0	0
	LOD (vol%)	–	0.264	0.052	0.020	0.024	–
			[SR: 0.161]	[SR: 0.033]	[iPLS: 0.0072]	[iPLS: 0.0064]	
	LOQ (vol%)	–	0.880	0.174	0.067	0.082	–
		[SR: 0.458]	[SR: 0.097]	[iPLS: 0.019]	[iPLS: 0.018]		
1st Validation (fine-tuning)	x_d (vol%)	–	1.11	0.27	0.107	0.108	–
	x_q (vol%)	–	3.24	0.80	0.331	0.336	–
	N	13	15	12	11	16	14
	RMSEP (vol%)	0.2	0.2	0.1	0.02	0.04	0.05
	RPD	2.84	11.01	3.40	4.80	2.79	3.38
	R ²	0.993	0.993	0.932	0.962	0.873	0.913
External Validation	N	20	24	17	18	27	20
	RMSEP (vol%)	0.4	0.2	0.03	0.03	0.05	0.03
		[SR: 0.4]	[SR: 0.3]	[SR: 0.03]	[iPLS: 0.008]	[iPLS: 0.007]	[SR: 0.03]
	RPD	5.83	11.8	15.7	3.38	2.38	4.85
R ²	0.971	0.991	0.990	0.919	0.847	0.959	

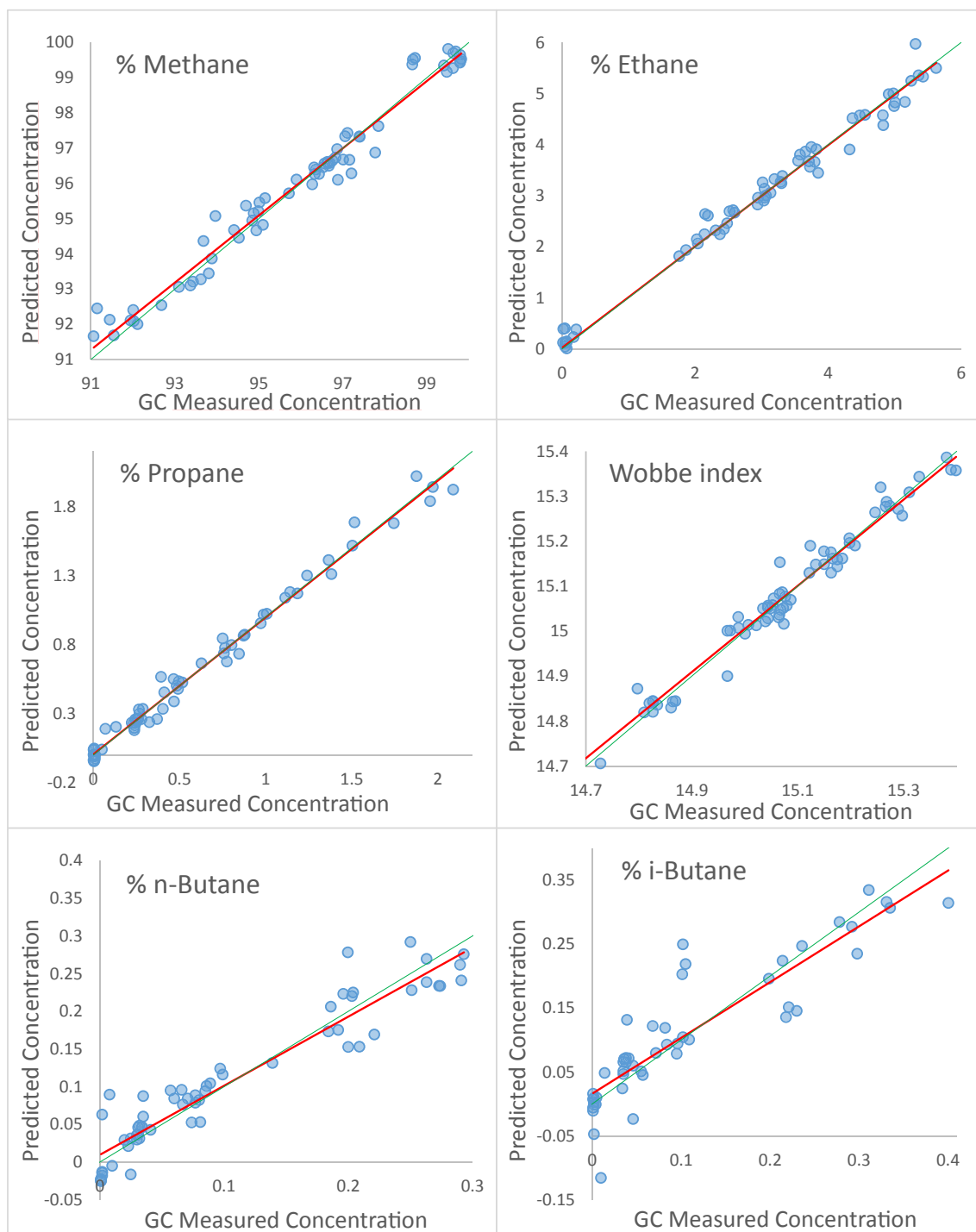


Fig. 3. Calibration accuracy lines for the PLS models selected for each predicted parameter. The green line depicts the theoretical perfect prediction (45° line) whereas the red one shows the actual predictive behaviour of the model. The units for the x and y axes are % vol molar concentration. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

0 % ethane concentration the samples used as ‘zero’ had concentrations ranging from 0.01 to 0.027 vol% ethane. With respect to the classical limit of detection (LOD) very few comparisons could be established with literature because of the scarcity of reported values, and none of them reported the modern definitions (x_d , x_q). All LODs are clearly higher than the chromatographic ones (Table 3), which is the reference methodology. However, positively enough, the mid-IR approach leads to lower LODs than the NIR ones.

3.3. Predictive model for % of propane

The model to predict the concentration of propane was developed using a calibration set consisting of 78 LNG samples in a range between 0 and 2.1 % volume molar concentration of propane. A model with 11 LVs (see Fig. 2) yielded a good calibration (Fig. 3 and Table 1). The need for this rather high number of LVs was attributed to the requirement for considering minor spectral signals which can correlate positively with propane (likely because its spectral bands overlap strongly with those from other NG components). In fact, a bit more than 99 % of the

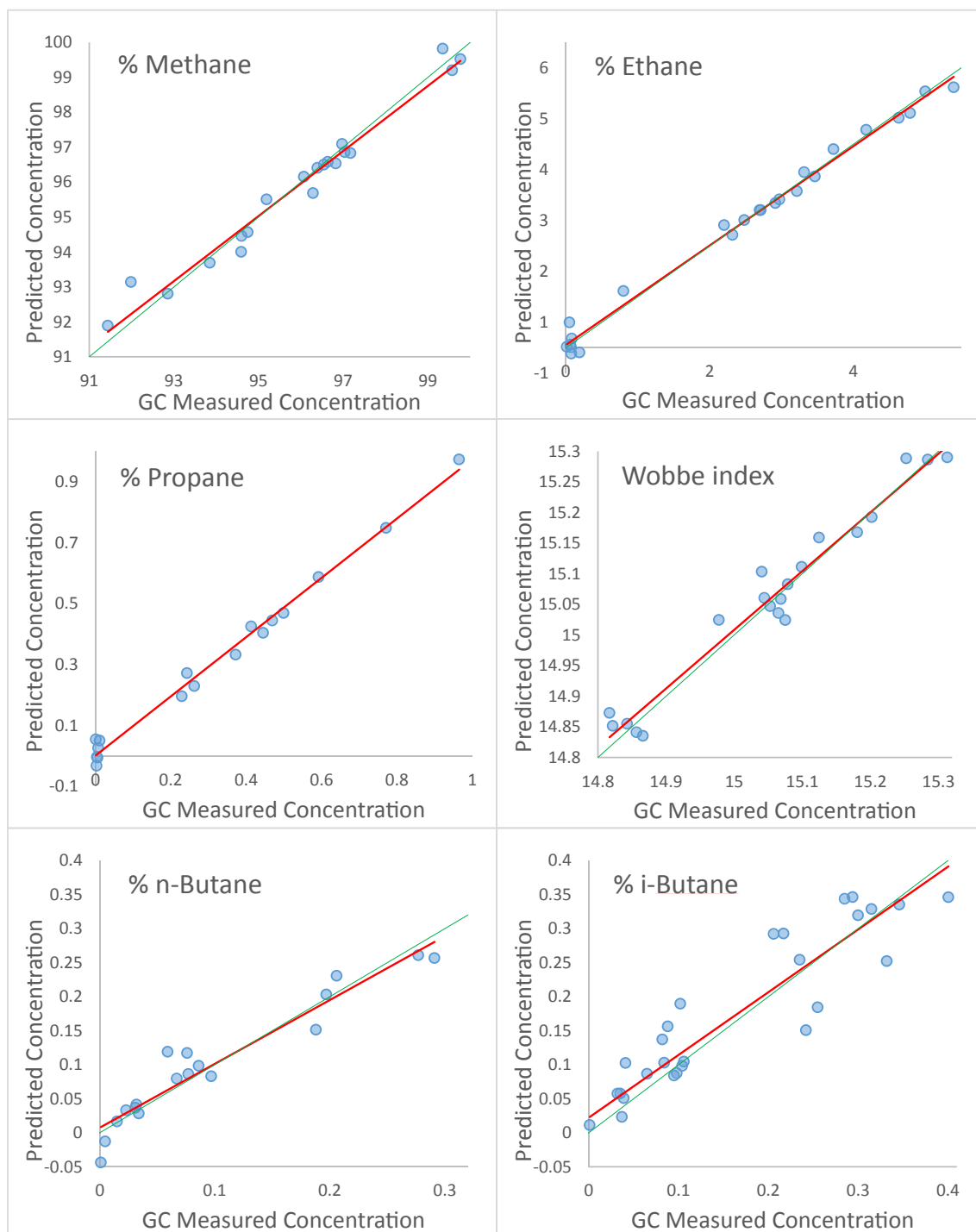


Fig. 4. Predictions for the external test set using the PLS selected model for each parameter. The green line depicts the theoretical perfect prediction (45° line) whereas the red one shows the actual predictive behaviour of the model. The units for the x and y axes are % vol molar concentration. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

information in the spectral domain was required to explain the concentration of propane ($R^2 = 0.998$, Table 1). No obvious suspicious samples were seen on the applicability domain plot (Figure SM1, supplementary material) and no relevant bias was observed for calibration or validation (Figs. 3 and 4, and Table 1).

The model was validated using external NG samples. The RMSECV values were similar to the RMSECV one (0.03 vol% – 0.1 vol%) so no overfitting occurred. The model was not biased (Table 1) and its precision was comparable to the GC reproducibility (Table 2). In fact, 73.3 % of the predictions of the validation samples were within the ISO

6975:1997 maximum GC reproducibility and, also, 100 % of them overlapped their confidence sample-specific intervals with the GC ones (Fig. 5).

The limits of detection and quantification were calculated (Table 1). As for ethane, there were not enough industrial samples with zero propane concentration. Thus, the LOD and LOQ were calculated considering samples with concentrations ranging from 0 to 0.004 vol%. The LOD was higher than the GC ones although quite similar to that reported by Haghi et al [13] and much better than that of Rivessi et al [21] (Table 3). The average error (RMSEP) obtained when validating this model is clearly

Table 2

Range-dependent overall-method reproducibility values calculated for the gas chromatography reference method (indicated as the reproducibility for the lowest and highest concentrations of each component). The percentages between parentheses indicate the number of external samples whose predictions using gas-phase FTIR + PLS are within these reproducibility values, for the full-spectrum and reduced models.

	GC calibration range(Vol.% or kWh/Nm ³)	GC method ISO 6975:1997 reproducibility values(% of predictions within the reproducibility ranges)
Methane	99.850–93.220	0.37–0.39 (PLS: 95; SR: 100)
Ethane	3.002–0.010	0.0092–0.11 (PLS: 37.5; SR: 42)
Propane	3.115–0.003	0.0032–0.56 (PLS: 73.3; SR: 53)
n-Butane	0.717–0.002	0.0032–0.034 (PLS: 77.8; iPLS: 83)
i-Butane	0.722–0.002	0.0032–0.038 (PLS: 63.0; iPLS: 96)
Wobbe index	14.866–14.552	0.04 (PLS: 80; SR: 85)

better than those reported for NIR (Table 3).

3.4. Predictive model for % of Butane.

The models to predict the concentrations of n- and i-butane were developed using calibration sets including 60 and 50 industrial LNG samples, respectively, whose concentration ranges were between 0 % and 0.3 vol%, and between 0 and 0.4 vol%, each. The optimized models considered 5 LVs for n-butane, and 4 LVs for i-butane (see Fig. 2). They yielded good calibrations, without bias and quite good performance parameters (Fig. 3 and Table 1). No obvious outliers were seen on the models (Figure SM1, supplementary material). The models were validated using external fine-tuning and test sets. The RMSEP values were similar to the RMSECV ones (0.02 vol%–0.03 vol%, n-butane, and 0.05 vol%–0.06 vol%, i-butane) so no overfitting occurred. In addition, those values were similar to the ISO 6975:1997 maximum GC reproducibility precision, being the number of predictions within those figures 77.8 % of the external validation samples for n-butane, and 63.0 % for i-butane (Table 2). Fig. 5 shows that 100 % of the confidence intervals overlap for the validation samples.

Despite quite good models were obtained, they have low RPDs (ca. 3, Table 1), which seems to be caused mainly by the reduced working ranges. The average errors (RMSEP) obtained when validating this model with true NG samples are slightly higher (although of the same order) than those reported using NIR using synthetic mixtures [13] although much better than those reported for the sum of i + n butanes [20,21] (Table 3). The limits of detection and quantification were also calculated (see Table 1). In this case there were 15 production samples without butane, so that they constituted a true zero. The LODs were better than those reported for NIR [13,21]; all IR-based approaches had bigger LODs than the GC ones (Table 3).

3.5. Predictive model for the Wobbe index

The model developed for the Wobbe index considered 65 NG samples ranging from 14.5 to 15.5 kWh/Nm³. This interval does not include the low values associated to some samples, that can be as low as 12.6 kWh/Nm³ in some countries [45]. Despite some very few samples had WIs between 13.0 and 14.5 kWh/Nm³ they disrupted the models. This was attributed to their contents on N₂ as it decreases dramatically the WI. The problem here is that N₂ is transparent to the mid-IR radiation, thus making it hard for the models to take it into account. This yielded a broad dispersion of the predictions at the lowest values of the calibration. Therefore, those particular samples were not considered in the models.

After several preliminary studies (Fig. 2 was not conclusive by itself) with the fine-tuning dataset 6 LV were fixed, which yielded a good calibration (Fig. 3 and Table 1), without bias and no outliers (Figure SM1, supplementary material). The RMSECV and RMSEP average errors for the calibration and the fine-tuning and external validation sets (Fig. 4) were similar (ca. 0.03–0.05 kWh/Nm³), suggesting that overfitting did not occur. These errors (0.28 % as relative

error, for the experimental range of values) compare very well to other publications reporting relative errors between 1 % and 0.03 % [25]. Other authors reported even higher relative errors, like 1.5 % [29] or 14 % [27]. Although Brown et al [28] reported average errors around 0.5 %, those corresponded to energy predictions, using BTU units.

As ISO 6975:1997 does not contemplate the WI, the precision figures calculated for this parameter using the MIR+PLS approach were compared to the experimental reproducibility (strictly, intermediate precision) obtained by Reganosa using GC (ca. 0.04 kWh/Nm³). They are similar (Table 2), and 80 % of the predictions of the validation samples became within the reproducibility range. Notwithstanding, 100 % of the sample-specific confidence intervals of the validation samples overlapped with the reference ones (Fig. 5).

3.6. Validation with synthetic gas mixtures

As mentioned in the experimental part, 27 gas mixtures from two European projects were considered. Some of them were used to check two new sensors, one based on electrochemical membranes and a TFIR system [7]. Despite some of these mixtures were only binary or ternary ones (and, so, quite different from the industrial NG samples employed in the models above), it was considered interesting to predict them as a benchmark activity to see whether the MIR + PLS approach could predict them. Table 3 summarizes the average prediction errors (as RMSEP) and despite they are of somewhat lower quality than those from the real NG samples (as expected because of the spectral differences), they are very encouraging. The RMSEPs (as they had not bias, they can be immediately compared with standard deviations) for methane and ethane are midway between those of the other two methods [7] while for propane, the MIR-PLS approach yields slightly better results. The predictions for the two isomers of butane yielded only semiquantitative results because many synthetic mixtures were out of the calibration range of the models and they contained much more butanes (0–2 vol% range) than our usual NG samples (0–0.45 vol% range).

3.7. Variable reduction methods

As mentioned in the experimental section, the spectra measured in this work contain as many as 9375 variables/spectrum because of the need to register the sharp IR spectral peaks of the gaseous components at high resolution. This can be a problem when time is an issue (here, at least 30 min/spectrum were needed to get a high signal/noise ratio, including the background), when implementing probes or portable equipment, or when some of those wavenumbers offer no relevant information and degrade the predictions. Hence, spectral variable reduction appears as a nice option. Disappointingly, as mentioned in the Supplementary Material, many variable selection strategies do not set absolute thresholds for their statistics [46] and these have to be established ad-hoc. Here, we took advantage of the many trials the algorithms performed to set a strategy rooted on classical quality control. As for traditional quality control charts, average values of the statistics associated to all the variables (e.g., the reliability (of the MCUVE approach)

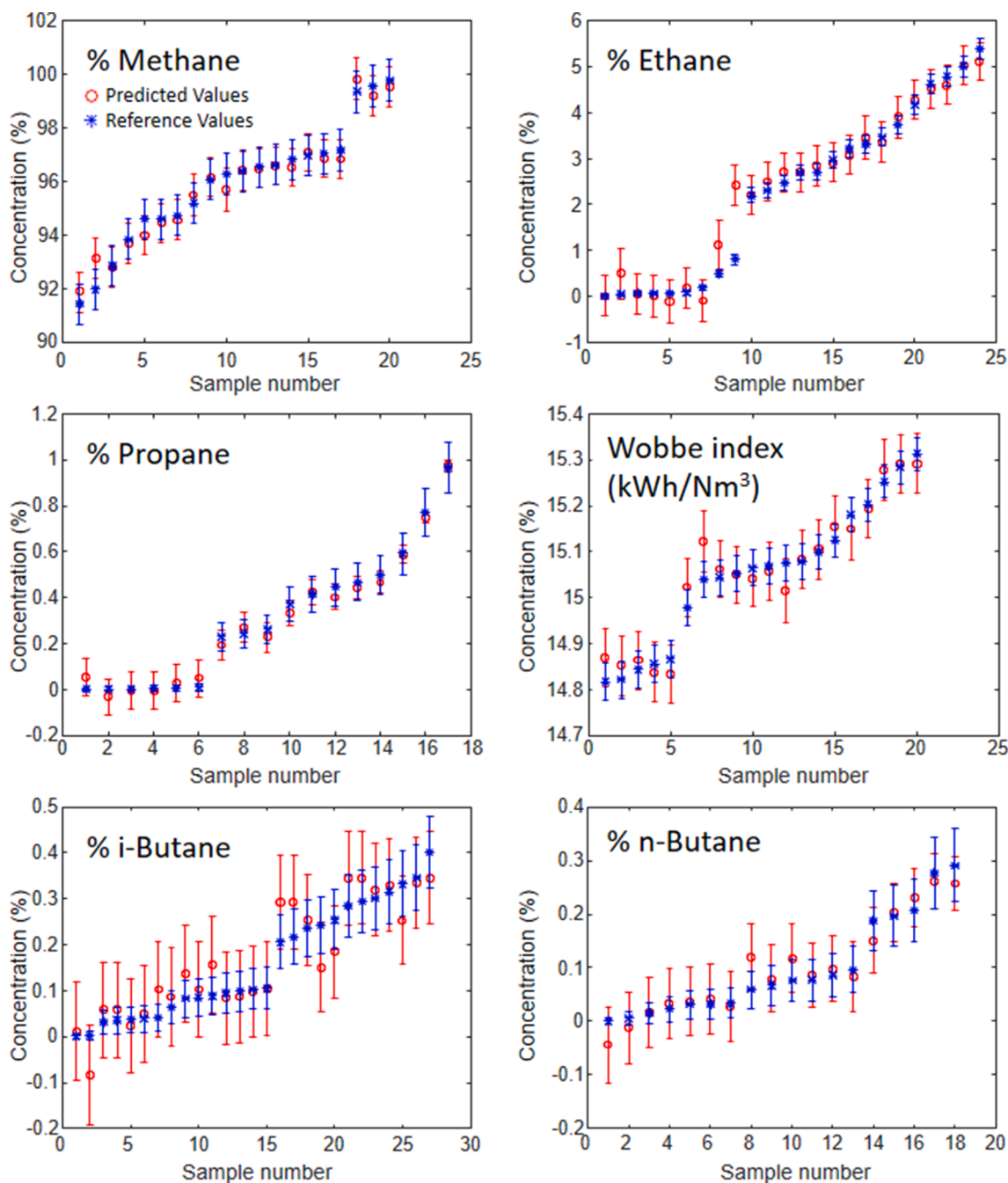


Fig. 5. Reference (blue asterisk) with the ISO 6975:1997 max. reproducibility (Reganosás in the case of the Wobbe index) and predicted (red circle) values with their respective 95 % confidence intervals for the external calibration samples. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

and the selection probability (for random frog) can be calculated, along with their 2 and 3 standard deviation upper limits. Hence, any variable outside the upper control limit is deemed to be selected; see next paragraphs for an example.

The number of selected spectral variables was varied from 10 to 400 for all five approaches and all analytical parameters (composition plus Wobbe index). Further, the number of latent variables was also optimized for each trial. As this generates a very large number of models, to choose a final one we proceeded as follows (for each analytical parameter): first, for each selection strategy the number of spectral variables leading to best predictions was chosen among the different trials (the number of latent variables in each PLS models were optimized as well); second, the best candidates of the five variable reduction methods were

compared; third, whenever several 'best' candidate models performed approximately the same, that with less spectral variables and/or with the spectral variables more concentrated in particular spectral regions would be preferred. This criterion was applied at the final stage of the selection because one of our objectives was to simplify the measuring stage in the industrial laboratory, which is trivial whenever the selected variables become close to each other.

As a general result, it was found that many models considering reduced suites of variables outperformed those considering full-spectra. However, the 'best' models disagreed on the number of wavenumbers they considered, as expected because of the different criteria involved in the approaches (see [Supplementary Material](#)), and they varied also with the property under consideration (as it is logical because relevant

Table 3

Average errors obtained in this work (RMSEP) compared to those reported in literature using NIR and other methods. The LODs are shown between parentheses (when available) and the calibration ranges, as percentage, between brackets. The chromatographic LODs are shown as a reference. All values represent vol% molar concentration of the constituent. Note that RMSEPs can be related to SD because the models in this work are not biased (see text for details). SD means standard deviation.

	Range		C1	C2	C3	i-C4	n-C4
LNG samples in this work	MIR:(PLS)	RMSEP	0.4	0.2	0.03	0.03	0.05
		(LOD)	– [99–89]	(0.26)[6–0]	(0.05)[2–0]	(0.02)[0.4–0]	(0.02)[0.4–0]
	MIR (reduced)	RMSEP	SR: 0.4[99–89]	SR: 0.3[6–0]	SR: 0.04[2–0]	iPLS: 0.008[0.4–0]	iPLS: 0.007[0.4–0]
		(LOD)	– [99–89]	SR: 0.161[6–0]	SR: 0.033[2–0]	iPLS: 0.0072[0.4–0]	iPLS: 0.0064[0.4–0]
Synthetic Mixtures in this work	MIR:	RMSEP	1.04[95–89]	0.49[14–0]	0.28[5–0]	–	–
Electrochemical sensor (SD) [7]	MIR:	SD	0.58[95–89]	0.62[10–0]	0.34[5–0]	0.15[2–0]	0.22[2–0]
TF-IR sensor (SD) [7]	MIR	SD	1.23[95–89]	0.13[10–0]	0.44[5–0]	0.34[2–0]	0.07[2–0]
Haghi et al [13]	NIR	RMSEP	0.20	0.19	0.16	0.012	0.012
		(LOD)	(0.90)[100–80]	(0.39)[12–0]	(0.33)[8–0]	(0.13)[2–0]	(0.15)[2–0]
Rohwedder et al [20]	NIR	RMSEP	0.37[82–69]	0.36[17–6]	0.67[14–5]	0.37[7–2]	–
Makhoukhi et al [18]	MIR/NIR	RMSEP	0.2[96–85]	0.2[10–2]	0.1[4–0]	–	–
Ribessi et al [21]	NIR	RMSEP	0.77	0.75	1.63	0.54	–
		(LOD)	(0.42)[90–30]	(0.59)[50–10]	(1.42)[30–3]	(1.67)[20–1]	–
Cao et al [22]	NIR	RMSEP	0.95[0.46–0 ppm]	–	–	–	–
Udina et al [29]	Thermic sensor	RMSEP	0.6[100–72]	1.0[20–0]	–	–	–
GC method	–	LOD	– [99–68]	0.01[12–0]	0.003[3–0]	0.002[0.7–0]	0.002[0.7–0]

variables for methane may not be so for –e.g.- i-butane). This complicates any comparison and makes it difficult to decide which approach is best in an absolute sense. As a consequence, a trade-off was made for each analytical parameter.

Table 1 depicts the variable reduction method of choice for each property, their RMSEC, RMSECV, RMSEP, and limits of detection and quantification. First of all, note the improvements achieved when the variable subsets are used as those performance parameters became half or a third those of the full-spectrum ones. Of most importance is the very large enhancement associated to i- and n-butane, which are particularly difficult to address because their bands overlap not only among them but with methane and ethane.

The feature reduction method selected for methane, ethane, propane and WI was SR (the selectivity ratio index, see Supplementary Material), with 3 LV (50 wavenumbers), 6 LV (100 wavenumbers), 6 LV (50 wavenumbers) and 6 LV (250 wavenumbers), respectively (see Fig. 6 and Figure SM2, supplementary material). Despite the wavenumbers selected for methane became not too grouped (Fig. 7), they indeed formed nice, definite regions for ethane, propane and WI (Figure SM3, supplementary material).

A good alternative for the former three properties may be VIP (variable importance in projection, Supplementary Material) as it chose limited spectral ranges (Fig. 7 and Figure SM3, supplementary material) although with slightly higher prediction errors. For the WI good

alternatives might be random frog or common PLS (although all the spectrum needs to be measured). iPLS performs quite well although at the expense of selecting very sparse sets of variables (so all the full spectrum would still be required). Random frog yielded also sparse selections while MCUVE (Monte Carlo uninformative variable elimination, Supplementary Material) and VIP lead to two very well defined groups around variables 5000–5500 and 1500–1800 (i.e., 2650–2900 and 4430–4580 cm^{-1} , respectively). See Supplementary Material for a general chemical interpretation of the most relevant regions. Fig. 8 exemplifies how thresholds for MCUVE and random frog were set following the ‘quality control chart’ criterion depicted above.

Note the very stable predictions SR yields for ethane and Wobbe index, where the dimensionality is not a critical factor (Figure SM2, Supplementary Material, in the figure it is called SRI to stress its indexing nature). This is a very positive result for quality control purposes as parsimony can be applied, however in this paper we only focused on absolute minima to simplify the comparisons and discussions.

Analogous situations were found for the other analytical parameters (Supplementary Material, Figures SM2 and SM3), i- and n-butane are predicted nicely by iPLS (200 wavenumbers and 6 LV in both cases; 4500–2450 cm^{-1} for i-butane and 4100–950 cm^{-1} for n-butane). The alternative for i-butane (although with higher RMSEP) was random frog (10 wavenumbers), with a very stable behaviour when dimensionality is

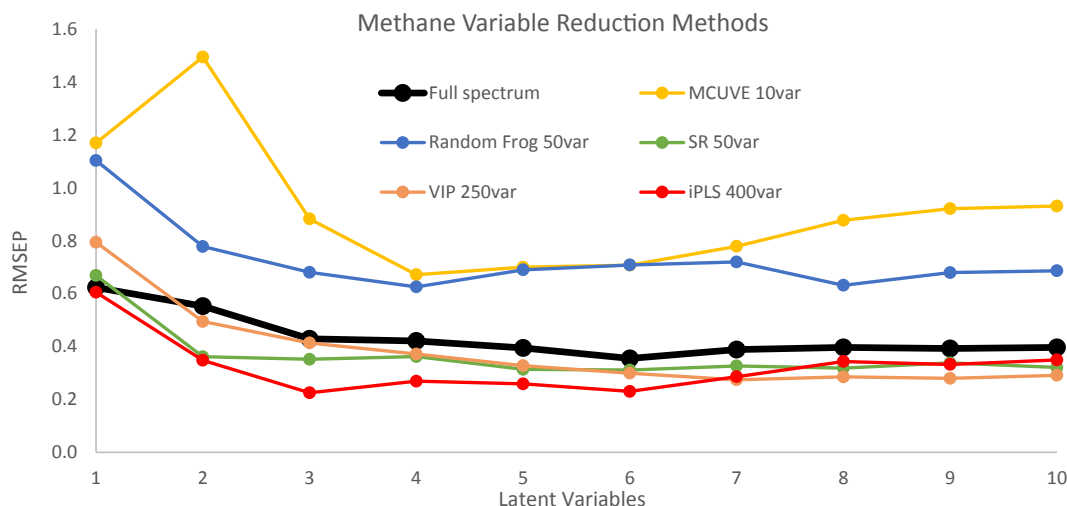


Fig. 6. Errors of prediction (RMSEP, vol%) for each latent variable and variable reduction method for the methane determination.

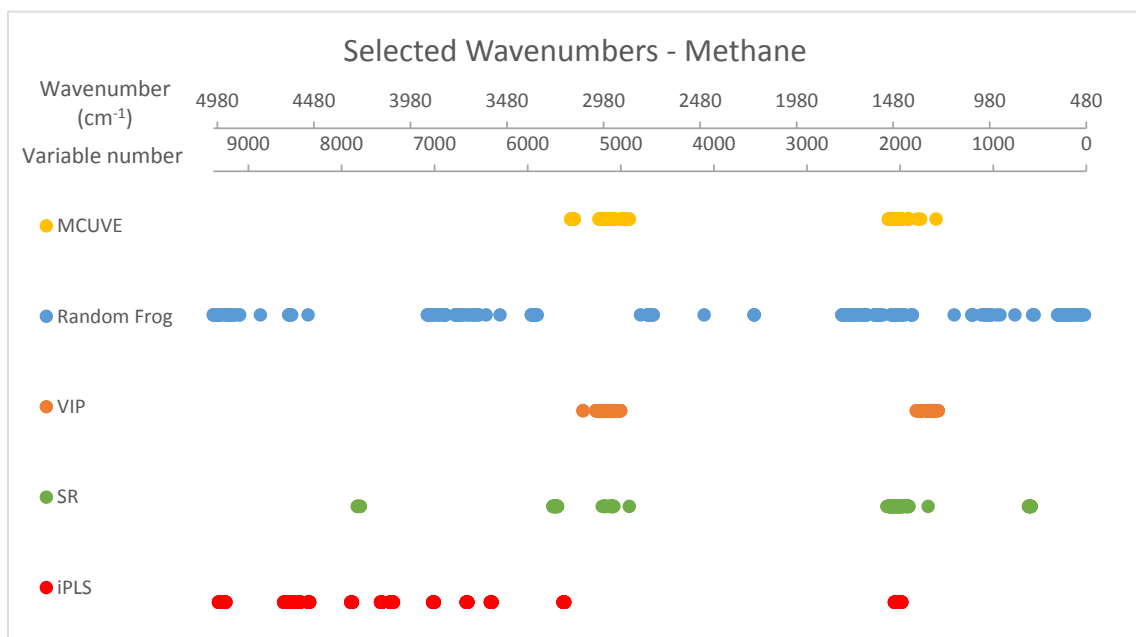


Fig. 7. Selected variables for each of the tested methods for the methane determination.

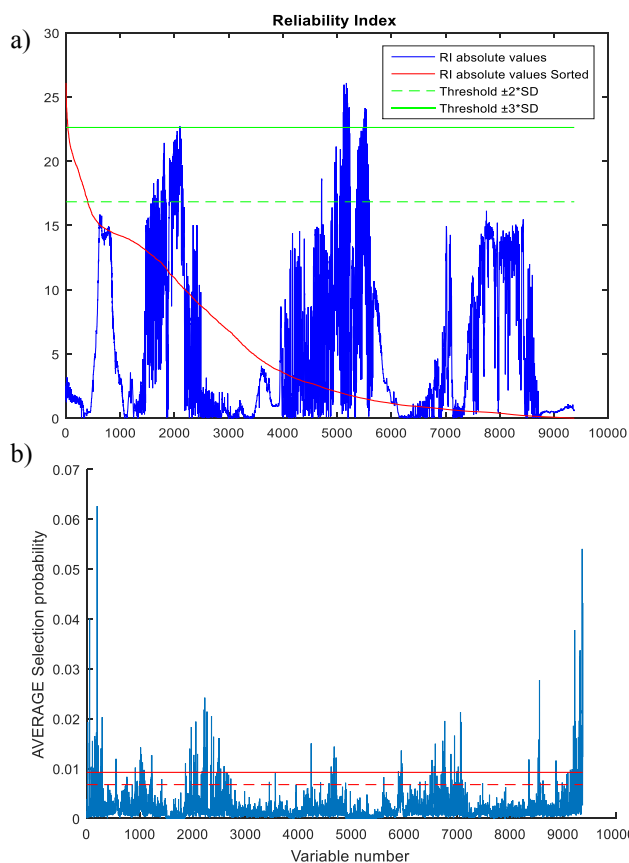


Fig. 8. Exemplification of how a selection threshold can be set considering the average and classical upper quality control limits ($\pm 3SD$) for the MCUVE (a) and random frog (b) indices calculated for methane (SD stands for standard deviation). See text for details.

considered and an average error almost as good. Nevertheless, those 10 variables spanned throughout the overall original spectrum, whereas for iPLS the intervals were collateral. For n-butane, SR (50 wavenumbers)

may be a reasonable alternative, although with ca. 50 % more error.

As a final remark, it is worth noting the very 'homogeneous' overall performance of iPLS throughout the various analytical parameters as it had a quite good behaviour almost always, but for the Wobbe index. However, it required high processing times ($>8h$ for a 9375 to 400 variables reduction) and it can only select intervals of variables. SR and VIP performed rather similarly to iPLS although much faster and, indeed, SR was the method of choice for methane, ethane and propane, mostly because it 'clustered' the selected wavenumbers (see, e.g. Fig. 7) and it appeared also as a good alternative for n-butane.

MCUVE and Random frog demonstrated an intermediate behaviour, often similar to iPLS, with the advantages that they required much reduced computing times and can select discreet variables. The former tends to group them slightly more than iPLS, while random frog tended to select much more dispersed wavenumbers.

4. Conclusions

This work demonstrates that the combination of mid-IR spectrometry and PLS regression yields regression models that predict the primary composition of natural gas reliably. The approach is cost effective because it requires standard laboratory instrumentation, industrial samples (not standard mixtures) and requires ca. 45 min to get the main composition of natural gas, along with an important physicochemical property, the Wobbe index (this included recording the sample spectrum, ca. 35 min, plus the software application to run the models). Further, it can be considered a green method because it does not demand chemicals (but some argon), uses very little sample (ca. 500 mL) and does not generate residues nor cleaning steps.

The models were unbiased in the typical industrial working ranges, with precisions comparable to the chromatographic reference method. The mid-IR-PLS approach compares advantageously to other NIR-based methods, with better average errors and better limits of detection (or, in the worst case, similar to the best NIR ones).

The models developed with reduced sets of variables clearly decreased the average predictions errors and limits of detection and quantification and, so, outperformed previous reports using other spectral regions. As a trade-off solution, the selectivity ratio index, SR, seemed the most satisfactory alternative because it was selected for four parameters and could be a good alternative for another one. iPLS

behaved also very well, achieving the lowest errors to determine the butanes (although it selects variables across all the spectrum). The prediction capabilities of the advanced random frog method were good but it selected very sparse variables.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fuel.2021.121500>.

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