



Full Length Article

Direct and simultaneous determination of four phenolic antioxidants in biodiesel using differential pulse voltammetry assisted by artificial neural networks and variable selection by decision trees

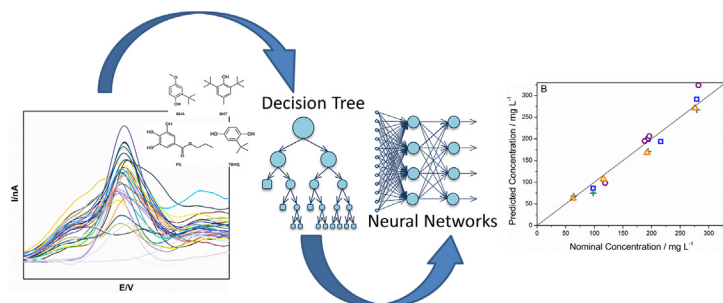


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GRAPHICAL ABSTRACT



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ABSTRACT

A new methodology using differential pulse voltammetry and artificial neural network (ANN) for simultaneous determination of butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl gallate (PG) and *tert*-butylhydroquinone (TBHQ) in biodiesel samples is proposed. A platinum ultramicroelectrode (ume) was used as working electrode and measures were taken directly in biodiesel:ethanol medium without previous preparation. On this condition, detection limits for the antioxidants separately are 20.5, 32.4, 35.5 and 26.5 mg L⁻¹ for BHA, BHT, PG and TBHQ, respectively. The artificial neural network model allowed the quantification of the individual concentrations overcoming the strongly overlapped voltammograms obtained for the mixture of the four antioxidants. For the model construction, a variable selection step through decision trees (DT) led to a reduction of prediction errors by 17.5%. The optimized DT-ANN model presented high correlation (0.97474, 0.99995, 0.98246 and 0.98928 for BHA, BHT, PG and TBHQ, respectively) between real and predicted values. Recovery percentages found were between 82.6% and 106.7%, except for two samples whose values were 76.0% and 114.7%. From the accuracy found between nominal and estimated concentration, it is inferred that the proposed methodology is a good alternative to quantify phenolic antioxidants in biodiesel samples.

Abbreviations: TBHQ, *tert*-butylhydroquinone; PG, propyl gallate; BHA, butylated hydroxyanisole; BHT, butylated hydroxytoluene; B100, biodiesel; ume, ultramicroelectrode; DPV, differential pulse voltammetry; GPES, general purpose electrochemical system; N(Hex)₄ClO₄, tetrahexylammonium perchlorate; ANN, artificial neural network; DT, decision tree

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1. Introduction

Biodiesel is a renewable fuel derived from different triglycerides sources as vegetable or animal oil and fats. Its characteristics as biodegradability, low sulfur and aromatics content and reduced combustion emissions attend the demand for sustainable energy sources. Further, its high flash point, good lubricity, the compatibility with the current distribution infrastructure, and miscibility with petrodiesel in any blending ratio improving its quality [1] have increased biodiesel interest over the past few decades. Despite its advantages, biodiesel has lower oxidation stability when compared to fossil fuels and thus it is more prone to suffer degradation and property change. Therefore, the addition of synthetic antioxidants becomes necessary to increase its oxidative stability. Among them, the most used are butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl gallate (PG) and *tert*-butylhydroquinone (TBHQ). The structures of these phenolic compounds (Fig. 1) allow the donation of protons to free radicals, thus inhibiting the oxidative process [2].

Products of oxidation process of degraded biodiesel affect automotive combustion systems. To ensure safe commercialization, monitoring of the biodiesel quality is fundamental. Standard accelerated oxidation methods, such as Rancimat (EN 14112), employed to evaluate antioxidant efficiency on biodiesel oxidative stability, require analysis time over 8 h [3]. Separation methods, capable of determining antioxidant content, like liquid chromatography, gas chromatography or capillary electrophoresis, generally demand preprocess steps which may cause contamination and sample loss, leading to false results [4].

Therefore, the development of analytical methods that provide a fast, cheap and safe response is of great relevance. Electrochemical methods are promising in that sense, since they permit direct analysis, feature fast and simple execution, and lower costs when compared to chromatographic techniques. These methods were already applied to resistive medium, such biodiesel; for example, electrochemical impedance spectroscopy was used in the evaluation of lubricity of biodiesel/diesel blends [5] and determination of water content in biodiesel [6]. Different voltammetric techniques were successfully used in either individual [7–10] and simultaneous determination of two [11,12] antioxidants in biodiesel. Among these, the pulse voltammetric techniques, such as differential pulse voltammetry (DPV), are more sensitive than linear voltammetry due to the decrease in the capacitive current contribution, being more suitable for measurements on resistive medium [13]. DPV has already been successfully applied in our previous work [4] for the simultaneous determination of TBHQ and PG in biodiesel samples using a Pt ultramicroelectrode (ume).

Nevertheless, the simultaneous voltammetric determination of a mixture of antioxidants is difficult due to the overlapping peaks in electrochemical responses, thus making inviable the use of individual calibration curves. To overcome this limitation, multivariate analysis tools are used together with voltammetry allowing the construction of predictive models. Widely used in spectroscopy, the application of these tools with voltammetric data has increased [14]. Among the most reported techniques are the Classical Least Squares (CLS) [15], Principal

Component Regression (PCR) [16,17], Partial Least Squares (PLS) [18,19], Multivariate Curve Resolution-Alternating Least Squares (MCR-ALS) [20,21] and Artificial Neural Networks (ANN) [22–25]. The latter is used mainly when the responses are not well described by a linear model.

Concerning antioxidant content determination, these techniques have been applied, in food and vegetable oil samples, for simultaneous determination of three [26,27] and four [28] synthetic antioxidants. Simultaneous determinations of natural antioxidants (tocopherols) in vegetable oil samples are also reported [29,30].

When the amount of data is large and the dimensionality is high, other tools are used as a preprocessing stage to reduce the number of variables and to extract more valuable information. Among the most used, Genetic Algorithm (GA) [31,32] is generally applied with PLS; Discrete Wavelet Transform (DWT) [33,34] and Principal Component Analysis (PCA) [35] are generally used prior to neural network training to reduce computational time in training process and generate a more robust model. Another tool that has gained space in data analysis applications is the Decision Tree (DT). DTs are considered general purpose prediction and classification mechanism [36]. Although it was not found any applications of DTs in the analysis of voltammetric data, the diversity of fields where they were successfully applied suggests the viability of using this technique for electrochemistry as well.

Considering the lack of analytical methodology, the objective of this work is the development of a fast and reliable procedure to determine the amount of antioxidants in biodiesel. Here, four antioxidants are quantified (BHA, BHT, PG, and TBHQ) in biodiesel samples by combining the sensitivity of DPV with the modeling capability of ANNs in ways to overcome the signal overlapping. The study also evaluates the viability of using DTs as a preprocessing tool for variable selection. As far as the authors know, simultaneous determination of BHA, BHT, PG and TBHQ, directly in biodiesel samples, has not been reported yet.

2. Material and methods

2.1. Reagents and apparatus

Antioxidant-free soybean biodiesel (B100) sample was provided by a local producer in southern Brazil. BHA (98.0%), BHT (97.0%), PG (98.0%) and TBHQ (97.0%) were purchased from Acros Organics (USA). Ethanol (99%) was purchased from PanReac AppliChem and Tetrahexylammonium perchlorate (> 99%) was obtained from Fluka Chemika. All reagents were used without further purification.

The voltammetric measurements were carried out using a potentiostat/galvanostat AUTOLAB PGSTAT 30 (Holland) interfaced with a microcomputer and controlled by GPES v4.9.005 (Eco Chemie, Utrecht, The Netherlands) software. The working electrode consisted of a Pt disk ume with 5 μm radius from EG&G PAR (Princeton Applied Research, Wellesley, MA, USA). The auxiliary and quasi-reference [37] electrodes were a Pt ribbon and a Pt wire, respectively. Data were treated using Origin 8.5 (OriginLab, Northampton, MA, USA) and MATLAB v9.0 (MathWorks, Natick, MA, USA) software.

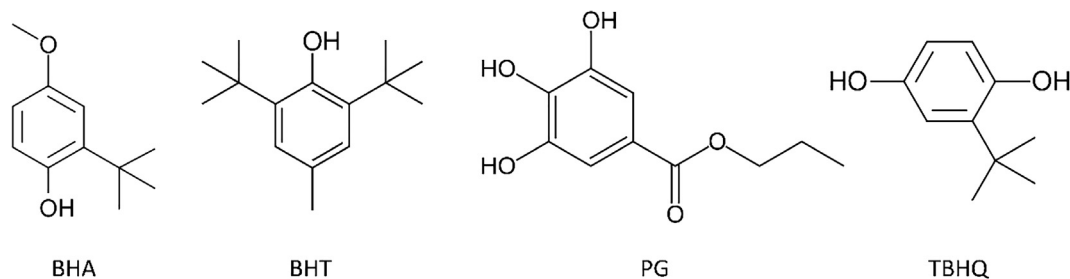


Fig. 1. Structure of the synthetic antioxidants.

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