



Composition and Physical Properties of the Natural Gas Supplied for Domestic Use through the Distribution Network

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Authors' contributions

This work was carried out in collaboration between all authors. Author MCFF designed the study, wrote the protocol, performed the statistical analysis and wrote the first draft of the manuscript. Authors BSF and LRSF managed the analyses of the study. Author JRPP managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

Aims: To assess the composition of the Natural Gas (NG) supplied for domestic consumption through the distribution network to correlate the physical properties linked to it were to be determined in order to investigate their fluctuations.

Study Design: The samples were analyzed in accordance with the method described in the ISO 6974-4 standard, "Natural Gas. Determination of Composition with Defined Uncertainty by Gas Chromatography".

Place and Duration of Study: Center of Technology Research, Fuels Laboratory, between January and December 2016.

Methodology: Over the course of the year, a total of eighty-four samples of natural gas for domestic use were analyzed. These were collected at a rate of one per month in seven cities in the geographical zone under study (Galicia, Spain), in which the number of users is significant.

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Results and Conclusion: The protocols for technical management of the Gas System have a section on quality specifications for Natural Gas at entry points to the system. This sets limits for only three of the physical properties of natural gas: Wobbe index, superior calorific value and relative density.

The figures obtained for Wobbe index, superior calorific value and relative density from the eighty-four samples studied showed that the quality of the Natural Gas distributed remained steadily within the acceptable limits throughout the whole year. The values for standard deviations bore witness to the fact that any variations did not significantly alter the quality of the Natural Gas supplied.

The concentrations of the odorant, THT, were always above the recommended value of 18.0 mg/Nm³, the fluctuations noted over the course of the year were such as to make it possible to see them as excessive. In some instances, a high concentration of odorant may lead users to erroneous impressions, so that they come to think that there are leaks from the gas-pipes or even that the gas is not burning properly.

Keywords: Natural Gas; composition; physical properties; gas chromatography; network distribution.

1. INTRODUCTION

Natural Gas (NG) is a non-renewable energy source, in the composition of which various gaseous hydrocarbons are included, predominantly methane, with smaller proportions of ethane, propane, butane, pentane and limited amounts of inert gases such as carbon dioxide and nitrogen. Its use has spread, primarily thanks to its high calorific value and to the fact that it burns much more cleanly than other traditional fuels [1,2]. Having a detailed acquaintance with its physical and chemical properties is of great importance both on a technical and on a financial level. This is because commercial transactions involving natural gas are based on the figure for its calorific value, this figure depending principally upon its chemical composition [3,4].

In Spain the Gas System [5,6], Fig. 1, developed late and slowly, owing to the limited production of gas within the country and to the geographical situation of Spain, distant from the European deposits in the North Sea and in Russia. The first re-gasification plant was built in the late 1960s in Barcelona, using as feedstock liquefied natural gas from Libya and Algeria. It was not until twenty years later that the plants at Huelva and Cartagena started operations and only in the 1990s that gas pipeline connections were made with France and that the North African gas pipeline linking Spain with gas reserves in Algeria was completed. At the beginning of this century re-gasification plants entered service in Bilbao (2003), Sagunto (2006) and Mugaros (2007), this latter being in Galicia. The Medgaz pipeline between Algeria and Almeria started operating in March 2011.

The oddity of the Spanish gas system, as compared to other European countries, is its high level of dependence on imports and the major role played by re-gasification plants in supply. There is also a considerable presence of underground storage installations, with a view to ensuring greater autonomy, security of supply and flexibility in the system. The development of gas infrastructures has been shaped by the large extent of the country, together with the distribution within it of population and industry. Current infrastructures for natural gas in Spain amount to six plants for the re-gasification of liquid natural gas, more than 11,000 kilometres of pipelines in the transmission grid, more than 80,000 kilometres of distribution pipes, two underground storage facilities, three deposits and six international connections (one each to Algeria and Morocco, two each to France and Portugal), together with other auxiliary installations, compressor stations and satellite liquefied natural gas plants.

The Gas System includes the installations making up the Basic Transmission Grid that is the liquefaction plants, re-gasification plants, primary transmission pipelines, underground storage facilities, and international connections. To these must be added the Secondary Transmission Grid, the Distribution Network and the other complementary installations needed to get gas to the individual final consumer from a pipeline in the basic or secondary grids.

The distribution network for natural gas in Galicia (a region in north-western Spain, 29,574 square kilometres in extent and with a population density of 93.78 inhabitants per square kilometre) essentially reaches the industrialized zones in



Fig. 1. Map of the Gas Infrastructure in Spain (Galicia is in the box at the top left)

Source: www.enagas.es

the region, where the majority of its population is concentrated.

Natural gas comes to Spain through international gas pipelines that distribute the gas throughout the territory, forming the main transport network or arrives the regasification plants on gas carrier ships in the form of liquefied natural gas (LNG), gasification and It enters the main network from where it is distributed to another smaller network that works at lower pressure, to reach the main consumption points. The distribution network forms a mesh, each point is supplied by more than one branch, so that supply is guaranteed in case of failure or maintenance at a point in the network.

The duality of the gas inlet system (natural gas, liquefied natural gas) together with the design of the grid supply system is the main cause of the possible existence of variations in the composition of natural gas and therefore in the physical properties linked to it: density, relative density, Wobbe index, higher and lower calorific value.

This makes evident the need to have available a quality-control system for the natural gas

distributed [7], the Spanish natural gas distribution network has on-line chromatographs for analysing the composition of the gas. The installation of such equipment for control is fundamental, and in countries like Brazil it has grown exponentially [4].

Remember that the processed natural gas received from the distributors has no smell. For safety reasons it is odorized, usually with organic sulfur compounds with a very intense odor, to detect leaks at very low concentrations before the accumulation of a dangerous concentration of gas in the air; in Spain tetrahydrothiophene THT is used. It is necessary to control that the concentration of odorant, the level of odorant is chosen to allow to perceive the gas before its concentration in air reaches 20% (alarm level).

2. MATERIALS AND METHODS

2.1 Equipment

A VARIAN CP-4900 Gas Micro-Chromatograph (MGC) equipped with a thermal conductivity detector and VARIAN STAR WORKSTATION

control software, using BIP helium as a carrier gas and configured for two channels:

- Channel A - 13 CB[‡] (12 m) / CP740483.
- Channel B - PPQ BF[‡] (10 m) / CP740150.

2.2 Primary Patterns

In the determinations, the CRM was used as the primary target for comparison, Table 1; this being a certified mixture of natural gas, prepared in accordance with the ISO 6142 standard, "Gas Analysis. Preparation of Calibration Gas Mixtures. Gravimetric Method" [8]

Table 1. Composition of the natural Gas used for calibration

Component	% v/v	± Δ % v/v
CH ₄	84.4510	0.195
C2	9.8120	0.099
C3	2.0050	0.021
I-C4	0.1750	0.004
N-C4	0.3049	0.007
I-C5	0.1119	0.003
N-C5	0.1139	0.003
C6+	0.0913	0.002
N ₂	1.9150	0.039
CO ₂	1.0200	0.021
THT	23.10	2.3

2.3 Sample Collection

This was carried out at regulation and measurement stations (RMS) in the Natural Gas distribution networks present in each of the cities that the study covered. This followed an adaptation of the requisites set out in the ISO 4257 standard [9]. A standardized one-litre canister was filled with natural gas at a pressure of 16 bar.

2.4 Method of Analysis

The samples were analysed in accordance, Table 2, with the method described in the ISO 6974-4 standard, "Natural Gas. Determination of Composition with Defined Uncertainty by Gas Chromatography - Part 4: Determination of Nitrogen, Carbon Dioxide and C1 to C5 and C6+ Hydrocarbons for a Laboratory and On-Line Measuring System Using Two Columns" [10,11]

In the case of the odorant, analysis took into account the ISO 13734 standard "Natural Gas. Organic sulfur compounds used as odorants. Requirements and test methods" [12].

2.5 Calculations

The calculations for determining the physical properties were governed by the indications contained in the following standards:

- ISO 6976. "Natural Gas. Calculation of Calorific Values, Density, Relative Density and Wobbe Index from Composition" [13].
- ISO 12213. "Natural Gas. Calculation of Compressibility Factor. Calculation Using Molar-Composition Analysis" [14].

2.5.1 Relative density

The density of a gas divided by the density of dry air of standard composition at the same specified conditions of pressure and temperature. The term ideal relative density applies when both gas and air are considered as fluids which obey the ideal gas law; the term real relative density applies when both gas and air are considered as real fluids.

Table 2. Ranges of application (ISO 6974-4)

Component	Mol Fraction Range %
N ₂ Nitrogen	0.001 to 15.0
CO ₂ Carbon dioxide	0.001 to 10
CH ₄ Methane	75 to 100
C2 Ethane	0.001 to 10.0
C3 Propane	0.001 to 3.0
i-C4 iso-Butane (2-methylpropane)	0.001 to 1.0
n-C4 n-Butane	0.001 to 1.0
i-C5 iso-Pentane (2-methylbutane)	0.001 to 0.5
nC5 n-Pentane	0.001 to 0.5
C6+ Hexanes - sum of all C6 and higher hydrocarbons	0.001 to 0.2

The relative density of the ideal gas is independent of any reference state, and is calculated from the equation:

$$d^0 = \sum_{j=1}^N x_j \frac{M_j}{M_{\text{air}}}$$

The relative density of the real gas is calculated from the equation:

$$d(t,p) = \frac{d^0 Z_{\text{air}}(t,p)}{Z_{\text{mix}}(t,p)}$$

$d(t,p)$ is the relative density of the real gas
 $Z_{\text{air}}(t,p)$ is the compression factor of dry air of standard composition
 $Z_{\text{mix}}(t,p)$ is the compression factor of the gas
 d^0 is the relative density of the ideal gas
 M_j is the molar mass of component j
 M_{air} is the molar mass of dry air of standard composition

2.5.2 Calorific value

As defined by ISO 6976, this is the amount of heat produced by complete combustion of one cubic metre of Natural Gas under normal conditions, measured at zero degrees centigrade at an absolute pressure of 1.01325 bar, with excess air at the same temperature and pressure as the natural gas, and where the combustion products are cooled at a yet to be defined benchmark temperature (usually 0°C for the Spanish system) and where all water formed during the combustion process completely condenses.

2.5.2.1 Calorific value on a molar basis

The ideal gas calorific value on a molar basis, at a temperature t_1 , of a mixture of known composition is calculated from the equation:

$$\overline{H}^0(t_1) = \sum_{j=1}^N x_j \overline{H}_j^0(t_1)$$

$\overline{H}^0(t_1)$ is the ideal molar calorific value of the mixture
 $\overline{H}_j^0(t_1)$ is the ideal molar calorific value of component j

For the purposes of ISO 6976 the real gas calorific value on a molar basis is taken as numerically equal to the corresponding ideal gas value.

2.5.2.2 Calorific value on a mass basis

The ideal gas calorific value on a mass basis, at a temperature t_1 , of a mixture of known composition is calculated from the equation:

$$\widehat{H}^0(t_1) = \frac{\overline{H}^0(t_1)}{M}$$

$\overline{H}^0(t_1)$ is the ideal molar calorific value of the mixture
 $\widehat{H}^0(t_1)$ is the real molar calorific value of the mixture
 x_j is the mole fraction of component j

M is the molar mass of the mixture, and is calculated from the equation:

$$M = \sum_{j=1}^N x_j M_j$$

For the purposes of ISO 6976 the real gas calorific value on a mass basis is taken as numerically equal to the corresponding ideal gas value.

2.5.2.3 Calorific value on a volumetric basis

The ideal gas calorific value on a volumetric basis, for a combustion temperature t_1 , of a mixture of known composition, metered at temperature t_2 and pressure p_2 , is calculated from the equation:

$$\widetilde{H}^0[t_1, V(t_2, p_2)] = \overline{H}^0(t_1) \frac{p_2}{R T_2}$$

The real gas calorific value on a volumetric basis, for a combustion temperature t_1 and pressure p_1 , of a mixture of known composition, metered at temperature t_2 and pressure p_2 , is calculated from the equation:

$$\widetilde{H}[t_1, V(t_2, p_2)] = \frac{\widetilde{H}^0[t_1, V(t_2, p_2)]}{Z_{\text{mix}}(t_2, p_2)}$$

$\widetilde{H}^0[t_1, V(t_2, p_2)]$ is the ideal molar calorific value on a volumetric basis of the mixture
 $\widetilde{H}[t_1, V(t_2, p_2)]$ is the real-gas calorific value on a volumetric basis of the mixture
R is the molar gas constant
 t_2 / p_2 working temperature and pressure metered
 T_2 is the absolute temperature

2.5.3 Compression factor

The compression factor is a correction factor which describes the deviation of a real gas from ideal gas behavior. Is defined as the actual (real) volume of a given mass of gas at a specified pressure and temperature divided by its volume, under the same conditions, as calculate from the ideal gas law.

$$Z_{mix}(t_2, p_2) = 1 - \left[\sum_{j=1}^N x_j \sqrt{b_j} \right]^2$$

$Z_{mix}(t,p)$ is the compression factor of the gas
 x_j is the mole fraction of component j
 $\sqrt{b_j}$ is the summation factor of component j, are given in "table 2-ISO 6976"
 M_{air} is the molar mass of dry air of standard composition

2.5.4 Wobbe Index

The Wobbe Index is an indicator of the interchangeability of fuel gases. Is defined as the superior calorific value on a volumetric basis at specified reference conditions, divided by the square root of the relative density at the same specified metering reference conditions.

The Wobbe Index of the ideal gas is calculated from the equation:

$$W^0 [t_1, V(t_2, p_2)] = \frac{\widetilde{H}^0 [t_1, V(t_2, p_2)]}{\sqrt{d^0}}$$

The Wobbe Index of the real gas is calculated from the equation:

$$W [t_1, V(t_2, p_2)] = \frac{\widetilde{H} [t_1, V(t_2, p_2)]}{\sqrt{d(t_2, p_2)}}$$

$\widetilde{H}^0 [t_1, V(t_2, p_2)]$ is the ideal molar calorific value on a volumetric basis of the mixture
 $\widetilde{H} [t_1, V(t_2, p_2)]$ is the real-gas calorific value on a volumetric basis of the mixture
 $W^0 [t_1, V(t_2, p_2)]$ is the Wobbe Index of the ideal gas
 $W [t_1, V(t_2, p_2)]$ is the Wobbe Index of the real gas
 $d(t,p)$ is the relative density of real gas

3. RESULTS AND DISCUSSION

Using the method chosen, a total of eighty-four samples of Natural Gas for domestic use were analysed. These were collected at a rate of one per month in each of the seven major population concentrations in the geographical zone under study, Galicia_Spain, in which the number of users supplied with gas is significant, Fig. 2.



Fig. 2. Galicia_Spain, sampling points

Each of the samples was analysed to determine its composition and concentration of odorant (THT) continuously over a period of at least four hours. This gave an optimum number of replications to ensure the reliability of the results obtained using the quality criteria established by the method.

For calibration, a certified reference material was used, the exact composition of which was known. All the samples were analysed so that, once their composition, and hence their physical properties, were known, it would be possible to check the variations in these relative to the limits set down in the specifications for natural gas quality at the entry points to the Gas System [15], Table 3.

It should be kept in mind that the norms state that the owner of the installation where gas enters the Gas System is under no obligation to supply users at exit points with natural gas having exactly the same characteristics as it had when introduced at entry points, provided that the agreed amounts in terms of energy content are supplied [15]. It should also be taken into account that Natural Gas has varying composition by origin [16]

Table 3. Quality specifications for Natural Gas at the entry points of the gas system

Property	Unit	Minimum	Maximum
Superior Calorific Value	kWh/m ³	10.23	13.23
Relative Density		0.555	0.700
Wobbe Index	kWh/m ³	13.368	16.016

Table values under the following reference conditions: [25 °C; V (0 °C , 101.325 kPa)]

Study of the chromatograms obtained allowed comparative determination of the composition of each of the samples analysed. As an example, the outcomes for the samples of natural gas taken in January 2016 are shown in Tables 4 and 5.

3.1 Methane (%v/v)

The composition of natural gas is very different according to its origin. The main constituent of natural gas is methane, which generally represents between 66 and 98% of the total volume of the mixture, the other gaseous hydrocarbons are present in proportion that rarely exceeding 15% of the total, Table 6 [17].

Once the gas has been extracted from the wells, before starting its transport to the consumption points, depending on their composition and the specifications of the gas for sale, a series of treatments be required to adjust the characteristics of combustion.

In the European market, natural gas is determined by the components indicated on Table 7.

In the study, over the course of 2016, the percentage of methane, Table 8, which is the main component of natural gas, had an average value of 91.529 % (v/v) with a average standard deviation of 4.014, within the range established in the European market [18].

The variation in the percentage of methane in the samples studied ran from 0.3% (v/v) in August to 6.7% (v/v) in November. The variation in the percentage of methane during year at the various sampling points stayed close to 6.5% (v/v) in all the cities except Orense and Pontevedra, where it was as high as 9% to 10% (v/v).

The greatest variation found in the composition of the samples of Natural Gas collected at the various sampling points related to those taken in November, Fig. 3 and Fig. 4.

These variations in the composition noted were related to the origin of the Natural Gas distributed at various times over the Network, and always remained within the expected range of values for this sort of sample.

3.2 Odorant, THT

Since Natural Gas is inflammable, must be easily detected by any non-specialized person without the need for any detector device. It is internationally recognized by most of the regulations, including the current regulation in Spain [15], as the minimum level of odor of a flammable gas the following:

"The gas must be odorised so that any leak can be easily detected by the normal human nose when there is a mixture whose volumetric concentration is one fifth of that corresponding to the lower limit of flammability."

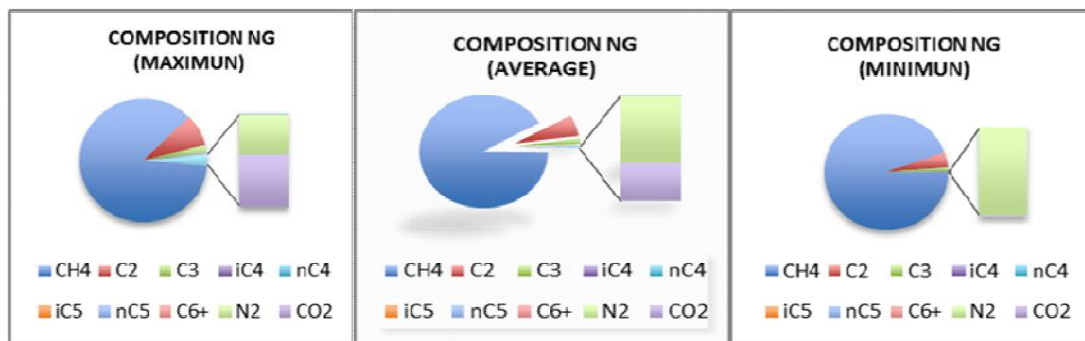


Fig. 3. Average distribution of components in Natural Gas, November_2016

Table 4. Composition of samples of Natural Gas, 2016_January

City	Composition (% v/v)										THT mg/Nm ³
	CH ₄	C2	C3	iC4	nC4	iC5	nC5	C6+	N ₂	CO ₂	
Vigo	92.896	5.225	1.491	0.191	0.120	0.001	0.001	0.000	0.111	0.000	25.6
Pontevedra	91.313	6.272	1.987	0.247	0.139	0.001	0.000	0.000	0.040	0.000	24.2
Santiago	92.656	5.408	1.540	0.193	0.123	0.001	0.001	0.000	0.079	0.000	22.3
Coruña	92.506	5.529	1.578	0.200	0.127	0.001	0.001	0.000	0.058	0.000	23.3
Ferrol	92.309	5.689	1.621	0.206	0.130	0.002	0.001	0.000	0.041	0.000	22.2
Lugo	92.468	5.565	1.583	0.200	0.126	0.001	0.001	0.000	0.055	0.000	23.0
Orense	92.327	5.615	1.610	0.230	0.126	0.001	0.001	0.000	0.090	0.000	23.3
Standard Deviation	0.501	0.327	0.163	0.021	0.006	0.000	0.000	0.000	0.027	0.000	1.1

Table 5. Physical properties calculated from the composition of Natural Gas samples, 2016_January

City	Relative Density	Density at 15°C kg/m ³	Wobbe Index kWh/m ³	Compressibil. Factor	Calorific Value	
					Inferior kWh/m ³	Superior kWh/m ³
Vigo	0.6000	0.7758	15.293	0.9971	10.676	11.846
Pontevedra	0.6108	0.7897	15.409	0.9970	10.859	12.043
Santiago	0.6014	0.7757	15.312	0.9971	10.702	11.874
Coruña	0.6024	0.7889	15.327	0.9971	10.722	11.896
Ferrol	0.6037	0.7805	15.343	0.9971	10.745	11.921
Lugo	0.6026	0.7791	15.330	0.9971	10.726	11.900
Orense	0.6037	0.7805	15.331	0.9971	10.737	11.912
Standard Deviation	0.0035	0.0057	0.036	0.0000	0.058	0.062

Table 6. The composition of natural gas according to its origin

Components (%v/v)	Dachava	Hassi R'Mel	Scochteren	Zelten	Kansas		
	Siberia	Algeria	Netherlands	Libia	USA	Iran	Canada
Methane	98.0	89.5	81.9	66.2	67.6	73.0	90.0
Ethane	0.7	7.0	2.7	19.8	6.2	21.5	
Propane		2.0	0.4	10.6	3.2		8.0
Butane		0.8	0.1	2.3	1.3		
Pentane and +		0.4	0.1	0.2	0.5		
H ₂ S						5.5	1.0
CO ₂	0.1	0.2	0.8		0.1		0.5
N ₂	1.2	0.1	14.0	0.9	21.1		0.2

Table 7. Components of natural gas, European market

Components	% (w/w)
Methane	70.0 - 98.0
Ethane	0.3 - 18.0
Propane	< 8.0
Butane	< 2.0
Pentane	< 0.2
N ₂	< 30.0
CO ₂	< 15.0
Other component	<0.1

It is established that the carriers of the primary network will deliver the odorised natural gas at the entrances to the transportation system, at the entrances to the distribution networks and to the consumers directly connected to their networks.

Distributors must ensure the smell characteristic of the gas that deliver to consumers, adding odorant compounds in the necessary proportion, when necessary, so that its presence is detected.

In Spain it is recommended that in the distribution networks carrying natural gas for domestic use the minimum THT content should be 18.0 mg/Nm³ of gas.

In the study, over the course of 2016, the concentration of THT, Table 9, had an average value of 22.9 (mg/Nm³) with an average standard deviation of 4.5, values within the range recommended.

3.3 Density at 15°C (kg/m³) and Relative Density

In the study, over the course of 2016, the density of the samples of natural gas analysed remained at an average of 0.7857, with an average standard deviation of 0.0332; the maximum being 0.8333 and the minimum 0.7498.

In the study, over the course of 2016, the relative density of the samples of natural gas analysed remained at an average of 0.6121, with an average standard deviation of 0.0330; the maximum being 0.6917 and the minimum 0.5799. These being values that fall within the limits set by Spanish regulation: [0,555 - 0.700kg/m³] [15,18], Table 3, Table 10 and Fig. 6.

When the variation in the relative density of the samples is considered month to month, it is observed that the highest variation was obtained in Pontevedra; the figures obtained for the standard deviation show that the relative density of the samples experienced only minimal changes.

3.4 Wobbe Index

Spanish standard UNE 60002 [19] between Superior Calorific Value and the square root of the relative density of the gas. The family of natural gases has a Wobbe index lying between 9,680 and 13,850 Kcal/Nm³ or 11.240 and 16.081 kWh/Nm³.

Table 8. Methane (%v/v) in Natural Gas samples, Galicia_2016

	Vigo	Pontevedra	Santiago	Coruña	Ferrol	Lugo	Ourense
Maximum	95.759	95.823	95.269	94.769	95.234	95.044	94.976
Minimum	88.901	85.698	88.742	88.023	88.714	88.767	85.681
Average	92.324	91.513	91.989	91.549	92.011	91.971	91.463
Standard deviation	2.124	2.760	1.764	2.007	1.705	1.718	2.466

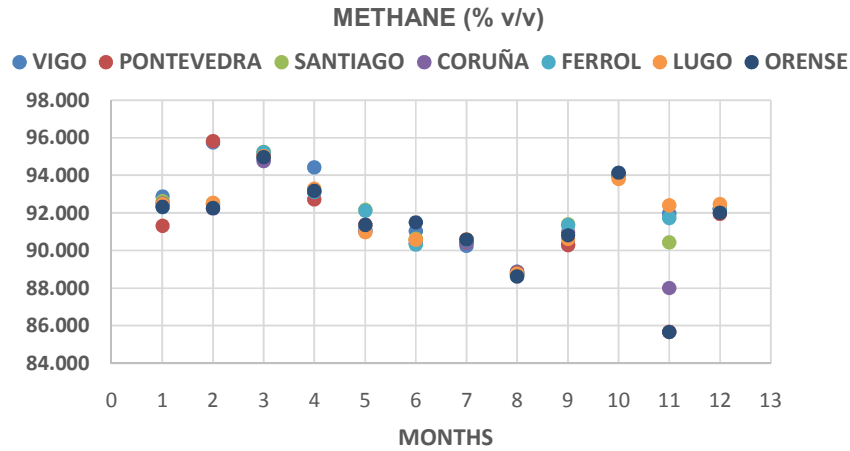


Fig. 4. Methane (%v/v) in the samples by city and month of collection

Table 9. THT (mg/Nm³) in Natural Gas Samples, 2016_Galicia

	Vigo	Pontevedra	Santiago	Coruña	Ferrol	Lugo	Ourense
Maximum	27.7	24.9	32.3	25.1	24.2	24.2	28.6
Minimum	19.0	19.0	19.2	18.0	19.5	19.6	18.8
Average	23.4	22.2	23.0	22.0	21.3	21.3	22.5
Standard deviation	2.5	1.7	3.4	1.8	1.9	1.5	2.5

Table 10. Density 15°C and Relative Density of NG samples, 2016_Galicia

	Vigo	Pontevedra	Santiago	Coruña	Ferrol	Lugo	Ourense
Density 15°C (kg/m³)							
Maximum	0.8080	0.8322	0.8097	0.8148	0.8097	0.8095	0.8333
Minimum	0.7501	0.7498	0.7545	0.7594	0.7548	0.7563	0.7573
Average	0.7802	0.7863	0.7832	0.7877	0.7833	0.7839	0.7871
Standard deviation	0.0180	0.0226	0.0158	0.0170	0.0153	0.0153	0.0205
Relative density							
Maximum	0.6249	0.6917	0.6262	0.6302	0.6302	0.6302	0.6445
Minimum	0.5801	0.5799	0.5836	0.5874	0.5874	0.5874	0.5857
Average	0.6034	0.6157	0.6059	0.6086	0.6086	0.6086	0.6087
Standard deviation	0.0139	0.0296	0.0121	0.0134	0.0134	0.0134	0.0158

Table 11. Wobbe Index (kW-h/m³) of NG samples, 2016_Galicia

	Vigo	Pontevedra	Santiago	Coruña	Ferrol	Lugo	Ourense
Maximum	15.457	15.486	15.498	15.486	15.487	15.500	15.457
Minimum	15.122	14.765	15.147	14.964	15.150	15.166	15.122
Average	15.314	15.275	15.319	15.320	15.343	15.351	15.314
Standard deviation	0.116	0.196	0.114	0.152	0.106	0.105	0.116

The Wobbe index remained at an average value of 15.272 kWh/m³ with a average standard deviation of 0.236, the maximum being 15,500 and the minimum 14,765 kW-h/m³. These being

values that fall within the limits set by Spanish regulation and the European market [13.368 – 16.016 kW-h/m³] [15, 18], Table 3, Table 11 and Fig. 7.

Consideration of the standard deviation of the month-on-month figures obtained in respect of each of the cities in which the samples were taken showed a practically constant value for this parameter. The standard deviation calculated annually for each city was not significant. The largest difference between maximum and minimum values for this parameter relative to the cities in which samples were gathered was found in November in two places situated at opposite ends of the gas pipeline.

The Wobbe index is a measure of the interchangeability of gases when they are used as a fuel. It compares the energy output of different gases during combustion. The Wobbe index is essential for analyzing the impact of a fuel changeover and is also a common specification of appliances that use gas and of

devices that transport gas. The Wobbe index may be calculated from the higher heating value and the relative density of the gas.

3.5 Calorific Value

The majority of users receive natural gas through a set of pipes, with a meter measuring the volume they consume. The price paid for natural gas is not calculated per unit of volume, but per unit of energy produced by burning the gas. The volume measurement is adjusted, using details of the calorific value to determine the amount of energy being consumed. Thus, end users are interested in the thermal energy that is generated by burning the gas supplied. Since this is linked to the relative proportions of the component gases, it is not a constant value for all the various different sources of natural gas.

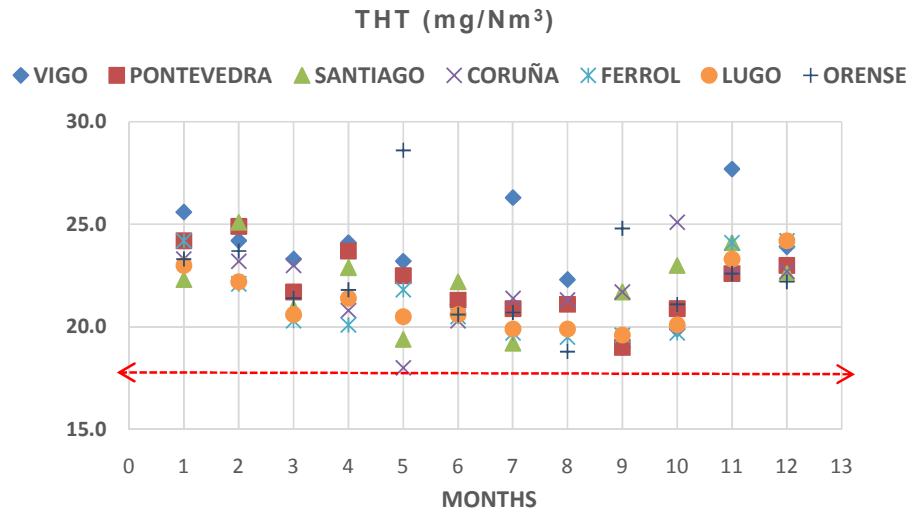


Fig. 5. THT (mg/Nm³) in samples by city and month of collection

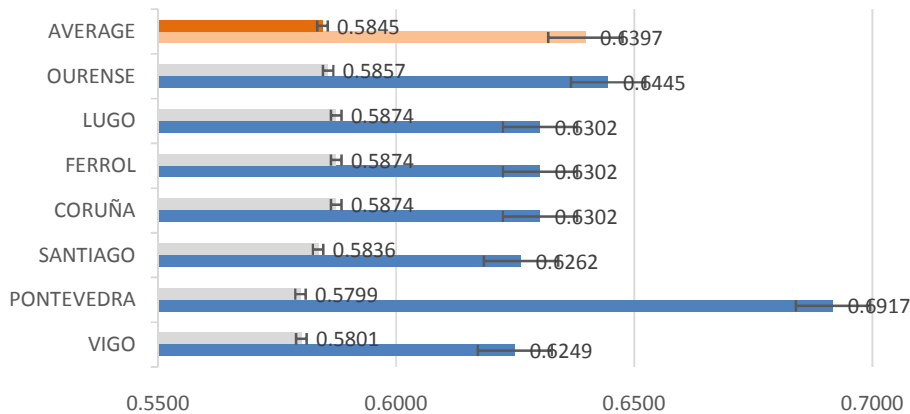


Fig. 6. Relative density (minimum-maximum)

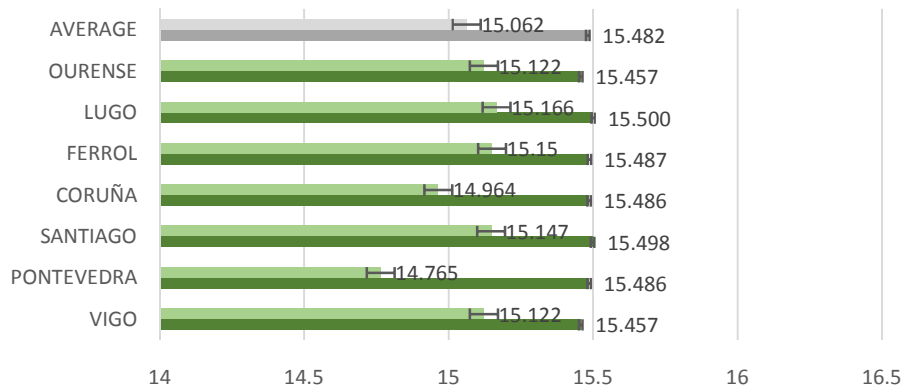


Fig. 7. Wobbe Index (minimum-maximum)

Over the course of 2016, the superior calorific value of Natural Gas stood at an average of 11.913 kWh/m³, varying over a range that ran from 11.518 to 12.265 kWh/m³. The standard deviation for the figures obtained for calorific value by sampling point in was 0.350 kWh/m³. This indicates that the parameter in question remained at a virtually constant value for the whole year, Table 12-13.

The figures for the superior calorific value for each of the samples studied fell within the limits

established by the standards currently valid in Spain and de European market: 10.23 at 13.23 kW-h/Nm³ [15,18].

The inferior calorific value for natural gas showed an average figure of 10.738 kWh/m³, having a range that ran from 10.369 to 11.066 kWh/m³. The standard deviation for the figures obtained for calorific value by sampling point over the course of year was 0.327 kWh/m³. This indicates that the parameter in question remained at a virtually constant value throughout.

Table 12. Superior calorific value (kWh/m³) of NG samples, 2016_Galicia

	Vigo	Pontevedra	Santiago	Coruña	Ferrol	Lugo	Ourense
Maximum	12.217	12.248	12.264	12.237	12.251	12.265	12.255
Minimum	11.518	11.519	11.571	11.639	11,576	11.600	11.615
Average	11.896	11.911	11.924	11.951	11,942	11.953	11.926
Standard deviation	0.226	0.217	0.195	0.193	0,198	0.197	0.187

Table 13. Inferior calorific value (kWh/m³) of NG samples, 2016_Galicia

	Vigo	Pontevedra	Santiago	Coruña	Ferrol	Lugo	Ourense
Maximum	11.023	11.051	11.066	11.041	11.054	11.066	11.058
Minimum	10.369	10.370	10.419	10.482	10.423	10.446	10.459
Average	10.722	10.737	10.750	10.774	10.765	10.775	10.751
Standard deviation	0.211	0.203	0.182	0.180	0.184	0.184	0.174

Table 14. Compressibility factor of NG samples, 2016_Galicia

	Vigo	Pontevedra	Santiago	Coruña	Ferrol	Lugo	Ourense
Maximum	0.9973	0.9973	0.9973	0.9973	0.9973	0.9973	0.9973
Minimum	0.9969	0.9969	0.9968	0.9969	0.9969	0.9968	0.9968
Average	0.9971	0.9971	0.9971	0.9971	0.9971	0.9971	0.9971
Standard deviation	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001	0.0001

Despite the variations noted in composition, the figures calculated for the superior and inferior calorific values of the samples remained practically constant throughout the period.

3.6 Compressibility Factor

The compressibility factor is a parameter of considerable relevance, since it establishes the relation between the molar volume of a real gas and the molar volume of the same gas considered as ideal. It takes into account the fact that natural gas is not an ideal gas. It is needed for calculating the factor that allows the conversion of the units of measurement of gas-meters from m^3 to Nm^3 , and the subsequent further conversion to the unit of measurement used in tariffs, kWh.

Consideration of the previous figures shows that this parameter had an average value of 0.9971, with an average standard deviation of 0.001; the maximum being 0.9973 and the minimum 0.9968, Table 14. When the standard deviation of the month-on-month values by city of collection is studied, a practically constant figure is to be seen. The standard deviation calculated for the year-long state of affairs was likewise not significant.

4. CONCLUSIONS

Within the European Union all operators of the gas infrastructure publish the parameters of gas quality necessary to grant access to their systems [7]. The Spanish regulations establishing the detailed protocols for technical management of the Gas System have a section on quality specifications for natural gas at entry points to the system. This sets limits for only three of the physical properties of natural gas among those that can be calculated from the values determined from its composition. These are: Wobbe Index, superior calorific value and relative density [15,18].

The variation in the composition of natural gas can lead to an increase in pollutant emissions and a loss of combustion efficiency among other problems; to avoid them, it is necessary to maintain without great variations the composition of the gas in the network and thus ensure stable values for the properties linked to it. The values obtained for these parameters from the eighty-four samples studied showed that the quality of the natural gas distributed in Galicia_Spain in 2011 remained steadily within the acceptable

limits throughout the whole year. The values for standard deviations that emerge bore witness to the fact that any variations occurring did not significantly alter the quality of the natural gas supplied. The data reflect good control over the quality of the natural gas supplied through the network in the area and time of study.

The concentrations of the odorant THT were always above the recommended figure of $18.0 \text{ mg}/Nm^3$, although the fluctuations noted over the course of the year were such as to make it possible to see them as excessive. In some instances, a high concentration of odorant may lead users to erroneous impressions, rather than what in fact is the case, so that they come to think that there are leaks from the gas-pipes or even that the gas is not burning properly.

World experience shows that important factor in the calculations for natural gas consumption between suppliers and consumers is not only the volume of natural gas, but the quality indicators. With gas market liberalization, gas properties are expected to vary more frequently and strongly. Quality of natural gas is currently a topical issue, considering the steady increase of gas consumption in the world in recent decades. Existent chromatographs and calorimeters are very accurate in gas quality determination, but general expenditure and maintenance costs are still considerable. Market demands alternative lower cost methods of natural gas quality determination for transparent energy billing and technological process control. [20].

In the last years, new methods are being proposed for measuring natural gas calorific value based on multi-parameter approximation of calorific value as a function of sound speed in natural gas, nitrogen and carbon dioxide concentration at standard temperature and pressure using artificial neural network [20,21,22].

Natural gas is emerging as the ideal fuel to increase its participation in the global energy balance, it is a fossil fuel that has been displacing petroleum derivatives until it represents an energy source of generalized use, both in a gaseous state and in a of liquefied gas. Saving policies, the rationalization of energy consumption and the international will to reduce atmospheric pollution are favoring the search for new technologies that will make it possible to extend their use.

One of the main lines of work, facing the future, is the use of natural gas as a fuel in the transport sector where its physicochemical properties make it an excellent fuel, due to its low level of air pollution and low impact acoustic of the motors. Around the world, more than one million vehicles powered by compressed natural gas are already circulating, producing up to 50% less CO₂ emissions and 80% less nitrogen oxides (NO_x) than gasoline or diesel powered vehicles, and do not emit lead, sulfur or aromatic compounds. The automotive fleet supplied with natural gas is expected to reach 50 million in 2020 [17].

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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