

New Headspace-Mass Spectrometry Method for the Discrimination of Commercial Gasoline Samples with Different Research Octane Numbers

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ABSTRACT: A method for the discrimination of different gasoline samples according to their RON has been developed using an HS-MS system. The working conditions for the HS-MS analytical procedure were optimized by experimental design. The variables optimized were incubation temperature, incubation time, and sample volume. The optimal conditions were as follows: 145 °C incubation temperature, 10 min incubation time, and 80 μ L sample volume. The optimized method was applied to a set of 30 gasoline samples with different RON values (95# and 98#). An hierarchical cluster analysis was applied in which the m/z (45–200 m/z) values were used as a variable to form groups. A perfect classification (100%) of the gasoline samples according to their RON was achieved. A linear discriminant analysis was carried out and the resulting linear discriminant function enabled a perfect classification of the gasoline samples according to the RON using only the m/z values of 88, 95, and 112. These results demonstrate the capacity of the new technique for the discrimination of gasoline samples according to their RON and the applicability of this method in this field. For the first time, HS-MS was used for this purpose. The main advantage of HS-MS vs previous methodologies is that no chromatographic separation and no sample manipulation are required. HS-MS is therefore faster than the current techniques used in these kinds of studies; it is also cheaper, ecofriendly, and easy to use for routine analysis.

1. INTRODUCTION

Gasoline, as a petroleum based product, is a flammable volatile mixture of hydrocarbons that includes paraffins (alkanes), cycloalkanes (naphthenes), and olefins (alkenes). Gasoline also contains compounds with oxygen, nitrogen, or sulfur. Additionally, some metals are present at trace levels.

Automotive gasoline is one of the most refined products, and the specific process used for gasoline production defines the final chemical composition of gasoline fractions and the resulting gasoline quality. The basic elemental composition of gasoline shows little variation from one type to another, and it may vary from location to location depending on the crude fuel feed used in the refinery. In fact, the variations in composition that have an effect on the properties of the gasoline lie in the proportion of the various compounds and the additives that each refinery adds, rather than in the elemental composition. Procedures such as cracking and alkylation are used to change the sizes of molecules in order to favorably affect the amount of material within a particular boiling point range. Procedures such as reforming and isomerization are used to improve the quality of the gasoline.¹

Different additives are added to the gasoline by the refineries in order to improve fuel performance, avoid problems in the engine, or reduce pollutant emissions. For instance, ethanol is usually added to gasoline to improve spark-ignition engine performance.² Other typical additives are antiknock agents, detergents, dispersants, or antioxidants.³

The gasoline production process must meet a variety of specifications, and the quality of the resulting gasoline must

satisfy the national standard requirements. Numerous different tests can be carried out to test the quality of the gasoline. The Research Octane Number (RON) is a measure of a fuel's resistance to knock or to ignite prematurely, and this is one of the critical measures of a gasoline's performance. The RON value is obtained using a Co-operative Fuel Research (CFR) engine according to ASTM D2699-08.⁴ The standard liquids used for the octane number tests are *n*-heptane, which has very poor knock resistance (with a rating set to 0), and isooctane (2,2,4-trimethylpentane), which exhibits excellent knock resistance (with a rating set to 100).¹ The antiknock performance of the fuel being tested is then compared to that of mixtures of the two standards. The Spanish gasoline market,⁵ and those of most European countries, includes 2 different types of gasoline that are differentiated by RON: 95# and 98#. The higher the RON, the higher the quality of the gasoline and therefore the higher the price.

A number of rapid methods to test the quality of gasoline using spectroscopic techniques such as NMR,⁶ NIR,^{3,7–11} FTIR,^{12,13} and flame emission spectroscopy¹⁴ have recently been developed. Raman spectroscopy has also been used for the quantitative analysis of gasoline properties, and recently, Li et al.¹⁵ performed a classification of gasoline brands and origins by Raman spectroscopy combined with a novel *R*-weighted LSSVM algorithm. However, most of the methods for testing

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the quality of gasoline are expensive, tedious, or time-consuming. Additionally, most of them deal with the whole gasoline sample; this means minor differences will be used for discrimination purposes. If using only volatile compounds, differences would be found more easily. Gasoline is a volatile mixture of hydrocarbons, and as a consequence, gas chromatography techniques have been widely used for the analysis of not only gasoline but also other ignitable liquids and their residues.^{16–23} The main drawbacks for gas chromatography based methods are related with the total time for the analysis. Additionally, most gas chromatographic systems have no options for a portable model; then samples must be taken to the lab and no in situ analyses can be run.

Apart from the importance of gasoline production within the petroleum market, the study of gasoline identification is of forensic significance for the investigation of arson and spills and the detection of gasoline adulteration.¹⁸ In arson, accelerants such as ignitable liquids are commonly used to initiate or accelerate a fire. The most commonly used ignitable liquids are petroleum based products such as gasoline, as they are easy to obtain and easy to ignite. In some cases, traces of ignitable liquid may remain at the fire scene, and these could be matched to samples that are associated with the suspect.¹⁷ The sum of ion spectra, i.e. the mass spectra calculated by summing the intensities of each nominal mass over all chromatographic times during a GC-MS, has been applied as the method to discriminate among several ignitable liquids during fire debris analysis.²⁴

In the environment, gasoline or petrol spills (intentional or accidental) are common, but it can be extremely difficult to identify the source.^{25,26} It is also worth mentioning that there are several illegal practices within the fuel market. For instance, the addition of lower price components, such as solvents, to fuel is a common type of fuel adulteration because of the significant difference in the taxation of gasoline and solvents. Apart from the lost tax revenue, this illegal activity causes environmental pollution and poor engine performance.^{22,27,28}

Despite the fact that gasoline classification is a very important task because of the expected economical, environmental, and technical profitability, very few papers have been published in this field. It was therefore of interest to establish a system to monitor the quality of gasoline and to develop analytical techniques for gasoline identification by source and type.

The primary results of a headspace (HS) based method that used a matrix of metal oxide semiconductor gas sensor, rather than a mass detector, are presented in ref 29. The system was used for the classification of gasoline, heating oil, and diesel oil. The results showed that it is possible to develop systems based on sensors and that the HS approach can be used for quality screening tests. The problem is that this kind of system requires the stabilization of different parameters.

In the work described here, a new analytical method based on HS-MS was optimized for the discrimination of car gasoline. The advantages of this methodology, apart from the wide applicability, are the rapidity of the analysis, the lack of need for sample preparation, and the absence of residues, as solvents are not employed. Besides, the method has high sensitivity, good accuracy, and a low cost and is easy to use for routine analysis. For these reasons, most applications of HS-MS to date have been related to food and beverage analysis.^{30–32}

To our knowledge, this method is the first to be reported in this field in which an HS-MS system has been applied. The HS-MS parameters were first optimized and then applied to a set of

commercial gasoline samples with different research octane numbers. It must be noted that this method does not produce chemical waste, can be run without sample preparation, and can be applied by technicians with a basic background.

2. MATERIALS AND METHODS

2.1. Gasoline Samples. Thirty gasoline samples were purchased from different gas stations corresponding to different Spanish refineries. The samples were divided into two different types according to their RON: 95# ($n = 15$) and 98# ($n = 15$).

2.2. HS-MS Spectra Acquisition. Analysis of the gasoline samples was performed on an HS-MS Alpha Moss (Toulouse, France) system composed of an HS 100 static headspace autosampler and a Kronos quadrupole mass spectrometer (MS). The samples were contained in 10 mL sealed vials (Agilent Crosslab), and they were then placed into the autosampler oven to be heated and agitated in order to generate the headspace. Headspace was finally taken from the vial using a gas syringe and injected into the mass spectrometer. The gas syringe was heated above the sample temperature (+5 °C) to avoid condensation phenomena. Between each sample injection, the gas syringe was flushed with carrier gas (nitrogen) to avoid cross-contamination.

The optimized experimental conditions for the headspace sampler were as follows: sample volume of 80 μ L, incubation temperature 145 °C, incubation time 10 min, agitation speed 500 rpm, syringe type 5 mL, syringe temperature 150 °C, flushing time 120 s, fill speed 100 μ L/s, injection volume 4.5 mL, and injection speed 75 μ L/s. The carrier gas was nitrogen. TBPFA (perfluorotributylamine) (2 μ L) was added to all the samples as an internal standard. TBPFA produces several peaks at different m/z ratios; then it allows for a full calibration in the MS region. The total time per sample was approximately 10 min. The components in the headspace of the vials were passed directly to the mass detector without any chromatographic separation or sample pretreatment. In this way, for any given measurement, the resulting mass spectrum gives a fingerprint of the gasoline. MS spectra were recorded in the range m/z 45–200. Instrument control was achieved using RGA (Residual Gas Analysis software package) and Alpha Soft 7.01 software.

2.3. Data Analysis and Software. The mass spectra were normalized at m/z 131, which is the significant signal of the internal standard (TBPFA).

Multivariate analysis of the data, which included principal component analysis (PCA), hierarchical cluster analysis (HCA), and linear discriminant analysis (LDA), was performed using the statistical computer package SPSS 17.0 (Chicago, IL, USA).³³ PCA was used to check if a reduced number of variables would provide similar information to the raw data from the MS spectra. HCA was used to study the group distribution for samples. LDA was used to determine equations allowing for classifying samples in different groups previously established.

Optimization of experimental variables was performed using the Box–Behnken statistical methodology by considering the standardized signal in the MS detector, i.e. the MS signal at any m/z ratio divided by the maximum signal for the internal standard. The results for the 15 analysis conditions carried out in duplicate for the three extraction variables (each variable has three levels: low, medium, and high), including 3 center points, are shown in Table 1 along with the respective responses.

The responses obtained from the various extractions were entered into a second-order polynomial equation into which each of the various parameters was introduced. A second-order polynomial equation was used because it allows evaluation of interactions between working variables. The polynomial equation is as follows:

$$Y = \beta_0 + \beta_1X_1 + \beta_2X_2 + \beta_3X_3 + \beta_{12}X_1X_2 + \beta_{13}X_1X_3 + \beta_{23}X_2X_3 + \beta_{11}X_1^2 + \beta_{22}X_2^2 + \beta_{33}X_3^2$$

In this equation Y is the aforementioned response, β_0 is the ordinate at the origin, X_1 is the volume of the sample, X_2 is the temperature during the headspace generation (°C), X_3 is the

Table 1. Box–Behnken Experimental Planning

Exp. No.	Volume (mL)	Temp (°C)	Time (min)	Response (abundance)	Est Values (abundance)
CP02	25	125	6.5	853	760
12	40	150	6.5	10310	10748
5	10	125	3	3847	4113
7	10	125	10	713	693
8	40	125	10	18602	15336
9	10	100	6.5	380	243
1	25	100	3	397	231
3	25	100	10	641	1099
11	10	150	6.5	201	107
CP01	25	125	6.5	676	760
10	40	100	6.5	2619	3427
CP03	25	125	6.5	750	760
4	25	150	10	2831	3659
2	25	150	3	438	380
6	40	125	3	5489	5509

incubation time (min), β_i are the linear coefficients; β_{ij} are the cross product coefficients, and β_{ii} are the quadratic coefficients.

The analysis of data for the Box–Behnken design including the partial least regression calculation (PLS) was carried out using Unscrambler X (Camo Software AS, Oslo NO). This software was used to estimate the effects of the variables on the final response, the variance analysis, the second order mathematical model, the optimum levels of the significant variables, and the surface graphs.

3. RESULTS AND DISCUSSION

3.1. Study of the Significant Areas of the Spectra.

Studies into the working conditions of HS-MS systems for the analysis of gasoline samples were not found in the literature. Therefore, before starting the method development process, the most useful areas in the mass spectra for gasoline discrimination must be identified. In order to find these significant spectral regions, a principal component analysis (PCA) was performed on the signals from the mass spectrometry detector for six samples corresponding to RON = 98 (3 samples) and RON = 95 (3 samples).

The samples were analyzed using the following method for HS generation: 140 °C incubation temperature, 5 min incubation time, and 20 μ L sample volume.

Signals from $m/z = 45$ to $m/z = 200$ were standardized using the internal standard signal. PCA provided the principal components, and the loadings of experimental values for the main principal components were then checked. The m/z signals that showed loadings higher than 0.7 in the PC1 were used as target values in the subsequent optimization process. In this way, working variables were optimized in order to maximize the signals with high values to discriminate between gasoline samples with different RON numbers.

3.2. Headspace Generation. Experimental Design. The experimental variables that had the most influence on headspace generation usually are operating temperature, operating incubation time, and sample volume. As explained before, there are not previous references for gasoline samples. However, mainly incubation temperature as well as incubation time have been reported as the most important working variables for other kinds of samples during headspace generation.^{31,34} As these variables can have strong interaction effects, an experimental design (Box–Behnken method) was proposed for the method development in order to obtain

information about their interactions. The experimental results were analyzed by the response surface methodology (RSM).

The experimental design was carried out by analyzing a commercial gasoline sample under the 15 different sets of experimental conditions shown in Table 1. The ranges for values of temperature, incubation time, and sample volume are shown in Table 1 along with the experimental planning according to the Box–Behnken experimental design. As can be seen, 15 experimental points were run randomly. Incubation times of 3 min, 6.5 min, and 10 min, temperature ranges of 100 °C, 125 °C, and 145 °C, and sample volumes of 10 μ L, 25 μ L, and 40 μ L were tested.

From the Box–Behnken design, a response model was developed and PLS correlations between the response and the experimental variable values were calculated. The correlation results are shown in Table 2, and the predicted values for each experiment are given in Table 1. The resulting correlation coefficient for the developed model was 0.8519.

Table 2. Coefficient Values in the Regression Model and Corresponding p -Values

	B-coefficient	p -value
B0	759.5	
vol (A)	4009.7	0.0016
temp (B)	1242.6	0.1183
time (C)	1602.0	0.0584
vol*temp (AB)	2417.5	0.0838
vol*time (AC)	3311.8	0.0067
temp*time (BC)	37.2	0.5803
vol*vol (AA)	3977.2	0.0060
temp*temp (BB)	−1658.9	0.1275
time*time (CC)	1676.1	0.0836

The mean relative error between the real values and predicted values was 26%, and this error was higher when the value obtained for the signal was lower. Likewise, for those experiments in which the signal values were above 650 units, the mean relative error was 10.6%, meaning that the resulting model can be used in the optimization of the working conditions to reach the highest values for the analytical response.

As can be observed from the results in Table 2, for individual variables, only the volume variable is significant (p -value < 0.05). Furthermore, the interaction between volume and time and the quadratic volume are also significant (p -value < 0.05). Regarding the regression model, the β coefficients are shown in Table 2 and the effect of the volume variable is positive, meaning that an increase in the signal can be achieved by increasing the volume. Temperature and time coefficients are also positive, although their significance was not appreciable in increasing the response.

In order to improve the optimization, interactions between experimental variables were analyzed. The effect of the interaction between two working variables in the response while keeping the third one constant is shown in Figure 1.

The volume and temperature response surface at constant incubation time (6.5 min) is shown in Figure 1. In general, the response increases on increasing the sample volume and temperature. Moreover, the interaction effects between these two variables can be seen. The increase in the response on increasing the sample volume occurs from a sample volume 25 μ L when the incubation temperature is 100 °C, while the

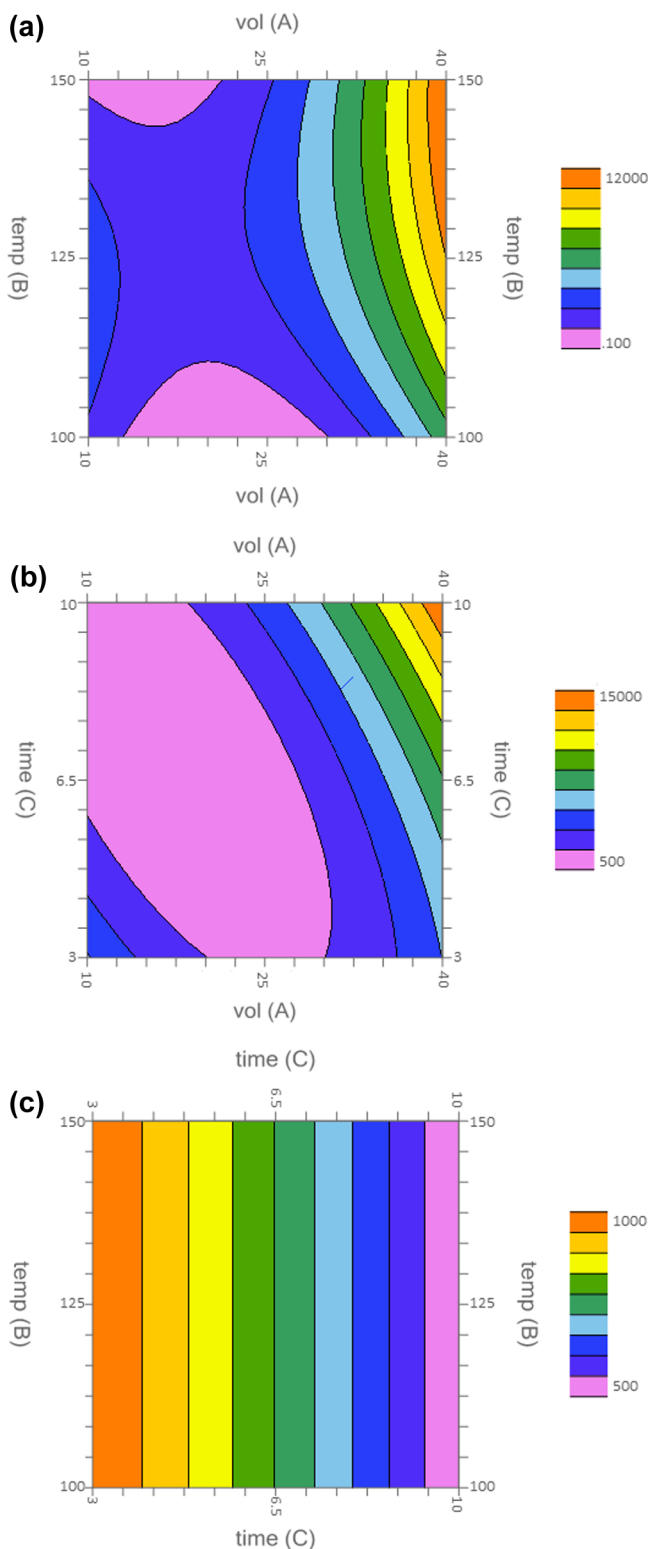


Figure 1. Response surface for the interaction between sample volume (μL) and incubation (a) temperature ($^{\circ}\text{C}$) and (b) time (min). (c) Response surface for the interaction between incubation temperature ($^{\circ}\text{C}$) and incubation time (min).

increase in the response can occur with smaller sample volumes if the incubation temperature is 145 $^{\circ}\text{C}$. The maximum response is obtained when high values for both variables (sample volume of 40 μL and incubation temperature above 130 $^{\circ}\text{C}$) are used.

The sample volume and incubation time response surface at constant incubation temperature (125 $^{\circ}\text{C}$) are shown in Figure 1. Once again, the increase in the response occurs on increasing the sample volume. In addition, a clear interaction effect can be observed between the incubation time and sample volume in relation to the response. The graphic shows the need to heat the sample for 10 min in order to obtain the maximum response, which is obtained when sample volumes of 40 μL and above are used. On using an incubation time lower than 10 min, it is not possible to reach the maximum response even though the sample volume is the highest. This means that it is necessary to increase both variables at once (incubation time sample volume) in order to obtain the optimal signal.

The incubation time and incubation temperature response surface at constant sample volume (25 μL) are shown in Figure 1. It should be noted that in this case there is no interaction between incubation temperature and incubation time. Therefore, the increase in the response occurs on increasing the incubation time, and this increase in the response shows the same trend regardless of the incubation temperature used.

Based on these results, sample volumes above 40 μL needed to be checked in order to guarantee a maximum response. The responses obtained on using sample volumes of 50 μL , 60 μL , 70 μL , 80 μL , and 100 μL and on heating the sample for 10 min at 145 $^{\circ}\text{C}$ are shown in Table 3. It can be seen that there is an increase in the response when the sample volume is increased from 40 to 80 μL . However, a similar increase cannot be observed when a sample volume of 100 μL is used. Therefore, a sample volume of 80 μL was selected as the optimal volume. As a result, the optimal conditions within the experimental range of the variables studied were 145 $^{\circ}\text{C}$, 10 min, and 80 μL .

3.3. Applicability in the Discrimination of Gasoline Samples. In order to check the applicability of the optimized method in the discrimination of gasoline samples according to their RON, a hierarchical cluster analysis (HCA) was carried out on gasoline samples with different RON analyzed by HS-MS. A set of 30 gasoline samples with different RON (95#, 15 samples and 98#, 15 samples) were analyzed using the optimized method. HCA was applied by using all the m/z (45–200 m/z) values as a variable for forming groups. The results of the HCA are represented in the dendrogram in Figure 2, which lists all of the samples and indicates the level of similarity (dissimilarity) at which any of the two clusters were joined. The Ward method was used for clusters preparation, and square Euclidean distance was used to measure distances between clusters. Other methods for cluster selection were also assayed, including the between-groups linkage method and the within-groups linkage method; all of them produce similar results. It can be seen that a perfect classification of the gasoline samples according to their RON was achieved.

Based on the tendency to cluster shown in Figure 2, an LDA (linear discriminant analysis) was performed. 50% of the

Table 3. Total Response (Abundance) Obtained Using Different Sample Volumes

	40 μL	50 μL	60 μL	70 μL	80 μL	100 μL
Response	25765 \pm 1987	82469 \pm 9384	119890 \pm 10200	151166 \pm 8253	183706 \pm 12113	186097 \pm 15397

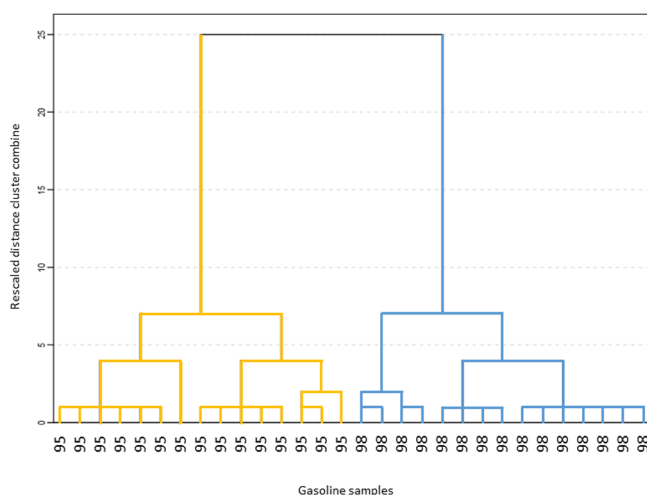


Figure 2. Dendrogram obtained from the hierarchical cluster analysis using the Ward method for measuring distances.

samples were randomly selected as a training set in order to obtain a discriminant function. The other 50% of the samples were then used as a validation set. In order to identify whether there are some specific m/z values in the mass spectra that are more significant than the others when classifying the gasoline according to the RON, a stepwise discriminant analysis was applied. The canonical discriminant function was as follows:

$$F = -3.115 - 63.632 \cdot (m/z \ 88) + 18.680 \cdot (m/z \ 95) + 55.175 \cdot (m/z \ 112)$$

The resulting linear discriminant function enabled a perfect classification (100% correct) of the gasoline samples to be obtained. The m/z values selected for the classification were 88, 95, and 112; then a shorter range in the mass spectrum could be applied for discrimination purposes.

4. CONCLUSIONS

A rapid analytical method has been developed for gasoline classification purposes. The optimized working conditions were as follows: 145 °C incubation temperature, 10 min incubation time, and 80 μ L sample volume. Lower incubation temperatures, incubation times, and sample volumes lead to lower responses in the MS, and therefore, appropriate working conditions must be used in order to obtain an effective discrimination of the two types of gasoline samples available on the market. A perfect discrimination of the samples was achieved after HCA and LDA; therefore, m/z values used in the process are directly related to the differences between gasoline samples with different RON values. The capacity of the HS-MS technique to discriminate gasoline samples according to their RON value has been proved.

This new method will allow for gasoline sample discrimination without sample preparation, in less than 15 min. It could be used for both control quality during gasoline production, because it is fast enough, and for inspection in already commercialized gasolines, because a perfect discrimination was achieved.

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Notes

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■ REFERENCES

- (1) Stauffer, E.; Dolan, J. A.; Newman, R. Flammable and Combustible Liquids. In *Fire Debris Analysis*; Stauffer, E., Dolan, J. A., Newman, R., Eds.; Academic Press: Burlington, 2008; Chapter 7, pp 199–233.
- (2) Foong, T. M.; Morganti, K. J.; Brear, M. J.; Da Silva, G.; Yang, Y.; Dryer, F. L. The octane numbers of ethanol blended with gasoline and its surrogates. *Fuel* **2014**, *115*, 727–739.
- (3) da Silva, M. P. F.; Brito, L. R. e.; Honorato, F. A.; Paim, A. P. S.; Pasquini, C.; Pimentel, M. F. Classification of gasoline as with or without dispersant and detergent additives using infrared spectroscopy and multivariate classification. *Fuel* **2014**, *116* (0), 151–157.
- (4) Standard test method for research octane number of spark-ignition engine fuel 2008 ASTM D2699-08. <http://www.astm.org/Standards/petroleum-standards.html>.
- (5) BOE-A-2010-13704, Real Decreto 1088/2010, de 3 de septiembre, 2010; Vol. 215, pp 76436–76445.
- (6) Flumignan, D. L.; Boralle, N.; De Oliveira, J. E. Screening Brazilian commercial gasoline quality by hydrogen nuclear magnetic resonance spectroscopic fingerprintings and pattern-recognition multivariate chemometric analysis. *Talanta* **2010**, *82* (1), 99–105.
- (7) Balabin, R. M.; Safieva, R. Z. Gasoline classification by source and type based on near infrared (NIR) spectroscopy data. *Fuel* **2008**, *87* (7), 1096–1101.
- (8) Balabin, R. M.; Safieva, R. Z. Biodiesel classification by base stock type (vegetable oil) using near infrared spectroscopy data. *Anal. Chim. Acta* **2011**, *689* (2), 190–197.
- (9) 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* (1–2), 27–35.
- (10) Falla, F. S.; Larini, C.; Le Roux, G. A. C.; Quina, F. H.; Moro, L. F. L.; Nascimento, C. A. O. Characterization of crude petroleum by NIR. *J. Petrol. Sci. Eng.* **2006**, *51* (1–2), 127–137.
- (11) Veras, G.; Gomes, A. D. A.; Da Silva, A. C.; De Brito, A. L. B.; De Almeida, P. B. A.; De Medeiros, E. P. Classification of biodiesel using NIR spectrometry and multivariate techniques. *Talanta* **2010**, *83* (2), 565–568.
- (12) Al-Ghouti, M. A.; Al-Degs, Y. S.; Amer, M. Determination of motor gasoline adulteration using FTIR spectroscopy and multivariate calibration. *Talanta* **2008**, *76* (5), 1105–1112.
- (13) Khanmohammadi, M.; Garmarudi, A. B.; Ghasemi, K.; de la Guardia, M. Quality based classification of gasoline samples by ATR-FTIR spectrometry using spectral feature selection with quadratic discriminant analysis. *Fuel* **2013**, *111* (0), 96–102.
- (14) De Paulo, J. M.; Barros, J. E. M.; Barbeira, P. J. S. Differentiation of gasoline samples using flame emission spectroscopy and partial least square discriminate analysis. *Energy Fuel* **2014**, *28* (7), 4355–4361.
- (15) Li, S.; Dai, L.-k. Classification of gasoline brand and origin by Raman spectroscopy and a novel R-weighted LSSVM algorithm. *Fuel* **2012**, *96* (0), 146–152.
- (16) ASTM. E1618-11 Standard Test Method for Ignitable Liquid Residues in Extracts from Fire Debris Samples by Gas Chromatography–Mass Spectrometry, West Conshohocken, PA, 2011.
- (17) Desa, W. N. S. M.; Daéid, N. N.; Ismail, D.; Savage, K. Application of unsupervised chemometric analysis and self-organizing feature map (SOFM) for the classification of lighter fuels. *Anal. Chem.* **2010**, *82* (15), 6395–6400.
- (18) Doble, P.; Sandercock, M.; Du Pasquier, E.; Petocz, P.; Roux, C.; Dawson, M. Classification of premium and regular gasoline by gas

chromatography/mass spectrometry, principal component analysis and artificial neural networks. *Forensic Sci. Int.* **2003**, *132* (1), 26–39.

(19) Rudnev, V. A.; Boichenko, A. P.; Karnozhytskiy, P. V. Classification of gasoline by octane number and light gas condensate fractions by origin with using dielectric or gas-chromatographic data and chemometrics tools. *Talanta* **2011**, *84* (3), 963–970.

(20) Sigman, M. E.; Williams, M. R. Covariance mapping in the analysis of ignitable liquids by gas chromatography/mass spectrometry. *Anal. Chem.* **2006**, *78* (5), 1713–1718.

(21) Sigman, M. E.; Williams, M. R.; Ivy, R. G. Individualization of gasoline samples by covariance mapping and gas chromatography/mass spectrometry. *Anal. Chem.* **2007**, *79* (9), 3462–3468.

(22) Skrobot, V. L.; Castro, E. V. R.; Pereira, R. C. C.; Pasa, V. M. D.; Fortes, I. C. P. Use of principal component analysis (PCA) and linear discriminant analysis (LDA) in gas chromatographic (GC) data in the investigation of gasoline adulteration. *Energy Fuel* **2007**, *21* (6), 3394–3400.

(23) Williams, M. R.; Sigman, M. E.; Lewis, J.; Pitan, K. M. Combined target factor analysis and Bayesian soft-classification of interference-contaminated samples: Forensic Fire Debris Analysis. *Forensic Sci. Int.* **2012**, *222* (1–3), 373–386.

(24) Sigman, M. E.; Williams, M. R.; Castelbuono, J. A.; Colca, J. G.; Clark, C. D. Ignitable Liquid Classification and Identification Using the Summed-Ion Mass Spectrum. *Instrum. Sci. Technol.* **2008**, *36* (4), 375–393.

(25) Gaganis, V.; Pasadakis, N. Characterization of oil spills in the environment using parallel factor multiway analysis. *Anal. Chim. Acta* **2006**, *573–574* (0), 328–332.

(26) Yuan, B.; Warneke, C.; Shao, M.; de Gouw, J. A. Interpretation of volatile organic compound measurements by proton-transfer-reaction mass spectrometry over the deepwater horizon oil spill. *Int. J. Mass Spectrom.* **2014**, *358* (0), 43–48.

(27) Mendes, G.; Barbeira, P. J. S. Detection and quantification of adulterants in gasoline using distillation curves and multivariate methods. *Fuel* **2013**, *112* (0), 163–171.

(28) Teixeira, L. S. G.; Oliveira, F. S.; dos Santos, H. C.; Cordeiro, P. W. L.; Almeida, S. Q. Multivariate calibration in Fourier transform infrared spectrometry as a tool to detect adulterations in Brazilian gasoline. *Fuel* **2008**, *87* (3), 346–352.

(29) Sobański, T.; Szczurek, A.; Nitsch, K.; Licznarski, B. W.; Radwan, W. Electronic nose applied to automotive fuel qualification. *Sens. Actuators, B: Chem.* **2006**, *116* (1–2), 207–212.

(30) Cocchi, M.; Durante, C.; Marchetti, A.; Armanino, C.; Casale, M. Characterization and discrimination of different aged 'Aceto Balsamico Tradizionale di Modena' products by head space mass spectrometry and chemometrics. *Anal. Chim. Acta* **2007**, *589* (1), 96–104.

(31) Cozzolino, D.; Cynkar, W.; Damberg, R.; Smith, P. Two-dimensional correlation analysis of the effect of temperature on the fingerprint of wines analysed by mass spectrometry electronic nose. *Sens. Actuators, B: Chem.* **2010**, *145* (2), 628–634.

(32) Cynkar, W.; Damberg, R.; Smith, P.; Cozzolino, D. Classification of Tempranillo wines according to geographic origin: Combination of mass spectrometry based electronic nose and chemometrics. *Anal. Chim. Acta* **2010**, *660* (1–2), 227–231.

(33) SPSS; SPSS Science, 233 S. Wacker Drive, 11th floor, Chicago, IL 60606-6307 (SPSS Inc.: Chicago, IL, USA).

(34) Santonico, M.; Bellincontro, A.; De Santis, D.; Di Natale, C.; Mencarelli, F. Electronic nose to study postharvest dehydration of wine grapes. *Food Chem.* **2010**, *121* (3), 789–796.