Determination of hydrogen content, gross heat of combustion, and net heat of combustion of diesel fuel using FTIR spectroscopy and multivariate calibration

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ABSTRACT

The precise determination of the heat of combustion is of great importance for trading automotive diesel. The net heat of combustion (NHC) of fuel is related to the hydrogen elemental composition of fuel as obtained by elemental analysis. Heat of combustion expressed as gross heat of combustion (GHC) and net heat of combustion (NHC) have been predicted from data obtained by proximate analysis (density, ash, water and sulphur content) (ASTM D4868). GHC was obtained using bomb calorimetry (ASTM D240). The results of ASTM D4868 and ASTM D240 were found in good agreement. GHC and NHC fall within the relatively narrow range 45.24–46.08 and 41.91–43.27 MJ/kg, respectively. GHCs of tested diesel samples are, on average, about 7% greater than NHCs. The present paper also present a simple analytical method for determination of hydrogen content, GHC, and NHC of automotive diesel fuel using FTIR spectroscopy and partial-least squares calibration (PLS-1). PLS-1 had a high prediction power for prediction of hydrogen from FTIR spectra of diesel samples. The spectral ranges used in calibration were 400–670 and 2846–2970 cm^{-1}. On the other hand, classical least squares calibration (CLS) was found invalid for determination of hydrogen content in diesel. The results obtained by the proposed analytical method were almost to those obtained by ASTM D4868 and ASTM D240. PLS-1 method, offers a simple and reliable analytical method for quantification of hydrogen content in diesel samples without running expensive analysis like those carried out using carbon, hydrogen, and nitrogen (CHN) instruments.

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1. Introduction

Petroleum diesel fuel is derived from crude oil by fractional distillation at temperature range 170–350 °C at normal pressure. Diesel fuel is a very complex mixture of thousands of individual compounds with carbon numbers between 9 and 23 (number of carbon atoms per hydrocarbon molecule). Most of these compounds are members of the paraffinic, naphthenic or aromatic class of hydrocarbons. These three classes have different chemical and physical properties. The different relative proportions of the three classes are one of the factors that make one diesel fuel different from another. It influences fuel properties and affects its performance.

Fuels are evaluated, in part, based on the amount of energy or heat that they release per unit mass or per mole during combustion of the fuel. Such a quantity is known as the fuel's heat of combustion or heating value. The heat of combustion of a substance is the heat evolved when that substance is converted to its final oxidation products by means of molecular oxygen [1].

The heat of combustion of diesel is an important parameter for the planning and the control of generators using this type of fuel. The so-called gross heat of combustion (GHC) or 'higher heating value', also called gross calorific value, is the enthalpy of complete combustion of a fuel with, for instance, all carbon converted to CO_2, and all hydrogen converted to H_2O.

The fuel can be either liquid or solid, and contain only the elements carbon, hydrogen, nitrogen, and sulphur. The products of combustion, in oxygen, are gaseous carbon dioxide, nitrogen oxides, sulphur dioxide, and liquid or gaseous water. There exists two different values of specific heat energy for the same batch of fuel. One is the high (or gross) heat of combustion (GHC) is given for standard conditions (1 atm, 25 °C) and the other is the low (or net) heat of combustion (NHC). GHC is the quantity of energy released when a unit mass of fuel is burned in a constant volume enclosure, with the products being gaseous, other than water that is condensed to the liquid state. NHC is the quantity of energy released when a unit mass of fuel is burned in a constant pressure, with all of the products, including water, being gaseous. GHC is measured in a bomb calorimeter for fuels. The difference between the GHC and NHC values is significant, about 8% or 9%. While in the USA GHC is generally used, NHC is more common in European

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countries [2]. Because engines exhaust water as a gas, the NHC is the appropriate value to use for comparing fuels.

The NHC value of diesel corresponds to a heating value in which the water remains a vapour and does not yield its heat of vaporisation. Thus the energy difference between the two values is due to the heat of vaporisation of water, and

$$GHC = NHC + (m_{water}/m_{diesel})h_v \qquad (1)$$

where m_{water} is the mass of liquid water in the combustion products, and h_v is the latent heat of vaporisation of water (40.8 kJ/mol).

The precise determination of the heat of combustion is of great importance for trading automotive diesel due to the fact that the heat of combustion is the most important parameter for determining the price of the automotive diesel to be paid the supplier by the user of the diesel fuel. Numerous empirical equations have been published to relate the NHC of fuel to the hydrogen elemental composition of fuel as obtained by elemental analysis (ASTM D240) (ASTM stands for American Standard for Testing and Material) [3]. Heat of combustion values have also been predicted from data obtained by proximate analysis (density, ash, water and sulphur content) (ASTM D4868) [4].

Recently, multivariate calibration has been applied for analysing many chemical systems including wastewater, foods, drugs formulations, and fuels without the need for separation of solutes prior their analysis as the case in chromatographic analyses [5–7]. Multivariate calibration is an effective calibration method in which the chemical information (absorption, emission, electrical etc.) of a set of standard mixtures recorded at different variables (wavelengths) are related to the concentration of the chemical compounds present in the mixtures [5]. The popular calibration way used in chemical analysis is the univariate calibration in which the chemical information of a set of solution recorded at one variable (i.e., wavelength) is related to the solute concentration in the solution. The most applied chemometric methods are Classical Least Squares (CLS), Inverse Least Squares (ILS), Principal Component Regression (PCR), Partial-Least Squares (PLS) and Net-Analyte Signal (NAS) [8]. In this work, the possible application of CLS, PCR and PLS-1 for determination hydrogen content in diesel samples will be investigated. The content of hydrogen in the samples was previously quantified with the aid of carbon, hydrogen, and nitrogen (CHN) analyser.

Therefore, the aim of this work was to determine GHC and NHC using bomb calorimetry (ASTM D240) and from data obtained by proximate analyses (density, ash, water and sulphur content) (ASTM D4868), respectively. The present paper also outlines a simple analytical method for determination of hydrogen content, GHC, and NHC of automotive diesel fuel using FTIR spectroscopy and PLS-1. Determination of hydrogen content in diesel fuels by FTIR/PLS-1 has never been discussed.

2. Experimental

2.1. Collection of diesel samples

Jordanian diesel samples were collected from different service stations in the Amman, Jordan area over a 2-week period and stored in brown glass bottles in the refrigerator at 3 °C. To ensure reproducibility of the analysis, the samples were analysed in duplicate over a 2-day period. Also important to note is that the composition of the diesel will depend not only on the Jordanian refinery, but also on the residual level in the tank when filled. Therefore, each diesel sample is chemically unique because of the inherent differences in the tank levels when filled. The unique chemical composition is useful in comparisons, as two samples that are statistically similar are more likely to originate from the same source.

2.2. Heat of combustion

2.2.1. Calibration

Prior to sample testing with the oxygen bomb calorimeter, the thermal mass of the system had to be defined. The bomb calorimeter was calibrated using the method described below by combusting a known mass, m, of standard benzoic acid which has a known heat of combustion of 26.453 kJ/g. Ten benzoic acid samples of size around one gram were tested. The calibration factor for the bomb calorimeter, C, was calculated from the benzoic acid calibrations as

$$C = \frac{(m \times 26.453 \text{ kJ/g})}{(T_{max} - T_0)} = 10.13 \pm 0.13 \text{ kJ/K}(n = 10) \qquad (2)$$

2.2.2. Instrumentation

An oxygen bomb calorimeter (IKA Calorimeter system C2000, Petrotest Instruments GmbH, Germany) was used to obtain the GHC of the automotive diesel. The Petrotest is a static and manual calorimeter with temperature resolution of 0.002 °C, capable of oxygen charging pressures up to 40 atm, and can liberate up to a maximum 33,400 J per charge. The fuel samples were placed directly in a stainless steel capsule (2.5 cm of diameter and 1 cm of deep) and burned with oxygen at a pressure of 3.0 MPa according to ASTM D240 [3].

Approximately 1 g of sample is placed inside a sample cup in a pressure vessel (oxygen bomb) which is in contact with an ignition wire conNHCted to two electrodes. The bomb is then sealed, purged, and pressurised up to 40 atm with pure oxygen. The sealed bomb is then placed inside a 2-L water bath which is inside an adiabatic container. Upon thermal equilibration of the system at ambient temperature, the sample is ignited and completely combusted. The GHC (kJ/g) of the sample at room temperature is calculated from the temperature rise of the water bath ΔT ($\Delta T = T_{max} - T_o$) (K), which is typically a few degrees Kelvin, the calibration factor C (J/°K), and the mass of the sample m (g) according to

$$GHC = (C\Delta T - e_1 - e_2)/m \qquad (3)$$

where e_1 and e_2 are the correction factors for the heat of combustion of the ignition wire and the heat of formation of acids, respectively, in units of kJ.

There are no direct methods for measuring the NHC – which is the GHC minus the latent heat of vaporisation of the water produced during the reaction. The NHC is relevant to flaming combustion where water is in the gaseous state at flame temperatures of ≈1000 K. As a result, the latent heat of water at 298 K is subtracted from the GHC because this amount of heat is required to maintain the combustion product water in the gaseous state.

2.3. Chemical analyses of the diesel samples

2.3.1. CHN analysis

The contents of carbon (C), hydrogen (H), and nitrogen (N) in diesel samples have been measured by standard methods of elemental analysis using a "EuroVector (EA3000, Italy)". The content of oxygen has been calculated as the difference between 100 and the sum of the other constituents. About 1 mg of sample was incinerated at 1000 °C in oxygen atmosphere in a tube furnace and the final reaction products CO_2, H_2O, and N_2 quantitatively determined by gas chromatography using a thermal conduction detector. Typical analysis errors for diesel samples are in the range of ±0.3 wt.%.

2.3.2. Ash content – ASTM D482

About 1 g of sample contained in a suitable vessel was ignited and allowed to burn until only ash and carbon remain. The

carbonaceous residue is reduced to an ash by heating in a muffle furnace (K 1252, Heraeus) at 775 °C until constant weight of the sample was reached, cooled and weighed. This procedure was carried out according to ASTM D482 [9]. Typical analysis errors for diesel samples are less than 2%.

2.3.3. Water content – ASTM D6304

An aliquot of the sample (20–50 μL) is injected into the titration vessel of a coulometric Karl Fischer apparatus (Metrohm 652 KF-Coulometer, Sweden) in which iodine for the Karl Fisher reaction is generated coulometrically at the anode. When all of the water has been titrated, excess iodine is detected by an electrometric end point detector and the titration is terminated. Based on the stoichiometry of the reaction, 1 mol of iodine reacts with 1 mol of water; thus, the quantity of water is proportional to the total integrated current according to Faraday's Law. This procedure was carried out according to ASTM D6304 [10].

2.3.4. Sulphur content, S – ASTM D4294

The sample is placed in the X-ray beam and the peak intensity of the sulphur Kα line is measured (sulphur-in-oil analyser SLFA-2100, HORIBA). The resultant net counting rate is the compared to previously prepared calibration curve or equation to obtain the concentration of sulphur in wt.%. This procedure was carried out according to ASTM D4294 [11]. This test method provides rapid and precise measurement of total sulphur in petroleum and petroleum products with a minimum of sample preparation. A typical analysis time is 1–2 min per sample.

2.3.5. Density – ASTM D1298

The sample is brought to 15 °C and test portion is transferred to a hydrometer cylinder that has been brought to approximately the same temperature. The appropriate hydrometer (No. 2 (0.76–082) and No. 3 (0.82–0.88)), also at the similar temperature, is lowered into the test portion and allowed to settle. After temperature equilibrium has been reached, the hydrometer scale is read, and the temperature of the test portion is taken. This procedure was carried out according to ASTM D1298 [12].

2.4. Instrumentation and software

Analytical spectra were taken using a Shimadzu IR Prestige-21/FTIR-8400S with a resolution of 4 cm^{-1} at 64 scans. The data interval provided by the instrument for a resolution of 4 cm^{-1} is 1 cm^{-1}. A small quantity (~2 μL) of the sample was deposited with the use of a Pasteur pipette between two well-polished KBr disks, creating a thin film. Duplicate spectra were collected for the same sample. All spectra were recorded from 4000 to 400 cm^{-1} and the spectra were collected using a Shimadzu IR Prestige-21 Windows Software. These tests were conducted at the laboratories of The Royal Scientific Society (RSS), Amman, Jordan. Then, the digitised absorbance values were transferred to a Pentium(IV) personal computer for subsequent analysis. The data treatment and the multivariate calculations were carried out using MATLAB (version 7.0). The algorithms used for CLS, PCR and PLS-1 were outlined in the literature [5,6].

2.5. Multivariate calibration methodology

Eight diesel samples were used in the chemometric study. Five samples use as calibration set while the remaining three samples were kept for validation. In the calibration phase, the FTIR absorbances of calibration samples which recorded at wavenumbers from 400 to 4000 cm^{-1} were collected in absorption matrix **A**. The corresponding hydrogen content which obtained using CHN analyser (in wt.%) of the calibration samples were collected in **c**

vector. After selecting the optimum wavenumbers for calibration, multivariate analysis by CLS, PCR, and PLS-1 was carried out to build a linear relation between **A** and **c**. The validation of the multivariate calibration methods was further tested by analysing hydrogen content in three diesel samples not considered in calibration stage. Referring to Table 1, samples 1–5 were used for building calibration models and samples 6–8 were used for validation.

3. Results and discussion

Heat of combustion can be estimated by calculation from selected properties or measured using bomb calorimetry. The methods typically used for diesel fuel are discussed below.

1. ASTM D4868 [4], standard test method for estimation of GHC and NHC of burner and diesel fuels. This test method covers the estimation of the GHC and NHC of petroleum fuel. The calculations use the fuel density, sulphur, water, and ash content. The equations for estimating GHC and NHC are:

$$GHC = (51.916 - 8.792d^2 \times 10^{-6})[1 - (x + y + s)] + 9.420s \qquad (4)$$

where GHC is the gross heat of combustion at constant volume, MJ/kg, d is the density at 15 °C, kg/m^3, x is the weight fraction of water (% divided by 100), y is the weight fraction of ash (% divided by 100), and s is the weight fraction of sulphur (% divided by 100).

Calculation the NHC of the diesel samples corrected for the sulphur, water, and ash contents was performed in accordance with following equation:

$$NHC = (46.423 - 8.792d^2 \times 10^{-6} + 3.170d \times 10^{-3})[1 - (x + y + s)] \\ + 9.420s - 2.449x \qquad (5)$$

This test method is purely empirical. It is applicable only to liquid hydrocarbon fuels derived by normal refining processes from conventional crude oil. According to the estimation of a hydrocarbon fuel from its density, sulphur, water, and ash contents is justifiable only when the fuel belongs to well-defined classes for which a relationship between these quantities have been derived from accurate experimental measurements on representative samples of theses classes [4].

2. ASTM D240 [3], standard test method for heat of combustion of liquid hydrocarbon fuels by bomb calorimeter. This test method covers the determination of the heat of combustion of liquid hydrocarbon fuels ranging in volatility from that of light distillates to that of residual fuels. Under normal conditions, this test method is directly applicable to such fuels as gasoline, kerosene, fuel oil, and diesel fuel.

In this test method the NHC is represented by the following equation:

$$NHC = GEC - 0.2122 \times H \qquad (6)$$

where H is the elemental hydrogen content in the sample, wt.%

The results of analysing the elemental compositions (C, H, N, S and O contents) together with the GHC and calculated NHC of the diesel samples are shown in Table 1.

The GHC and NHC fall within the relatively narrow range 45.24–46.08 and 41.91–43.27 MJ/kg, respectively. The NHC of the diesel fuel is, on average, about 7% greater than the NHC.

The last column of Table 1 are the NHC of the diesel fuels calculated with Eq. (6) from hydrogen content for each diesel fuel sample. It is seen that the NHC decreases with increasing the hydrogen content of the diesel fuel.

Table 1
Elemental compositions, GHC and calculated NHC of the diesel samples.

Sample no.	Elemental composition (wt.%)					Heat of Combustion(MJ/kg)	
	C[a]	H[a]	N[a]	O[c]	S[b]	GHC[d]	Calculated NHC[e] (NEC = GEC−0.2122 ×H)
1	81.97	14.75	0.17	2.10	1.0079	45.57	42.44
2	79.54	15.68	0.16	3.70	0.9174	45.24	41.91
3	79.29	15.04	0.16	4.59	0.9249	45.77	42.58
4	81.72	14.49	0.16	2.63	0.9997	45.63	42.56
5	78.87	13.75	0.13	6.42	0.8274	45.81	42.89
6	84.48	15.26	0.18	0.0	1.0757	45.59	42.35
7	80.14	14.01	0.12	5.06	0.6700	45.89	42.92
8	72.27	13.23	0.15	13.85	0.5013	46.08	43.27

[a] Determined by using CHN analyser, S.D. $\leqslant$ 0.003.
[b] Determined by using sulphur analyser, S.D. $\leqslant$ 0.0001.
[c] Determined by subtraction, O%wt. = 100−(C% + H% + N% + O%), S.D. $\leqslant$ 0.003.
[d] Determined by ASTM D240.
[e] Calculated based on the hydrogen content.

3.1. Development of a correlation

The development of a correlation appeared very simple in view of a number of correlations is developed from the plot of NHC vs. H using the results presented in Table 1. A plot of the NHC in MJ/kg against the corresponding hydrogen values is presented in Fig. 1. To start with, it will be seen that a simple linear relation of the type $y = mx + c$ can be confidently drawn (Fig. 1), this being almost perfectly linear with little or no significant scatter. In fact, the correlation coefficient (r^2) between NHC and hydrogen has been found to be 0.9191. Thus, the equation could be written as:

$$NHC = 49.586 - 0.4798H (r^2 = 0.9191) \qquad (7)$$

No relation has been observed between GHC or NHC and carbon, nitrogen, or sulphur content in diesel fuel. A plot of the GHC in MJ/kg against the corresponding NHC is presented in Fig. 2. The correlation coefficient (r^2) between GHC and NHC has been found to be 0.9601. Thus, the equation could be written as:

$$NHC = 1.6032GHC - 30.645 (r^2 = 0.9601) \qquad (8)$$

Eq. (8) might be used as an equation in order to calculate the value of NHC of Jordanian diesel fuel.

3.2. Comparative precision

ASTM D4868 [4] estimates the GHC and NHC of automotive diesel fuel from its density, sulphur, water and ash contents. This test method is intended for use in cases where an experimental determination of heat of combustion is not available and cannot be made conveniently, and where an estimate is consider satisfactory. Heating value per volume is directly proportional to density when other fuel properties are unchanged. Each degree increase in American Petroleum Industry (API) gravity (0.0054 specific gravity decreases) equates to approximately two percent decrease in fuel energy content [14].

ASTM International specifications limit how much the heating value of a particular fuel can be increased. Increasing density involves changing the fuel's chemistry – by increasing aromatics content – or changing its distillation profile by raising the initial boiling point, end point, or both. Increasing aromatics is limited by the cetane number requirement (aromatics have lower cetane numbers), and changing the distillation profile is limited by the 90% distillation temperature requirement.

Based on the results of the chemical analyses performed, the GHC and NHC of the samples were calculated. The equations used for this calculation are mentioned above (Section 3). Table 2 shows the values of density, sulphur, waster and ash contents of the diesel samples. The estimated values of GHC and NHC of the samples are also shown in the table. When the results from ASTM D4868 [4]
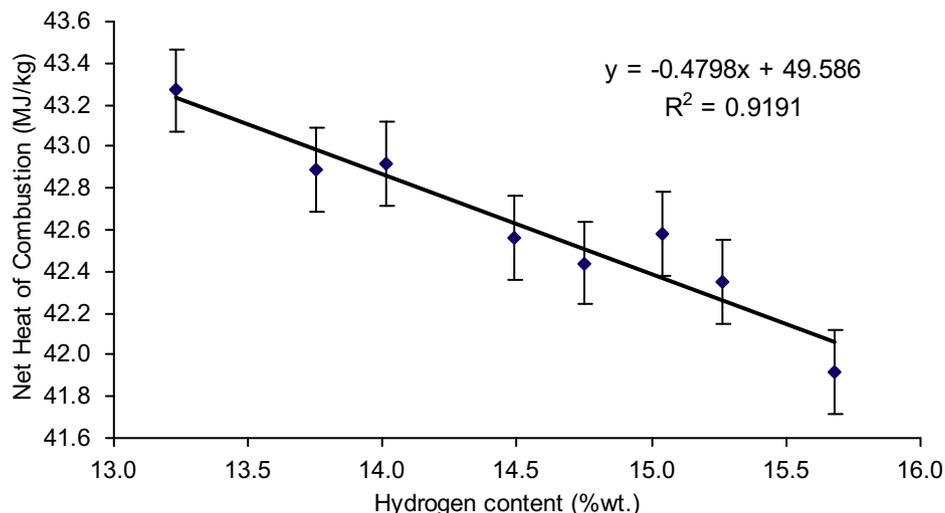

Fig. 1. Relationship between hydrogen content of the samples and their NHC values.
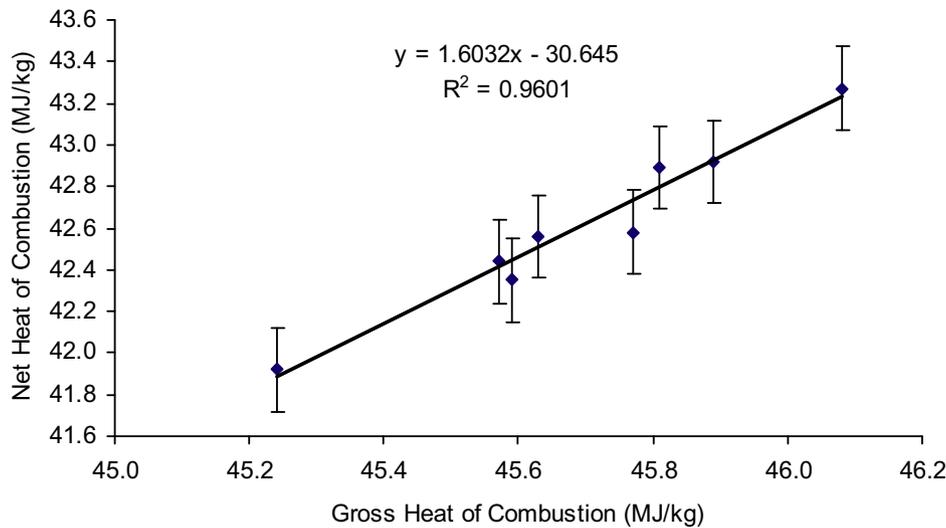
Fig. 2. Relationship between GHC and NHC.

Table 2
The values of density, sulphur, water, ash contents, GHC, and NEC of the diesel samples. Results are averaged of five determinations.

Sample no.	Density (kg/m³)[a]	Ash content (wt.%)[b]	Water content (wt.%)[c]	Sulphur content (wt.%)[d]	GHC (MJ/kg)[e]	NHC (MJ/kg)[e]
1	833.7	0.019	0.0088	1.0078	[*]45.43(0.51)	42.60(0.52)
2	834.9	0.022	0.0142	0.9174	45.44(0.62)	42.62(0.25)
3	832.9	0.038	0.01000	0.9249	45.46(0.36)	42.63(0.21)
4	820.6	0.015	0.0106	0.6700	45.74(0.28)	42.87(0.36)
5	807.7	0.012	0.0168	0.5013	45.98(0.36)	43.07(0.55)
6	832.7	0.022	0.0072	0.9997	45.44(0.92)	42.62(0.62)
7	828.2	0.032	0.0107	0.8274	45.56(0.83)	42.72(0.74)
8	840.3	0.019	0.0099	1.0757	45.30(0.72)	42.51(0.93)

[*] Average (S.D.), $n = 5$.
[a] At 15 °C (ASTM D1298). S.D. $\leqslant 0.5$.
[b] ASTM D482. S.D. $\leqslant 0.0002$.
[c] ASTM D6304. S.D. $\leqslant 0.0001$.
[d] ASTM D4294. S.D. $\leqslant 0.0001$.
[e] ASTM D4868.

and ASTM D240 [3] are evaluated separately, the results are both in good agreement. The difference between the averages of both methods is small and not significant. The GHC and NHC values predicted from Eqs. (4) and (5) have seldom been found to deviate from the experimental values (Table 2) by more than 0.7%. To decide whether the results of the two methods are comparable or not, t- and f-tests should be carried out. The statistical results were summarised in Table 3.

It is evident from the t-test that there is no significant difference between two methods in GHC and NHC determination. The f-test results also confirm that the two methods are of comparable precision.

As seen from above discussion, the precise determination of hydrogen content in diesel samples is of importance in determination of NHC. The following subsections will describe an effective approach to asses the efficiency of the employed multivariate calibration for prediction of hydrogen content in diesel fuel without the need of using CHN analyser.

3.3. Determination of the correlation matrix

It is important to investigate if there is any correlation between the studied variables (S, O, N, H, and C wt.%) and GHC or NHC. As mentioned earlier, a high correlation between hydrogen content

Table 3
Comparative determination of GHC and NHC by ASTM D4868 and ASTM D240 methods. Results are average of five determinations, t (0.05, 8) = 2.31, f (0.05, 4, 4) = 9.605.

Sample	GHC (MJ/kg)				NHC (MJ/kg)			
	ASTM D4868	ASTM D240	t-test	f-test	ASTM D4868	ASTM D240	t-test	f-test
1	45.43(0.51)[*]	45.57(0.63)	1.66	1.53	42.60(0.52)	42.44(0.81)	2.00	2.43
2	45.44(0.62)	45.24(0.71)	2.18	1.31	42.62(0.25)	41.91(0.75)	1.63	9.00
3	45.46(0.36)	45.77(0.82)	1.52	5.19	42.63(0.21)	42.58(0.98)	2.36	21.78
4	45.74(0.28)	45.89(0.16)	0.82	3.06	42.87(0.36)	42.92(0.82)	2.09	5.19
5	45.98(0.36)	46.08(0.22)	2.01	2.68	43.07(0.55)	43.27(0.63)	1.63	1.31
6	45.44(0.92)	45.63(0.46)	1.45	4.00	42.62(0.62)	42.56(0.15)	2.26	17.08
7	45.56(0.83)	45.81(0.55)	0.96	2.28	42.72(0.74)	42.89(0.42)	0.82	3.10
8	45.30(0.72)	45.59(0.24)	1.10	9.00	42.51(0.93)	42.35(0.69)	1.77	1.81

[*] Average (S.D.), $n = 5$.

and NHC is expected in fuel samples. Table 4 shows the correlation values between fuel components and corresponding heat of combustions. Table indicated that NHC–GHC, NHC-H%, and C%–O% variables have distinguished correlations (>0.95). The effect of sulphur, nitrogen, and oxygen contents in the diesel samples has been taken into account in estimating the hydrogen content in the samples. This effect is observed in Table 4.

The correlation between C% and O% was not studied because it is not related to GHC and NHC. In fact, equations revealed that both GHC and NHC can be both accurately estimated if hydrogen content of the samples is known. As will be shown next, hydrogen content can be determined using FTIR spectroscopy coupled with PLS-1 calibration without the need for using expensive instruments like CHN analysers.

Table 4
Correlation matrix between the variables estimated for diesel samples.

	GHC	NHC	S	O	N	H	C
GHC	1.00						
NHC	0.97	1.00					
S	0.75	0.78	1.00				
O	0.68	0.76	0.92	1.00			
N	0.58	0.59	0.68	0.47	1.00		
H	0.87	0.96	0.79	0.78	0.64	1.00	
C	0.57	0.64	0.89	0.98	0.41	0.66	1.00

3.4. Spectral overlap and importance of multivariate calibration for hydrogen determination

FTIR spectroscopy is usually employed for identification of functional groups in organic compounds. FTIR spectroscopy is probably the fastest and cheapest spectroscopic technique ever used for identification purposes. Basically, it is based on measurement of well defined and sharp characteristic frequencies associated with certain functional groups.

The FTIR spectra of diesel samples are presented in Fig. 3. As indicated in Fig. 3, all samples were active in IR region and this is attributed to the hydrocarbons which contains many IR-active functional groups. The high similarity between spectra is obvious and there was no linear relationship between hydrogen contents in samples and absorbances at any of recorded wavenumbers. This will limit the application of univariate classical calibration. In this paper, a simple analytical procedure is presented to determine hydrogen content using FTIR spectroscopy and multivariate calibration. As will be shown soon, PLS-1 method has outperformed other tested calibration methods for determination of hydrogen content; therefore, a brief description of this method is presented herein.

PLS-1 is a simple and convenient calibration method for resolving mixtures, which in principle could be applied for the current system. Due to the high collinearity in matrix **A**, the simple multivariate calibration method like CLS may be invalid for determina-
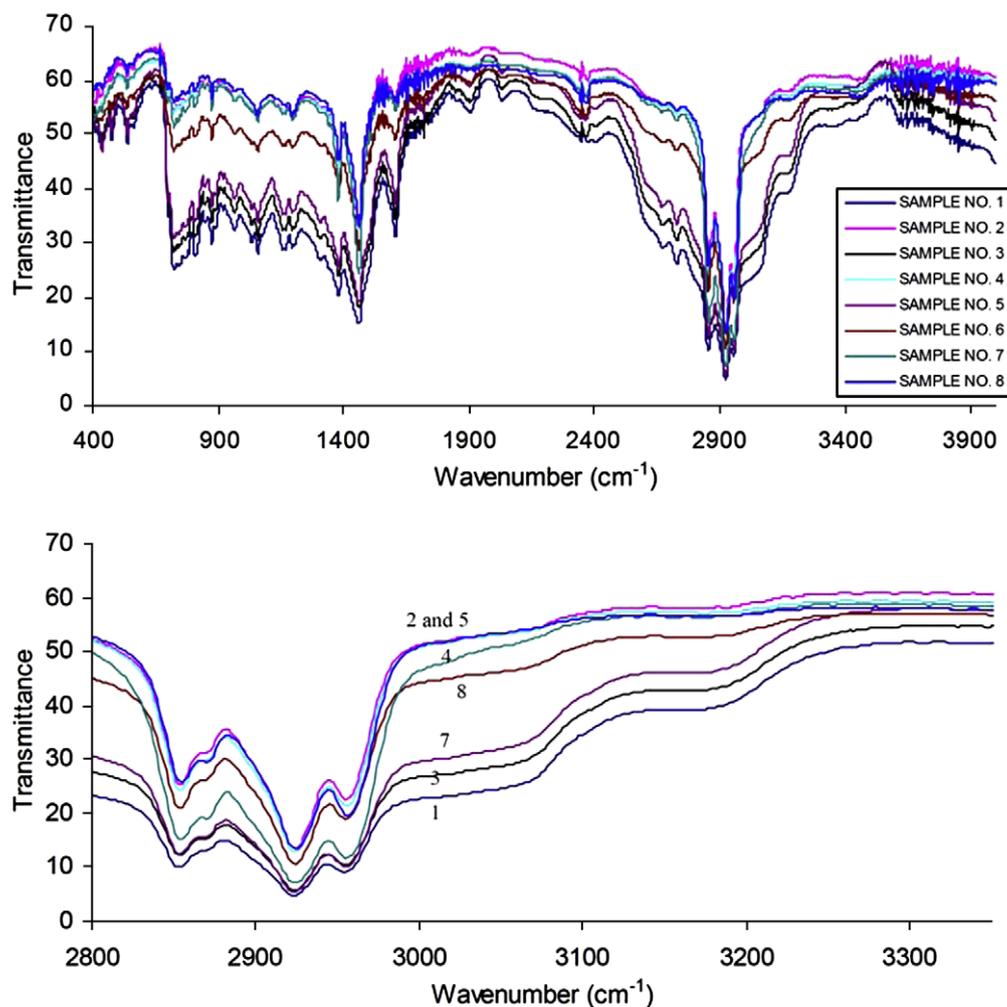

Fig. 3. FTIR spectra of the eight diesel samples depicted at different spectral regions.

tion of hydrogen content in diesel samples. Collinearity (i.e., the linear relationships between absorbance at multiple wavenumbers) is a serious drawback that may negatively affect the accuracy and precision of the calibration method. A good estimation of collinearity in a data matrix is the condition number [6], matrix of high collinearity has a high condition number and can not be involved in simple calibration methods. The condition number of matrix **A** was 1150, which reflected the high degree of collinearity and the high spectral overlap between the spectra of the diesel samples as well (See Fig. 3). In PLS-1 regression, the high collinearity in matrix **A** could be eliminated and the calibration quality could be largely improved. Simply, in PLS-1 method, matrix **A** is decomposed using the concentrations vector of diesel to be calibrated. With the aid of PLS-1 algorithm, $\mathbf{W}_{n \times h}$, $\mathbf{P}_{h \times n}$ matrixes and $\mathbf{q}_{h \times 1}$ vector were obtained. Where h represents the number of optimum PLS-1 latent variables needed to perform accurate calibration. The calibration parameters **b** and b_o were obtained as following [13]:

$$\mathbf{b} = \mathbf{W}(\mathbf{P^t W})_{\mathbf{q}} \tag{9}$$

And,

$$\mathbf{b_0} = \bar{c} - \mathbf{a^t b} \tag{10}$$

where c and **a** are average content (in wt.%) of hydrogen in the calibration mixture and the average spectrum of the calibration mixtures, respectively. t stands for matrix transpose.

To predict hydrogen content from the spectrum of unknown sample, the following equation was used:

$$\mathbf{c} = \mathbf{b}_0 + \mathbf{a}_{un}\mathbf{b} \tag{11}$$

where $\mathbf{a}_{un}$ is the measured spectrum of the unknown sample. To improve the quality of PLS-1 calibration, the absorbances and concentrations were mean-centered before running the analysis [13]. The presence of outlier(s) was also investigated in calibration and prediction sets by estimating Mahalanobis Distance [5]. The Mahalanobis Distance values for standard diesel samples (Table 1) were 1.64, 1.94, 1.42, 1.72, 2.35, 2.25, 2.58, and 2.61 for sample 1, 2, 3, 4, 5, 6, 7, and 8, respectively. The closeness of Mahalanobis Distance values indicated that no outliner is present and the samples are homogenous and all are suitable for multivariate calibration [15,16].

3.4.1. Wavelength selection for prior multivariate calibration

Most of multivariate calibration methods, in fact, are considered as full-spectrum methods because, in some instances, the entire data in a given spectrum would be included in numerical analysis. Some modern FTIR and UV–Vis spectrophotometers could generate 6000 inputs per spectrum. Including all spectral data points is not necessary to improve the quality of analysis; moreover, it has been shown for many systems that reduction of data points could improve the accuracy and precision of numerical analysis [17]. Hence, various criteria have been developed to allow for effect wavelength selection prior multivariate calibration [18]. In this work, the method proposed by Alba et al. [19] was effectively employed to select the optimum wavelength regions multivariate calibration. Simply, the correlation coefficients between hydrogen content (in calibration set) and the corresponding absorbance at each wavenumber were estimated. The correlation plot is presented in Fig. 4.

As can be noted from Fig. 4, there are two regions in which a fair correlation between hydrogen contents and wavenumbers is present. These regions are 400–670 cm^{-1} and 2840–2970 cm^{-1}. It is interesting to notice that the second region (2840–2970 cm^{-1}) containing important characteristics bands for C–H vibrations including 2960, 2950, 2925, 2915, 2870, and 2855 cm^{-1}. These bands are attributed to sp^3 CH$_3$ (asymmetric), sp^2 CH$_2$ (olefinic), sp^3 CH$_2$ (asymmetric), sp^3 CH, sp^3 CH$_3$ (symmetric), and sp^3 CH$_2$ (symmetric). The spectral region 3400–3600 cm^{-1} is totally excluded from multivariate calibration due to their negative correlation with hydrogen content.

3.4.2. Determination of hydrogen content in diesel samples using multivariate calibration

After selecting the suitable wavenumbers for calibration, CLS, PCR, and PLS-1 methods were applied. The strategy of analysis was as following: (a) obtaining the calibration parameters from calibration samples and (b) using calibration parameters for prediction of hydrogen content in both calibration and validation samples. The quality of calibration of the methods was assessed by calculating recovery values, relative standard deviation, and relative error of prediction. Relative error of prediction was obtained as [5]:

$$\mathrm{REP\%} = 100 \times \left(\frac{\sum_{i=1}^{n}(C_{i,\,\mathrm{pred}} - C_{i,\,\mathrm{act}})^2}{\sum_{i=1}^{n}(C_{i,\,\mathrm{act}})^2} \right)^{1/2} \tag{12}$$
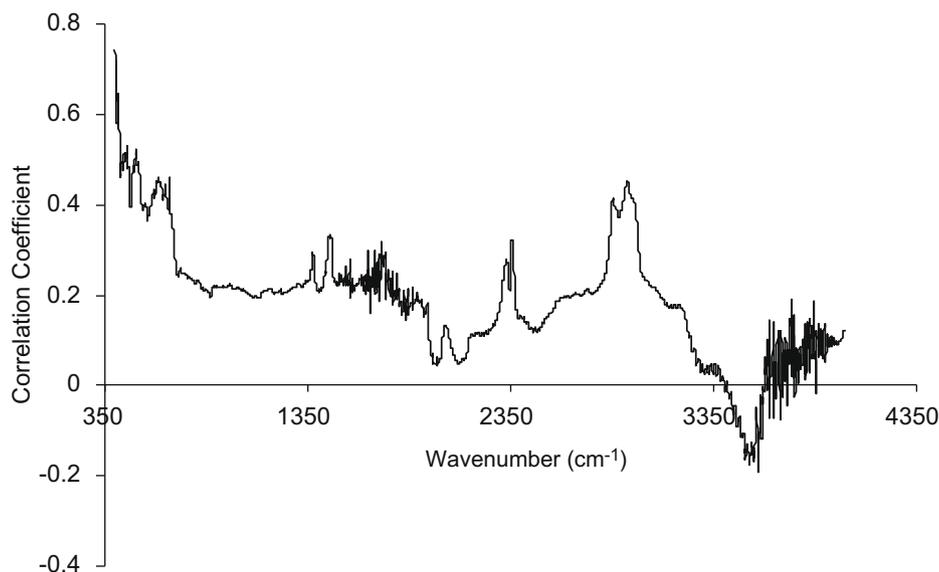

Fig. 4. Correlation coefficient – wavenumber plot.

Table 5
Assessment of calibration quality of employed methods for determination of hydrogen content.

Sample	H (wt.%)[a]	Found by CLS	Found by PCR[b]	Found by PLS-1[c]
Internal validation				
1	14.75	12.52	14.20	14.73
2	15.68	17.36	15.21	15.65
3	15.04	11.36	14.32	15.00
4	14.01	16.35	13.45	13.97
5	13.23	9.32	12.11	13.28
Recovery(R.S.D.)		91.6(20.9)	95.2(2.2)	99.9(0.4)
REP%		20	5.0	0.3
External validation				
6	14.49	11.36	14.13	14.46
7	13.75	16.82	12.32	13.77
8	15.26	21.3	14.82	15.29
Recovery(R.S.D.)		113.4(31.5)	94.7(4.4)	100.1(0.22)
REP%		29.7	6.2	4.0

[a] Determined by CHN analyser.
[b] Calibration was carried out using 6 principal components (see discussion below).
[c] Calibration was carried out using 5 latent variables (see discussion below).
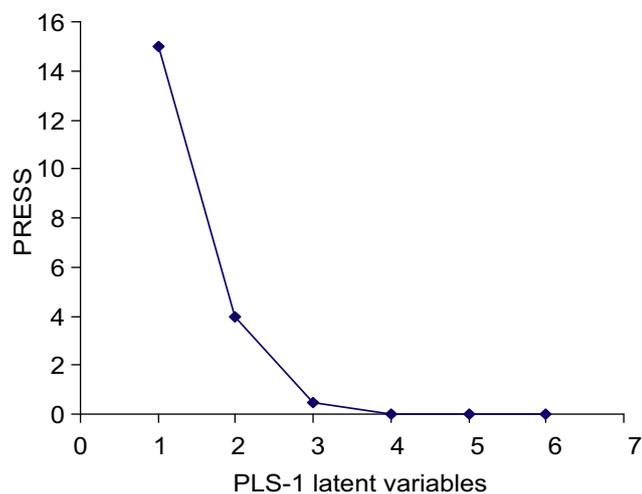

Fig. 5. A plot between numbers of latent variables vs. PRESS obtained from cross-validation technique.

where n, C_{pred}, and C_{act} are the total number of validation samples (7 in this study), predicted concentration and the actual hydrogen content, respectively. The results of internal and external validation with other statistical results were given in Table 5.

As can be noted from Table 4, PLS-1 has a high calibration capacity either for calibration set or validation set. This method accurately estimated the hydrogen content compare to the other methods. On the other hand, CLS is not recommended for analysis the current system, the internal and external relative prediction errors of this method was very high (20–30%). With an internal rel-

ative prediction error of 0.3 and external relative prediction error of 4.0, PLS-1 is the method of choice because it offers a simple and reliable analytical method for determination of hydrogen content in the diesel samples without the need for application of expensive instruments like CHN analyser.

3.4.3. Selection of the optimum number of factors (h) for PCR & PLS-1 calibration methods

The optimum number of factors (h) should be selected in order to avoid overfitting when using PCR & PLS-1 calibration methods. This can be done by applying leave-one-out cross-validation procedure as developed by Haaland and Thomas [6,7]. Simply, from a given set of m calibration samples, the PLS-1 calibration on m-1 calibration set is performed. Using this calibration, the content of hydrogen in the sample left out during the calibration is predicted. This process was repeated m times, until each sample has been left out once. The content predicted (C_{pred}) of hydrogen in each sample is then compared with the actual value (C_{act}) of this reference sample. The sum of squared prediction errors for all calibration samples, or PRESS = $\Sigma(C_{i,pred} - C_{i,act})^2$ was calculated each time a new factor (h) is added to the PLS-1 model. Usually, the optimum number of factors is obtained by computing the ratios $F = \text{PRESS}(h < h^*)/\text{PRESS}(h)$ (h^* corresponds to the minimum PRESS), and selecting the number of factors leading to a probability of less than 75% that $F > 1$ [6]. In the current system, a number of 5 factors were found optimum for determination of hydrogen content using PLS-1 calibration. Fig. 5 shows the PRESS plot obtained by optimising the calibration matrix of the absorption spectra of the samples with the PLS-1 method. On the other hand, the optimum number of principal components that used in PCR calibration was 6.

Table 6
Determination of hydrogen content, GHC, and NHC for five diesel samples obtained by ASTM D240 and the proposed FTIR/PLS-1 method. Results are average of five determinations, t (0.05, 8) = 2.31, f (0.05, 4, 4) = 9.605.

Sample	H%				GHC				NHC			
	[*]CHN analyser	FTIR/PLS-1	t-test	f-test	Eq. (8)	FTIR/PLS-1	t-test	f-test	Eq. (7)	FTIR/PLS-1	t-test	f-test
1	12.98 (0.35)	12.89 (0.52)	1.20	2.21	46.01 (0.62)	46.19 (0.63)	2.00	1.03	43.13 (0.62)	43.40 (0.65)	1.83	1.10
2	15.13 (0.53)	15.07 (1.0)	0.68	3.55	45.33 (0.55)	45.53 (0.72)	1.95	1.71	42.31 (0.84)	42.36 (0.52)	1.10	2.61
3	14.66 (0.63)	14.63 (0.85)	2.27	1.82	45.60 (0.52)	45.67 (0.82)	1.47	2.49	42.51 (0.52)	42.57 (0.28)	1.00	3.44
4	13.38 (0.51)	13.36 (0.92)	1.66	3.25	45.97 (0.25)	46.05 (0.53)	1.12	4.49	43.11 (0.68)	43.18 (0.71)	2.12	1.09
5	15.92 (0.82)	15.83 (0.36)	1.85	5.18	45.27 (0.62)	45.31 (0.66)	1.73	1.13	41.86 (0.82)	41.99 (0.44)	1.19	3.47

[*] Average (S.D.), n = 5.

3.4.4. Determination of hydrogen content, GHC, and NHC for the diesel samples not included in the calibration study

Obviously, the next step is to apply the proposed analytical method for determination of hydrogen content, GHC, and NHC of the diesel samples not included in the study. Five samples of diesel were selected from different petrol stations. The samples were kept at cooled place until analysis time. For each sample, elemental composition, GHC, and NHC were determined. PLS-1 was applied for determination of hydrogen content of the samples form their FTIR spectra and finally GHC & NHC were both estimated using Eqs. (7) and (8). Five determinations were carried out for each individual diesel sample. Table 5 illustrates the results.

As clearly indicated from Table 6, FTIR/PLS-1 method is an effective method that can estimate H%, GHC and NHC without the need for running expensive analysis like those involved in the current standard methods. The results of *t*-tests indicate that no significant difference between ASTM D240 and the proposed method for determination of H%, GHC and NHC for the five diesel samples. The *f*-test indicated that both methods are of similar precision. It is worth mentioning that the proposed method can only be applied (with care) for diesel fuels of hydrogen contents within the range 13–16 wt.%.

4. Conclusion

The heat of combustions of diesel fuel is an important value to be measured. A linear correlation was found between hydrogen content in Jordanian diesel fuel and the corresponding NHC. Both GHC and NHC were determined using ASTM D4868 and ASTM D240 standard methods. Two empirical Eqs. (7) and (8) in the text were found useful for estimating GHC and NHC if the hydrogen content is known for the fuel. A simple and accurate multivariate was developed for sake of determination of hydrogen content in diesel fuel without running expensive analysis like those carried out in CHN analyser. Five samples of diesel were analysed by FTIR/PLS-1 method, the results clearly prove that the later method is effective and can be used with a high precision. The proposed

method can only be applied to diesel fuel samples of hydrogen content from 13 to 16 wt.%.

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