A Simple FIA-System for the Simultaneous Determination of Phenolic Antioxidants with Multiple Pulse Amperometric Detection

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Introduction

Among the primary synthetic antioxidants, the phenolic compounds BHA (butylated hydroxyanisole) and BHT (butylated hydroxytoluene) are widely used to interrupt the chain of free radicals involved in the autooxidation that constitutes the most common form of deterioration of fats used in the food industry[1]. The determination of these antioxidants in foods is necessary to ensure the fulfillment of legal requirements as well as quality-control procedures in the food industry. Multiple pulse amperometry (MPA) is a technique that, under certain experimental conditions[2], allows the simultaneous determination of compounds with different oxidation and reduction potentials. Thin films of boron-doped diamond (BDD) have emerged as excellent electrode materials for several electrochemical applications, especially electroanalytical ones, mainly due to unique properties[3]. The present work reports a simple strategy for the simultaneous determination of BHA and BHT in food using a BDD electrode and flow injection analysis (FIA) with MPA detection.

Results and Discussion

The electrochemical flow cell consisted of two acrylic blocks with holes for introduction and exit of solutions and plug-ins for the working electrode [BDD], reference electrode [Ag/AgCl (KCl 3.0 mol L^{-1})], and counter electrode [stainless-steel tube]. Preliminary studies employing simple amperometric detection were done for the construction of the hydrodynamic voltammograms and optimization of all chemical and FIA variables (Table 1).

Table 1: Investigated ranges of the chemical and FIA variables and their optimum values

Variable	Studied range	Optimum value
Oxidation potential of BHA (mV)	350 - 950	850
Oxidation potential of BHT (mV)	700 - 1250	1150
Sample Volume (µL)	50 - 600	250
Carrier Flow rate (mL min^{-1})	0.6 – 2.7	2.4
KNO_3 concentration* (mol L^{-1})	0.01 – 0.5	0.01

*prepared with an aqueous-ethanolic (70/30 %, v/v)

Using the MPA, a double-potential waveform, at $E_{det.1}$ = 850 mV (200 ms) and $E_{det.2}$ = 1150 mV (200 ms) vs. Ag/AgCl (KCl 3.0 mol L^{-1}), was employed at a BDD electrode for the simultaneous determination of BHA and BHT by flow injection analysis. $E_{det.1}$ and $E_{det.2}$ caused the oxidation of BHA and BHT, respectively; hence, concentration subtraction could be used to determine both species. The current peaks obtained with the flow injection system at the two oxidation potentials ($E_{det.1}$ and $E_{det.2}$) are shown in Figure 1 for different conditions; from these results, it is clear that the value of the BHT concentration is proportional to the value of current obtained by subtracting the current at $E_{det.1}$ from that at $E_{det.2}$ (I_{BHT} = $E_{det.2}$ - $E_{det.1}$), while the BHA concentration is directly proportional to the value of current obtained at $E_{det.1}$.

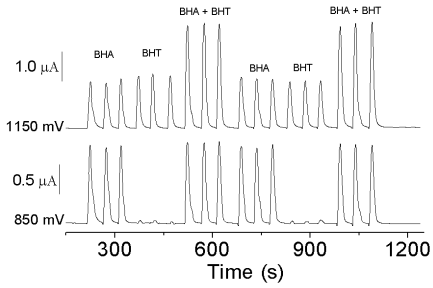

Figure 1: Peaks obtained with the flow injection system for BHA, BHT, and the mixture BHA + BHT; all concentrations at 5.0 x 10^{-5} mol L^{-1} in aqueous-ethanolic (70/30 %, v/v) 0.01 mol L^{-1} KNO_3.

Using FIA and MPA, a linear response to BHA at $E_{det.1}$ was obtained across the concentration range 5.0 × 10^{-8} – 3.0 × 10^{-6} mol L^{-1}, with a limit of detection of 3.0 × 10^{-8} mol L^{-1}. A linear response to BHT at I_{BHT} = $E_{det.2}$ - $E_{det.1}$ was obtained across the concentration range 7.0 × 10^{-7} – 7.0 × 10^{-5} mol L^{-1}, with a limit of detection of 4.0 × 10^{-7} mol L^{-1}. The proposed method was successfully applied in the simultaneous determination of BHA and BHT in food products, with results similar to those obtained using a high-performance liquid chromatography method.

Conclusions

MPA and FIA with a BDD electrode were successfully used for the simultaneous determination of the antioxidants BHA and BHT. The proposed method is simple, quick, and can be carried out with good precision and accuracy.

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