Analytica Chimica Acta 796 (2013) 130–136

Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

Quantitative analysis of biodiesel in blends of biodiesel and conventional diesel by comprehensive two-dimensional gas chromatography and multivariate curve resolution

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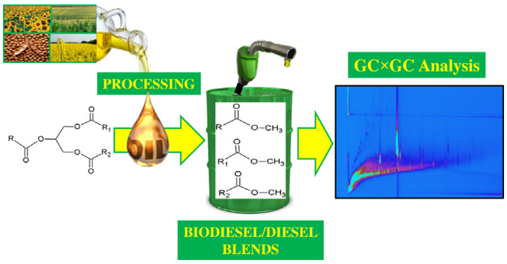
HIGHLIGHTS

- Comprehensive two-dimensional gas chromatography was used to obtain the fatty acid methyl esters profile.
- Multiway principal component analysis was employed to aid variable selection.
- Modeling and prediction of the percentage composition of biodiesel and diesel blends was performed by multivariate curve resolution.
- The proposed methodology was successfully employed to predict the concentration of biodiesel and diesel blends regardless of the biodiesel's origin.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 17 May 2013
Received in revised form 30 July 2013
Accepted 31 July 2013
Available online 6 August 2013

Keywords:
Biodiesel
Blends of biodiesel and conventional diesel
Comprehensive two-dimensional gas chromatography
Multivariate curve resolution
Multiway principal component analysis

ABSTRACT

In this paper, a method to determine the composition of blends of biodiesel with mineral diesel (BXX) by multivariate curve resolution with Alternating Least Squares (MRC-ALS) combined to comprehensive two-dimensional gas chromatography with Flame Ionization Detection (GC × GC-FID) is presented. Chromatographic profiles of BXX blends produced with biodiesels from different sources were used as input data. An initial evaluation carried out after multiway principal component analysis (MPCA) was used to reveal regions of the chromatograms were the signal was likely to be dependent on the concentration of biodiesel, regardless its vegetable source. After this preliminary step MCR-ALS modeling was carried out only using relevant parts of the chromatograms. The resulting procedure was able to predict accurately the concentration of biodiesel in the BXX samples regardless of its origin.

1. Introduction

Alternative and renewable fuels have recently received increased attention due to the predicted shortage in oil supplies and consequent rise in oil price and the effects associated with ambient air pollution [1,2]. In this context, biodiesel represents one of the

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http://dx.doi.org/10.1016/j.aca.2013.07.071

most significant alternatives to conventional petrodiesel fuel [1]. In addition, biodiesel is defined as a mixture of fatty acid methyl, or ethyl, esters and are processed from biological materials such as several vegetable oils, recycled cooking oils, animal fats and waste products [1,3–5].

The direct use of biodiesel in engines can present various problems [6,7]. Hence, biodiesel is frequently mixed with petroleum distillates to attain blends defined by BXX, where XX stands for the percentage of biodiesel (v/v). The use of biodiesel in several countries of the European Union has been growing each year [4], in part, because biodiesel is characterized by diesel like properties, but does not contain hazardous constituents such as sulfur, nitrogen and polycyclic aromatic compounds [1].

The determination of the content of biodiesel in diesel fuel is performed according to the ASTM D 7371 procedure by employing infra-red spectroscopy analysis [1]. However, the determination of this percentage can also be carried by using specific fatty acid methyl esters (FAME) present in the biodiesel. Hence, the elucidation of the FAME profile in diesel blends is necessary. According to the UNI EN 14331 procedure the FAME profile is determined by gas chromatography (GC) using a capillary column coated with a polar stationary phase, such as poly(ethyleneglycol), after a LC pre-separation step [1]. Often sample fractionation prior GC analysis is performed due to the potential coelution of characteristic and important biodiesel compounds with saturated alkanes from mineral diesel such as C18:0 with C25, C18:3 with C26 e C20:0 with C27 [1].

In this context, comprehensive two-dimensional gas chromatography (GC × GC) has been proven to be effective at characterizing biodiesel blends due to its increased peak capacity and enhanced detectability [8–12]. The separation is usually employed using a combination of stationary phases – non-polar and polar stationary phase in the first and second dimension, respectively – in order to generate FAME secondary retention times that are greater than those of the highly concentrated alkanes in the petroleum diesel. Naturally, the use of more powerfull instrumentation for the separation of complex samples, such as GC × GC, generate more complex experimental measurements. Hence, this often requires high order multivariate data analysis methods to improve the correlation of the two-dimensional chromatographic profiles with the property of interest, the BXX of biodiesel/diesel blends [13–17].

The GC × GC-FID (FID, Flame Ionization Detection) generates a 3-way array $\underline{\mathbf{X}}$ (I, J, K), were I = samples, J = ^{1}D chromatographic profile and K = ^{2}D chromatographic profile. In the current study, multiway principal component analysis (MPCA) is proposed for pattern recognition. However, the main goals of MPCA analysis are: (i) to find the chromatographic regions responsible for the differentiation of BXX blends, processed from different raw materials (soy biodiesel, unprocessed soybeans, soybean recovered after domestic use, corn, sunflower and canola); and (ii) to eliminate these regions prior multivariate curve resolution with Alternating Least Square (MCR-ALS) modeling. Thus, MCR-ALS modeling of the biodiesel chromatographic profiles were used for the prediction of the BXX mixtures. It is hoped that this combination, MPCA prior MCR-ALS, should allow the development of a model able to predict accurately the concentration of biodiesel in the BXX sample regardless of its origin.

1.1. MPCA

Multiway principal component analysis is a extension of PCA for high order data set, in which the data cube $\underline{\mathbf{X}}$ is unfolded to an array $\underline{\mathbf{X}}$ (I, J, K) and PCA analysis is subsequently performed [18]. It is a powerful unsupervised pattern recognition technique that allows the identification of natural cluster formation and outlier detection. PCA decomposes the $\underline{\mathbf{X}}$ data matrix in scores and loadings matrices which provide information about the samples and variables respectively (Eq. (1)) [18,19]. For the present case, the scores will provide information about sample clustering and loadings provide the chromatographic profile related to each cluster.

$$X = T_k \times P_k^T + E_k, \ k = \text{ideal factor number} \tag{1}$$

The simultaneous analysis of both scores and loadings allows the grouping detection in data set and improve chemical interpretation of the differences between complex samples, which enables recognition and classification of biodiesel from various sources [20].

1.2. MCR-ALS

MCR-ALS is a bilinear method, widely used in multidimensional analysis, that is able to work as a second order algorithm and is frequently combined with data obtained from GC × GC-FID for the quantification of compounds in complex mixtures [21–24]. In this method, the instrumental response obtained for a set of samples is transformed in a cube of data $\underline{\mathbf{X}}$ (I, J, K), which are unfolding in a matrix $\mathbf{X}$ (I, J, K) with I = samples and $J \times K$ = chromatographic profile, and then decomposed as described in Eq. (2) [24], where matrix C provides the relative concentrations from pure chromatographic profiles from the mixture and S^T provides the solved profiles.

$$X = C_k \times S_k^T + E_k, \ k = \text{ideal factor number} \tag{2}$$

A Alternating Least Square (ALS) procedure is used to iteratively adjust C and S^T matrices starting from a initial estimative of the pure analyte instrumental profile. The algorithm allows the mathematical recovery of the chromatographic profiles which best explains the observed variance of the data set. Thus, the simultaneous interpretation of both, the relative concentration provided by the scores values, and the profiles of each pure compound provided by the loadings values, lead to the quantitative information for all the analytes of interest into the BXX mixture [23,24].

The accuracy and precision of the calibration models can be evaluated by the root mean square error of the percentage deviation, RMSPD (Eq. (3)) and the root mean square error of prediction, RMSEP (Eq. (4)), where y_{pred} and y_{ref} are the predicted and the real concentrations, ith is the sample number and n is the number of prediction samples.

$$\text{RMSPD} = 100 \times \sqrt{\sum\nolimits_{i=1}^{n} \frac{(y_{\text{pred}(i)} - y_{\text{ref}(i)})}{y_{\text{ref}(i)}} \times \frac{1}{n}} \tag{3}$$

$$\text{RMSPE} = \sqrt{\frac{1}{n} \sum\nolimits_{i=1}^{n} (y_{\text{pred}} - y_{\text{ref}})^2} \tag{4}$$

2. Materials and methods

2.1. Samples and materials

All vegetable oils used for preparation of biodiesels – soybean, corn, canola and sunflower - were obtained locally. Samples of soybean biodiesel were also prepared using un-refined raw oil and recovered oil previously used on conventional cooking. Mineral diesel was also obtained on the local market. Mixtures of C8:0 to C24:0 FAME (fatty acid methyl esters), HPLC-grade methanol and reagent grade sodium hydroxide were also used (Supelco, Bellefonte, USA).