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Full Length Article

Antioxidants detection in aviation biokerosene by high-performance liquid chromatography using gold nanoparticles anchored in reduced graphene oxide

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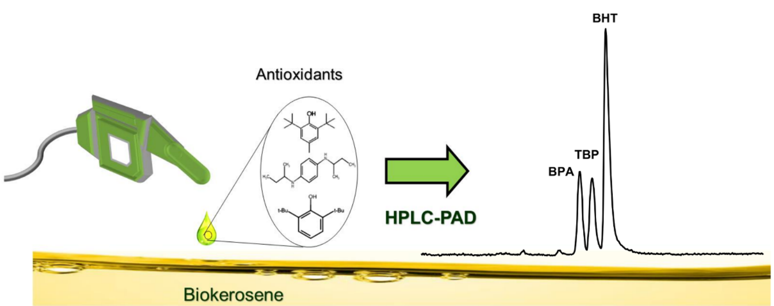
GRAPHICAL ABSTRACT



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ABSTRACT

This paper report the development of a new HPLC-pulsed amperometric detector (HPLC-PAD) for the determination of antioxidants using glass carbon electrode (GCE) modified with reduced graphene oxide (rGO) and gold nanoparticles (AuNPs). The modified electrode exhibited efficient electro-oxidation when it was applied in the analysis of three important antioxidants: N, N'-di-sec-butyl paraphenylenediamine (BPA), 2,6-Di-*tert*-butylphenol (TBP) and 2,6-Di-*tert*-butyl-4-methylphenol (BHT). The chromatographic separation was performed with an isocratic elution composed of acetonitrile/water (90:10% v/v) and 1% acetic acid. The chromatograms showed good separation of all components in periods of time less than 10 min. The developed method presented linear ranges of 5.0×10^{-6}–1.3×10^{-4} mol L^{-1} (BPA), 2.5×10^{-6}–1.0×10^{-4} mol L^{-1} (TBP) and 7.5×10^{-7}–1.3×10^{-4} mol L^{-1} (BHT), and the analytical curves presented limits of detection of 1.2×10^{-7}, 1.7×10^{-7} and 7.8×10^{-8} mol L^{-1} for BPA, TBP and BHT, respectively. The values obtained for the recovery studies conducted ranged from 97.3 ± 1.5% to 101.5 ± 2.1%. The results showed that the method is reliable, since it presented high sensitivity, precision and accuracy. The developed method was successfully applied for the determination of antioxidants in a sample of biokerosene, consisting of isoparaffins synthesized from fermented and hydroprocessed sugars. The determined concentrations were TBP $3.1 \times 10^{-5} \pm 5.5 \times 10^{-6}$ mol L^{-1} and BHT $3.3 \times 10^{-5} \pm 2.9 \times 10^{-6}$ mol L^{-1}.

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1. Introduction

Biofuels are considered a promising alternative when one thinks of ways to overcome the current challenges of the global energy sector, which include increased greenhouse gas emissions and dependency on fossil fuels [1,2]. Swings in oil prices make the development of new energy sources essentially relevant, particularly for air and road transportation [1,3,4]. Many governments are currently encouraging the production of biofuels through subsidies and tax exemptions, setting targets and standards for the addition and complemenatarization of these fuels in the composition of fossil fuels [3–5].

There are a wide range of alternative energy sources for land transportation; these include biofuels, biogas, fuel cells and electromobility [6,7]. Meanwhile, the aviation sector depends largely on Jet A-1 fuel (kerosene of fossil origin) as the main source of energy [1,8]. To overcome the challenges involving the excessive dependency on Jet A-1 fuel and its negative impacts on the environment, the aviation industry has sought to develop more energy-efficient aircrafts and biofuels with properties similar to those of mineral kerosene [1,2,4]. Many pathways have been proposed for obtaining new aviation fuels, the main one involves the use of biomass as feedstock [9,10]. However, other non-biomass-dependent renewable technologies have also been investigated, such as solar-thermochemical fuels and power-to-liquids (PtL) [10]. Several options for the production of kerosene from organic matter (i.e. biomass) have been investigated by researchers in the field [1,2,11]. The main routes for converting biomass into biofuels hydrocarbons involve mechanical, biological, thermal and chemical processes [4,7,9].

Biokerosene is defined as aviation fuel derived from alternative sources such as biomass, waste gas, solid waste, coal and natural gas [12]. ASTM certification (ASTM D7566-19) has defined five types of synthetic paraffin kerosene (SPK), used as blending components for aviation kerosene of fossil origin: Fischer-Tropsch hydroprocessed synthesized paraffinic kerosene (FT-SPK); synthesized paraffinic kerosene from hydroprocessed esters and fatty acids (HEFA-SPK); synthesized kerosene with aromatics (SPK/A); alcohol-to-jet synthetic paraffinic kerosene (ATJ-SPK) and synthesized *iso*-paraffins from hydroprocessed fermented sugars (SIP) [13].

For biokerosene to be certified as commercial fuel for aeronautical purposes, some underlying stringent specifications are required to be met; these include satisfying, for instance, the American regulations (ASTM D7566) on biokerosene, which establish the quality standards of biokerosene. The low oxidation stability of biofuels, caused by exposure to air, moisture, metals, light, heat and storage time, has a direct influence over their physico-chemical properties [14–16]. The addition of synthetic antioxidants in biofuels is found to be indispensable because it provides biofuels with greater resistance to oxidation, longer storage time and thermal stability [16,17]. Synthetic antioxidants, such as N, N'-di-sec-butyl paraphenylenediamine (BPA), 2,6-Di-*tert*-butylphenol (TBP) and 2,6-Di-*tert*-butyl-4-methylphenol (BHT) have been frequently used for these purposes [16–18].

The quality of biokerosene is directly associated with the presence and concentration of antioxidants which are added to biokerosene in the concentration range of 17 mg L^{-1}–24 mg L^{-1} after the manufacturing process and prior to storage [13,16]. To ensure the effectiveness of the quality control process, the use of reliable and highly sensitive analytical methods capable of quantifying small concentrations becomes primarily important. Studies published in the literature report the use of a wide range of analytical methods for the determination of antioxidants in several matrices via the application of gas chromatography (GC) [19–22]; spectrophotometry [23]; electrochemical techniques [24–28]; and high performance liquid chromatography (HPLC) with UV detector [29–32], diode array detector [33,34], and fluorescence detector [35]. Furthermore, studies in the literature have also reported the use of electrochemical technique for the detection of antioxidants after chromatographic separation [36,37]. However, to date, no studies have been reported in the literature describing methods for the determination of antioxidants in aviation biokerosene.

Nanostructured materials have been employed in order to improve the analytical determination of antioxidants [38,39]. Graphene has been widely used because of its electronic, optical, mechanical and thermal properties [40,41]. Noble metal nanoparticles, such as Pt, Au and Ag, have received considerable attention in catalysis because of their unique physical and chemical properties [42,43]. Gold nanoparticles (AuNPs) have also been widely used in various applications due to their excellent conductivity and large surface area [38,44,45]. Based on these properties, HPLC-based electrochemical detection technique using electrodes modified with nanostructured materials offers numerous application advantages; this explains the popularity of the technique among researchers and its ample use for the detection of several analytes in other matrices [37,46,47].

In this work, the analytical performance of the glassy carbon electrode modified with reduced graphene oxide and gold nanoparticles (GCE/rGO-AuNPs) was investigated. The effectiveness of the modified electrode coupled to high performance liquid chromatography was investigated for amperometric determination of antioxidants in aviation biokerosene, without previous sample treatment.

2. Experimental

2.1. Reagentes

All reagents used in the experiments were of analytical grade. The water used to prepare the solutions was deionized in a Milli Q system (acquired from Millipore, Billerica, MA, USA) with a resistivity of 18.2 MΩ cm^{-1}. Graphene oxide (GO, 4.0 mg mL^{-1}), sodium hydroxide ($NaOH \geq 98\%$), chloroauric acid ($HAuCl_4$), sodium sulfate ($Na_2SO_4 \geq 99\%$), and the antioxidants, namely, N, N'-di-sec-butyl paraphenylenediamine ($BPA \geq 95\%$), 2,6-Di-*tert*-butylphenol ($TBP \geq 99\%$) and 2,6-di-*tert*-butyl-4-methylphenol ($BHT \geq 99\%$), were obtained from Sigma-Aldrich. Nitric acid (HNO_3, $\geq 65\%$), ethanol ($C_2H_5OH \geq 96\%$), acetonitrile ($CH_3CN \geq 99\%$) were obtained from Merck. Standard solutions of BPA, TBP and BHT were prepared by dissolving appropriate amounts of the antioxidants in ethanol.

2.2. Electrochemical measurement

The electrochemical experiments were carried out using a conventional cell with three electrodes: Ag/AgCl (KCl 3.0 mol L^{-1}), platinum wire, and glassy carbon electrode modified with reduced graphene oxide and gold nanoparticles (GCE/rGO-AuNPs) were used as reference, auxiliary and working electrodes, respectively. The conventional cell with the three electrodes was connected to a PGSTAT-30 AUTOLAB potentiostat/galvanostat controlled by NOVA 1.11 software. Electrochemical impedance spectroscopy (EIS) was performed using the FRA module. All experiments were conducted at room temperature.

2.3. Modification of GCE surface with rGO and AuNPs

The surface of the GCE was previously polished with α-alumina (0.3 μm), and cleansed by sonication in ethanol and Milli-Q water for 5 min. The working electrode was modified with reduced graphene oxide based on a previously published work [47]. A suspension of graphene oxide of 0.50 mg mL^{-1} in 0.1 mol L^{-1} Na_2SO_4 was electrodeposited on the surface of the working electrode with constant potential of −1.5 V for 500 s. The electrode was then dried at room temperature.

The gold nanoparticles were electrodeposited on the surface of the modified GCE with rGO by chronoamperometry; this was done based on methods described in the literature [45]. The parameters found to affect the formation of nanoparticles, including $HAuCl_4$ concentration, potential, and deposition time, were optimized; this can be found in Fig.