Measurement 74 (2015) 56–63

Contents lists available at ScienceDirect

Measurement

journal homepage: www.elsevier.com/locate/measurement

Determination of the carbon and hydrogen contents of gasoline using a combustion method and the estimation of their measurement uncertainty

Wan-Gyu Lim [a,b,*], Sang-Sup Lee [b], Jong-Han Ha [a]

[a] Research Institute of Petroleum Technology, Kpetro, Cheongju 363-883, Republic of Korea
[b] Department of Environmental Engineering, Chungbuk National University, Cheongju 361-763, Republic of Korea

ARTICLE INFO

Article history:
Received 21 October 2014
Received in revised form 15 June 2015
Accepted 23 June 2015
Available online 4 July 2015

Keywords:
Gasoline
Carbon content
Hydrogen content
Combustion method
Uncertainty

ABSTRACT

An analytical method of determining the carbon and hydrogen contents of gasoline was studied using a combustion method. Four pure organic hydrocarbons were selected and tested as calibration standards. Three hydrocarbon reagents, n-hexane, n-heptane, and isooctane, were found to be appropriate calibration standards. Two different calibration methods – one-point and four-point – were used to calibrate the analysis instrument and both methods showed satisfactory results. The measured carbon and hydrogen values were normalized to 100% minus the oxygen content and these values were more precise than the measured ones. The present paper also presents an evaluation of the measurement uncertainty. The uncertainty estimate for the four-point calibration was larger than that for the one-point calibration. The analysis of the contributions of the uncertainty sources showed that the purity of the calibration standard and the injected volume had a large effect on the overall uncertainty. The other parameters had virtually no influence.

1. Introduction

Gasoline is a highly volatile liquid fuel which is obtained by the fractional distillation of crude oil in the temperature range of 30–105 °C at atmospheric pressure. Gasoline is a complex mixture of several hundred compounds having carbon numbers between 3 and 13 (number of carbon atoms in each molecule). Gasoline consists of combinations of carbon and hydrogen which are attached to one another in many different ways. These hydrocarbons can be classified into four groups, paraffins, olefins, naphthenes, and aromatics. Paraffins have the highest H/C ratio (hydrogen to carbon ratio) and aromatics have the lowest. Olefins have intermediate H/C ratios and naphthenes have H/C ratios between those of paraffins and olefins.

The H/C ratio of gasoline, or its relative hydrogen and carbon contents, is an important parameter for calculating the fuel economy in gasoline-powered automobiles. The fuel economy of gasoline-fueled vehicles can be calculated by the carbon balance method, which requires information on the gasoline fuel properties, particularly the carbon and hydrogen contents [1]. An empirical method is used to obtain the hydrogen content of gasoline fuel when calculating its fuel economy. The carbon content is calculated using the estimated hydrogen content. However, this empirical method is basically applicable to aviation fuels and there exists the possibility that the estimates may be greatly in error [2].

The carbon and hydrogen contents are also used for determining the CO_2 emission factors for fuel combustion. The emission factors for CO_2 reflect the carbon content of

* Corresponding author at: Research Institute of Petroleum Technology, Kpetro, Cheongju 363-883, Republic of Korea. Tel.: +82 432407914; fax: +82 432407998.
E-mail address: wklim@kpetro.or.kr (W.-G. Lim).

http://dx.doi.org/10.1016/j.measurement.2015.06.020
0263-2241/

the fuel and are in units of kg CO_2/TJ on a net calorific value basis [3,4]. The net calorific value is obtained from the gross calorific value by correcting it using the hydrogen content of the fuel [5]. The CO_2 emission factors of a fuel are determined by measuring its carbon content, but no specific measurement method has been established for gasoline fuel. ASTM D4808, which utilizes nuclear magnetic resonance spectroscopy [6], and ASTM D1018, which uses a wick lamp [7], can be used to measure the hydrogen content of gasoline fuel, but there is no standard method to measure carbon content of gasoline fuel.

The combustion method is widely used to determine the carbon, hydrogen, and nitrogen contents in organic and inorganic materials [8–11]. In this method, a portion of the sample is weighed and combusted in a combustion tube to convert the carbon to carbon dioxide and hydrogen to water vapor. The subsequent, quantitative determination of these gases is performed by appropriate methods, such as by using thermal conductivity detectors and infrared detectors. ASTM D5291 is the most widely used method for determining carbon and hydrogen in petroleum products but it is not recommended for the analysis of volatile materials such as gasoline, gasoline-oxygenate blends, or gasoline type aviation turbine fuels [12]. This is because the procedure includes weighing a portion of the sample in a metallic capsule, but it is very difficult to weight a portion of volatile samples, due to their evaporation. Therefore, there needs to be a way to extend the application of combustion method to volatile materials such as gasoline fuel.

Recently, the uncertainty in calibration and measurements has been applied in many areas including pharmaceutical analysis, food chemistry, air quality measurements, and chemical measurements [13–16]. It is an effective method of demonstrating the quality of the analysis results by indicating the extent to which the result can be relied on for the purpose in hand. General rules for evaluating and expressing uncertainty in measurements were formally established in the ISO Guide [17]. The EURACHEM document shows how the concepts in the ISO Guide are applied in chemical measurements [18].

In this work, an analysis technique for the carbon and hydrogen contents of gasoline was studied using a combustion method. A glass syringe was used for transferring the test specimen into the instrument in place of a metallic capsule. The one-point (1P) and four-point (4P) calibration methods with four different short-chain hydrocarbon reagents were used to calibrate the instrument. The measurement uncertainty was estimated to assess the reliability of the finally obtained results. The combined uncertainty, which accounts for all of the uncertainty sources, was used for this purpose. The uncertainty budgets were also estimated to analyze the contributions of the uncertainty components to the overall uncertainty.

2. Materials and methods

2.1. Materials

Six gasoline samples were obtained from three different oil refineries in Korea. Each refinery offered two gasoline samples; one is regular gasoline with a research octane number (RON) between 91 and 93 and the other is premium gasoline with a RON of more than 100. The premium gasoline had a higher density than the regular gasoline. The properties of the gasoline samples are given in Table 1.

2.2. Chemical analysis of the gasoline samples

The composition of gasoline was analyzed by the gas chromatographic method using an AC Reformulyzer (AC Analytical Controls, USA) according to ASTM D6839 [19]. The contents of paraffins, olefins, naphthenes, aromatics, and oxygenates in the gasoline were determined. The oxygen content was calculated from the oxygenate content. The quantity of methyl-*tert*-butylether (MTBE) was measured in this work, because it was the only oxygen-containing compound in the gasoline samples. The nitrogen content was measured by the chemiluminescence method using a TN-110 total nitrogen analyzer (Mitsubishi chemical, Japan) according to ASTM D4629 [20]. The determination of the sulfur content was done by the ultraviolet fluorescence method using a TS-100V trace sulfur analyzer (Mitsubishi chemical, Japan) in accordance with ASTM D5453 [21].

2.3. Carbon and hydrogen analysis

A Flash 2000 organic elemental analyzer (Thermo Fisher Scientific, Italy) was used for all analyses. The elemental analyzer was equipped with an inlet for syringe injection, a catalyst based reactor (operated at 900 °C), a multi-separation column (operated at 70 °C), and a thermal conductivity detector (operated at 70 °C). The reactor was prepared with a 45 cm × 18 mm (OD) × 14 mm (ID) quartz tube filled with silvered cobaltous cobaltic oxide, reduced copper, and chromium oxide. A 2 m × 6 mm (OD) × 5 mm (ID) multi-separation column was used for the separation of the products generated during the combustion process. High purity grade helium and oxygen with a purity of 99.999% (V/V) were used as the carrier gas and oxidation gas, respectively. The flow rate of the helium carrier gas was 100 mL/min for the reference and 130 mL/min for the detector. The oxygen flow rate was 240 mL/min. The oxygen was introduced into the system for 5 s during the analyses. A 10 μL glass syringe was used to take the test portion from the gasoline sample and 2 μL of gasoline was injected through the inlet-port septum into the instrument. The mass of the test specimen was calculated by multiplying the density of the gasoline sample by the volume used.

2.4. Uncertainty estimation

The estimation of uncertainty was carried out using the method described in the ISO GUM and EURACHEM document. The measurand was specified and the mathematical model was built based on the relationship between the measurand and the input quantities upon which it depends. The uncertainty sources were identified by listing