CHEMOMETRIC TOOLS ASSOCIATED TO FTIR AND GC-MS FOR THE DISCRIMINATION AND THE CLASSIFICATION OF DIESEL FUELS BY SUPPLIERS

I. BARRA*, M. KHARBACH, Y. CHERRAH, A. BOUKLOUZE

Pharmaceutical and Toxicological Analysis Research Team, Laboratory of Pharmacology and Toxicology, Faculty of Medicine and Pharmacy – Rabat, Morocco.

* E-mail: issam.barra@um5s.net.ma

Introduction

Since the beginning of the industrial era, oil has been massively used for energy production which caused a considerable pollution of the atmosphere. In this sense the quality of these products should be controlled and must meet the specifications and requirements of the market. The determination of several quality parameters of petroleum products recommended by national and international regulations requires a large number of physicochemical tests such: viscosity, distillation fractions, sulfur content, index cetane and octane number. These tests require sophisticated equipment, qualified personnel, cost and time consuming.

Spectroscopic techniques such as Mid Infrared Spectroscopy (MIR), Near Infrared Spectroscopy (NIR) and Raman, as well as chromatographic couplings (GC-MS) can be a suitable techniques instead the cited above for improving quality control of these products petroleum [1][2].

The aim of this work was to establish two PLS-DA models obtained from FTIR spectra and GC-MS data respectively and compare their suitability for the discrimination and the classification of diesel fuels by suppliers.

Samples collection

52 diesel samples were purchased from the 4 biggest brands (Afriquia, Shell, Total and Winxo) located in different regions of Morocco. The collection was made in 30ml glass vials and stored in suitable conditions before being analyzed.

Material and methods

A FTIR spectrometer (Bruker Optics, Ettlingen, Germany) connected to an attenuated total reflectance (ATR) accessory was employed to record the FTIR spectra in the range 4000–400 cm -1. A Thermo Electronics gas chromatograph coupled to mass spectrometer ISQ 7000 Single Quadrupole (Thermo Fisher Scientific wissenschaftliche Geräte GmbH, Inc., Austria) was used to collect GC-MS data.

Resultats

Classification By FTIR-PLS-DA

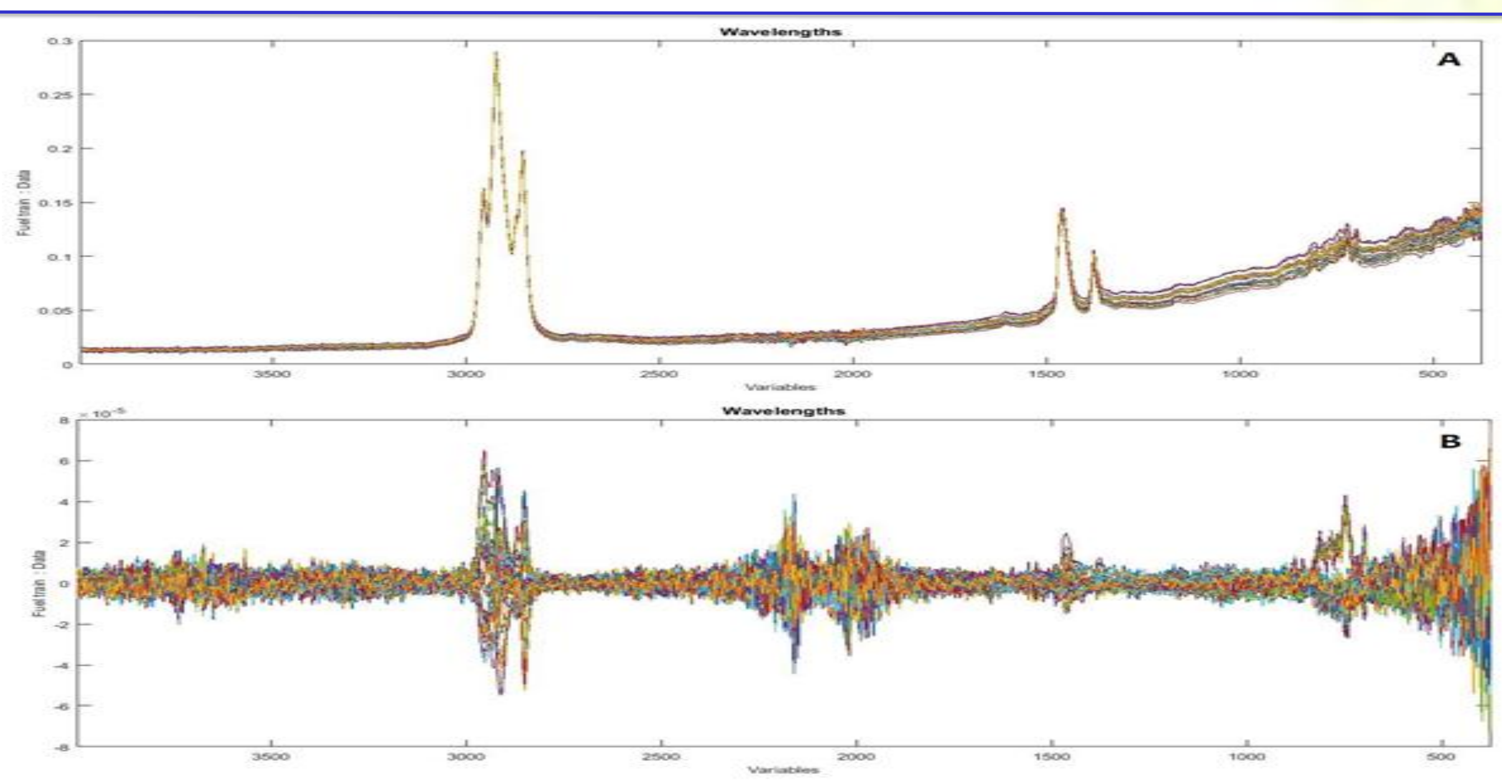

Figure 1. the effect of preprocessing techniques on the MIR-FTIR data. (A): before preprocessing, (B) after preprocessing.

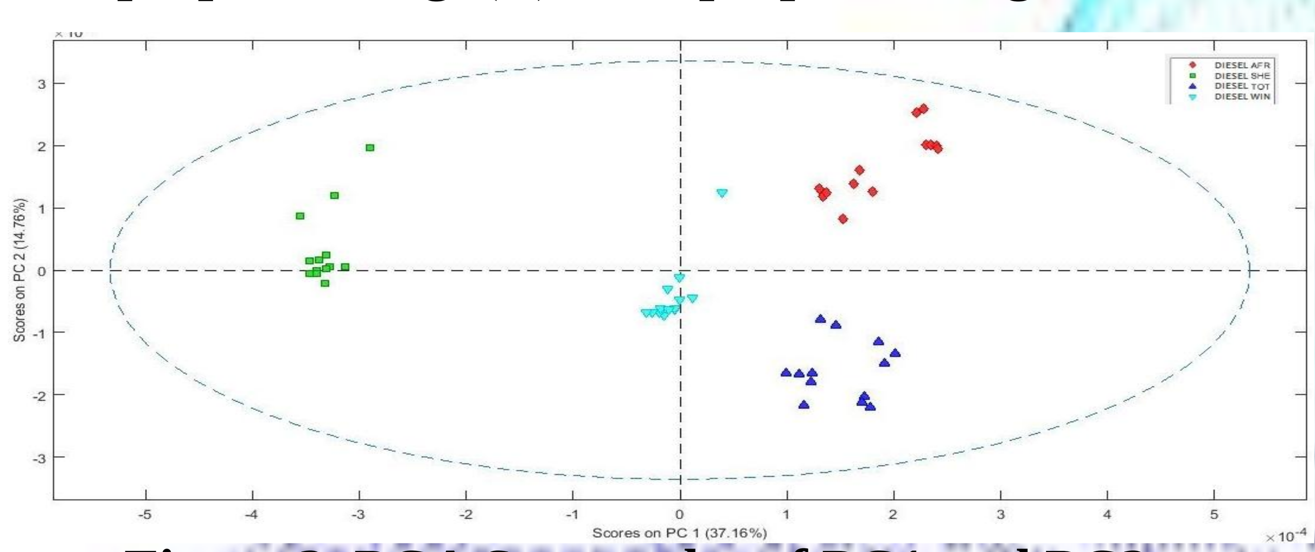

Figure 2. PCA Scores plot of PC1 and PC2

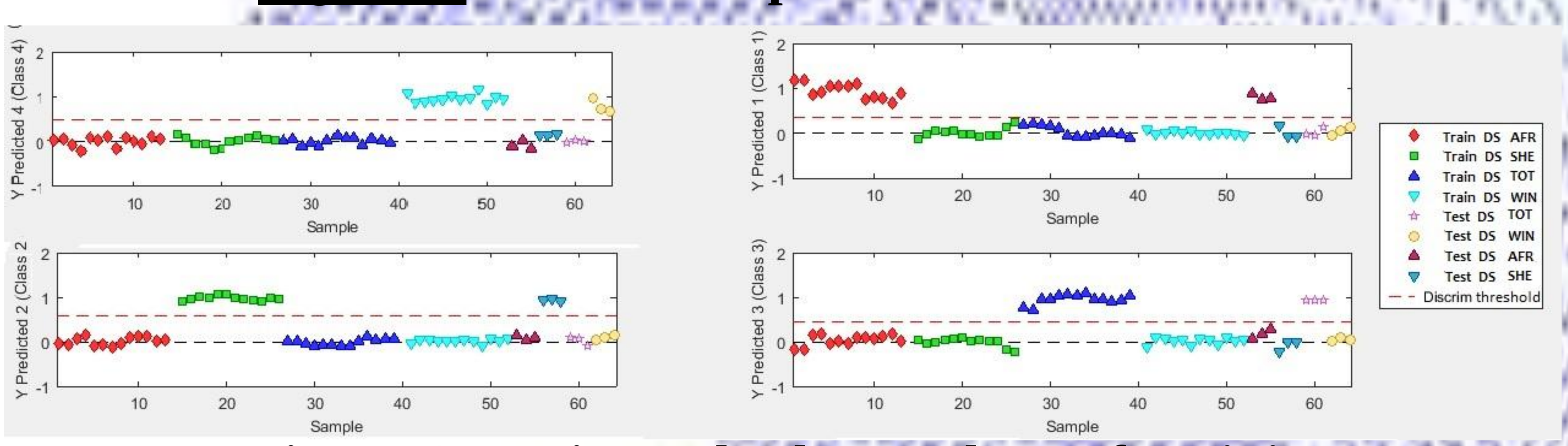

Figure 3. Estimated Class Values of training and test sets obtained by PLS-DA model

Tableau 1. paramètres de discrimination du modèle FTIR-PLS-DA

Param\Fuel	Diesel AFR	Diesel SHE	Diesel TOT	Diesel WIN
Latent variables	3	3	3	3
RMSEC	0.118901	0.0669197	0.102564	0.0928363
RMSEP	0.129968	0.0932471	0.126827	0.151776
Sensitivity (calibration model)	1.00	1.00	1.00	1.00
Specificity (calibration model)	0.973	1.00	1.00	1.00
Sensitivity (prediction model)	1.00	1.00	1.00	1.00
Specificity (Prediction model)	1.00	1.00	1.00	1.00
Threshold	0.358	0.568	0.458	0.497

Classification By GC-MS-PLS-DA

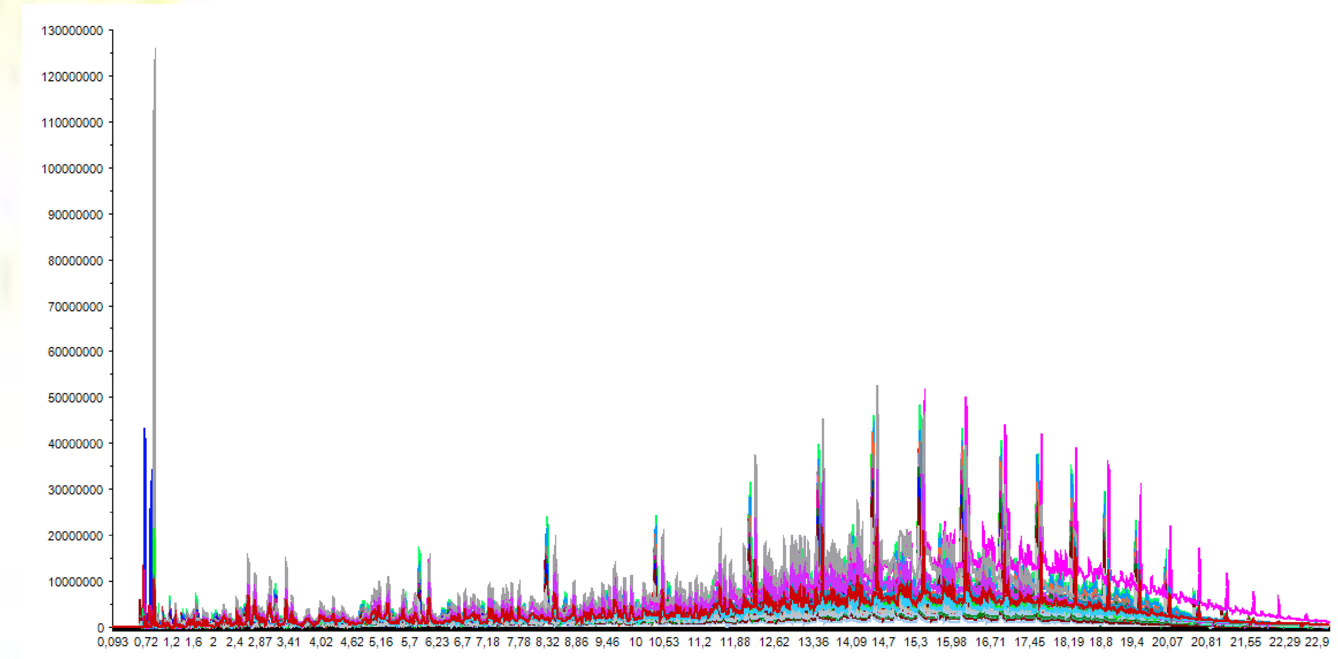

Figure 4. Chromatograms of diesel samples

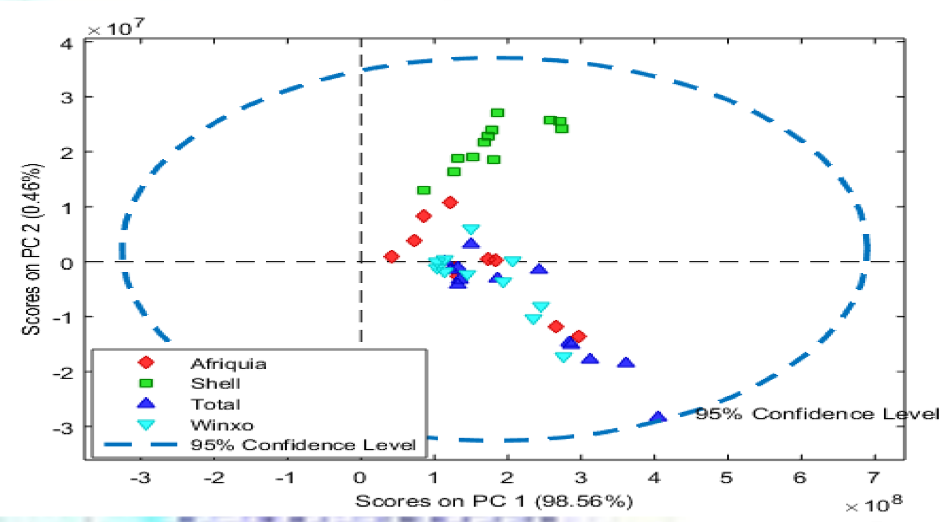

Figure 5. PCA scores plot of PC1 and PC2

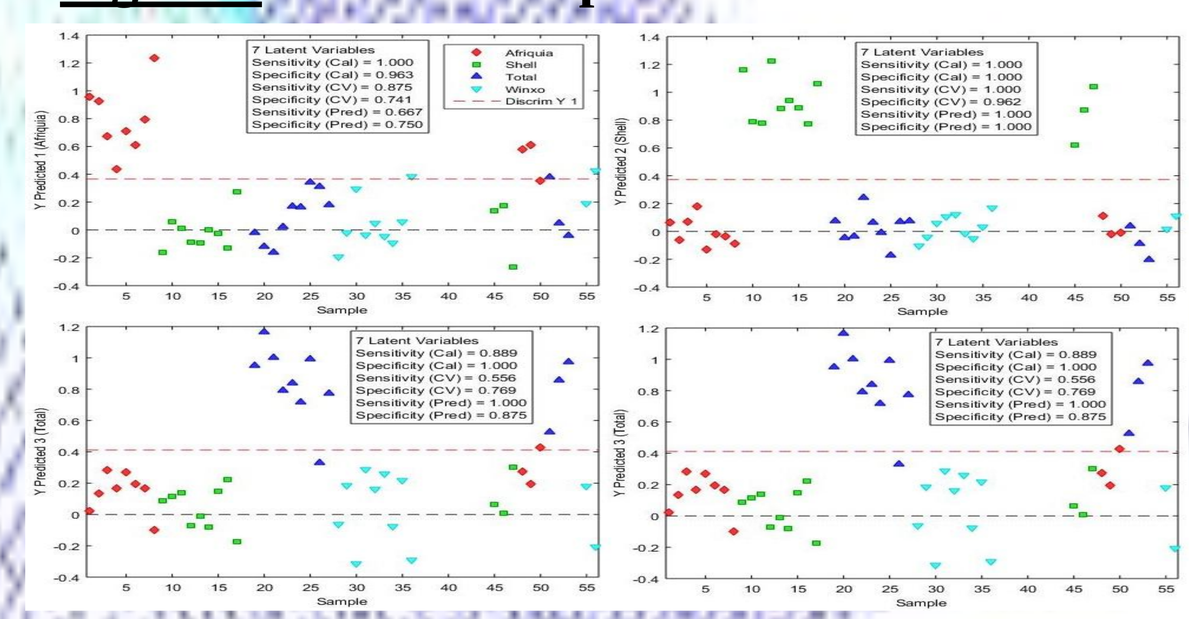

Figure 6. Estimated Class Values of training and test sets obtained by PLS-DA model

Tableau 2. paramètres de discrimination du modèle GC-MS-PLS-DA

Param\Fuel	Diesel AFR	Diesel SHE	Diesel TOT	Diesel WIN
Latent variables	3	3	3	3
RMSEC	0.2363	0.2575	0.3019	0.2669
RMSEP	0.6123	0.304	0.5100	0.3017
Sensitivity (cal)	1.000	1.000	1.000	1.000
Specificity (cal)	1.000	1.000	1.000	1.000
Sensitivity (pred)	0.667	1.000	1.000	1.000
Specificity (Pred)	1.000	1.000	0.778	1.000

Conclusions

The usefulness of coupling FTIR spectra and GC-MS fingerprints to PLS-DA for the discrimination and classification of diesel fuels from four suppliers (Afriquia, Shell, Total and Winxo) was demonstrated.

The two models gave satisfactory results. However, the FTIR-PLS-DA model can be recommended in routine use, thanks to its cheapness, simplicity and time saving.

References

[1] A. Al-Ghouti, Y. S. Al-Degs, and M. Amer, “Application of chemometrics and FTIR for determination of viscosity index and base number of motor oils,” Talanta, vol. 81, no. 3, pp. 1096–1101, 2010.

[2] M. De Luca et al., “Derivative FTIR spectroscopy for cluster analysis and classification of morocco olive oils,” Food Chem., vol. 124, no. 3, pp. 1113–1118, 2011.