

## A Review Article: Applications of Electroanalytical Techniques

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### Abstract

*Electroanalytical techniques are thought to be the most significant area of analytical chemistry, which identify the properties as well as quantify the given analyte(s) within an electrochemical cell. The high sensitivity, high analysis speed, low sample and solvent consumption, high scan rate, low operating cost of electro analysis make it highly advantageous in all situations. A summary of electroanalytical techniques is provided, with an emphasis on their most common uses in the identification of distinct analytes. These techniques include cyclic voltammetry (CV), square wave voltammetry (SWV), differential pulse voltammetry (DPV), electrochemical impedance spectroscopy (EIS), and voltammetry in square waves (SWV). This review explains the electrochemical applications of electroanalytical techniques in different fields. CV is widely used for studying the electrochemical properties of molecules, particularly in redox reactions. It provides detailed information about the oxidation and reduction processes of the analytes. SWV offers enhanced sensitivity and is particularly useful in trace analysis of complex matrices. DPV is employed for its high sensitivity and resolution in detecting low concentrations of analytes. EIS is used for characterizing the electrical properties of materials and interfaces, often in the study of corrosion, batteries, and sensor development. The versatility and efficiency of these techniques make them indispensable in environmental monitoring, pharmaceutical analysis, and material science, among other fields.*

**Keywords:** Electroanalytical techniques, Cyclic voltammetry (CV), Square wave voltammetry (SWV), Differential pulse voltammetry (DPV), Electrochemical impedance spectroscopy (EIS)

### INTRODUCTION

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Electroanalytical techniques are analytical methods which identify an analyte by measuring its current, potential or resistance in electrochemical cell having the analyte [1]. Electrochemistry provides a variety of techniques for analyte measurement, such as electrochemical impedance spectroscopy (EIS), differential pulse voltammetry (DPV), cyclic voltammetry (CV), square wave voltammetry (SWV) [2]. For the quantitative and qualitative analysis of biochemical, chemical and physical systems electroanalytical techniques are very useful [3]. In some cases, these quantitative analytical studies are applied to detect and sense the analyte (e.g., blood glucose concentration). However, in recent years, a significant amount of technique development has been done to study electrocatalysis in electrolyzers and fuel cells, intercalation in batteries, electrolyte/electrode interface, plating and corrosion, and even

properties of nanomaterials [4]. The most popular methods for characterizing the electrochemical processes are CV and EIS, which are also utilized for determining the analyte concentration. CV is carried out by measuring the current produced by the redox process and scanning a working electrode potential. Among all the voltammetric approaches, SWV and DPV are the most utilized pulse schemes and are recognized to be sensitive. Instead of sweeping the potentials as is the case with CV, these approaches operate by pulsing the working electrode's potential between two predetermined values. Consecutive potential pulses are applied in both the DPV and SWV procedures, with the current being recorded at the conclusion of each potential pulse.

Another electrochemical technique called amperometry is used to measure the current flowing at the working electrode's surface at a stable potential. It is highly sensitive and selective [2].

For a long time, these electroanalytical methods have multiple applications in different fields.

For instance, in important environmental, food, pharmaceutical, herbal, and biological domains, analytes, such as environmental pollutants, food additives, medicines, and cancer biomarkers are regularly evaluated [5]. Besides, these techniques can be used in some other applications i.e., capacitors and sensor studies, etc. [6]. The reactivities underlying redox processes, lifetimes and basic interactions can be widely understood by the application of electroanalytical methods [7–8]. These technologies have also included new biologically and chemically and modified electrodes for the measurement of non-redox-active compounds, advancements in voltammetric techniques, and combinations of methods to perform in situ or operando analysis [9]. Modern analytical chemistry labs use voltammetric techniques because of recent developments in apparatus, automated analytical data processing, and most importantly, creative electrochemists [10–11]. The robustness and versatility of electroanalytical procedures can be attributed to their advantages, which include high sensitivity, affordability, accuracy and easy to use [5, 12]. Additionally, the low detection limits of electroanalytical techniques allow for the study of subpicogram quantities of drug products and metabolites. These techniques also need very small sample volumes, frequently in the microliter range [13–14]. Thanks to these techniques, enable to detect the target analytes in various samples.

## REVIEW OF LITERATURE

Electroanalytical techniques play a significant role in different research areas, such as clinical, medicinal and pharmaceutical [15]. Voltammetry is one of these, it calculates the current as a function of current. A wide range of electroanalytical chemistry techniques are included in the word 'voltammetry,' including polarography, pulsed voltammetry, CV, linear scan voltammetry, and stripping voltammetry [23]. Among these technologies, voltammetric methods that use chemically modified electrodes (CMEs) based on nanomaterials for drug determination have garnered a lot of attention lately.

In a variety of commercial and research contexts, CV is a flexible electrochemical method for analyzing redox state. The common uses include label-free biomolecule detection of hormones and other biomolecules, as well as the assessment of pharmaceutical medication quality and the measurement of phenolics and antioxidants in wine and food [17]. As it offers comprehensive and valuable information on a compound's redox nature, it is regarded as a representative in-vitro approach to explain the redox nature of a substance in body tissues and fluids. By examining a chemical's redox nature through changes in potential or current, one can examine how the compound binds to DNA and perhaps aid in the investigation of the compound as a novel therapeutic candidate [18]. Barbosa et al. [19] investigated Fenclorim, an herbicide, utilizing CV at Carbon Nano Tubes Paste Electrodes and other electrochemical techniques. They monitored the current voltage curves of fenclorim 0.5 mM in universal buffer systems with a pH range of 2.0 to 6.0, they were able to investigate the impact of pH on the voltammograms. Based on the results collected, the method worked well in cases where fenclorim had a single, distinct wave or peak. Furthermore, the two-

electron irreversible reduction of the azomethine group could account for this phenomenon. A plan was created to improve the process's comprehension [5].

Al-rashdi and colleagues used CV to study the electrochemical properties of tinidazole. An irreversible reduction peak was seen in tinidazole at approximately  $-440$  mV. Tinidazole's differential pulse voltammetric peak current exhibited a linear dependence on concentration within the  $5.0$ – $200$   $\mu\text{M}$  range. The lower limits of detection and quantification were found to be  $5.1 \times 10^{-7}$  and  $1.7 \times 10^{-6}$   $\mu\text{M}$ , respectively [20].

Square-wave voltammetry (SWV) of 'surface redox reactions' is thought to be an easy-to-use and effective method for measuring a wide range of medications, physiologically active compounds, and other significant chemicals [21]. Square-wave voltammetry (SWV), which offers improved analytical performance and the capacity to provide both kinetic and mechanistic information about electrochemical processes, combines the benefits of cyclic and pulse voltammetry [22]. In addition, it is widely used for the quantitative measurement of many different substances, including pharmaceuticals, biomolecules, antioxidant, contaminants in the environment, etc. Although SWV is known to be an extremely quick voltammetric technique, electroanalytical procedures often call for a brief analysis period in addition to their marked sensitivity [4, 23].

Hence, the latest reviews regarding the electrochemical sensors for forensic drug analysis, electrochemical biosensors, electrochemical methods for determining the antioxidant capacity of food, and the use of bismuth electrodes in contemporary electroanalysis provide a helpful compilation of references on the analytical application of SWV [22].

Taleb et al. presented on the development of an electrochemical sensor that used a highly orientated pyrolytic graphite electrode transformed by self-organized gold nanoparticles. The sensor was used to analyze silver and copper ions using SWV. In terms of availability, ease of use, and detection limit, the sensor demonstrated exceptional performance [24].

SWV is also a useful method for the examination of certain bacteria in actual samples. Carpani et al. reported on the use of SWV to measure the amount of *Pseudomonas aeruginosa* and *Escherichia coli* bacteria in untreated water samples. For this, a microelectrode array was employed, and the epoxy glue-impregnated reticulated vitreous carbon electrode allowed for the precise identification of the studied bacterial cultures. There was no need for a water sample to be pretreated because the procedure was quick, easy, and selective [25].

Svorc et al. reported a simpler, relatively cheaper and more sensitive method of determination of paracetamol using anthraquinone modified carbon paste electrode AQM/CPE by square wave voltammetric method with a limit of detection  $0.13$   $\mu\text{M}$  [26].

Al-rashdi et al. investigated quercetin, polyphenol by square wave anodic stripping voltammetry. There was a linear concentration range of  $67.66$  to  $338.3$  ppb quercetin under ideal testing circumstances. The quercetin detection limit at  $15$  s accumulation time was  $6.77$  ppb [20].

DPV provides low limit of detection LOD and high sensitivity. DPV is abundantly used technique in bioanalysis, and more importantly before altering the measured current potential, DPV measurements can mitigate the impacts of charge current. Compared to commercial chromatographic procedures, DPV is significantly more precise and sensitive, especially for quantitative detection. Additionally, DPV allows for the simultaneous quantitative evaluation of many elements or substances, as well as the identification of complex electrode reaction mechanisms and adsorption phenomena [27].

Siddiqui et al. reported the electrochemical behavior of clioquinol, a compound having a wide range of therapeutic applications, Utilizing a glassy carbon electrode, cyclic, differential pulse, and square-wave voltammetry over a wide range of pH [3].

Farahi et al. developed a quick and sensitive technique to measure the paraquat (pq), an herbicide, in  $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$  solution using a silver rotating electrode. Two negative peaks were seen in paraquat at around 1.0 and 1.7 V. Several factors, including step amplitude, amplitude, frequency, and deposition duration, were examined, and the best ones were selected for the DPV investigation. The results of adding paraquat concentration were plotted on a calibration curve, with a range of  $1.0 \times 10^{-3} \text{ mol}$  and  $1.0 \times 10^{-8} \text{ L}^{-1}$ . Moreover, calibration curve was created to determine the quantification limits and detection values. For peak 1 values were  $7.1 \times 10^{-9} \text{ mol L}^{-1}$  as well as  $23.9 \times 10^{-9} \text{ mol L}^{-1}$ , respectively, while for peak 2, the values were  $2.8 \times 10^{-9} \text{ mol L}^{-1}$  and  $9.2 \times 10^{-9} \text{ mol L}^{-1}$ . The method is effective in identifying low concentrations of Pq, according to the author's conclusion (Farahiet al., 2014).

Al-rashdi et al. reported doxycycline hyclate was measured using DPV. In Britton-Robinson doxycycline hyclate has a distinct irreversible oxidation peak at pH 3.0. With estimated limits of detection and quantification of  $6.56 \times 10^{-8}$  and  $2.19 \times 10^{-7} \text{ molL}^{-1}$ , respectively, the peak current rose linearly in the concentration range of  $2.0 \times 10^{-7}$ –  $3.0 \times 10^{-6} \text{ molL}^{-1}$ . Doxycycline hyclate's pharmaceutical form was successfully established by following the suggested approach.

EIS is the very important electroanalytical method used to study electrode materials related to Li-ion batteries, hetrojunction solar cells and electro or photocatalysis [27]. EIS is a non-destructive method that can be used as a prognostic or diagnostic tool during different stages of a battery's life: for internal temperature monitoring, quality control, state estimation, which includes state of charge (SOC), stat of health (SOH), and stat of function (SOF), and characterization for use in second-life applications [1].

Brett reported ZnO-nanorod-based DNA biosensor was created to detect complimentary targeting single-stranded DNA of the BCR/ABL fusion gene as an illustration of how EIS is used to DNA sensing using a redox probe. Using  $1.0 \text{ mM} [\text{Fe}(\text{CN})_6]^{3-/4-}$ , EIS was employed to examine the immobilization and hybridization of single-stranded DNA at the electrode surface. In accordance with the dependency of the change in  $R_{ct}$  on the logarithm of its concentration, the complementary targeting single-stranded DNA of BCR/ABL could potentially be quantified within the concentration range of  $1.0 \text{ pM/L}$  to  $1.0 \text{ nM/L}$  [28].

Ângelo et al. conducted a study using a commercially available photocatalyst (P25 from Evonik®, Germany) with the corresponding  $\text{TiO}_2$  /graphene composite. The photocatalytic performance was evaluated using the standard ISO 22197-1:2007, which validated the P25 graphene composite. The Randles electrical analogue was selected for corresponding to the experimental results in the EIS, which included a three-electrode setup. Because graphene enhances the charge mobility, the composite sample showed lower values of  $R_{CT}$  and  $C_{SC}$  when compared to P25, confirming increased faradaic the photocurrent and increased photocatalytic capacity for NO degradation. Furthermore, the 2.9 eV band gap of the  $\text{TiO}_2$ /graphene photocatalyst allows for the absorption of a larger spectrum of wavelengths [29].

According to a study by Wang et al., the  $\text{NiCo}_2\text{O}_4$  BHNAs-NF electrode's semicircle was greater within the low-frequency range than the  $\text{NiCo}_2\text{O}_4$ @C BHNAs-NF electrode's. It was shown that the  $R_{ct}$  of later was comparatively lower than later [30]. The high-frequency signals area revealed that the  $\text{NiCo}_2\text{O}_4$ @C BHNAs-NF electrode had a bigger slope of the straight line than the  $\text{NiCo}_2\text{O}_4$  BHNAs-NF electrode, indicating an improved efficacy for the diffusion of ions. So, the results of these studies

clearly demonstrated that the electrode with the carbon covering had better specific capacity, cyclic stability, and rate performance [30].

## DISCUSSION

In the modern era, electrochemistry is focusing on the development of electroanalytical techniques. These electroanalytical methods are used to detect and identify the analytes(s) within an electrochemical cell by measuring its current, potential as well as resistant. These techniques are very helpful for quantitative as well as qualitative analysis of samples. Most common electroanalytical techniques are CV, square-wave voltammetry, pulse differential voltammetry and electrochemical impedance spectroscopy. These technologies have also included new biologically and chemically modified electrodes for the measurement of non-redox-active compounds, advancements in voltammetric techniques, and mixtures of techniques for in situ or operando analysis. Electroanalytical techniques are very advantageous due to high speed, low cost, easiness in operation, low consumption of sample and solvent and high sensitivity. Furthermore, the investigation of subpicogram amounts to drug products and metabolites is made possible by the low detection limits of electroanalytical techniques. Additionally, these methods require extremely tiny sample volumes typically in the microliter range. These techniques pose a variety of applications in pharmaceuticals, clinical, medicinal, food, batteries and in solar system.

## CONCLUSION

Low operating cost, high scan rate, fast analysis speed, high sensitivity, small sample and solvent consumption make these techniques highly beneficial. These techniques play a widespread role in the detection of tumor biomarkers, environment pollutants, pharmaceuticals, food additives and herbal products. The durability and versatility of electroanalytical processes have been further improved by recent developments in equipment, automated data processing, and the inventiveness of electrochemists. These methods' low detection limits enable the analysis of trace level analytes with only microliter sample volumes, such as subpicogram amounts of drug products and metabolites. Overall, the review highlights the potential role electroanalytical methods in modern chemistry and applications in diverse areas.

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