

IMPLEMENTATION OF ELECTROCHEMISTRY IN CHEMICAL ANALYSIS

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Abstract

Chemical analysis is part of chemistry that concern on sensor of material. There was develop some method in analytical chemistry. Spectrophotometry method was develop early. The some new method was develop in the 2000 century. One of the method is electrochemistry. Electrochemistry has been used for chemical analysis in multiple fields through electroanalytical techniques. Electroanalytical techniques are prominent analytical technique due to high sensitivity, reduction in solvent and sample consumption, high-speed analysis and low operating cost. A review of the electroanalytical techniques, namely, potentiometry, cyclic, differential pulse, square wave and stripping voltametric techniques, are reported. This review gives application of different electroanalytical techniques in chemical analysis.

Keywords: electrochemistry, analytical technique, voltammetry, potentiometry

1. Introduction

Electrochemistry approaches have been used successfully in numerous applications ranging from food analysis, through environmental and process monitoring to medical diagnostics [1,2] which is represented by electroanalytical techniques. Electrochemistry is concerned with the interplay between electrical and chemical effects involving chemical changes caused by the passage of an electric current and the production of electrical energy by chemical reaction [3]. Hence, electroanalytical techniques use electrical measurement for analytical purposes. Electroanalytical techniques are known as powerful and versatile analytical techniques owing to their high performance, sensitivity, reliability, and speed of analysis along with low cost instrumentation [4]. In contrast to many analytical techniques that involves homogenous bulk solution, electrochemical process take place at the electrode-solution interface. Furthermore, extremely low detection limit can be achieved due to the accumulation (pre-concentration) step of electroanalysis techniques [5]. Recent decades, electroanalytical techniques have seen fast

advances in the discovery electroactive compounds, synthesis, and sensitive electrochemical sensor [6,7].

The purpose of this review is to give the information about the implementation of electrochemistry in chemical analysis.

2. Electroanalytical Techniques

A variety of electroanalytical techniques have impacted multiple fields, including diagnostics, environmental analysis, food sciences, enzymatic kinetics and pharmacology [8]. Among the various known electroanalytical techniques, potentiometry and voltammetry are the most prominent ones widely used for ion and biomolecules sensing.

2.1 Potentiometry

Potentiometry is analytical technique based on measuring the potential of electrochemical cells without drawing negligible current [9]. Electrochemical cell of potentiometry is composed of ISE as working electrode, whose potential is highly sensitive to a specific ion to be measured and reference electrode, whose potential is stable constant [10]. It can be summarized as:

reference electrode: salt bridge ::sample solution || working electrode

The measurement enables the selective detection of ions in presence of various other substances and achieves lower detection limit [11].

2.2 Voltammetry

Voltammetry involves measurement of current as a response to an applied of constant of varying potential at the working electrode. The potential is applied in a cell of three electrodes (working electrode, auxiliary electrode, and reference electrode) and the resulting current flowing through electrochemical cell will be recorded. This technique allows quantitative analysis of analyte with extreme sensitivity due to the measured current is directly proportional of the concentration analyte [12]. The application of potential cause redox reaction of an analyte at the surface of working electrode, results in the mass transport of new material to the electrode surface and the current can be obtained. Even though the various types of voltammetric techniques may appear to be very different at first glance, their fundamental principles and application derive from the same electrochemistry approaches [13]. Voltammetric techniques have been developed in recent

decades. A brief overview of the basic concepts of the various commonly employed electroanalytical techniques is summarized below.

2.2.1 Cyclic Voltammetry

Cyclic voltammetry (CV) is widely used for qualitative information about electrochemical reaction such as study of redox processes, monitoring reaction intermediates, and stability assessment of reaction products. In this technique, during the applied potential in both forward and reverse direction, the current resulting is measured. Depending on the analysis, singles or multiple cycles can be used [14].

2.2.2 Pulse Voltammetry

Pulse voltammetry techniques are developed to improve the speed and lowering the detection limits of analysis. In this technique, the potential is varied in a series of steps (or pulse) following which the charging current has largely decayed. After the potential step, the measured current consists solely of the faradaic current (charging current being negligible) Thus, use of pulse-based technique allows for elimination of the unwanted capacitive current from the faradaic current [12]. Differential pulse and square wave voltammetry are the most widely used.

2.2.2.1 Differential Pulse Voltammetry (DPV)

In this technique, the potential is scanned with a series of pulses with fixed small amplitude (10–100 mV) and superimposed on a slowly changing base potential. The current is determined at two points for each pulse; the first point is registered before the pulse application, and the second is taken at the end of the pulse. These sampling points are selected to allow for the decay of the nonfaradic (charging) current. The difference between current measurements at these points is determined for each pulse and plotted as a function of the base potential. [12,14].

2.2.2.2 Square Wave Voltammetry (SWV)

Square wave voltammetry has a symmetrical square wave pulse of amplitude E_{sw} superimposed on a staircase (stepped) potential ramp in such a way that the forward square wave pulse coincides with the underlying staircase. The current is measured twice during each square-wave cycle, once at the end of the forward pulse, and then at the end of the reverse pulse. The difference between the two measurements is plotted versus the applied staircase potential. The

resulting peak-shaped voltammograms displays excellent sensitivity and effective discrimination against background contributions [12]. This technique has comparable shorter times of measurement than differential pulse voltammetry, hence it is possible to increase the precision of analyses and lowering detection limit.

2.2.3 Stripping Voltammetry

Stripping voltammetry is two step techniques, first one is preconcentration step involves the electrolytic deposition of analyte on working electrode. Then, followed by stripping step (measurement step), which involves the dissolution (stripping) of the deposit from working electrode. As a result of the preconcentration step, stripping voltammetry achieved the lowest detection limits of all voltammetric procedures. The three most commonly used methods are anodic stripping voltammetry (ASV), cathodic stripping voltammetry (CSV) and adsorptive stripping voltammetry (AdSV)

2.2.3.1 Anodic Stripping Voltammetry (ASV)

In anodic stripping voltammetry, the working electrode behaves as a cathode during preconcentration step and as an anode during the stripping step. During an anodic potential sweep analyte being oxidized back to its original form and resulting in a sharp peak. The peak currents are correlated to the concentration of each analyte and the position of peak potential is characteristic for each analyte. This technique is widely used for the determination of trace metal and has a practical detection limit in the part per trillion ranges.

2.2.3.2 Cathodic Stripping Voltammetry (CSV)

In cathodic stripping voltammetry, the working electrode behaves as an anode during preconcentration step and as a cathode during the stripping step. This technique has been used to determine inorganic anions such as halides, selenide, and sulfide, oxyanions, and organic compounds.

2.2.3.3 Adsorptive Stripping Voltammetry (AdSV)

Adsorptive stripping voltammetry has similar step to anodic and cathodic voltammetry, except that the preconcentration step of the analyte then occurs by physical adsorption on the electrode surface or by a specific reaction on a chemically modified rather than by electrolytic deposition.

This technique has been showed to be highly favorable for measuring many organic and inorganic compounds.

3. Electrochemical Sensors

The performance of electrochemical measurements is strongly influenced by the material of the working electrode. Numerous materials have been used as working electrode in the electroanalytical techniques that play a critical role in the construction of high-performance electrochemical sensing platforms for detecting analytes through electroanalytical techniques.

3.1 Potentiometric Sensor

The potentiometry measurement primarily used ion selective electrode (ISE) as working electrode. Ion selective electrode is a transducer that converts the activity of a specific ion dissolved in a solution into an electrical signal (potential). The voltage theoretically depends on the logarithm of ionic activity, according to the Nernst equation. The sensing part of the electrode is usually an ion-specific membrane, along with a reference electrode. The analytical information is obtained from the potential difference between the ion selective electrode and a reference electrode.

3.2 Voltammetric Sensor

The apparatus in the voltammetry measurement consist of three electrode cell included working electrode, auxiliary electrode and reference electrode. The reaction of analytes take place on the working electrode, thus the performance of voltammetric measurement is strongly influenced by the material of working electrode. From solid electrode to biosensor electrode have been investigated to develop the selective, reproducible, and raging voltammetric sensor.

3.2.1 Solid Electrodes

Mercury electrodes used to be working electrode in the voltammetric measurement, owing wide cathodic potential window and highly reproducible, making them very attractive choice as working electrode. However, the highly toxic nature of mercury insists on the necessary search for the alternative electrode materials. Solid material must possess electrical conductivity, chemical and electrochemical stability over a wide range of conditions, rapid electron transfer for a wide variety of redox systems, and reproducible electrical, microstructural, and chemical properties to function as working electrode [15]. Platinum, gold, and carbon have been

successfully used as solid electrode in numerous voltammetric measurements. They require precise electrode pretreatment and polishing to obtain reproducible results. The nature of these pretreatment steps depends on the materials involved [16].

3.2.2 Chemically Modified Electrodes (CMEs)

All electrode materials have own functionality with respect to their potential window. The modification of electrode surface is targeted to improve selectivity, sensitivity, chemical and electrochemical stability, as well as a larger usable potential window and improved resistance to fouling [16]. In combination with chemically modified electrode, the voltammetric measurement turned into outstanding analytical technique which regularly used in the fields of clinical, industrial, environmental, and agricultural analyses. The modification of electrode depends on incorporation of a modifier to the electrode surface or into the matrix of the electrode with suitable method [17].

3.4 Biosensor

Electrochemical biosensor can be defined as electrochemical sensor which contains a biological recognition element, often called a bioreceptor, and a transducer [4]. As subclass of chemical sensor, it contains a biological recognition such as enzymes, proteins, antibodies, nucleic acids, cells, tissues or receptors, that selectively reacts with target analyte and produces an electrical signal that is related to the concentration of the analyte being studied [18]. The combination of electroanalytical techniques and biosensor provide tremendous performance evaluated based on its sensitivity, limit of detection (LOD), linear and dynamic ranges, reproducibility, selectivity, and its response to interference. Biosensors have been used for clinical, food, environment, and national defense applications through potentiometric and voltammetric measurements. Recent years, electrochemical biosensors have seen significant growth with the development of enzyme biosensors and DNA detection.

4. Analytical Applications

Electroanalytical techniques have been developed for various cations, anions and biomolecules. A review about several applications of different electroanalytical techniques is presented in this review.

4.1 Electrochemical Detection of Trace Metal Ions

Metal ions are associated with various chemical species, some of them have a great influence on toxicity and the other ones have great advantages for human being. Therefore, it is importance to detect to trace metal ions.

Suyanta et al. have been developed carbon paste electrode modified with 3-methyl-2-hydrazinobenzothiazole (MBTH) was developed for the determination of La(III) by differential adsorptive stripping voltammetry. This development achieved limit of detection (LOD) 1.0 pM with linear range of 1.0 pM – 70.0 pM [19]. The modified electrode showed good reproducibility. In a study carried out by Ghoreishi et al. the working electrode was modified using graphite powder and multiwalled carbon nanotubes to detect La(III) in the presence of calcon carboxylic acid . This work used differential pulse voltammetry resulted 1.3 nM La(III) for detection limit [20].

Saidin et al. reported the use of square wave anodic stripping voltammetry with MWCNT paste electrode modified with the fenchone diazine tetracarbonylmolybdenum(0) complex to detect Cu(II). This technique obtained limit of detection (LOD) 80 pM with concentration range of Cu(II) in the 0.1 nM – 0.1 μ M [21]. Cyclic voltammetry measurement has been used by Wardani et al. that employed ZLH-CPPA modified CNT paste electrode to detect Cu(II). This work achieved the concentration range of 1.0 nM – 1.0 μ M and 10.0 μ M – 1.0 mM Cu(II) with a limit of detection (LOD) 0.1 nM Cu(II) [22]. Another work of Saidin et al. have worked using potentiometry technique that employed ion selective membrane based on 2,6-diacetylpyridine-(1R)-(-)-fenchone diazine ligand. This method obtained linear response in the concentration range of 10.0 μ M to 0.1 M with limit of detection of 2.5 μ M [23].

In order to investigate arsenic, Bhanjana et al. have performed cyclic voltammetry and chronoamperometry measurement that employed ZrO₂/Nafion/Au electrode. This work demonstrated an ultra sensitivity detection of As(III) with limit of detection 5 ppb and linear concentration range of 5 ppb – 60 ppb [24]. Yang et al. also developed modified electrode for determination of As(III) in mild condition. This work employed Au₈₉Cu₁₁bimetallic nanoparticles modified GCE through square wave anodic stripping voltammtry (SWASV) and obtained high sensitivity measurement with LOD of 2.09 ppb [25].

In order to detect mercury, Zhou et al. employed Au–TiO₂ nanoparticles/Chitosan/gold (Au–TiO₂ NPs/Chit/gold)-modified electrode through differential pulse anodic stripping voltammetry technique. This modified electrode exhibited a wide linear response range of 5.0 nM –400.0 nM Hg(II) and the limit of detection is 1.0 nM Hg(II). Another study by Bala et al. used square wave voltammetry with glassy carbon electrode modified with PTO. The result of this study revealed to have limit of detection of 23.4 pM and linear concentration range of 10 pM – 0.1 μM [27].

4.3 Electrochemical Detection of Anions

Electrochemical detection of cyanide ion using potentiometry with chemically modified carbon paste electrode was developed by Abbaspour et al. This work obtained linear concentration range of 15.0 μM – 10.0 mM and its limit of detection is 9.0 μM [28]. Noroozifar et al. have been developed modification of glassy carbon electrode with SHFNPs and MWCNT. The GC/MWCNT-SHFNPs was used for the determination of cyanide using square wave voltammetry. This work successfully used for determination of cyanide in concentration range of 40.0 nM – 150.0 μM and limit of detection was found to be 8.3 nM [29].

Electrochemical detection of chloride ion is important due to its wide application in everyday life. A novel method using linear sweep voltammetry with Ag/{PDDA/Ag}m/APTS/ITO electrode has been done by Chu et al. The measurement responded linearly with the concentration of chloride ion in the range of 10.0 nM – 1.0 μM and limit of detection was 5.2 nM [30]. Suyanta et al. have been developed ion selective electrode to detect chloride ion in water samples. This work obtained linear concentration range of 10.0 μM – 0.1 M with limit of detection of 1.23 μM [31]. Meanwhile, the study for determination of iodide ion has been done by Çiftçi et al. using potentiometry technique. This study obtained linear concentration range of 1.0 μM – 0.1 M and the limit of detection was found to be 0.8 μM [32].

The increasing presence of phosphate species derived from fertilizer in the environment leads to great concern on health problem. Hence, the study of determination of phosphate in water sample has been done by Lawat et al. This study achieved limit of detection 20.0 μM phosphates and a linear concentration range of 20–200 μM through potentiometric measurement used PPy–NO₃/BSA/GLA–PNP–XOD biosensor [33]. Meanwhile, Ejhieh et al. developed a phosphate-selective electrode based on surfactant-modified zeolite (SMZ) particles into carbon-paste. This

work exhibited linear concentration range to phosphate species in the range of 15.8 μM – 10.0 mM with limit of detection of 12.8 μM [34].

Nitrate contamination of surface and ground water is a pervasive, worldwide problem, while nitrite is an important indicator of fecal pollution in water. Hence, monitoring the presence of nitrate species has received great attention in recent years. Afkhami et al. have been developed square wave stripping voltammetry measurement to detect nitrite and nitrate in mixture. This work constructed modified carbon paste electrode using L-SCMNPs to obtain accurate and selective measurement. The limit of detection was found to be 0.625 μM and 87 μM for NO_2^- and NO_3^- , respectively [35]. Lu et al. also used square wave voltammetry for the determination of nitrate in $\text{PM}_{2.5}$ samples using carbon-fiber micro-disk electrode. This work revealed to obtain linear concentration range of 3.0 μM – 2.0 mM with limit of detection 1.10 μM [36].

4.3 Electrochemical Detection of Biomolecules

Electrochemical detection of biomolecules has attracted an enormous interest for the early diagnosis and treatment of diseases. The glucose detection using cyclic voltammetry and linear sweep voltammetry measurement has been done by Chang et al. This work developed gold nanoparticles modified glassy carbon (AuNPs/GC) electrode that exhibited a wide linear range from 25 mM – 0.1 mM with limit of detection down to 0.05 mM [37]. Meanwhile, Zhao et al. used anodic stripping voltametric technique for glucose sensing coupled with Pt_3Pd NPs modified glassy carbon electrode. This work obtained linear concentration range of glucose in the 2.0 nM – 300.0 μM and the limit of detection down to 2.0 nM [38].

The simultaneous determination of ascorbic acid, dopamine and uric acid has been reported due to these biomolecules usually coexist together in biological samples. Yang et al. have reported simultaneous measurement of dopamine, ascorbic acid and uric acid using differential pulse voltammetry with electrochemically reduced graphene oxide (ERGO) modified glassy carbon electrode (ERGO/GCE). This work revealed that dopamine, ascorbic acid and uric acid could be detected selectively and sensitively at ERGO/GCE with linear concentration range of 500.0 μM – 2.0 mM, 0.3 mM – 2.0 mM and 0.5 μM – 60.0 μM , respectively. The limit of detection (LOD) for dopamine, ascorbic acid and uric acid separately was 0.5 μM , 0.3 mM, and 0.5 μM , respectively [39]. Meanwhile, Wu et al. developed electrochemical sensor based on amino-group

functionalized mesoporous Fe_3O_4 ($\text{Fe}_3\text{O}_4\text{-NH}_2$)@graphene sheets to simultaneously determine dopamine, ascorbic acid and uric acid. This work obtained linear concentration range of 0.2 – 38.0 μM , 5.0 μM – 1.6 mM and 1.0 μM – 0.85 mM, respectively, using differential pulse voltammetry method. In addition, the limit of detection was found to be 0.126 μM , 0.074 μM and 0.056 μM for the determination of dopamine, ascorbic acid and uric acid, respectively [40].

5. Conclusions

As discussed above, we attempt to give a brief overview of the implementation of electroanalytical techniques for chemical analysis. Voltammetric techniques were observed to be more predominantly used as compared to the potentiometric ones. Various electrode materials, especially nano-dimensional, were employed to modify the electrode surface and improve the selectivity and sensitivity of the electrochemical sensor. Furthermore, electroanalytical techniques have been developed to improve detection of biomolecules for clinical applications.

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