



Review

A review of pulsed electrochemical detection following liquid chromatography and capillary electrophoresis



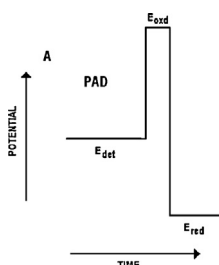
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HIGHLIGHTS

- Reviews the fundamental and basic tenants of pulsed electrochemical detection.
- The latest advances in pulsed electrochemical detection technology and its applications.
- Contains a bibliography of applications since 1997.

GRAPHICAL ABSTRACT



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ABSTRACT

Pulsed electrochemical detection (PED) has progressed as a highly sensitive and selective detection technique following aqueous-based separation systems over the past three decades. The application of on-line pulsed potential cleaning to electrocatalytic noble metal electrodes has significantly increased the number of applications formerly achieved with conventional electrochemical (EC) detection. Electrochemical cells are easily miniaturized, providing the ability to apply detection by PED at microelectrodes and onto microchips utilizing electrophoretic separations. In addition, recent advances in PED waveforms and instrumentation have enabled the detection technique to be easily coupled with high pressure separation systems which require rapid detection to maintain separation integrity. As a result, advanced applications for the determination of carbohydrates as well as the expansion of PED for the detection of other organic aliphatic compounds have been recently accomplished. This review will focus on developments and methods utilizing PED following liquid chromatography (LC) and capillary electrophoresis (CE). Publications are reviewed in chronological order to emphasize the advancement of the detection method and the sustained relevance of its applications.

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1. Introduction

Over the past 30 years, PED has served as a direct mode of detection for the determination of variety of compounds in aqueous media. The combination of rapid, on-line pulsed potential cleaning to electrocatalytic noble metal electrodes has introduced a new aspect to the division of amperometric detection following aqueous-based separation systems. In addition to the technique's inherent sensitivity, PED has been recognized to maintain sustainable analyte signals as a result of the application of anodic and cathodic polarizations intended to maintain an active electrode surface for the duration of detection.

Preceding the introduction of PED, direct current (dc) amperometric detection had been considered to be the predominant method of detection for a variety of inorganic metals and organic aromatic compounds following a prior mode of separation. The majority of applications which utilized dc amperometry were concentrated on the detection of organic aromatic compounds as a result of the species' inherent electroactivity at solid anode electrodes (e.g., Au, Pt, and C). The greater electroactivity observed by aromatic compounds is attributed to inherent electronic pi-resonance, functioning to stabilize free radical intermediates of oxidative one-electron reactions at the electrode surface [1,2]. As a result, the activation energy barrier of the electrochemical reaction is lowered significantly, therefore producing higher rates of oxidation of analytes at inert, or highly resistant electrodes [3].

The stabilization of aromatic compounds achieved via electronic pi-resonance is not observed with organic aliphatic compounds at solid anode electrodes. Hence, very low oxidation rates at inert electrodes are recognized due to the lack in stabilization of free-radical intermediates formed during the detection process. However, it was observed that the activation energy barrier for the oxidation of aliphatic compounds could be significantly reduced with the use of noble metal electrodes such as Au or Pt [3]. Noble metal electrodes such as these offer partially unsaturated d-orbitals which function to adsorb analytes on to the surface of the electrode for detection; this form of detection is referred to as electrocatalytic. As a result, electrochemical oxidation of aliphatic compounds was determined to be not only feasible but highly sensitive with the use of electrodes that facilitate surface adsorption.

The favored adsorption of aliphatic compounds at noble metal electrodes generates an overall increase of oxidation rates for both analytes and interferences. This typically results in the accumulation of products at the electrode surface rendering an inactive electrode that prevents further detection. Hence, the detection signal is observed to rapidly deteriorate when electrocatalytic noble metal electrodes such as Au and Pt become fouled with carbonaceous material. PED serves to apply alternate anodic and cathodic polarizations in a cyclic manner to maintain a clean and reactive surface capable of providing reproducible analyte signals. The technique enables the sensitive detection of aliphatic compounds otherwise considered to be electrochemically inactive by dc amperometry.

This paper will begin with a brief review of the historical aspects of PED following aqueous-based separation by LC and CE systems. The primary focus of this review will emphasize the recent advancements in PED technology, considering the development of advanced waveforms and the use of microsystems in combination with PED. In addition, applications of significant advances in the use of PED within the last 15 years will also be reviewed.

2. Historical developments of PED

The origins of pulsed potential cleaning are delineated to the beginning of the 20th century, at which the reactivation of fouled noble metal electrodes towards the development of hydrocarbon fuel cells was under investigation. Amongst the first to apply pulsed potential cleaning to Pt electrodes were Hammett [4] in 1924 and Armstrong et al. [5] in 1934 for the anodic oxidation of H₂ and cathodic reduction of O₂, respectively. Kolthoff and Tanaka [6] studied the polarization curves of Pt electrodes subject to a variety of supporting electrolytes, providing the foundation for future studies involving electrode reactivation by potential oxidative and reductive pulses. With the advancements of LC during the 1960s and 1970s, efforts in the development of pulsed potential reactivation of noble metal electrode surfaces were stimulated. These studies eventually lead to the observation of a reproducible signal response resulting from the oxidation of an aliphatic alcohol with concomitant alternate potential cleaning [7]. In 1981, Johnson and co-workers and students at Iowa State University [7,8]

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