

Cite this: *Analyst*, 2012, **137**, 5919

www.rsc.org/analyst

PAPER

# A study of adulteration in gasoline samples using flame emission spectroscopy and chemometrics tools

Jaqueline M. de Paulo,<sup>a</sup> Gisele Mendes,<sup>a</sup> José E. M. Barros<sup>b</sup> and Paulo J. S. Barbeira<sup>\*a</sup>

Received 2nd April 2012, Accepted 27th September 2012

DOI: 10.1039/c2an35441a

This work presents a low cost system based on Flame Emission Spectroscopy (FES) that enables the prediction of fuel adulteration. The spectral data acquired using FES were associated with chemometric tools – Partial Least Squares Discriminant Analysis (PLS-DA) and Partial Least Squares (PLS), aiming to predict gasoline adulterations with different solvents. The classification of the Brazilian adulterated gasoline samples with turpentine, thinner, kerosene, rubber solvent and ethanol was carried out through a PLS-DA model built using five latent variables (LV) with an accumulated variance of 100% on *X* and 76.78% on *Y*. The combination of these techniques provided the discrimination of distinct groups for each one of the studied adulterants. Subsequent to the classification, samples of adulterated gasoline with the same solvents with contents varying from 1 to 50% (v/v) were analyzed through FES and multivariate calibration curves were employed in order to predict the contents of the respective solvents. The results obtained by the combination of FES and PLS provided the determination of gasoline adulterants with small calibration and validation errors and also lower values than the ones reported in the literature using other spectroscopic techniques.

## 1. Introduction

The adulteration of automotive gasoline with low cost solvents is a common practice in many parts of the world.<sup>1</sup> In Brazil, the commercialization of solvents often does not involve additional taxes or these are very low; on the other hand, fuels are suffering high taxation from the State, and thus these products become more expensive in relation to other solvents. Furthermore, other factors that favor this practice are how solvents are easily acquired in the market and their high solubility in gasoline.<sup>2</sup> The addition of illegal compounds to fuels can lead to serious losses to the consumer, such as, environmental risks due to the increase of vapor and toxic gas emission like CO and NO<sub>x</sub>, lower durability of the vehicle engines and also unfair competition in fuel prices causing states to lose in tax collection.

The most commonly used solvents in gasoline adulteration include diesel oil, kerosene and refined petrochemicals, excessive amounts of ethanol, toluene, xylene, hexane, among other solvents from the light aliphatic class such as rubber solvent (C6–C8), aromatics and heavy aliphatics like turpentine (C13–C15) and kerosene (C19–C16).<sup>3</sup>

There is a great struggle in identifying adulteration in gasoline, which is related to the fact that the majority of the industrial

solvents used in this practice are themselves constituents of gasoline.<sup>4</sup>

Thus, in order to ensure quality control of fuels in Brazil, the National Agency of Petroleum, Natural Gas and Biofuels (ANP – *Agência Nacional do Petróleo, Gás Natural e Biocombustíveis*) regulates and inspects fuels through the analysis of some physicochemical properties.<sup>5</sup> Moreover, the ANP invested in a program which marked the solvents, thus establishing the mandatory addition of markers to solvents and other products, as well as, the prohibition of markers in gasoline.<sup>6</sup> In this way, the detection of the marker in gasoline indicates that it has been adulterated with some kind of solvent, although it is a rather laborious process, which requires a 20 min chromatographic analysis, a tight logistic for the markers, and the monitoring process which becomes highly expensive.

Besides the standard methods designated by the ANP, several works in the literature have been described using techniques for the determination of adulteration in fuels. Among them the most commonly used techniques are the Fourier transform infrared spectroscopy (FTIR),<sup>7–13</sup> nuclear magnetic resonance (NMR),<sup>14,15</sup> Raman spectroscopy<sup>16,17</sup> and gas chromatography (GC).<sup>4,18</sup>

These techniques give rise to multivariate data, while statistical methods for univariate systems become insufficient for the treatment of the data generated.<sup>19</sup> Thus, chemometric methods such as Partial Least Squares (PLS), Principal Component Regression (PCR), Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA) have been employed

<sup>a</sup>Departamento de Química, Universidade Federal de Minas Gerais, Minas Gerais, MG, Brazil. E-mail: barbeira@ufmg.br

<sup>b</sup>Escola de Engenharia, Universidade Federal de Minas Gerais, Minas Gerais, MG, Brazil

combined with conventional methods, enabling the acquirement of more data information.<sup>20–22</sup>

The scientific literature has reported a large number of studies demonstrating the broad application of chemometric methods in conjunction with various conventional analytical techniques of gasoline analysis to detect adulteration.

Pereira *et al.*,<sup>1</sup> employed PCA and Linear Discriminant Analysis (LDA) in conjunction with FTIR to identify adulterated samples and the type of solvent used in the adulteration. In another study, the Soft Independent Modelling of Class Analogy (SIMCA) was applied to data obtained through infrared spectroscopy by Teixeira *et al.*<sup>23</sup> in screening gasoline. Wiedemann *et al.*<sup>4</sup> conducted a study to detect adulteration in gasoline samples using the results obtained from the physico-chemical data and gas chromatography of the samples combined with HCA. Monteiro *et al.*<sup>14</sup> used hydrogen nuclear magnetic resonance (<sup>1</sup>H NMR) of samples of commercial gasoline with PCA and HCA to distinguish between conform and nonconform samples. The results showed that there is a tendency for nonconform samples to group with the increase of content solvent added.

Another simple technique used in fuel studies is flame emission spectroscopy (FES).<sup>24,25</sup> This technique enables the radicals present in the flame, as well as, the large number of species formed in the presence of metals to be detected in various wavelengths.

The radiation emission of these radicals is known as chemiluminescence. In hydrocarbon fuel flames, the most intense emissions are associated with C<sub>2</sub>\*, CH\* and OH\* species. The asterisk denotes the electronic state associated with each molecule.

The characterization of these radicals present in hydrocarbon flames is widely studied and described by quite complex kinetic models involving a variety of reactions triggered by free radicals formed in the steps of initiation and propagation reactions during combustion. Generally, models representing methane combustion, the simplest hydrocarbon chain used as a flame in this work, use more than 300 reactions<sup>26–28</sup> to define combustion products, which demand a computationally great task. Even more complex models are described for long chained hydrocarbons, as is the case with gasoline and the solvents used in adulterations proposed by this study.

Thus, in order to meet the need for evaluating the quality of fuels, this paper aims to propose an analytical method able to classify and quantify the adulteration of fuels with solvents by combining FES with the chemometric techniques Partial Least Squares Discriminant Analysis (PLS-DA) and Partial Least Squares Regression (PLS) for the classification and prediction of adulteration levels of solvents present in Brazilian gasoline.

## 2. Materials and methods

The samples were prepared by adding ethanol, 25% (v/v), to a gasoline A (hydrocarbon mixture without ethanol) from REGAP (Refinaria Gabriel Passos – Petrobras). Then different solvents (turpentine, thinner, kerosene, rubber solvent and ethanol) were added in concentrations of 0 to 50% (v/v) totaling 250 samples. Petrobras provided all the solvents too, with the exception of the thinner, which was acquired in local trade (Dissolminas 3500).

The analytical signals were obtained from the continuous emission spectra recorded by an EPP 2000 spectrometer (StellarNet, Inc.), in the range of 260–860 nm. The emission spectra were obtained by burning the samples in a laminar flow burner, using synthetic air as the oxidant and methane as the fuel, operational conditions of which are described in Table 1.

For each (*n*) sample the obtained spectra were organized into a data matrix so that a row vector (*n* × 1219) was built for each sample. All the data were mean centered and treated using PLS-DA.

The models were built with the matrices considering the intensity of all the generated signals. Cross-validation “leave-one-out” and external validation were used to validate the PLS-DA model. The Kennard–Stone algorithm was used to select samples of the calibration and validation sets, using 167 samples for calibration and 83 samples for the validation of the model. The choice of the number of latent variables was made based on the lowest Root Mean Square Error Cross Validation (RMSECV) value.

Subsequent to the classification, PLS models were built for each solvent – turpentine, kerosene, thinner, rubber solvent and ethanol – individually. 50 samples were prepared with concentrations in the range of 0–50% (v/v) as previously described. The Kennard–Stone algorithm was employed to build the PLS models, using 33 samples for the calibration set and 17 for the validation of the model. The data were mean centered. Cross-validation “leave-one-out” and external validation were used for the validation of the model.

## 3. Results and discussion

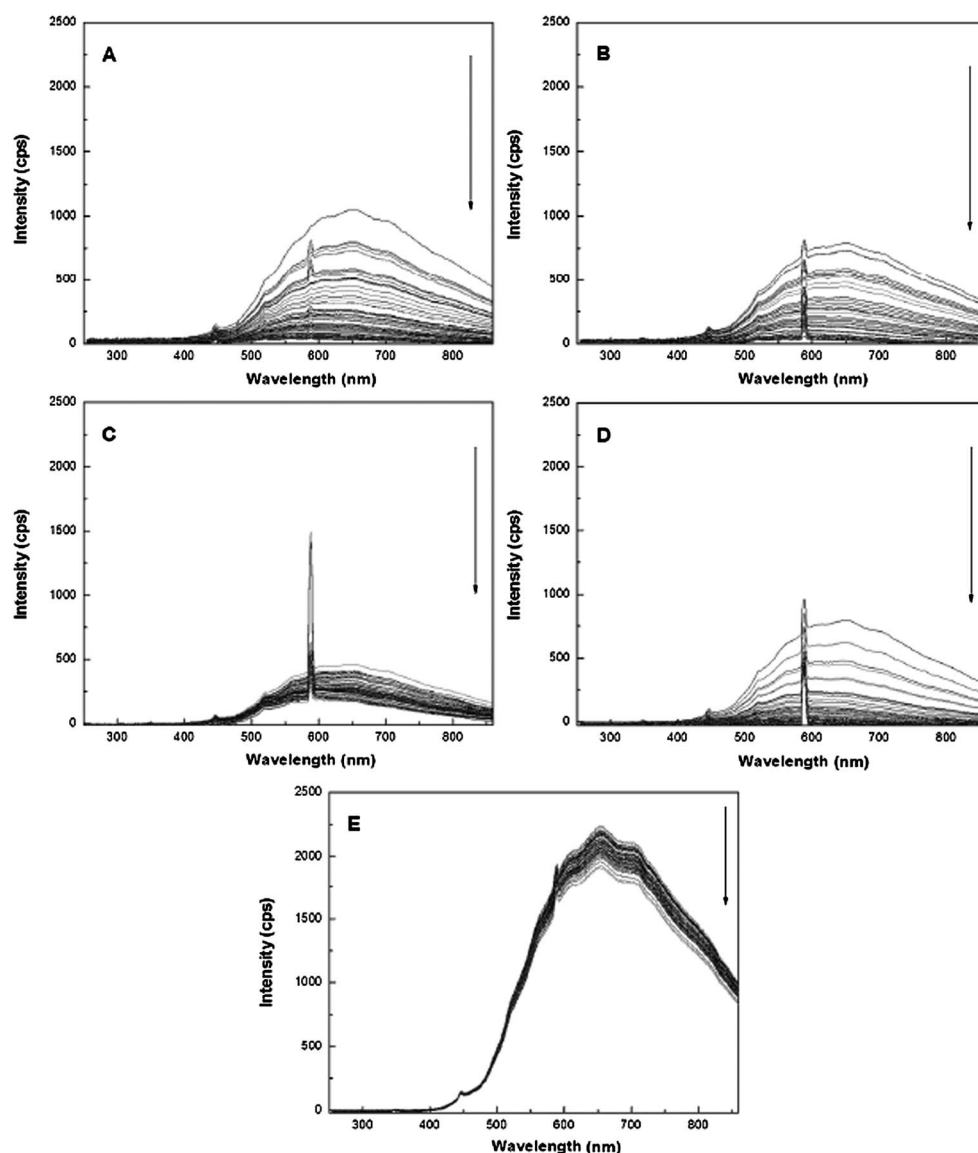
The spectra recorded for the samples of adulterated gasoline with different solvents are shown in Fig. 1. It is possible to detect the species formed during the burning of gasoline, forming different radicals from the fragmentation of the molecules in the flame. However, most signals overlap, forming spectra recorded as continuous emission characteristic of black-body spectra, but dependent on the type of sample present in the flame, the pressure conditions, type of spray, flame temperature, among other factors that interfere with the emission of radicals.

In all spectra (Fig. 1), there is a peak at near 575 nm assigned to the emission of the C<sub>2</sub>\* radical, that corresponds to the vibration band of the 3Π<sub>g</sub>–3Π<sub>u</sub> electronic transition. Sometimes this band is enhanced by the overlapping signal of sodium (580 nm) originating from contamination from the production system and the storage of ethanol,<sup>29</sup> which is present in high concentrations in the thinner (Fig. 1C). In general, the presence of these

**Table 1** Experimental conditions for flame emission spectrometry

Parameter	Condition
Air flow rate <sup>a</sup>	1.25 NLPM
Fuel flow rate <sup>b</sup>	11.00 NLPM
Sample flow rate	1.0 mL min <sup>−1</sup>
Air pressure	1.25 bar
Fuel pressure	5.50 bar

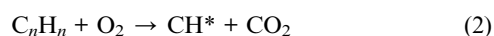
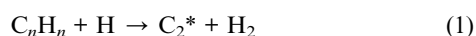
<sup>a</sup> Synthetic air (79% v/v N<sub>2</sub> and 21% v/v O<sub>2</sub>). <sup>b</sup> CH<sub>4</sub> (89% v/v).



**Fig. 1** Emission spectra obtained for gasoline samples doped with different solvents. (A) Kerosene; (B) turpentine; (C) thinner; (D) ethanol; (E) rubber solvent. Arrows indicate the increase in the concentration of solvents added.

signals is very important and allows differentiation of the spectra of samples doped with different solvents.

In the spectra recorded for all solvents (Fig. 1) there is also a signal of low intensity, at 350 nm and 450 nm, assigned to  $C_2^*$  radicals. The results shown in Fig. 1 are in agreement with the literature, where usually the combustion reactions of hydrocarbons are presented following the formation of  $C_2^*$  and  $CH^*$  radicals and are commonly described by eqn (1) and (2).



According to eqn (1) the formation of the  $C_2^*$  radical is related to the presence of H which is produced in high quantities in flames with excessive amounts of fuels like the gasoline flames studied in this work.<sup>30</sup> The formation of  $CH^*$  radicals described in eqn (2) depends on the presence of oxygen in the flame. The

emission spectra obtained for adulterated samples with different solvents are due to the formation of these radicals in the flame.

In the case of heavy aliphatic solvents, such as turpentine (C13–C15) which is a kerosene fraction (C9–C16), the formation of these radicals follows similar kinetic mechanisms, which leads to very similar spectra (Fig. 1A and B).

Moreover, different kinetic mechanisms are responsible for the formation of radicals in samples doped with rubber solvent which comprises of light aliphatic solvents (C6–C8), olefins and saturated compounds in concentrations higher than those observed in other solvents studied. In this case, the high intensity of the signals obtained for samples doped with rubber solvent is due to the high concentration of radicals in the flame, allowing the differentiation of this class of adulterant from the others.

In general, the identification of adulterations is not an easy task. In many cases the bands due to the transitions of each species overlap and the identity of each becomes quite difficult.

**Table 2** Percent variance captured by the regression model (PLS-DA)

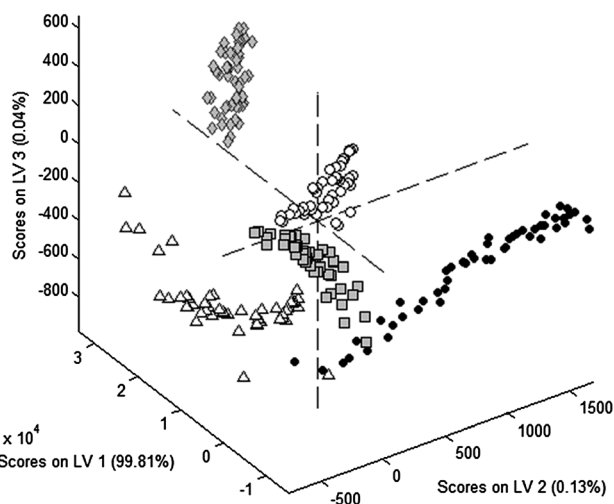
Latent variable (LV) number	X-Block		Y-Block	
	Explained variance	Accumulated variance	Explained variance	Accumulated variance
1	99.81	99.81	21.20	21.20
2	0.13	99.93	20.51	41.71
3	0.04	99.97	17.32	59.03
4	0.02	99.99	16.04	75.07
5	0.01	100.00	1.70	76.78

Thus, the spectral data (Fig. 1) were treated using the PLS-DA chemometric tool.

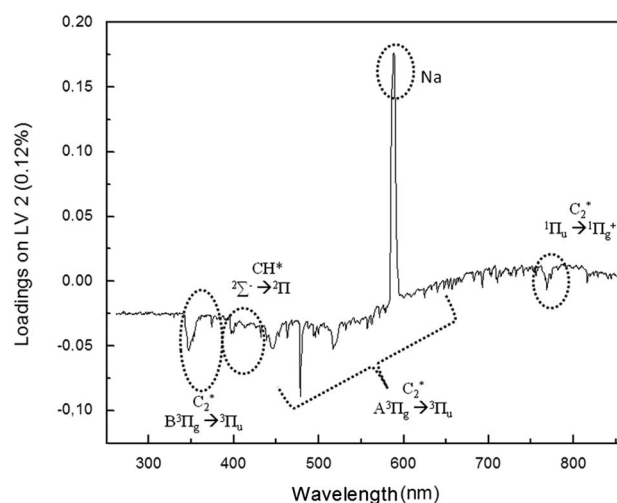
Initially, the signals obtained for each solvent were arranged in a matrix of data, as described above. To build the PLS-DA model, the choice of latent variables was based on small values of RMSECV. Thus, five Latent Variables (LV) were used to build the PLS-DA model allowing a cumulative variance of 100% in *X* and 76.78% *Y* (Table 2).

The graph of scores, shown in Fig. 2 indicates that the first latent variable (LV1) is responsible for separating the set of samples doped with the rubber solvent from the samples doped with ethanol, turpentine and thinner. In the same figure, it is observed that LV2 is responsible for separating the set of samples doped with rubber solvent from those doped with kerosene and turpentine, while LV3 is responsible for the separation of samples doped with ethanol, kerosene, turpentine and thinner.

The classification found for each class of solvents (Fig. 2) can be explained through the loading graphs at LV2 and LV3. As shown in Fig. 3 and 4, the signals responsible for the classification obtained in the model using the PLS-DA are mainly due to the presence of  $C_2^*$  radicals. The bands of  $C_2^*$  radicals, known as the Swan system, are observed at 473.7, 516.2 and 563.5 nm, and are formed during the combustion of fuel-rich mixtures, as described in eqn (1).<sup>34</sup> In some cases there is an overlap near 563.5 nm influenced by sodium concentration in the samples doped with different solvents. As discussed above, samples



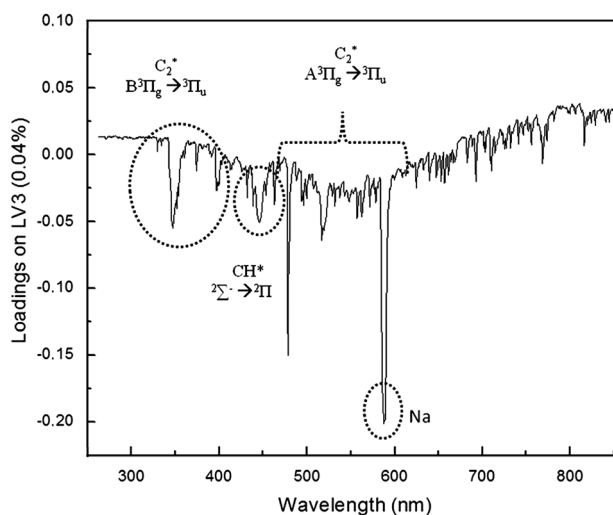
**Fig. 2** Graph of scores of the first three principal components obtained for gasoline samples doped with different solvents. ( $\Delta$ ) kerosene; ( $\blacksquare$ ) thinner; ( $\bullet$ ) ethanol; ( $\circ$ ) turpentine; ( $\blacklozenge$ ) rubber solvent.



**Fig. 3** Graph of loadings (LV2) obtained for gasoline samples doped with different solvents and analyzed by flame emission spectroscopy.

doped with ethanol and thinner exhibit significantly higher concentration of sodium than other solvents. Analyzing the spectroscopic profile obtained for samples doped with rubber solvent it appears that the  $C_2^*$  peak (563.5 nm) is almost fully overlapped by the presence of other radicals in the flame (Fig. 1E). In samples doped with kerosene and turpentine (Fig. 1A and B) spectral differentiation is only possible through the use of PLS DA (Fig. 2).

So the most important variable is characterized by transitions observed for the radical  $C_2^*$ . In wavelengths ranging from 450 to 580 nm it is possible to verify the transition  $A^3\Pi_g \rightarrow ^3\Pi_u$  with a significant contribution in LV2 (Fig. 3). For all other peaks, it appears that they present practically the same importance. The observed signal at 350 nm is due to transitions  $^1\Pi_g \rightarrow ^1\Pi_u$  of radical  $C_2^*$ . There is also a characteristic peak of the Phillips band system of 770 nm due to the transition  $^1\Pi_u \rightarrow ^1\Sigma_g^+$  observed in LV2. Low signal intensity is observed at 400 nm characteristic of the presence of radical  $CH^*$ .<sup>35,36</sup>



**Fig. 4** Graph of loadings (LV3) obtained for gasoline samples doped with different solvents and analyzed by flame emission spectroscopy.



**Table 3** Sensitivity and specificity by the PLS-DA model

Parameter	Kerosene	Turpentine	Thinner	Ethanol	Rubber solvent
Sensitivity (calibration)	1.000	0.971	1.000	1.000	1.000
Specificity (calibration)	1.000	1.000	0.956	0.970	0.993
Sensitivity (prediction)	1.000	1.000	1.000	1.000	1.000
Specificity (prediction)	1.000	1.000	0.937	0.984	0.983
Classification error (calibration)	0.000	0.015	0.022	0.015	0.003
Classification error (prediction)	0.000	0.000	0.032	0.008	0.008

**Table 4** RMSEC, RMSEP and  $R^2$  values, obtained in the determination of adulterants in gasoline by the PLS model

Solvent	$R^2$	RMSEC	RMSEP
Kerosene	0.996	0.92	0.97
Turpentine	0.996	0.88	0.93
Thinner	0.986	1.14	2.54
Ethanol	0.991	0.34	0.48

The main difference observed between samples doped with rubber solvent and those doped with kerosene and turpentine is due to the chemical composition since the former is characterized as a light aliphatic solvent while the latter are considered heavy aliphatic solvents. The separation between these classes of samples is strongly influenced by the presence of  $C_2^*$  radicals in the flame. The burning mechanisms for different classes of solvents follow different routes, allowing variations in the concentrations of these radicals to be detected spectrophotometrically, enabling the separation of these classes.

Similarly the transitions responsible for the separations observed in LV3 (Fig. 4) are largely due to the presence of the  $CH^*$  and  $C_2^*$  radicals from the fragmentation of heavy aliphatic solvents (turpentine and kerosene) and yet again characteristic contributions from the sodium peak, especially in samples doped with ethanol and thinner.

Table 3 shows the sensitivity and specificity parameters of the PLS-DA model. The results indicate 97% accuracy in predicting the samples adulterated with turpentine and 100% for samples doped with other solvents. The classification and validation errors for the entire set of samples were lower than 0.03% v/v.

Once the adulterant was identified and the transitions responsible for the separation of groups defined, PLS

multivariate calibration models were employed in order to quantify the content of each solvent added to the gasoline. The results combining FES and PLS are presented below. Table 4 shows the parameters obtained using PLS to quantify the presence of adulterants in gasoline samples.

The parameters obtained for the PLS model for each solvent show that the greatest errors of calibration (RMSEC) and validation (RMSEP) were observed for samples doped with the thinner. Nevertheless, both for samples doped with the thinner and those doped with kerosene the RMSEC and RMSEP values were lower than those reported in recently published papers using the GC and FTIR techniques (Table 5).

In this work, the PLS model for the samples doped with ethanol provided lower RMSEC and RMSEP values (Table 4) compared to the values obtained by other authors in the prediction of ethanol content in gasoline using different analytical tools.

In the same manner as observed in the prediction of the alcoholic content, thinner and kerosene, the present results for samples doped with turpentine present calibration and validation errors smaller than those obtained using FTIR (Table 5).

In general, results obtained by combination of FES and PLS enabled the determination of adulterants in gasoline, low calibration errors and prediction and even lower values than those reported in the literature using different spectroscopic techniques.

## 4. Conclusions

The classification of adulterated samples with different solvents is mainly due to the distribution of  $CH^*$  and  $C_2^*$  radicals and presence of sodium in the flame. Although this classification involves complex kinetic mechanisms of radical formation it is possible to be carried out with the combination of FES with chemometric tools such as PLS-DA without the need for detailing the kinetic models involved. In this work, PLS-DA provided the classification of a set of doped samples with kerosene, rubber solvent, thinner, turpentine and ethanol using five latent variables. Through the PLS-DA model it was possible to determine the sensibility and sensitivity with values close to one for all sets of samples, which indicates that the methodology proposed in this work is a good method of classification and prediction of adulterations in gasoline samples. Through the PLS model it was possible to propose calibration and validation models for several solvents. The results indicated RMSEC values smaller than one for all solvents and 1.14 only for samples adulterated with the thinner. Furthermore, the methodology proposed in this work can be employed with the aim to detect

**Table 5** Recent results obtained for PLS quantification of adulterants in gasoline

Solvent	RMSEC	RMSEP	Technique	Ref.
Kerosene		3.3	GC	31
Thinner		3.3		
Ethanol		8.2		
Turpentine	1.9	1.6	FTIR	23
Kerosene	1.8	1.6		
Thinner	1.8	1.6		
Ethanol		0.69	Distillation curves	29
Ethanol	0.38	0.68	FT-NIR and FT-Raman	32
Ethanol	2.7		Mass and capacitance transducers	33

gasoline adulterations in a fast, simple and low cost manner while using small volumes of samples.

## References

- 1 R. C. C. Pereira, V. L. Skrobot, E. V. R. Castro, I. C. P. Fortes and V. M. D. Pasa, *Energy Fuels*, 2006, **20**, 1097.
- 2 P. J. S. Barbeira, Using statistical tools to detect gasoline adulteration, *Eng. Térmica*, 2002, **2**, 48.
- 3 F. S. Oliveira, L. S. G. Teixeira, M. C. U. Araújo and M. Korn, *Fuel*, 2004, **83**, 917.
- 4 L. S. M. Wiedemann, L. A. d'Avila and D. A. Azevedo, *J. Braz. Chem. Soc.*, 2005, **16**, 139.
- 5 Agência Nacional de Petróleo, *Gás Natural e Biocombustíveis*, Portaria 309, 27/12/2001.
- 6 Agência Nacional de Petróleo, *Gás Natural e Biocombustíveis*, Portaria 274, 20/12/2002.
- 7 J. M. Andrade, S. Muniategui and D. Prada, *Fuel*, 1997, **76**, 1035.
- 8 D. R. Battiste, S. E. Fry, F. T. White, M. W. Scoggins and T. B. McWilliams, *Anal. Chem.*, 1981, **53**, 1096.
- 9 E. Bessler, *Ciênc. Cult.*, 1977, **28**, 928.
- 10 F. A. Honorato, B. B. Neto, M. F. Pimentel, L. Stragevitch and R. K. H. Galvão, *Fuel*, 2008, **87**, 3706.
- 11 J. J. Kelly, C. H. Barlow, T. M. Jinguji and J. B. Callis, *Anal. Chem.*, 1989, **61**, 313.
- 12 P. Valderrama, J. W. B. Braga and R. J. Poppi, *J. Agric. Food Chem.*, 2007, **55**, 8331.
- 13 J. L. Wong and B. Jaselskis, *Analyst*, 1982, **107**, 1282.
- 14 M. R. Monteiro, A. R. P. Ambrozini, L. M. Lião, E. F. Boffo, L. A. Tavares, M. M. C. Ferreira and A. G. Ferreira, *Energy Fuels*, 2009, **23**, 272.
- 15 J. Mühl and V. Srica, *Fuel*, 1987, **66**, 1146.
- 16 W. M. Arden, T. B. Hirshfeld, S. M. Klainer and W. A. Mueller, *Appl. Spectrosc.*, 1974, **28**, 554.
- 17 P. E. Flecher, W. T. Welch, S. Albin and J. B. Cooper, *Spectrochim. Acta, Part A*, 1997, **53**, 199.
- 18 V. L. Skrobot, E. V. R. Castro, R. C. C. Pereira, V. M. D. Pasa and I. C. P. Fortes, *Energy Fuels*, 2007, **21**, 3394.
- 19 R. G. Brereton, *Chemometrics: Data Analysis for the Laboratory and Chemical Plant*, John Wiley and Sons, England, 2003.
- 20 P. Geladi and B. R. Kowalski, *Anal. Chim. Acta*, 1986, **185**, 1–17.
- 21 P. J. S. Barbeira, R. C. C. Pereira and C. N. C. Corgozinho, *Energy Fuels*, 2007, **21**, 2212.
- 22 R. Kramer, *Chemometric Techniques for Quantitative Analysis*, New York, 1998.
- 23 L. S. G. Teixeira, F. S. Oliveira, H. C. Santos, P. W. L. Cordeiro and S. Q. Almeida, *Fuel*, 2008, **87**, 346.
- 24 D. Carinhana Jr, L. G. Barreta, C. A. Bertran and A. M. Santos, *J. Braz. Chem. Soc.*, 2010, **21**, 1770.
- 25 I. C. Heghie, C1–C4 Hydrocarbon Oxidation Mechanism, Dissertation, University of Heidelberg, Germany, 2006.
- 26 A. B. Bendtsen, P. Glarborg and K. Dam-Johansen, *Combust. Sci. Technol.*, 2000, **151**, 31.
- 27 C. K. Westbrook and F. L. Dryer, *Combust. Sci. Technol.*, 1981, **27**, 31.
- 28 J. Andersen, C. L. Rasmussen, T. Giselsson and P. Glarborg, *Energy Fuels*, 2009, **23**, 1379.
- 29 H. G. Aleme, L. M. Costa and P. J. S. Barbeira, *Talanta*, 2009, **78**, 1422.
- 30 D. Carinhana Jr, L. G. Barreta, C. J. Rocha, A. M. Santos and C. A. Bertran, *J. Braz. Chem. Soc.*, 2008, **19**, 1326.
- 31 M. P. Pedroso, L. A. F. Godoy, E. C. Ferreira, R. J. Poppi and F. Augusto, *J. Chromatogr., A*, 2008, **1201**, 176.
- 32 L. S. Mendes, F. C. C. Oliveira, P. A. Z. Suarez and J. C. Rubim, *Anal. Chim. Acta*, 2003, **493**, 219.
- 33 N. K. L. Wiziack, A. Catani, M. Santonico, A. D'Amico, R. Paolesse, L. G. Paterno, F. J. Fonseca and C. Di Natale, *Sens. Actuators, B*, 2009, **140**, 508.
- 34 C. A. Bertran, C. S. T. Marques and L. H. Benvenutti, *Combust. Sci. Technol.*, 1998, **139**, 1.
- 35 K. J. Laidler and K. E. Shuler, *Ind. Eng. Chem.*, 1951, **43**, 2758.
- 36 A. G. Gaydon, *The Spectroscopy of Flame*, London, 1957.