Gasoline Quality Assessment Using Fast Gas Chromatography and Partial Least-Squares Regression for the Detection of Adulterated Gasoline

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ABSTRACT: To find out if gasoline is adulterated, it is essential to analyze the sample's information efficiently; however, current official test methods are time consuming and costly. Much research has been conducted to supplement these difficulties using multivariable analysis and instruments such as spectrophotometers or gas chromatography (GC). However, spectrophotometers are unable to determine the chemical components, and conventional GC systems take more than 30 min to obtain sufficient data from gasoline samples. In this work, fast GC and a partial least-squares regression (PLSR) were used as analytical methods to determine research octane number (RON), aromatic compounds, methanol, and other oxygenates in under 6 min. The samples of gasoline unadulterated and adulterated with benzene, toluene, xylenes, and methanol were predicted using PLSR, which showed a good correlation between the reference values greater than 0.97. The methodology was validated, estimating specific figures of merit for quantitative multivariate analysis, showing a good value of the root-mean-square error of prediction (RMSEP) and good relative error of prediction (REP %) in the range 0.0−13.0%. Therefore, these results indicate that the fast GC and PLSR model could be an alternative analytical method to effectively manage the gasoline quality.

1. INTRODUCTION

Motor gasoline is one of the dominant transportation energy sources. According to the International Energy Outlook (EIA, 2016), gasoline occupied 39% of the total liquid fuel market in 2012 and is expected to hold the position of dominant transportation fuel until 2040.[1] However, the gasoline market has faced some controversial issues, including growing demands for better gasoline quality and reduced environmental impacts. To meet these requirements more effective tests are required to determine if gasoline is adulterated since adulterated gasoline is hazardous to both human health and a vehicle's internal combustion system corrosion.[2]

The adulterated gasoline is an illegal fuel type to make a profit by blending with cheap adulterants because of the different taxation systems in many countries. The adulterated gasoline can normally be made by adding organic solvents, such as light aliphatic (C4−C8), and mixed aromatic compounds or refined single components such as methanol, benzene, toluene, xylenes, *n*-hexane, and *n*-heptane to meet fuel specifications intentionally.[3,4] It is difficult to decipher between gasoline unadulterated and adulterated with different components because those adulterants are not possible to detect by visual inspection only, since they have high solubility in gasoline. To ensure fuel quality in the Republic of Korea, the Korea Petroleum Quality and Distribution Authority has regulated national fuel quality and has regularly inspected fuel properties and components from production sites through to end-user applications since 1984.

There are several ways to determine if gasoline is adulterated. The most common method involves checking the research octane number (RON) and chemical components. However, conducting these tests is undesirable since

they require a large amount of sample, a long operation time, and manual intervention. For example, the single RON test requires a minimum of 500 mL of gasoline sample and a similar amount of standards (iso-octane and *n*-heptane) as well as more than 30 min of run time.[5−7]

Various analytical methods, which mostly combine chemometrics and analytical instruments, have been developed to reduce both the operation time and the mass of sample required. For example, multivariate calibrations combined with spectrophotometers have been adopted to estimate the sample's physicochemical properties in the beginning.[8−11] The first step of the multivariate calibration is usually developing the models by combining the reference spectra and concentration results or other specific results of interest. Afterward, calibration models are validated with actual values from new samples which are not used in the calibration process.[12] Partial least-squares (PLS), multiple linear regression (MLR), and principal component regression (PCR) are widely used chemometric models for multivariate analysis.[13,14] Recent computational developments can make it possible to use these multivariate models for more complex sample data. For example, oil and oil-derived products can be analyzed using gas chromatography-mass spectrometry (GC-MS) or two-dimensional gas chromatography (GC X GC).[15−18] Thus, many works have been done to determine the correlation between these analytical techniques and gasoline standard methods with respect to the detection of adulterated gasoline. For example, Kelly et al. evaluated octane numbers using near-

infrared spectrometry (NIR) associated with PLS multivariable calibration,[19] Mendes et al. used PLS regression with GC-MS and distillation curves to predict octane numbers,[3] and Parastar et al. conducted quality assessment using GC X GC and flame ionization detection associated with PLS.[4]

Even though many achievements have been made with spectrophotometers and GC techniques (GC-MS, GC X GC), they still have drawbacks with respect to effectively identifying gasoline adulteration. Although results are obtained quickly, spectrophotometer chemometric results are limited in that they mainly focus on gasoline's physical properties, such as RON, distillation fractions, and specific gravity. Alternatively, GC provides detailed information on a sample's chemical composition but requires more than 30 min to obtain a single chromatogram and sometimes requires trained technicians for analysis. It would be helpful to determine a method that provides the required information quickly. Therefore, this paper aims to reduce the operation time using an analytical method based on fast GC associated with the PLS model.

In this work, RON, aromatic compounds, methanol, and oxygenates were chosen as the calibration model items to verify adulterated gasoline. RON is one of the main properties used to describe gasoline quality. It indicates a gasoline's resistance to autoignition depending on specific operation conditions. Aromatic compounds (benzene, toluene, xylenes) and methanol are typical components used to boost RON in the adulterated gasoline, but these chemical compounds have negative effects on human health and vehicle's fuel systems. According to the Worldwide Fuel Charter, aromatic compounds tend to accelerate deposit formations on the engine and these deposits influence tailpipe emissions, including carbon dioxide, that have a linear relationship with aromatic content.[20] Benzene especially is classified as a hazardous air pollutant by the Environmental Protection Agency (EPA) and is known as a human carcinogen.[21] Methanol is also strictly prohibited because it is such a corrosive material that can cause degradation in metal-based fuel systems and plastics and rubber parts.[20] Oxygenated organic compounds, methyl tertiary butyl ether (MTBE), and tertiary amyl methyl ether (TAME) along with ethanol are mixed with gasoline to improve the octane number and engine performance.[20] These oxygenates can be a useful parameter to determine if gasoline is adulterated because the oxygenate compounds are only produced through the petrochemical process and normal gasoline maintains specific components and amounts of oxygenates depending on its refinery site.

2. EXPERIMENTAL SECTION

2.1. Samples. In this study, 75 gasoline samples were collected. Forty-six samples were from gas stations or 5 different refinery sites, and the rest were blended by hand using typical adulterant substrates like solvents, aromatic compounds, methanol, and oxygenates. The blending ratios were based on data obtained from the fuel quality management system from Korea Petroleum Quality and Distribution Authority. Each sample was prepared in 3 L quantities and stored under refrigeration (3−5 °C) to prevent any volatile components loss.

2.2. Materials and Methods. *2.2.1. Research Octane Number (RON).* The most representative test procedures are outlined in ASTM D2699-15 using the Cooperative Fuels Research (CFR) engine, which has the specific single cylinder equipped with fuel−air mixture temperature and variable compression ratio controller.[5,7] For motor gasoline, the RON is domestically determined to be between 91 and 94 based on national automotive fuel specifications. Our method

operating conditions and procedures are equivalent to those outlined in ASTM D2699-16.[6,22]

2.2.2. Other Components: Aromatic Compounds, Methanol, and Oxygenate Compounds. There are several test methods from ASTM and ISO to detect these compounds in gasoline. In this study, ASTM D6730-01 was used. This method covers gasoline-graded spark-ignition engine fuels with a maximum boiling point of 225 °C and identifies the components using GC with a 100 m capillary column and a 1–4 m precolumn. The run time is 180 min per sample, and a cryogenic system is required to cool the oven temperature down to 5 °C at the beginning of each run.[23] The Agilent 7890A GC with an autosampler was used to analyze the samples, and liquid carbon dioxide was used as the cryogenic coolant.

2.2.3. Fast GC. The gasoline sample chromatograms were obtained using the fast GC-FID system (AC 8612) which was originally manufactured by Analytical Controls, Netherlands, with the Agilent 7890A GC platform to simulate gasoline boiling point distributions. The system had a fused capillary DB-1 column from J&W Scientific (10 m × 0.1 mm i.d. × 0.20 μm film thickness) and used helium as the carrier gas at a constant flow rate of 0.77 mL/min. Samples of 0.1 μL were injected in split mode (split ratio 1:600) using a 5 μL Hamilton microsyringe. The analysis was processed for 5.8 min using the following oven conditions: initial temperature of 35 °C for 0.65 min, temperature increased to 45 °C at a rate of 100 °C/min, temperature held at to 45 °C for 0.75 min, temperature increased again to 60 °C at a rate of 100 °C/min, temperature held at 60 °C for 0.75 min, and temperature ramped to 230 °C at a rate of 50 °C/min. The detection temperatures were 350 °C, and the data acquisition rate was 50 Hz. Each gasoline sample signal was exported to CSV format as a row vector (1 × 6956), and a data matrix was made by combining all sample (75) data (75 × 6956).

2.2.4. Data Modeling and Accuracy Check. To develop the calibration model using PLS regression, Unscrambler software (version 8.0, Camo) was used. All data results, including GC, RON, aromatic compound concentration (benzene, toluene, xylenes), and oxygenates values, were correlated to each other to build the PLS regression model. The PLS algorithm is using actual property results and all chromatograms to generate a calibration matrix.

The PLS model during the modeling relates the matrix data contained in X block (elution time data matrix X, for the present work) and values of the interest property (vector y containing the reference values of each interest property analyzed in the present work, such as RON, benzene, toluene, xylenes, total aromatics, methanol and other oxygenates), which are decomposed, and creates a new coordinate axes system denoted latent variables (LVs) to maximize the covariance between X and y according to eqs 1 and 2[24,25]

$$X = \sum_{i=1}^{n} t_i p^T + E \tag{1}$$

$$y = \sum_{i=1}^{n} t_i q^T + f \tag{2}$$

where t_i is the score vector, p_i and q_i are the loadings for h LVs, and E and f are the error matrices containing the nonmodeled information on X and y, respectively. The estimates for the interest property ($\hat{y}$) for a set of samples are obtained by multiplication of the preprocessed gas chromatograms (x, for example) by the regression vector b, obtained by the combination of calibration parameters W, P, and q using eq 3[26]

$$\hat{y} = xW(PW)^{-1}q = xb \tag{3}$$

where W is the weight matrix of X and P and q are loadings of X and y, respectively, obtained in the calibration step for HLVs by the PLS model. RMSEC is necessary to measure how correct the calibration is done. However, it does not prove the future samples' accuracy. Therefore, RMSECV and RMSEP are applied to validate and to predict the model's accuracy using eqs 4 and 5, respectively

Table 1. Measured RON and Components Summary of Gasoline Samples

gasoline samples		RON	aromatics				oxygenates	
			B[a] (vol %)	T[b] (vol %)	X[c] (vol %)	total[d] (vol %)	methanol (wt %)	other[e] (vol %)
normal −43ea	min	90.56	0.13	1.21	1.73	7.55	0.00	0.00
	max	92.00	0.56	3.96	4.42	22.04	0.00	2.13
	avg	91.17	0.43	2.02	2.52	12.38	0.00	1.67
adulterated −27ea	min	84.93	0.32	1.60	1.82	9.78	0.00	0.00
	max	94.70	0.64	7.23	6.98	19.59	5.68	2.97
	avg	89.77	0.44	2.90	3.03	13.29	0.94	1.60
external prediction sets-5ea	1	91.40	0.45	2.26	2.96	13.04	0.00	1.76
	2	91.27	0.48	2.28	3.31	12.27	0.00	1.62
	3	91.13	0.36	1.41	1.83	7.87	0.00	1.82
	4	87.60	0.56	2.02	2.18	10.52	0.00	1.59
	5	92.60	0.42	2.25	5.00	14.51	3.59	1.63

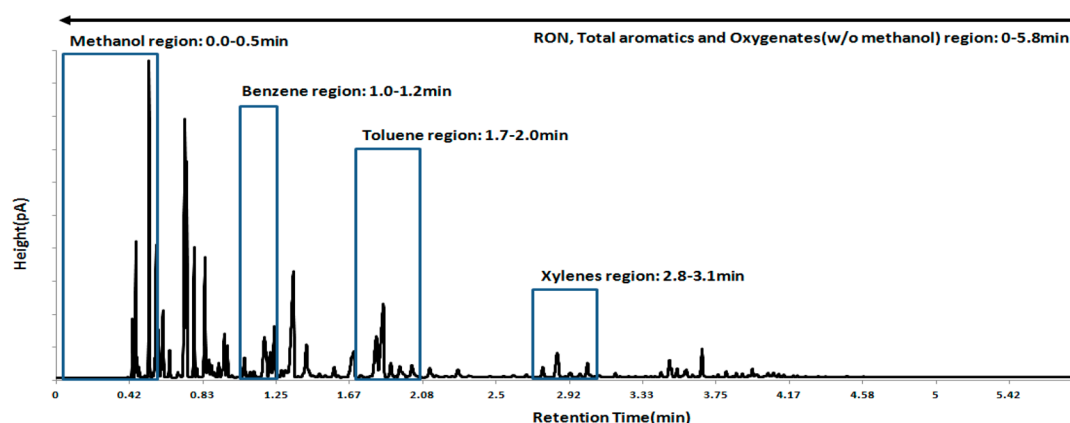[a]Benzene. [b]Toluene. [c]Xylenes. [d]All aromatic compounds between C6−C9. [e]MTBE + TAME.

Figure 1. Selected gasoline chromatogram regions time for PLS modeling

Table 2. Statistical Variables for PLS Modeling

modeled variables	RON	aromatics				oxygenates	
		B[a]	T[b]	X[c]	total[d]	methanol	others[e]
LVs[f]	11	14	4	2	6	8	9
RMSEC	0.221	0.020	0,173	0.12	0.659	0.245	0.045
RMSECV	0.256	0.025	0,189	0.128	0.727	0.291	0.085
REMSEP	0.550	0.026	0.204	0.150	0.808	0.348	0.123
−slope[g]	0.986	0.944	0.981	0.989	0.938	0.973	0.978
−offset[h]	1.315	0.025	0.043	0.031	0.769	0.011	0.039
−R[2i]	0.993	0.971	0.991	0.994	0.968	0.986	0.989
REP (%)	0.00−0.33	0.00−7.69	0.87−11.88	0.87−11.88	1.67−5.43	0.00−3.00	0.61−12.92

[a]Benzene. [b]Toluene. [c]Xylenes. [d]All aromatic compounds between C6−C9. [e]MTBE + TAME. [f]Latent Variables. [g]Coefficient to explain the correlations between measured values and predicted values during calibration. [h]Coefficient to explain the correlations between measured values and predicted values during calibration. [i]Coefficient to explain the correlations between measured values and predicted values during calibration.

$$RMSECV = \sqrt{\frac{\sum_{i=1}^{n}(y_1 - \hat{y}_1)^2}{n}} \quad (4)$$

$$RMSEP = \sqrt{\frac{\sum_{i=1}^{N}(y_i - \hat{y}_i)^2}{N}} \quad (5)$$

where n is the number of calibrated samples and N is the number of test samples.[5]

The relative error percentage (REP %) was used to evaluate the calibration's accuracy for each different property. The error can be expressed as the differences in measured and predicted data divided by the average of the measured data[27]

$$REP\% = \frac{|Predicted - Measured(Actual)|}{Measured(Actual)} \quad (6)$$

The model was validated with exhaustive cross validation (leave one out CV, LOO−CV) and predicted its accuracy using REP % from 5 external samples.

3. RESULTS AND DISCUSSION

3.1. Analysis of RON and Major Components. Measured data for all gasoline samples are summarized in Table 1. From these results, adulterated gasoline samples demonstrated wider ranges of RON than normal gasoline samples because aromatic compounds, toluene, xylenes, and methanol, were intentionally used to improve the RON and
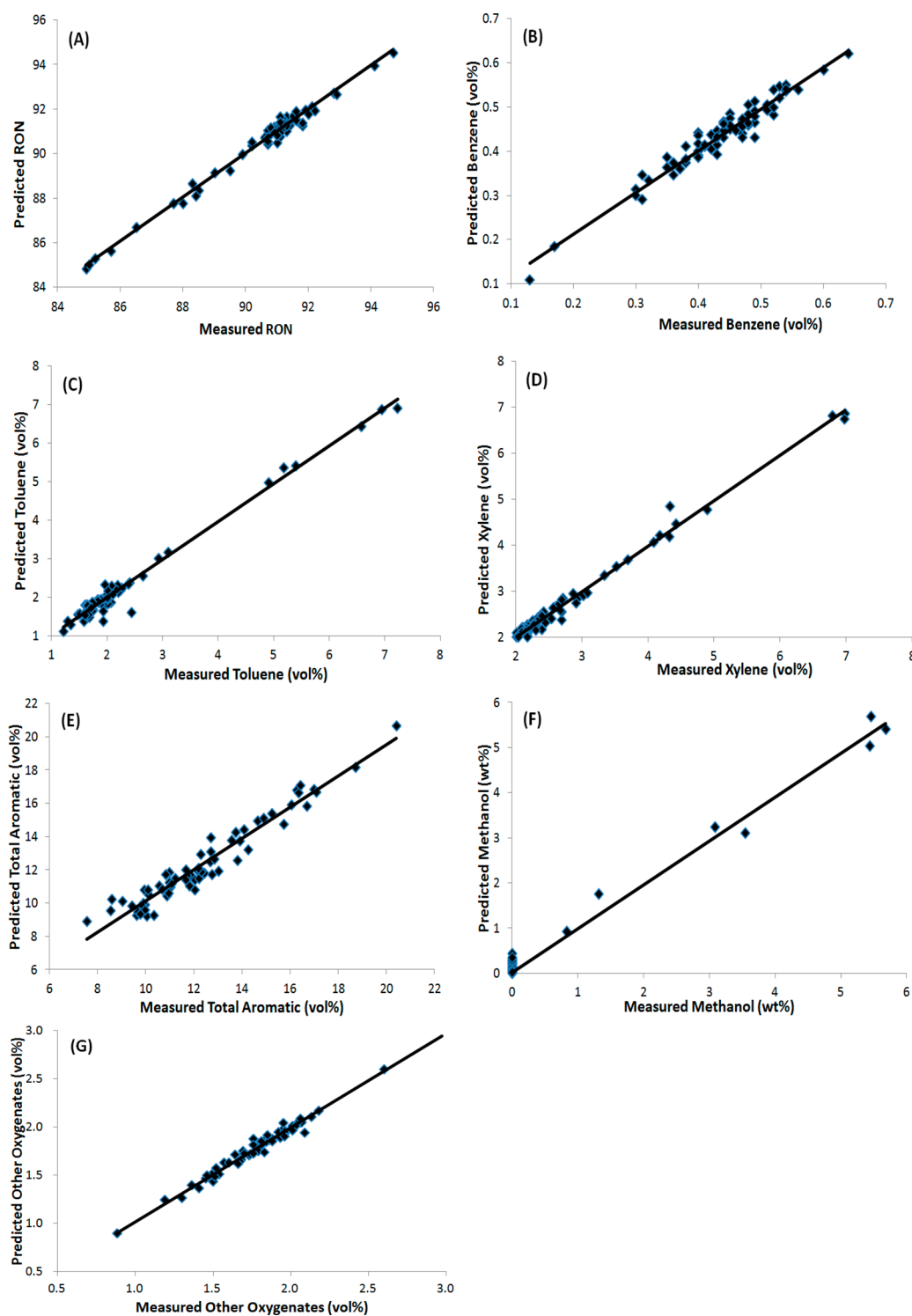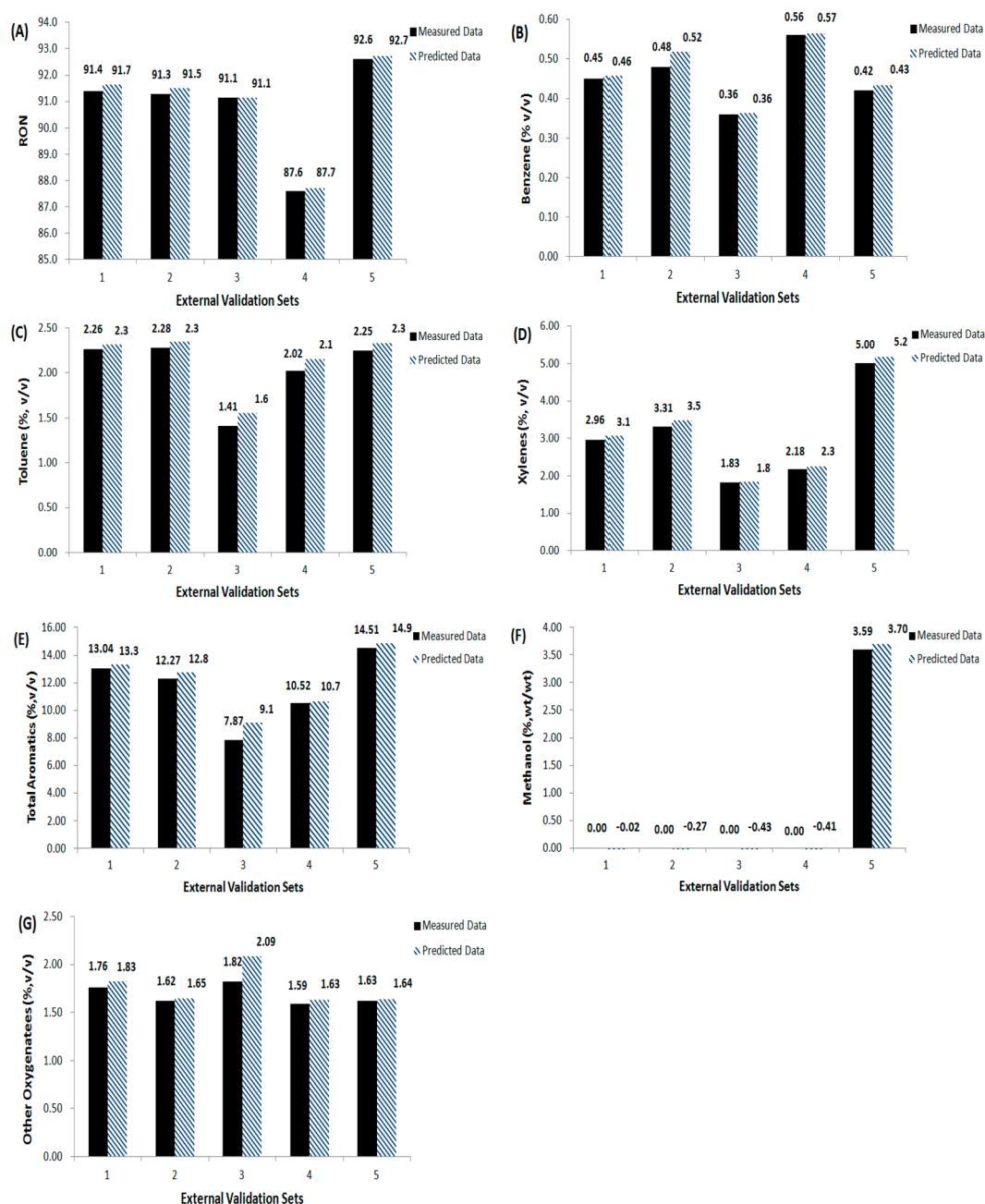
Figure 2. Predicted values against measured values for each calibration model for (A) RON, (B) benzene, (c) toluene, (D) xylenes, (E) total aromatics, (F) methanol, and (G) other oxygenates.

compensate for the RON decrease due to blending with the paraffinic solvents. The total aromatics listed in Table 1 refer to all possible aromatic compounds between C6 and C9 within gasoline stocks, such as ethylbenzene. Oxygenates were separated into methanol and other oxygenates to distinguish between different impacts when the methanol was blended as an adulterant.

3.2. Determination of Chromatogram Retention Time. The gasoline fast GC chromatogram had approximately

100 peaks with the conditions used. Many of the peaks could be a match for components based on standard materials spiking or database software provided by the manufacturer. Many gasoline components were overlapped when the fast GC result was compared with ASTM D6730-01 condition, which has more than 200 gasoline peaks. The possible retention time is shown in Figure 1. RON, total aromatics and oxygenates except methanol, were applied during the whole analysis time from 0 to 5.8 min. However, methanol was eluted at 0−0.5 s,

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Figure 3. Prediction results using external samples and calibration models for (A) RON, (B) benzene, (c) toluene, (D) xylenes, (E) total aromatics, (F) methanol, and (G) other oxygenates.

benzene was 1.0−1.2 s, toluene was 1.7−2.0 s, and xylenes were 2.8−3.1 s. These selected regions could increase the PLS model's accuracy by eliminating irrelevant signals and noninformative noises.[28]

3.3. Development of the PLS Calibration Model. All gasoline sample chromatograms and measured data were converted and combined to generate the PLS regression model. Multivariate calibration modeling was conducted with 70 normal and adulterated samples. Some variables, such as the LVs, RMSEC, RMSECV, RMSEP, and coefficients for the relation between measured results and predicted results (slope, offset, R^2),[29] explain the relations between measured and predicted results. For example, if the model results of the slope and R^2 are close to 1, the calibration models have ideal correlations with the two results.[30]

The calibration model results for each component are described in Table 2. As shown Figure 2A, samples' RONs were well distributed from 84 to 96 and slope and R^2 were 0.986 and 0.993, respectively. In the case of benzene from Figure 2B, samples were concentrated in the center between 0.3% and 0.6%. Data on toluene and xylenes were mainly located around 1% (v/v) and 3% (v/v); only a few samples, which were adulterated, had more than 5%. However, these revealed high correlations with toluene and xylenes plots having slopes and R^2 values of 0.981 and 0.989 and 0.991 and 0.994, respectively. Even though total aromatic content had an even distribution for concentration, the correlations between actual and predicted data were concentrated at low concentrations. This could be the cause for the relatively low slope and R^2 values for the total aromatic content. Calibration

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models for methanol and other oxygenates had high correlations between measured and predicted data with R^2 values of 0.986 and 0.989, respectively. Methanol's sample numbers were smaller than other items because normal gasoline has no methanol; therefore, the methanol was blended in adulterated samples from 1% (w/w) to 6% (w/w) to focus on quality rather than quantity inspection.

3.4. Prediction Results Using External Validation Sets. These PLS calibrations were validated again using five external samples. Three of the samples were normal gasoline, and two of the samples were blended with adulterants to evaluate the calibration modeling by simulating situations with low RON and added methanol.

The prediction results were quite accurate throughout the entire sample ranges. RON results had less than 0.33% error within the range from 87.6 to 92.6 (Figure 3A). Aromatic components (benzene, toluene, xylenes, and total aromatics) and other oxygenates had less than 13.00% error at the selected sample ranges. In the case of methanol, we set any negative predicted data to zero because the negative results only appeared when the samples had no methanol and because it was acceptable to do so for screening purposes for the calibration model.

From these data it can be concluded that PLS regressions using fast GC have a high probability of effectively determining if gasoline is adulterated by providing detailed information about the gasoline's components and properties.

4. CONCLUSION

In this work, PLS regression (a type of multivariate calibrations) with fast GC was used to predict several properties simultaneously to determine adulterated gasoline. Samples were collected from production sites or prepared by blending with adulterants based on an actual quality inspection database to represent the real-world situations. Specific regions were set in the chromatogram for some component calibrations to improve accuracy by eliminating noise.

The results showed high correlations between measured data and predicted data with more than 97% for all of the R^2 values. To validate the calibration results, an external data set was used and compared with the results. The percent error for RON was less than 0.2%, and all other components had less than 5% error within given sample ranges. Although a detailed feasibility study would be required to apply this method in actual field analysis circumstances, it is worth the undertaking as this new approach to enhance the operational efficiency of gasoline adulteration inspection has multiple benefits.

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Notes
The authors declare no competing financial interest.

■ REFERENCES

(1) *International Energy Outlook 2016*; U.S. Energy Information Administration; 2016; https://www.eia.gov/outlooks/-ieo/pdf/0484(2016).pdf [accessed Oct 3, 2017].

(2) Lee, J.; Balakrishnan, S.; Cho, J.; Jeon, S. H.; Kim, J. M. Detection of adulterated gasoline using colorimetric organic microfibers. *J. Mater. Chem.* **2011**, *21*, 2648−2655.

(3) Mendes, G.; Aleme, H. G.; Barbeira, P. J. S. Determination of octane numbers in gasoline by dis-tillation curves and partial least squares regression. *Fuel* **2012**, *97*, 131−136.

(4) Parastar, H.; Mostafapour, S.; Azimi, G. Quality assessment of gasoline using comprehensive two-dimensional gas chromatography combined with unfolded partial least squares: A reliable approach for the detection of gasoline adulteration. *J. Sep. Sci.* **2016**, *39*, 367−374.

(5) De Paulo, J. M.; Mendes, G.; Barros, J. E. M.; Barbeira, P. J. S. A study of adulteration in gasoline samples using flame emission spectroscopy and chemometrics tools. *Analyst* **2012**, *137*, 5919−5924.

(6) ASTM international *Standard test method for research octane number of spark-ignition engine fuel*. ASTM D2699-16; ASTM International: West Conshohocken, PA, 2016.

(7) Daly, S. R.; Niemeyer, K. E.; Cannella, W. J.; Hagen, C. L. Predicting fuel research octane number using Fourier-transform infrared absorption spectra of neat hydrocarbons. *Fuel* **2016**, *183*, 359−365.

(8) Kardamakis, A. A.; Pasadakis, N. Autoregressive modeling of near-IR spectra and MLR to predict RON values of gasolines. *Fuel* **2010**, *89*, 158−161.

(9) Pierce, K. M.; Schale, S. P. Predicting percent composition of blends of biodiesel and conventional diesel using gas chromatography−mass spectrometry, comprehensive two-dimensional gas chromatography−mass spectrometry, and partial least squares analysis. *Talanta* **2011**, *83*, 1254−1259.

(10) Gonzaga, F. B.; Pasquini, C. A low cost short wave near infrared spectrophotometer: Application for determination of quality parameters of diesel fuel. *Anal. Chim. Acta* **2010**, *670*, 92−97.

(11) Wiedemann, L.; Davila, L.; Azevedo, D. Adulteration detection of Brazilian gasoline samples by statistical analysis. *Fuel* **2005**, *84*, 467−473.

(12) ASTM International. *Standard practices for infrared multivariate quantitative analysis*. ASTM E1655-05; ASTM International, West Conshohocken, PA, 2005.

(13) Barbeira, P. J. S.; Pereira, R. C. C.; Corgozinho, C. N. C. Identification of gasoline origin by physical and chemical properties and multivariate analysis. *Energy Fuels* **2007**, *21*, 2212−2215.

(14) Balabin, R. M.; Safieva, R. Z.; Lomakina, E. I. Gasoline classification using near infrared (NIR) spectroscopy data: Comparison of multivariate techniques. *Anal. Chim. Acta* **2010**, *671*, 27−35.

(15) Mostafapour, S.; Parastar, H. N-way partial least squares with variable importance in projection combined to GC × GC-TOFMS as a reliable tool for toxicity identification of fresh and weathered crude oils. *Anal. Bioanal. Chem.* **2015**, *407*, 285−295.

(16) Flumignan, D. L.; Anaia, G. C.; Ferreira, F. d. O.; Tininis, A. G.; Oliveira, J. E. Screening brazilian automotive gasoline quality through quantification of saturated hydrocarbons and anhydrous ethanol by gas chromatography and exploratory data analysis. *Chromatographia* **2007**, *65*, 617−623.

(17) Kehimkar, B.; Hoggard, J. C.; Marney, L. C.; Billingsley, M. C.; Fraga, C. G.; Bruno, T. J.; et al. Correlation of rocket propulsion fuel properties with chemical composition using comprehensive two-dimension-al gas chromatography with time-of-flight mass spectrometry followed by partial least squares regression analysis. *J. Chromatogr.* **2014**, *1327*, 132−140.

(18) Teixeira, L.; Oliveira, F.; Dossantos, H.; Cordeiro, P.; Almeida, S. Multivariate calibration in Fourier transform infrared spectrometry as a tool to detect adulterations in Brazilian gasoline. *Fuel* **2008**, *87*, 346−352.

(19) Kelly, J. J.; Barlow, C. H.; Jinguji, T. M.; Callis, J. V. Prediction of gasoline octane numbers from near-infrared spectral features in the range 660−1215 nm. *Anal. Chem.* **1989**, *61*, 313−320.

(20) *Worldwide Fuel Charter-fifth edition*; European Automobile Manufacturers Association; 2013; https://www.acea.be/uploads/publications/Worldwide_Fuel_Charter_5ed_2013.pdf [accessed Sep 3, 2017].

(21) ASTM International. *Standard specification for automotive spark-ignition engine fuel*. ASTM D4814-16; ASTM International, West Conshohocken, PA, 2016.

(22) Korean Agency for Technology and Standards. *Motor fuels-Determination of knock characteristics-research method*. KS M2039-06; Korean Agency for Technology and Standards: Seoul, 2006.

(23) ASTM International. *Standard test method for determination of individual components in spark ignition engine fuels by 100-metre capillary (with precolumn) high resolution gas chromatography*. ASTM D6730-01; ASTM International: West Conshohocken, PA, 2016.

(24) Vandeginste, B. G. M.; Massart, D. L.; Buydens, C. M. L.; Jong, S.; Lewi, P. J.; Smeyers-Verbeke, J. *Hand book of Chemometrics and Qualimetrics: Part B*; 1st ed.; Elsevier: Amsterdam, Netherlands, 1988.

(25) Wold, S.; Sjöström, M.; Eriksson, L. PLS-regression: a basic tool of chemometrics. *Chemom. Intell. Lab. Syst.* **2001**, *58*, 109−130.

(26) Naes, T.; Isaksson, T.; Feran, T.; Davies, T. *A user-friendly guide to multivariate calibration and classification*; NIR Publications: Chichester, UK, 2002.

(27) Feng, F.; Wu, Q.; Zeng, L. Rapid analysis of diesel fuel properties by near infrared reflectance spectra. *Spectrochim. Acta, Part A* **2015**, *149*, 271−278.

(28) Li, H.; Liang, Y.; Xu, Q.; Cao, D. Key wavelengths screening using competitive adaptive reweighted sampling method for multi-variate calibration. *Anal. Chim. Acta* **2009**, *648*, 77−84.

(29) Monteiro, M. R.; Ambrozin, A. R. P.; Da Silva Santos, M.; Boffo, E. F.; Pereira-Filho, E. R.; Lião, L. M.; et al. Evaluation of biodiesel−diesel blends quality using 1H NMR and chemometrics. *Talanta* **2009**, *78*, 660−664.

(30) Olivieri, A. C.; Faber, N. K. M.; Ferre, J.; Boque, R.; Kalivas, J. H.; Mark, H. Uncertainty estimation and figures of merit for multivariate calibration. *Pure Appl. Chem.* **2006**, *78*, 633−661.