



Pulsed amperometric detection at glassy carbon electrodes: A new waveform for sensitive and reproducible determination of electroactive compounds



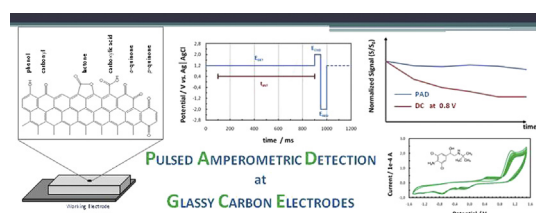
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HIGHLIGHTS

- Pulsed amperometric detection at glassy carbon electrodes.
- Three-step potential waveform to prevent the carbon electrode fouling during repeated analyses.
- Sensitive and reproducible quantitative determination of beta-agonists, phenols and polyphenols.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, the application of a new pulsed amperometric detection (PAD) waveform at a glassy carbon electrode, operating in typical chromatographic mobile phases, is proposed for the sensitive and reproducible determination of aryethanolaminic and phenolic moiety based compounds (e.g. beta-agonists and polyphenols). Preliminary experiments by cyclic voltammetry were carried out to investigate the electrochemical behaviour and to select the detection and cleaning electrode potentials. The proposed potential-time profile was designed to prevent the carbon electrode fouling under repeated analyses, thus ensuring a reproducible and sensitive quantitative determination, without the need of any mechanical or chemical electrode cleaning procedure. The waveform electrochemical parameters, including detection and delay times, were optimized in terms of sensitivity, limit of detection and response stability. The optimized waveform allowed the sensitive and stable detection of model compounds, such as clenbuterol and caffeic acid, that showed detection limits of $0.1 \mu\text{g L}^{-1}$ and $14 \mu\text{g L}^{-1}$, quantification limits of $0.4 \mu\text{g L}^{-1}$ and $46 \mu\text{g L}^{-1}$, and linearity up to $100 \mu\text{g L}^{-1}$ ($r = 0.9993$) and 10mg L^{-1} ($r = 0.9998$), respectively. Similar results were obtained for other compounds of the same classes, with precision values under repeatability conditions ranging from 3.0 to 5.9%. The proposed method can be then considered as an excellent alternative to the post-column detection of beta-agonists, phenols and polyphenols.

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1. Introduction

Since the first papers by Johnson and La Course in the 80's [1,2], pulsed amperometric detection (PAD) at metal electrodes has been exploited for the sensitive and reproducible determination of several compounds (e.g., carbohydrates, aminoacids, and organosulfur species) [1–6]. The proper choice of the electrode material,

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potential waveform and electrolyte solution is a fundamental aspect to enhance the electrode performance and sensitivity [5]. In addition to gold and platinum, generally used for scarcely electroactive compounds, most applications employ carbon-based electrodes (e.g., carbon paste, graphite, glassy carbon), sometimes modified in order to improve the response at constant potential (DC) [7,8]. In particular, glassy carbon electrode (GCE) has been very popular because of its excellent electrical and mechanical properties, a wide operational potential range, extreme chemical inertness, and relatively high reproducibility performances.

Several methods based on electrochemical detection at carbon electrodes were reported for the determination of beta-agonists [9–14] and phenolic compounds [15–18]. Compared to noble-metal electrodes, GCE shows very interesting anti-fouling properties [1], even though this phenomenon is often noticed on its working surface, especially with DC detection, due to the strong adsorption on GCE surface of sample matrix components and/or analyte oxidation products. This process causes a decrease of the sensitivity and a time-dependent deterioration of the response [10,19,20], and an electrode regeneration by a mechanical or electrochemical polishing is required at the beginning of each working session [21–23]. Indeed, starting from the 1980s these problems have been already evidenced, and surface activation procedures were found necessary to obtain reproducible and well-defined electrochemical behaviours. Various strategies were proposed [24] in order to activate the GCE surface, such as preanodization and precathodization at high potentials [25], chemical modifications by incorporating redox species [26], and daily electrochemical cycling [27]. These approaches were based on electrode pretreatment steps for enhancing heterogeneous electron transfer and increasing sensitivity and resolution; however, higher background currents were observed after preanodization. As a restoring method against the surface passivation phenomena, which can cause highly irreproducible measurements, repetitive treatments by pulsed laser light of graphite and glassy carbon electrodes were proposed [28]. This procedure is very efficient, but requires a structural modification of the conventional electrochemical cell with a window that allows the laser light to impact onto the electrode surface.

PAD offers great advantages respect to DC amperometry, due to the pulsed potential waveform that continuously cleans and reactivates the working electrode [1]. Different potential waveforms at working metal electrodes have been proposed for the determination of compounds whose anodic detection is supposed to involve a catalytic action of the surface oxides [1,6,29,30]. The electrochemical responses of electroactive compounds are greatly affected not only by the electrode material, but also by the electrolyte solution [5,31,32]. This influence becomes of fundamental importance when the electrochemical detection is used after the chromatographic separation, required for multi-analyte determinations in real samples.

Since 2007 we have demonstrated the proof of concept of the PAD at GCE operating in typical mobile phases containing organic solvents for the detection of beta-agonists [33], thus overcoming problems of the off-line preactivation [24–27] or in-situ laser irradiation [28]. Recently, PAD at GCE has been used for the post-column detection of drugs and herbicides [34], but, even in this case, the electrode fouling problem has not been overcome. Therefore, because of both a decreased response sensitivity and scarce reproducibility, a long electrode chemical pretreatment step was necessary.

In the present work an electrochemical approach, based on a new PAD waveform applied at glassy carbon electrodes and operating in typical chromatographic mobile phases for the sensitive and reproducible detection of aryethanolaminic and phenolic compounds is described. Preliminary experiments by cyclic voltammetry were carried out to investigate the electrochemical behaviour of the model compounds and to select the best detection and cleaning electrode potentials of the waveform.

2. Materials and methods

2.1. Reagents

Clenbuterol, terbutaline, fenoterol, caffeic acid, phenol, 4-ethylphenol, ferulic acid, rutin, syringic acid, gallic acid, *p*-coumaric acid, tyrosol (see Fig. 1) and acetonitrile of HPLC grade were purchased from Sigma–Aldrich (Stenheim, Germany). Acetic acid glacial,

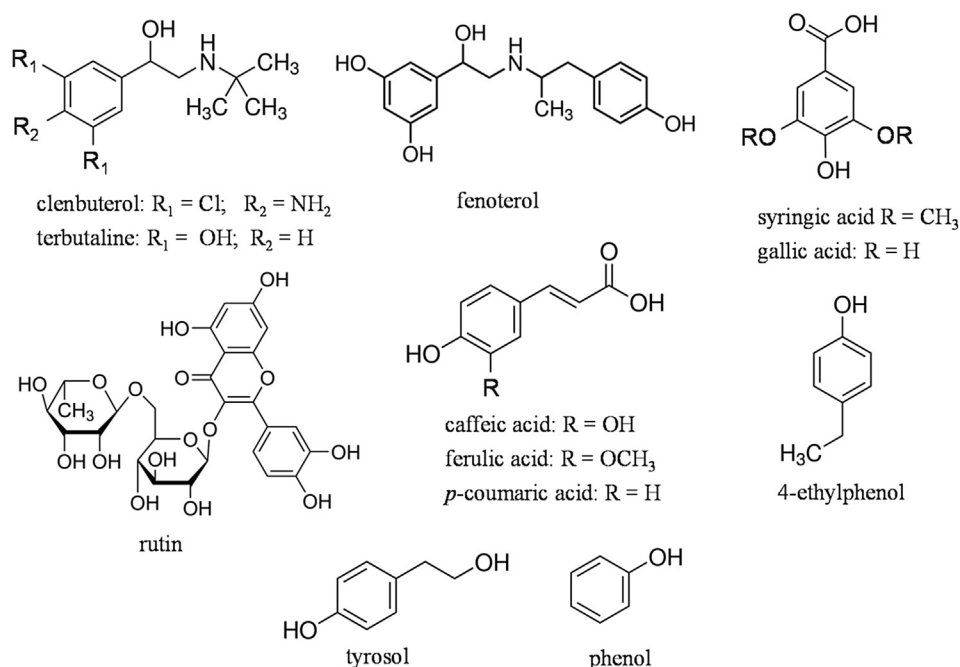


Fig. 1. Molecular structures of aryethanolaminic and phenolic compounds.

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