



## Organic-resistant screen-printed graphitic electrodes: Application to on-site monitoring of liquid fuels



Eduardo S. Almeida <sup>a</sup>, Luiz A.J. Silva <sup>a</sup>, Raquel M.F. Sousa <sup>a</sup>, Eduardo M. Richter <sup>a</sup>, Christopher W. Foster <sup>b</sup>, Craig E. Banks <sup>b</sup>, Rodrigo A.A. Munoz <sup>a,\*</sup>

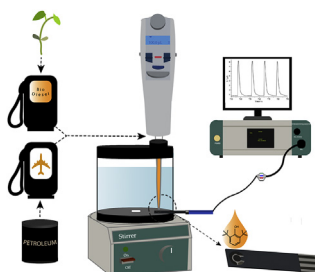
<sup>a</sup> Universidade Federal de Uberlândia, Universidade Federal de Uberlândia, Av. João Naves de Ávila, 2121, Uberlândia, MG, 38408100, Brazil

<sup>b</sup> Manchester Metropolitan University, Faculty of Science and the Environment, School of Science and the Environment, Division of Chemistry and Environmental Science, Manchester, M1 5GD, England, UK

### HIGHLIGHTS

- Organic-resistant screen-printed graphitic electrodes (SPGE) for (bio) fuels.
- Screen-printing of conductive and insulator inks on thin polyester substrate.
- Continuous detection of antioxidants in electrolyte with 99% v/v ethanol.
- SPGE coupled with batch-injection analysis allows over 200 injections (100  $\mu$ L).
- Similar results to GC and HPLC analyses of biodiesel and aviation jet fuels.

### GRAPHICAL ABSTRACT



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### ABSTRACT

This work presents the potential application of organic-resistant screen-printed graphitic electrodes (SPGEs) for fuel analysis. The required analysis of the antioxidant 2,6-di-*tert*-butylphenol (2,6-DTBP) in biodiesel and jet fuel is demonstrated as a proof-of-concept. The screen-printing of graphite, Ag/AgCl and insulator inks on a polyester substrate (250  $\mu$ m thickness) resulted in SPGEs highly compatible with liquid fuels. SPGEs were placed on a batch-injection analysis (BIA) cell, which was filled with a hydro-ethanolic solution containing 99% v/v ethanol and 0.1 mol L<sup>-1</sup> HClO<sub>4</sub> (electrolyte). An electronic micropipette was connected to the cell to perform injections (100  $\mu$ L) of sample or standard solutions. Over 200 injections can be injected continuously without replacing electrolyte and SPGE strip. Amperometric detection (+1.1 V vs. Ag/AgCl) of 2,6-DTBP provided fast (around 8 s) and precise (RSD = 0.7%, n = 12) determinations using an external calibration curve. The method was applied for the analysis of biodiesel and aviation jet fuel samples and comparable results with liquid and gas chromatographic analyses, typically required for biodiesel and jet fuel samples, were obtained. Hence, these SPGE strips are completely compatible with organic samples and their combination with the BIA cell shows great promise for routine and portable analysis of fuels and other organic liquid samples without requiring sophisticated sample treatments.

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\* Corresponding author.

E-mail address: [raamunoz@iqufu.ufu.br](mailto:raamunoz@iqufu.ufu.br) (R.A.A. Munoz).

## 1. Introduction

Currently there is a replacement scenario of fossil fuels by renewable sources of fuel. Countries such as Brazil and USA have established goals to replace 20 and 30% of fossil fuels, respectively, over the next 5–10 years. However, this substitution will take a long period. For this reason, both fossil fuels and biofuels need a quality control for marketing and market acceptance [1]. Such a quality control is not just restricted to contaminants (organic and inorganic) but also is required to evaluate the presence of additives responsible to maintain the fuel characteristics during transport, storage and final consumption. Antioxidant additives are widely used in fossil fuels and biofuels in order to avoid deterioration processes via oxidation mechanisms/processes. Antioxidants with phenolic structures are the most commonly used in biodiesels [2] and in aviation jet fuels [3].

The addition of antioxidants in jet fuel is regulated by the standard ASTM-D1655. These compounds have been determined in aviation fuels by gas chromatography with mass spectrometry (GC-MS) [4–7], high-performance liquid chromatography (HPLC) with electrochemical [3,8] and spectrophotometric detection in the UV region [9,10], and differential-pulse voltammetry [11]. The determination of antioxidants in biodiesel by electroanalytical techniques is highlighted in a recent review [2] giving emphasis on the pioneering work of Tormin et al. [12], in which the amperometric determination of the antioxidant *tert*-butylhydroquinone in biodiesel was accomplished after large sample dilution in a hydro-ethanolic electrolyte solution. Another approach was reported for the determination of the antioxidant pyrogallol in biodiesel using differential-pulse voltammetry [13]. Both methods employed conventional glassy-carbon disc working electrodes.

The development of portable analytical systems for on-site monitoring of the quality control of fuels is mandatory. Electroanalysis attends this demand especially when associated with screen-printed electrodes (SPEs), which are disposable and easy-to-use sensors that can be operated by portable mini-potentiostats connected to laptops. SPEs can be applied for a large variety of analytes, as highlighted in recent reviews [14,15]. However, few applications of SPEs involved fuel analysis. Caramit et al. reported the use of multi-walled carbon nanotube modified SPEs for the determination of antioxidants in biodiesel, but samples were 200-fold diluted in aqueous electrolyte containing a surfactant [16]. Our research group proposed the use of screen-printed gold electrode for metal determination in fuel bioethanol after sample dilution in aqueous electrolyte in such a way that the final ethanol concentration was 25% (v/v) [17]. Similarly, Saciloto et al. presented a SPE sensor using a graphite-polyurethane composite for metal determination in fuel ethanol after sample dilution to result in a final ethanol concentration in 20% (v/v) [18]. Therefore, these previous works on fuel analysis using SPEs revealed that samples are required to be diluted in aqueous electrolyte in order to perform accurate electrochemical measurements. The presence of organic solvents, especially non-polar solvents, in electrolyte affects electrochemical measurements due to their low constant dielectric, but also because inks used to construct SPEs may be dissolved by such solvents. This effect explains the high dilution ratios required for biodiesel analysis reported in the literature [13,16]. The application of SPEs for the quantification of fuel dyes in fossil fuel samples such as gasoline and kerosene required prior sample preparation involving solid-phase extraction due to the incompatibility of SPEs with such complex samples [19,20].

This work demonstrates the application of organic-resistant screen-printed graphitic electrodes (SPGEs) for the determination of the antioxidant 2,6-di-*tert*-butylphenol (2,6-DTBP) in biodiesel and aviation jet fuels. Screen printing on a polyester substrate

revealed to SPGEs highly compatible with organic solvents. This is the first report of a SPE sensor applied for measurements in a highly organic medium (99% v/v ethanol), which is a strong demand for fuel analysis especially when on-site analysis is required. SPGEs were placed on a portable batch-injection analysis (BIA) system for the amperometric detection of 2,6-DTBP. The BIA system is an analogue of flow-injection analysis (FIA); however, an electronic micropipette replaces the pump and valves used in FIA systems and the micropipette tip is placed close to the working electrode, which is immersed in blank electrolyte solution [21].

## 2. Experimental

### 2.1. Reagents, stock solutions and samples

High-purity deionized water ( $R \geq 18 \text{ M}\Omega \text{ cm}$ ) obtained from a Milli Q water purification system (Millipore, Bedford, MA, USA) was used for preparing all aqueous solutions. Concentrated perchloric acid (70%, m/v) and ethanol (99.9%, v/v) were obtained from Vetec (Rio de Janeiro, Brazil). The antioxidant 2,6-*tert*-butylphenol (2,6-DTBP), ferrocene (99%) and tetrabutylammonium perchlorate (TBAClO<sub>4</sub>, for electrochemical analysis) were obtained from Aldrich (USA). Working standard solutions were prepared immediately before use by appropriate dilution of the stock solution. A standard stock solution containing 2,6-DTBP ( $1 \times 10^{-2} \text{ mol L}^{-1}$ ) was prepared in ethanol containing 0.1 mol L<sup>-1</sup> HClO<sub>4</sub>. All reagents were used without further purification (analytical grade). Samples of aviation jet fuel were donated by the Radio Patrol Air Battalion (Brazilian Air Force), located at Uberlândia Minas Gerais, Brazil. Biodiesel samples were produced in laboratory from fat pork and Macauba oil (*Acrocomia aculeate*) through alkaline transesterification.

### 2.2. Instrumentation, electrochemical cell and electrodes

Amperometry measurements were performed using a  $\mu$ -Autolab Type III potentiostat (Metrohm Autolab B. V., Utrecht, The Netherlands). A PC with Nova 1.10 software for Windows 8<sup>®</sup> was used to control the instrument.

SPGEs were fabricated in-house on polyester flexible substrates (Autostat, 250  $\mu\text{m}$  thickness). Each SPGE was designed in a three-electrode configuration printed on the same planar platform consisting of a graphite disc-shaped working electrode ( $\varnothing = 2.8 \text{ mm}$ ), a graphite counter electrode, and a silver pseudo-reference electrode as previously described [22]. Briefly, the carbon-graphite ink (Gwent Electronic Materials Ltd, UK) was printed on the substrate and cured at 60 °C for 30 min. Similar consecutive steps of printing and curing (same temperature and time) were executed to print the Ag/AgCl paste (Gwent Electronic Materials Ltd, UK) and finally a dielectric paste (insulator) on the same substrate.

The BIA cell (with internal volume of 100 mL) adapted for screen-printed electrodes was fabricated in-house as described previously [21]. Additionally, a commercial version of this cell was recently introduced by Dropsens (Oviedo, Spain). Briefly, this cell was constructed in polypropylene and the SPGE is inserted at the bottom side using a rubber O-ring to prevent leaks and to limit the region over the three electrodes. The cover of the cell permits the insertion of an electronic micropipette that firmly fits over the cell in order to provide reproducible injections. The micropipette tip was placed at around 2 mm from the working electrode of the SPGE.

### 2.3. Electrochemical measurements

Injections of standard solutions or diluted samples were carried

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