

Development, Optimization and Validation of Gas Chromatographic Fingerprinting of Brazilian Commercial Diesel Fuel for Quality Control

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A three-step development, optimization and validation strategy is described for gas chromatography (GC) fingerprints of Brazilian commercial diesel fuel. A suitable GC–flame ionization detection (FID) system was selected to assay a complex matrix such as diesel. The next step was to improve acceptable chromatographic resolution with reduced analysis time, which is recommended for routine applications. Full three-level factorial designs were performed to improve flow rate, oven ramps, injection volume and split ratio in the GC system. Finally, several validation parameters were performed. The GC fingerprinting can be coupled with pattern recognition and multivariate regressions analyses to determine fuel quality and fuel physicochemical parameters. This strategy can also be applied to develop fingerprints for quality control of other fuel types.

Introduction

Diesel oil is a fuel derived from petroleum and is basically composed of paraffinic, olefinic, naftenic and aromatic hydrocarbons and substances containing sulfur, nitrogen and oxygen in low concentration (1). Its carbon chains range from C8 to C40 and its boiling points range from 160 to 380°C (2). The chemical composition of diesel depends both on the nature of the crude oils from which it is derived and the refinery processes it has undergone (1).

Brazilian specifications and quality control for commercializing diesel as an automotive fuel are regulated by Agência Nacional do Petróleo, Gás Natural e Biocombustíveis (ANP, Regulation 15) (3). This regulation establishes several physicochemical parameters that require large amounts of sample, use of specific and dedicated equipment and skilled operators. Other disadvantages include the use of manual operations, which can be tedious and prone to operational errors. Because of this, developing simple, fast, and efficient methods using alternative analytical techniques to screen the quality and authenticity of commercialized fuels is necessary and recommended for routine applications in quality control monitoring programs.

According to ANP, diesel is the fuel most often sold in Brazil, marketing 41% in volume of petroleum processed in 2009, and 44% commercialized in southeastern Brazil (4). It reflects the importance of this fuel in the country, primarily due to the widespread use of heavy transportation like trucks, buses and ships. Because of this, the aim of this paper is to make a method available to fingerprint the quality of diesel.

American Society for Testing and Materials (ASTM) offers many official gas chromatography (GC) to guarantee the quality control of different compounds, which explains the wide variety of GC applications for petroleum-related materials. The increase of studies involving GC is attributable to modern automated instruments equipped with high-performance packed or capillary columns, as well as universal or selective detectors, and other accessories (5).

The analysis of complex mixtures such as diesel is a great challenge due to the huge number of hydrocarbon compounds present in these matrices. A detailed analysis of hydrocarbon groups in diesel can be obtained coupling a supercritical fluid extraction (SCF) with GC, due to their good compatibility (6). The chromatographic analysis of diesel sometimes requires complex temperature programs (7–8) and complex systems, such as a two-dimensional gas chromatography (GC × GC), to achieve better resolution and selectivity in comparison with traditional techniques (9).

It is commonly known that the use of response surface methodology (RSM) can increase the efficiency of an experiment in which several parameters may control the outcome. In GC, several parameters can be improved, such as the type of column, the oven temperature, injector temperature, detector type and conditions, and ramping program and rate, to provide a separation with adequate resolution in an acceptable quantity of time.

Researchers have applied RSM as a tool to optimize several operating parameters of diesel engines (10) such as speed, engine load and engine operation time (11), related to NOx emissions.

Thermodynamics models that predict temperatures from isothermal data have also been described (12–13), however they are declining because are only applicable to one-step linear programming. The simple optimization coupled to thermodynamic calculations allows a complete simulation of GC separation without chromatographic experiments, but requires knowledge of more fundamental thermodynamics (14–15). Several full factorial designs, such as Plackett-Burman and central composite (response surface) are more popular in capillary separations with the intention of modelling the best experimental conditions (selectivity, resolution and time of gradient), but only the Doehlert matrix as experimental design has been used for optimization of programmed temperature in petroleum derivatives GC analysis (16–17).

Additionally, RSM is too often applied in the extraction of certain compounds, in many matrices, for further determination. Hernández-Soriano *et al.* reported optimization in the

extraction of five insecticides from soil samples, finding the optimum values of the most important variables involved in the processes (18); Januszkiewicz *et al.* obtained optimized conditions in a chromatographic system to perform the microextraction and quantification of the flavor of commercial Cheddar cheese (19); Aguilar *et al.* applied RSM to optimize solid-phase microextraction conditions to determine 13 organochlorine pesticides from water (20).

The objective of this paper was to apply an experimental design method for the improvement of programmed temperature GC–flame ionization detection (FID) analysis using a DP-Petro capillary column to analyze Brazilian commercial diesel. Both global and partial resolutions are based on pairwise resolutions and are defined as the sum or resolutions in order of peak index appearance in the complete and fractional chromatogram, similarly to the procedure described by Flumignan *et al.* (21) and Aragão *et al.* (22). By the use of RSM, it was possible to develop a method with improved conditions for the chromatographic separations. The emphasis of this work is to show the capability of this experimental approach to improve the resolution in a reduced analysis time in programmed capillary GC.

Our lab has published studies that describe the applicability of RSM in the optimization of gas chromatographic fingerprinting of Brazilian commercial gasoline (21). Other chemometric tools have also been applied, in both gas chromatographic and nuclear magnetic resonance fingerprintings: soft independent modeling of class analogy (SIMCA) pattern recognition method and partial least squares regressions have been applied to screen the quality (23–27) and to predict several physicochemical parameters of gasoline (28), respectively.

Experimental

Sample collection

Eighty-eight (88) diesel oil samples were collected in several cities of São Paulo State, Brazil during the first fortnight of April 2007 in 1-L polyethylene terephthalate (PET) amber flasks with sealing caps. The samples were transported to the laboratory below 30°C in refrigerated boxes, following ANP monitoring procedures (29). The samples were analyzed by two different approaches, namely, physicochemical analysis, including ANP standard methods, and chromatographic analysis. By the time of GC analysis, samples were collected in 1.5-mL glass vials closed with PTFE-lined septa and crimped tops. During the analysis process, the samples were stored in a freezer at temperatures between –29 and –24°C to avoid volatilization and keep their integrity, and the lab had a controlled temperature between 20 and 25°C.

Physicochemical analysis

All randomly collected diesel samples were analyzed according to ANP Regulation 15 standard methods (3), such as relative density (ASTM D4052); atmospheric distillation temperatures required to reduce the original volume of the sample to 10% (T10), 50% (T50) and 85% (T85) (ASTM D86); flash point (ASTM D93) and sulfur content (ASTM D4294). These physicochemical parameters were used as variables to elaborate the

spreadsheet for exploratory analysis. Densimeter Antón-Paar DMA 4500 v. 4.600.b, automatic distillers Normalab NDI 440 v. 1.70C, Pensky-Martens closed cup flash point tester Q292A and energy dispersive X-ray fluorescence spectrometer EDX-800 were employed in these analyses.

Selection of representative samples for GC by hierarchical cluster analysis

Hierarchical cluster analysis (HCA) is an excellent statistical tool for the preliminary analysis of data, because it is useful in finding homogeneous clusters on the basis of measured characteristics (variables). The usual approach is to compute a measure of the similarity for each pair of objects based on the values of the variables describing the objects followed by the application of a hierarchical clustering method (30).

In this work, all physicochemical parameters (relative density, T10, T50, T85, flash point and sulfur content) were used as variables in the exploratory analysis. These variables were autoscaled, which means that each variable was mean centered and its variance set to 1. This is used due to the different orders of magnitude of the variables. The clusters were grouped on the basis of Euclidean distance measurements and the incremental criterion of linkage was applied, whether the groups are joined causing a minimum loss of information. The similarity line, which establishes clusters, assigned the value 0.7. HCA was performed using Pirouette 3.11 software (Infometrix Co., Tulsa, OK) (31) and it was applied to the spreadsheet. The dendrogram constituted of 88 samples resulting in three clusters (Figure 1). This allowed the selection of 15 representative samples from these clusters, which were submitted to the chromatographic analysis. This selection was performed to minimize cost and time of chromatographic analysis.

Gas chromatographic analysis

All 15 selected representative commercial diesel samples showed the same chromatographic profiles, but with compounds in different concentrations that arise from the same processing (catalytic cracking). From these samples, one sample (number 12) was selected via chromatographic analysis, which presented a greater complexity to develop the method; in other words, a larger number of chromatographic peaks (Table 1). All general fingerprinting data were obtained using FID, because the detection of organic compounds in complex samples is most effectively done by this type of detector. This allows these compounds to be detected with greater sensitivity and selectivity, and the response tends to be linear across a wide range of concentrations. Analyses were conducted on an automated GC–FID Shimadzu model GC-17A containing an AOC20i autosampler and data manipulation was accomplished by GCSolutions workstation software (Shimadzu, Kyoto, Japan). Chromatographic separation was carried out in a DB-Petro fused-silica capillary column (50 m × 0.15 mm i.d. × 0.50 μm; J&W Scientific, EUA) with 100% polydimethylsiloxane as the stationary phase. The carrier gas was helium at a constant flow and the sample aliquots were injected in the split mode without pre-treatment, solvent delay and no internal standard was added. Moreover, the injector and detector temperatures were maintained at 300°C. The initial analytical

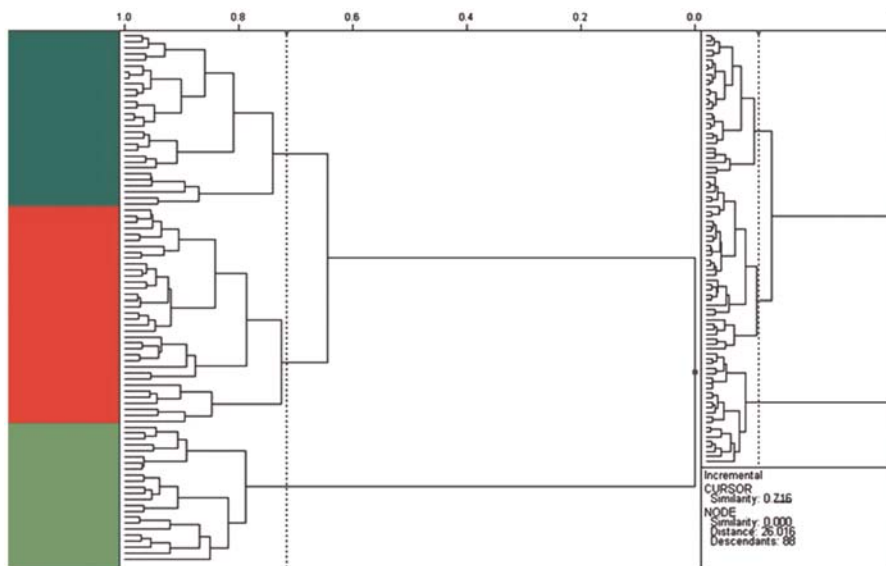


Figure 1. Dendrograms obtained for selection of the representative diesel oil samples.

chromatographic conditions, before the optimization strategy, was as follows: injector split, 1:100; volume injection, 0.3 μL ; flow of carrier gas He, 30 mL/min; oven temperature, 50°C, which was maintained for 5 min and then increased 5°C/min to 320°C; total time of analyses, 140 min.

Optimization strategy

The optimization was performed in two steps. First, a full three-level factorial design was performed to improve the variables in the system. In the first stage, the influence of the carrier gas flow rate and oven heating ramps were studied to determinate the resolution of the chromatographic fingerprinting. The flow rates of the carrier gas were from 0.8, 1.5 and 3.0 mL/min (pressures 200, 300 and 400 kPa, respectively) and under general conditions, the oven column temperature was initially kept at 50°C and then programmed using three times of analysis (with three different heating ramps for each analysis): (i) 125 min (2, 3 and 5°C/min), (ii) 116.7 min (2, 4 and 6°C/min) and (iii) 103.6 min (2, 7 and 10°C/min). Two other experiments were performed to complete this step. The gas pressure of the carrier gas was kept at 300 kPa and the heating ramps were fixed as follows: (i) from 1 to 7°C/min, (ii) 4°C (already improved) and (iii) from 12 to 15°C/min. In this time, the volume injection was kept at 0.3 μL and the split ratio was kept at 1:100. The global and partial resolutions are based on pair-wise resolutions and were obtained by GCSolutions software. They are defined as the sum of resolutions in order of peak index appearance in the complete and fractional chromatogram, similar to the procedure described by de Aragão *et al.* (22). Also, in the pair-wise resolutions, the overlapping was never ignored or assumed to constitute a single peak. In the partial resolutions (namely, initial, intermediate and final), the sum of resolutions was obtained from three different regions constituted by different chromatographic profiles. Finally, the duration time of the isothermal final temperature (320°C) step was not considered to be a factor, but necessary

Table I

Representative Commercial Diesel Samples selected by HCA, using the ANP Physicochemical Parameters, and their respective Number of Chromatographic Peaks

Sample	R.D. ($\text{kg}\cdot\text{m}^{-3}$)	Distillation			Sulfur content (% m/m)	Flash Point (°C)	Peaks
		T10 (°C)	T50 (°C)	T85 (°C)			
1	857.0	194.9	285.1	361.0	0.16	41.0	469
2	858.0	194.8	283.2	360.8	0.17	45.0	452
3	854.0	198.8	286.0	357.8	0.17	42.0	473
4	860.0	194.2	286.4	362.2	0.18	46.0	479
5	860.0	196.1	286.3	360.8	0.16	42.0	465
6	856.0	191.5	284.7	360.8	0.16	44.0	458
7	858.0	194.1	285.3	365.5	0.18	49.0	468
8	859.0	192.1	282.1	357.1	0.16	51.0	460
9	857.0	197.4	283.3	361.1	0.16	55.0	471
10	856.0	189.2	280.1	351.4	0.14	41.0	455
11	856.0	186.9	286.5	363.3	0.17	43.0	472
12	852.0	173.1	269.5	349.6	0.13	40.0	481
13	855.0	176.2	269.3	348.0	0.15	42.0	464
14	855.0	175.7	275.7	352.4	0.15	41.0	461
15	851.0	180.3	275.9	360.0	0.16	42.0	477
BLEND	858.0	187.2	281.3	359.8	0.16	45.0	472

to elute all heavier compounds present in all samples. In all experiments, the goal was to achieve an acceptable chromatographic resolution in the shortest possible analysis time, which is recommended for routine applications in quality control.

In the second factorial design, the same global resolution criterion was used to study the improvement of the injector conditions and to analyze its effect on the system using three different sample aliquots: 0.3, 0.6 and 1.0 μL , injected in three split modes: 1:100, 1:150 and 1:250. The experimental data were processed using Statistic 6.0 software (Statsoft Co., Tulsa, OK) (32), which generated all response surfaces.

Chromatographic validation

The optimized method was validated by its sensitivity, linearity, precision and limits of detection and quantification, in

accordance with recommendations of the Brazilian National Institute of Metrology, Standardization and Industrial Quality (INMETRO) (33) and other publications (34, 35). A mixture of different alkanes standards in isooctane were used in equal amounts (w/w): dodecane (C12), tetradecane (C14), hexadecane (C16), octadecane (C18), docosane (C22) and triacontane (C30). All standards were of chromatographic grade ($\geq 99\%$ purity) and were obtained from Fluka Chemica (Buchs, Switzerland). The concentrations for each compound varied between 0.02 and 2% (m/m). These working solutions were obtained through successive dilutions of the original solutions and injected in triplicate.

Results and Discussion

Selection of diesel samples for GC analysis

The application of HCA allowed 15 representative samples of the different clusters (Figure 1) to be selected proportionally: five from the dark-green cluster, six from the red cluster and four from the light-green cluster. They were chosen according their least similarity related to the ANP physicochemical parameters. This selection minimized the total time and cost of the chromatographic analyses and were representative data sets. Table I shows the characteristics of the samples selected by HCA, including a blend with all 15 samples. All samples were compliant with ANP specifications. From among the representative diesel samples selected by HCA, it was possible, through preliminary chromatographic analysis, to select one sample (number 12) that showed greater complexity; in other words, the highest number of chromatographic peaks (Table I). The blend did not show the larger number of peaks because the less concentrated compounds may have been diluted in the rest of the diesel array. In this way, it was possible to visualize the worst global resolution obtained from this complex chromatographic fingerprinting, and therefore optimize the system.

Optimization of chromatographic analysis

The chromatogram of the more complex sample obtained with the initial conditions was divided in three parts: the first with a low resolution, the second with intermediate resolution and the third with a very high resolution due to the elution of a homologous hydrocarbons series, with wide range of separation. In each region, the partial resolutions (Table II) were obtained by the sum of pair-wise resolutions and realized in the global resolution. In some peak pairs, overlapping occurs between a few peaks. However, in the pair-wise resolutions, the overlapping was never ignored or assumed to constitute a single peak and, therefore, all detected peaks were used in calculation of the resolutions. Experimental design was performed to improve the chromatographic resolution in a short running time, with the detection of a larger number of peaks (free of overlaps).

The three-level full factorial design performed to optimize carrier gas flow rate and oven heating ramps and the two extra experiments made after that are described in Table III. In this table, the responses are given as the chromatographic global and partial resolution, and their correlation with the quantitative chromatographic peaks. These data were utilized to

Table II
Data obtained with the Initial Conditions

Flow Rate (mL.min ⁻¹)	Time (min)	Global Resolution	Partial Resolution			Heating Ramp (°C.min ⁻¹)	Peaks
			1	2	3		
3.04	140	2.65	1.85	1.90	9.77	2	373

Table III
Design Matrix and Results of Both Partial and Global Resolutions and Number of Peaks

Flow Rate (mL.min ⁻¹)	Heating Ramps (°C.min ⁻¹)			Partial Resolution			Global Resolution	Peaks
	1	2	3	1	2	3		
	0.83 (-)	2 (+)	2 (+)	2 (+)	2.05	1.57	5.71	2.49
	3 (0)	4 (0)	7 (0)	1.94	1.28	2.57	1.97	351
	5 (-)	6 (-)	10 (-)	1.99	1.24	2.15	1.87	300
1.56 (0)	1	4	12	2.09	1.82	3.09	2.30	433
	2 (+)	2 (+)	2 (+)	1.99	1.78	7.17	2.60	390
	3 (0)	4 (0)	7 (0)	1.87	1.41	3.30	2.12	397
	5 (-)	6 (-)	10 (-)	1.93	1.28	2.38	1.93	363
	7	4	15	1.97	1.18	2.72	1.87	362
3.04 (+)	2 (+)	2 (+)	2 (+)	1.85	1.90	9.77	2.65	373
	3 (0)	4 (0)	7 (0)	1.86	1.44	3.33	2.11	384
	5 (-)	6 (-)	10 (-)	1.82	1.20	2.40	1.84	383

generate the response surfaces to improve resolution and the number of peaks obtained.

For the three parts in which the chromatograms were divided with different heating ramps, partial resolution values were observed to be very high, between 1.20 and 9.77, while the global resolution varied between 1.84 and 2.65. Nevertheless, the long analysis time (140 min) is not recommended for routine applications and must be improved. Therefore, the goal was to achieve an acceptable chromatographic resolution ($1.2 \leq R_s \leq 1.5$) in the shortest possible analysis time.

The carrier gas flow rate was defined as 1.56 mL/min (300 kPa) for this method, a value that, together with the values to be set to heating ramps, provide partial resolutions appropriate for analysis of diesel oil samples, as shown in Figure 2.

Figure 2A shows that the maximum of the partial resolution is observed at approximately 1°C/min. It decreases until values near 4°C/min and increases again, with another maximum at approximately 8°C/min. This may be because with the increasing heating and flow rate, peaks grow closer and coelute. In consequence, the separation of this pair of coeluted peaks and an adjacent one becomes greater, increasing the partial resolution values. A heating ramp of 2°C/min was chosen for the first part of the chromatogram because with these values, the respective partial resolution is satisfactory.

Figure 2B shows that partial resolution values assume greater values for smaller heating ramps and decreases with increasing ramps. For values greater than 7°C/min, there is a tendency for the resolution to assume greater values, probably due to the coelution between peaks. Therefore, a heating ramp of 4°C/min was chosen for the second part of the chromatogram to avoid coelution, despite a minimum resolution in the response surface, because their values become somewhat larger than 1.5, suitable for chromatographic analysis.

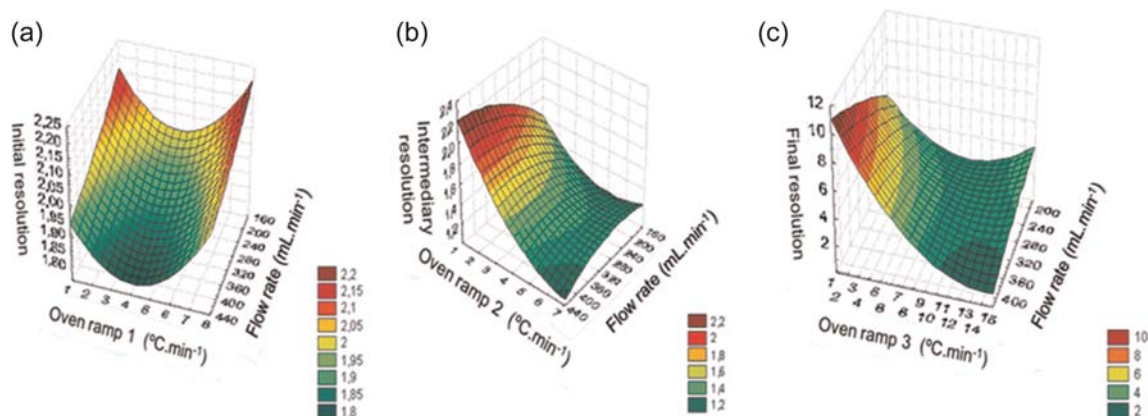


Figure 2. Three-dimensional response surface plot considering partial chromatographic resolution as analytical response: initial resolution (A); intermediary resolution (B); final resolution (C).

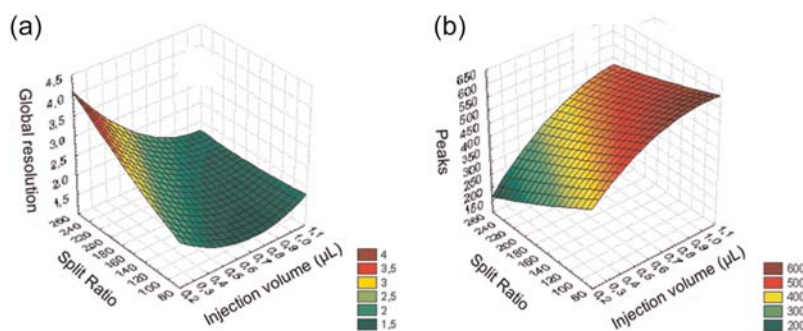


Figure 3. Three-dimensional response surface plot considering peak numbers and global chromatographic resolution as analytical responses using split ratio and injection volume variables.

Figure 2C shows the same behavior: decreasing in resolution when greater heating ramps are utilized. A heating ramp of 12°C/min was chosen for the same reason: detection of more peaks with suitable resolution.

Because diesel oil has heavier compounds, the duration of the final isothermal temperature was defined as 30 min. Finally, in the second factorial design, the experimental design was performed to improve two variables of the injector: volume injection and split ratio. Three levels were studied for both parameters, which were 0.3, 0.6 and 1.0 µL for volume injection and 1:100, 150 and 1:250 for split ratio. According to the chromatograms obtained, the global resolutions were calculated and then the response surfaces were elaborated for both global resolution and number of the peaks, as shown in Figure 3.

A volume of 0.4 µL and a split ratio of 1:100 were chosen because under these conditions, a large number of peaks are guaranteed to be detected; additionally, column saturation is avoided by injecting large amounts of the sample, thus increasing the useful life of the chromatographic system.

The experiment performed under improved conditions resulted in the fingerprinting chromatogram (Figure 4), with a 108-min analysis time and satisfactory global resolution ($R_s \approx 2.65$), and is therefore being recommended for routine applications. Moreover, almost 481 chromatographic peaks were detected in the analysis of representative Brazilian commercial diesel samples. This methodology, when compared to the

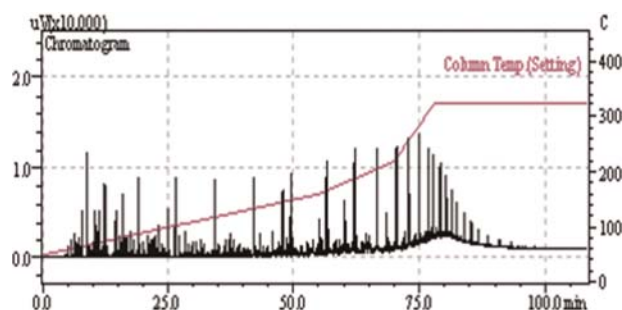


Figure 4. GC-FID fingerprints of Brazilian commercial gasoline performed under optimized analytical conditions. Column, DB-Petro by J&W Scientific (50 m × 0.15 mm i.d. × 0.50 µm); injector, split 1:100, 300°C; injection volume, 0.4 µL; flow of carrier gas, He, 1.56 mL/min; oven temperature, 50°C at 2°C/min, then to 160°C at 4°C/min, then to 220°C at 12°C/min, finally to 320°C (30 min); detector, FID, 300°C.

initial conditions, shows reduced analysis time and better chromatographic resolution, which improves the peak identification and quantification, even when applied to complex matrices like diesel fuels.

Method validation

GC-FID fingerprinting determination is not a quantitative method. The identification and interpretation of GC

Table IV

Validation parameters evaluated in the optimized method

Standards	Calibration Curve	r^2	LOD ($\mu\text{g.g}^{-1}$)	LOQ ($\mu\text{g.g}^{-1}$)	Precision RSD (%)
C₁₂	$y = -254.95 + 42021.63x$	0.99993	0.013	0.039	1.904
C₁₄	$y = -195.20 + 41309.53x$	0.99993	0.013	0.039	0.783
C₁₆	$y = -203.98 + 41603.95x$	0.99989	0.016	0.048	1.046
C₁₈	$y = -245.31 + 41947.84x$	0.99986	0.019	0.057	1.331
C₂₂	$y = -337.15 + 41837.37x$	0.99982	0.020	0.060	1.527
C₃₀	$y = -221.56 + 42314.76x$	0.99990	0.015	0.045	1.735

Note: y: peak height; x: concentration ($\mu\text{g.g}^{-1}$); r^2 : determination coefficient; LOD: limit of detection; LOQ: limit of quantification

fingerprints, is largely a qualitative practice and dependent upon the skill and experience of the individual(s) involved. The performance characteristics and validation aspects are different from general assaying methods. The authentication and identification can be accurately performed using the chromatographic fingerprints obtained, even if the batches or the concentrations are not the same in different samples.

Six paraffin standards were chosen, light, intermediate and heavy, representative of the three parts selected for the validation of the chromatographic method. These paraffins were: C₁₂, C₁₄, C₁₆, C₁₈, C₂₂ and C₃₀. The selection criteria for paraffins was that each paraffin eluted in a range of heating rates of the chromatographic run, and constitute the predominant class of hydrocarbons in the diesel matrix.

The improved method in the GC system was evaluated by linearity, sensitivity, intra-day repeatability calculated as relative standard deviation (RSD) and limit of detection (LOD) and quantification (LOQ). All of these results are shown in Table IV.

The analytical curves showed good linearity for all standards in the concentration range of 0.02–2% m/m ($n = 5$ points). Linearity for all components of the mixture is satisfactory in the concentration range studied, because all components show correlation coefficient values (r) higher than 0.99, the minimum acceptable (33). Sensitivities were very similar because the FID is very sensible to organic molecules and the standards have low volatilities. The intra-day repeatability represents an estimate of the variability of the measurements done on the same day. This was described as the value of the RSD, the standard deviation as a percentage of the mean calculated concentration ($n = 3$ replicates). Results are considered satisfactory because they are within the limits accepted by the recommendations for validation of chromatographic methods, in which precision has to be set $\pm 15\%$ (33). The LOD, defined as a signal equal to three times the baseline noise, and the LOQ, defined as signal equal to 10 times the baseline noise, were obtained for all standards present in the paraffin mixture ($n = 3$ replicates). LOD is equal to or smaller than 0.020% m/m and LOQ is to equal or smaller than 0.060%. Hydrocarbons belong to the same class and show very similar LOD and LOQ, because they exhibit the same behavior in terms of ionization and their responses are very close.

Therefore, due its robustness when samples with different compositions are analyzed, the methodology can be applied as an alternative method for the quality control of Brazilian commercial diesel oil.

Analytical application

Other work in our lab has been reported for the development, optimization and validation of chromatographic parameters for the analysis of commercial gasoline samples (21). With the established conditions, the fingerprinting method was coupled with multivariate pattern recognition and regressions to screen the quality of Brazilian commercial gasoline (23, 24) and to predict several physicochemical parameters (28). The developed method is an alternative, simple, fast and efficient way to trace the quality and authenticity of commercialized fuels and is recommended for routine applications in quality control monitoring programs.

Conclusion

The experimental design allowed the development and optimization of an efficient and fast chromatographic method for the separation of constituents of diesel fuel samples by a programmed temperature capillary column. RSM is a powerful tool for modelling a large amount of responses in a given experimental domain. The developed method is recommended for routine applications, because global and partial resolution were satisfactory and the total analysis time is less than 110 min for the complex mixtures of diesel fuel; additionally, the method presents good validation results. The best conditions for the chromatographic analysis were as follows: injector and detector temperature, 300°C; injection volume, 0.4 μL ; He carrier gas pressure, 300 kPa and split ratio, 1:100; oven temperature, 50°C, increased 2°C/min to 160°C, increased 4°C/min to 220°C and, finally, increased 12°C/min to 320°C, maintained 30 min; with column DB-Petro 50 m, 0.20 mm in diameter and 0.50 μm dimethylpolysiloxane internal coating; and total time of analyses, 108 min.

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