

Review

Analytical Application Using Modern Electrochemical Techniques

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Electrochemical analysis is a powerful analytical technique that is utility in Pharmaceutical industry, metal industry, and environmental applications. Electro analysis of high advantages due to high sensitivity, reduction in solvent and sample consumption, high-speed analysis, low operating cost and high scan rate in all cases. A review of the modern electro analytical techniques, namely, cyclic, linear sweep, square wave and stripping voltametric techniques, are reported. This review gives industrial, Pharmaceutical, and environmental applications used for each mode of electro analysis techniques. (269 references, from 1922-2013).

Keywords: Electro analytical; Cyclic voltammetry; Stripping techniques; Pulse techniques, pharmaceutical applications.

1. INTRODUCTION

Electrochemical techniques are powerful and versatile analytical techniques that offer high sensitivity, accuracy, and precision as well as large linear dynamic range, with relatively low-cost instrumentation. After developing more sensitive pulse methods, the electroanalytical studies are more regularly used on industrial, environmental applications and on the drug analysis in their dosage forms and especially in biological samples. However, electroanalytical techniques can easily solve many problems of pharmaceutical interest with a high degree of accuracy, precision, sensitivity, and selectivity employing this approach. Some of the most useful electroanalytical techniques are based on the concept of continuously changing the applied potentials to the electrode-solution interface and the resulting measured current (Kissinger and Heineman 1996; J. Wang 2006; Smyth and Vos 1992;

Ozkan, Uslu, and Aboul-Enein 2003; Bard and Faulkner 2001; Kellner et al. 2004; Hart 1990 ; Bengi Uslu and Sibel A. Ozkan 2010,). Most of the chemical compounds were found to be as electrochemically active [261], During the past years, there has been extraordinary acceleration of progress in the discovery, synthesis, sensitive electrochemical analysis [262-269].

The aim of the present review is to give the basic information about electroanalytical analysis methods, working electrodes, techniques, and their industrial, pharmaceutical, and environmental applications. An attempt was made to choose some readily available publications describing some advances in methodology and applications.

1. HISTORICAL BACKGROUND OF SOME SELECTED MODERN ELECTROCHEMICAL TECHNIQUES

The term voltammetry refers to a class of electroanalytical techniques, and it is used to designate the current-voltage measurement obtained at a given electrode. Polarography is a special case of voltammetry referring to the current-voltage measurement acquired using dropping mercury electrode with a constant flow of mercury drop. Czech chemist called Jaroslav-Heyrovsky [1] first introduced Polarography in 1922, for which he received the 1959 Nobel Prize in chemistry. The using of mercury drop as electrode provides us uniform area and fresh uncontaminated electrode surface for use over a range of applied potential. Voltammetry is based on voltage-current-time relationship arising in a cell of three electrodes: working electrode, reference electrode and auxiliary or counter electrode. This relationship could be explained when potential (E) is applied to the working electrode and the resulting current (i) flowing through the electrochemical cell will be recorded. The applied potential could be changed or the resulting current will be recorded over a period of time (t) [2]. The potential applied to the working electrode serves as driving force for the reaction; it is controlled the parameter that causes the chemical species present in solution to be electrolyzed (reduced or oxidized) at the electrode surface.

The instrument, which monitors current-voltage curves (polarograph), was invented by Heyrovsky and Shikata [3]. The resulting current-voltage plot is called voltamogram where current is displayed in vertical axis and potential in horizontal axis. A special branch of voltammetry is stripping analysis [4-7], which make possible to determine a very small concentrations of analyte (subnanograms); i.e., an analysis of 10^{-10} M solution. Zbinden [8] suggested the general idea of stripping analysis in 1931.

Stripping analysis involve the analyte is concentrated into or onto the surface of the working electrode. The preconcentration step is followed by electrochemical measurement of the preconcentrated analyte or stripped from the electrode surface by the application of a potential scan [9]. The combination of the preconcentration step and measurement step generates the extremely favorable signal to background ratio. The characterization property of stripping analysis is the presence of "built in" preconcentration step [10]. The presence of preconcentration step makes stripping analysis much more sensitive than direct polarographic techniques. In addition, this technique offer wide linear range and direct study of trace concentration of the analyte. Modern variants of classical stripping

started to appear in 1947-1960, fast linear sweep voltammetry was the first [11-13] followed by the development of square wave and pulse Polarography by Barker *et al* [14-16].

1.1. Stripping voltammetry techniques (As modern electrochemical methods):

There are several many techniques of stripping. Here, will discuss many different forms of stripping analysis used for analytical purposes:

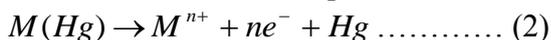
1.1.1. Anodic Stripping Voltammetry (ASV):

Anodic stripping voltammetry is most widely form of stripping analysis. It is used for the trace analysis of the analyte (metal ions or organic compound). ASV consist of two steps; pre concentration step, where the analyte is pre concentrated by electro deposition into the small-volume mercury electrode. This reaction can be represented as following [17]:



As shown from this equation the analyte is reduced at the mercury electrode forming amalgam at negative (cathodic) potential.

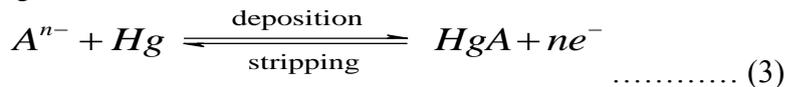
In the second step, the amalgamated analyte is reoxidized and stripped out of the electrode by applying a positive (anodic) potential. As a result of this reaction, peak current will be produced and recorded. This reaction can be represented as following [17]:



The resulting voltamogram provides us analytical information of the interest. The peak current (*I_p*) is proportional to the analyte concentration in the sample of reproducible deposition conditions is assumed. The peak potential (*E*) serves to identify the analyte in the sample [18].

1.1.2. Cathodic Stripping Analysis (CSV):

Cathodic stripping voltammetry is used to determine many of organic and inorganic compounds that forms insoluble salts with electrode material [19, 20]. It consider as mirror image of ASV. It involves positive deposition of the analyte when anodic potential is applied to the working electrode followed by stripping in a negative-going potential scan. The reaction in this step is shown as following:



The sensitivity of CSV depends on the amount of that can be plated in a given period, the density of the formed insoluble salt film and the dissociation rate of the insoluble mercury compound during the stripping step [21].

1.1.3. Adsorptive Stripping Voltammetry (AdSV):

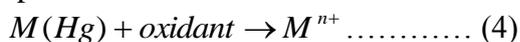
Adsorptive stripping voltammetry is quite similar to ASV and CSV methods. The primary difference could be explained as using adsorption in pre concentration step. Adsorptive stripping voltammetry can be employed in the trace analysis of a wide variety of organic and inorganic analyte [22].

In case of metal ions, it could be easily determined by AdSV when it reacts with suitable ligand to form a complex which is adsorbed on the electrode surface. Also, metal ions will be determined by AdSV when it reacts with ligand adsorbed on the electrode surface.

Organic compounds may be determined by AdSV. The adsorption process play important role in the accumulation process. When the organic compound contains electrochemically reducible or oxidizable function groups, it react with oxidized electrode material and the formed compound is adsorbed.

1.1.4. Potentiometric Stripping Analysis (PSA):

In Potentiometric stripping analysis, stirring play important role in stripping step to facilitate the transport of oxidant



Oxidation will be occurs when constant anodic current passed through the working electrode. As the oxidation proceeds, the variation of the working electrode potential is recorded and the stripping curve is obtained [23].

The transition time (t_M) consumed during the oxidation process is quantitative measure of the concentration of the analyte:

$$t_M \propto C_{M^{n+}} t_d / C_{ox} \dots\dots\dots (5)$$

This means that when the oxidant concentration (C_{ox}) decrease, the obtained signal will be increase.

1.2. Cyclic Voltammetry (CV):

Cyclic voltammetry (CV) has becomes an important and widely used in many areas of electro analytical chemistry. It is rarely used for the quantitative determination but it is widely used for study of redox reactions and get much information about the chemical reactions occurs [23]. Cyclic voltammetry is a rapid voltage scan technique in which the direction of voltage scan is reversed. While the applied potential at working electrode in both forward and reverse directions the resulting current is recorded. The scan rate in the forward and reverse direction is normally the same. CV can be used in single cycle or multicycle modes .

The measured parameters in cyclic voltammetry are anodic and cathodic peak potential (E_{pa} and E_{pc}), anodic and cathodic peak current (I_{pa} and I_{pc}) and the half peak potentials ($E_{p/2}$) at which the cathodic and anodic currents reach half of their peak value.

1.3. Pulse Voltammetry:

1.3.1. Normal Pulse Voltammetry (NPV):

This technique consists of a series of potential pulses of increasing amplitude. The measurement of peak current produced usually carried out at near the end of each pulse [16]. In NPV and at certain period, the resulting current equal zero. This may be explained as between the pulses, the electrode is kept at a constant potential at which there is no chemical reaction occurs in the cell [23].

1.3.2. Differential Pulse Voltammetry (DPV):

Comparison between NPV and DPV indicate that in DPV potential pulse is fixed and is superimposed on slowly changing base potential. the current is measured at tow points; before the application of the pulse, and at the end of the pulse [23]. The first current is subtracted from the second, and the current difference $\{\Delta i = i(t_2) - i(t_1)\}$ is plotted versus the applied potential. The highest of the produced peak current is proportional to the concentration of analyte:

$$i_p = \frac{nFAD^{1/2}C}{\sqrt{\pi a_m}} \left(\frac{1 - \alpha}{1 + \alpha} \right) \dots\dots\dots (4)$$

Where $\alpha = \exp [(nF/RT) (\Delta E/2)]$ and ΔE is pulse amplitude.

1.4. Square Wave Voltammetry (SWV):

The square wave-potential-time was first introduced by Barker [15]. In SWV waveform consist of regular square wave, superimposed on the base of staircase potential, and is applied to the working electrode [24]. The current is doubled during each square wave cycle, once at the end of the forward pulse and the other at the end of the reverse pulse. The difference between the two measurements is plotted versus the base potential.

The major advantage of SWV is its speed. Comparison of square wave and differential pulse voltammetry for reversible and irreversible cases indicated that the square-wave currents are 4 and 3.3 times higher, respectively, than the analogous differential-pulse response [25].

1.5. Instrumentation used for stripping analysis:

The apparatus used for stripping analysis consist of simple potentiostat circuits used for three-electrode cell. The three electrode cell is made up of three electrodes immersed in a solution containing the analyte and the nonreactive electrolyte called supporting electrolyte [26]. The usual cell used is that covered beakers (10-100 mL volume), but with continuous development of stripping science, the shape of cell change and being depend on the type of used working electrode and the limit of concentration want be measured [27].

1.5.1. Types of working electrode:

1.5.1.1. Mercury electrodes:

For stripping analysis, the working electrode must be stationary, and have a favorable redox behavior of the analyte, reproducible area and low background current over wide range of potential [27]. The most used electrode, which fulfills these requirements, is hanging dropping mercury electrode (HDME) and mercury film electrode (MFE).

1.5.1.2. Solid electrodes:

The limited anodic potential of mercury electrodes has precluded their utility for monitoring oxidizable compounds. Accordingly, solid electrodes with extended anodic potential windows have attracted considerable analytical interest. There are many different types of solid electrodes used as working electrodes such as gold [28], platinum [29], glassy carbon electrode [30], carbon paste electrode [31], carbon fiber electrode [32], and epoxy-bonded graphite electrode [33]. Unlike mercury electrodes, solid electrodes present a heterogeneous surface with respect to the electrode chemical activity [34]. Such surface heterogeneity leads to deviations from the behavior expected from homogenous surfaces.

An important factor in using solid electrodes is the dependence of the response on surface state of the electrode. Accordingly, the use of such electrodes requires precise electrode pretreatment and polishing to obtain reproducible results. The nature of these pretreatment steps depends on the materials involved [35-38].

1.5.1.3. Chemically Modified electrodes (CMEs):

Used working electrode may be insensitive to be applying in a certain field. Modification will be used to improve the properties of the selected working electrode. The main idea of the modification depends on incorporating of a reagent on the electrode surface or into the matrix of the selected electrode [23, 39].

The most famous method for the incorporation of a modifier to the electrode surface is covering the electrode surface with suitable polymer film. This may be occurs by covering the

electrode surface with the solution of the selected polymer and allowing the solvent to evaporate. Also, electropolymerization may be used to make the polymer film on the electrode surface.

As a new type of CMEs, pre concentrated CMEs were described [39-42]. Such modified electrodes have surface characterized by ability for reacting and binding the target analyte. Pre concentrating agent used in such modifications is usually incorporated in the electrode matrix (as done with carbon paste electrode [43, 44]) or may be binding with functionalized polymeric film on the electrode surface [23].

1.6. Sensors and biosensors

Sensor can be defined as a tool that detects or measures a physical property and records, indicates or otherwise responds to it. There are three types of sensors; chemical sensors, physical sensors and biosensors. Physical sensors are concerned with measuring physical quantities such as temperature and pressure. A chemical sensor is a device, which is responds to a particular analyte in a selective way through chemical reaction and can be used for qualitative or quantitative determination of the analyte. Chemical sensor may be described as transduction element covered with chemical or recognition layer. This layer interacts with the target analyte and the chemical changes resulting from this interaction are translated by the transduction element to electrical signal [23].

Electrochemical sensors are really a subclass of chemical sensors where the electrode is used as transduction element. The field of electrochemical biosensors has seen significant growth in the past few years, with the development of enzyme biosensors and DNA detection principles leading the way. Biosensor can be defined as a device incorporating a biological sensing element connected to a transducer. The analyte that this sensor detects and measures may be organic, inorganic and biological components. Different types of sensors have many analytical applications [45-52].

1.7. Potentiometry

Potentiometry is a classical analytical technique provides us information about the composition of the sample through the potential appearing between tow electrodes [23]. Recently, this method was developed by suggestion of use ion selective electrode (ISE). This electrode characterized by its selectivity and sensitivity. The equipment used in potentiometric measurement consists of ion selective electrode (ISE), reference electrode and potential measuring device.

The main idea of ion selective electrode is use membrane-based devices. The composition of such membrane will bind the analyte ions with high sensitivity and selectivity leaving the co-ions behind [23]. Such electrodes show fast response, wide linear range, not affected by color or turbidity, not destructive and very inexpensive.

2. ANALYTICAL APPLICATION OF SOME SELECTED MODERN ELECTROCHEMICAL TECHNIQUES

Electroanalytical techniques (specially stripping analysis) are well known as excellent procedures for the determination of trace chemical species. These techniques have been developed for various cations, anions and organic molecules. Several articles that reviewed the application and the use of such voltammetric techniques in the determination of pharmaceuticals and metals in different samples have been reported. A review about the methodology and application of different electroanalytical techniques has been presented [53].

2.1. Electroanalytical application for the determination of pharmaceutical compounds:

The electrochemical techniques, especially voltammetry, have gained steadily an importance during recent years. Such electrochemical techniques have been applied for the determination of pharmaceutical compounds in dosage forms (tablets, capsules, injections and suspension) and biological samples (real and spiked urine samples, blood and serum). Various types of pharmaceutical compounds analyzed by voltammetric techniques and these types like:

2.1.1. Gastro-intestinal drugs:

Electrochemical oxidation of metoclopramide hydrochloride has been reported [54], where the metoclopramide hydrochloride was determined by second-derivative adsorptive anodic stripping voltammetry with a nafion-modified glassy carbon electrode. The stripping peak current was proportional to the concentration of metoclopramide hydrochloride over the range 0.4–154.7 ng mL⁻¹ and the detection limit was 0.027 ng mL⁻¹ with 4-min. accumulation time. The method has been successfully applied to the determination of MCP in human serum.

Our group have been introduced a simple, reliable and selective square wave anodic stripping voltammetric method at carbon paste electrode for the determination of metoclopramide hydrochloride in pharmaceutical dosage forms (tablet) and in biological fluids (spiked and real urine samples) [55]. A linear concentration ranges from 0.067 to 0.336, 0.067 to 0.269 and 0.067 to 0.269 ng mL⁻¹ of metoclopramide hydrochloride, at accumulation times 60, 120 and 180 s, respectively, can be determined successfully.

The polarographic determination of cisapride by nitration with KNO₃ in H₂SO₄ was suggested [56]. The method is based on using Britton–Robinson buffer of pH 6.5 in presence of KNO₃/H₂SO₄ mixture as nitrating agent. The drug showed two reduction peaks in differential pulse polarography at –0.2 and –0.8 V.

Differential pulse polarographic and anodic stripping voltammetric (ASV) techniques were utilized for the determination of cinitapride [56]. The two procedures are based on using acetate buffer or KNO₃ as supporting electrolyte. At accumulation time 30 s, scan rate 4 mV s⁻¹ and accumulation potential of 0.0 V, cinitapride show peak potential at –0.3 V.

The electrochemical behavior of sulphiride at a HMDE was investigated. Linear sweep cathodic stripping voltammetry was used to determine sulphiride in the presence of acetate buffer of pH 10.5 [57]. The linear concentration range is from 0.68 to 17.1 ng mL⁻¹ sulphiride. Furthermore, a theoretical detection limit of 0.068 ng mL⁻¹ sulphiride was calculated.

Differential pulse stripping voltammetric method was developed for the determination of paracetamol and phenobarbital in pharmaceuticals assisted by chemometrics [58]. Both of these analytes gave well-defined oxidation peaks in the Britton–Robinson buffer (pH 5.72) at a glassy carbon electrode. A linear relationship between current and concentration of paracetamol [ranges: 0.09-0.93 mg L⁻¹ ($r^2 = 0.999$) and 0.9-11.7 mg L⁻¹ ($r^2 = 0.999$)], and phenobarbital [1.0-22.0 mg L⁻¹ ($r^2 = 0.999$)]. The proposed method was applied for the determination of paracetamol and phenobarbital in several commercial tablets with satisfactory results.

Direct electrochemical method based on the electrochemical oxidation of paracetamol was described for the determination of paracetamol in plasma [59]. A nanogold modified indium tin oxide (ITO) electrode was used for the determination of paracetamol at pH 7.2 [60]. Linear calibration curve is obtained over the range 2×10^{-7} - 1.5×10^{-3} M with a correlation coefficient of 0.997. The detection limit (3σ) was estimated to be 1.8×10^{-7} M. The practical analytical utility of the method is illustrated by determination of paracetamol in pharmaceutical preparations.

Square-wave adsorptive cathodic stripping voltammetric procedure was described for the trace determination of chlordiazepoxide in bulk form, pharmaceutical formulation and human serum at a mercury electrode [61]. This procedure show lower limits of detection (LOD) (4.4×10^{-10} M and 6.6×10^{-10} M) and limits of quantitation (LOQ) (1.5×10^{-9} M and 2.2×10^{-9} M), respectively in pharmaceutical formulation and spiked human serum.

2.1.2. Antibiotics and antibacterial drugs:

A highly sensitive adsorptive stripping voltammetric method was described for the determination of rifloxacin in tablets spiked plasma and urine [62].

Carbon paste electrode modified with poly(N-vinylimidazole) and poly(4-vinylpyridine) was used for the determination of amoxicillin in solid dosage forms without any separation step [63-65].

The electrochemical response of azithromycin has been attributed to oxidation of tertiary amino groups [66]. A simple and selective square-wave voltammetric method has been developed for the determination of azithromycin in pure form, in pharmaceutical preparation and in biological samples [67]. This method was accomplished with hand-make carbon paste electrode. The limits of detection and quantification of the pure drug are 0.463 and 1.544 ppb (with the correlation coefficient, $r=0.9785$ and the standard deviation, S.D.=0.1 ($n=5$), for the accumulation time of 60 s), respectively. The method was successfully applied to the determination of the drug in urine and two forms of pharmaceutical formulations.

Adriamycin was determined using carbon paste electrode in presence of cetyltrimethyl ammonium bromide (CTAB) [68]. The suggested method show linearity range of 2.5×10^{-8} - 5×10^{-6} mol L⁻¹ with detection limit 4×10^{-10} mol L⁻¹ at accumulation time 3 min.

Voltammetric study of the interaction of lomefloxacin (LMF)-Mg(II) complex with DNA and its analytical application at a mercury electrode is reported [69]. In $\text{NH}_3\text{-NH}_4\text{Cl}$ buffer (pH~9.1), the adsorption phenomena of the LMF-Mg(II) complex were observed by linear sweep voltammetry. In the presence of calf thymus DNA (ctDNA), the peak current of LMF-Mg(II) complex decreased considerably, and a new well-defined adsorptive reduction peak appeared at -1.63 V. The new peak currents of LMF-Mg(II)-DNA system increased linearly correlated to the concentration of DNA in the 4×10^{-7} - 2.6×10^{-6} g mL⁻¹ range when the concentrations of LMF-Mg(II) complex was fixed at 5×10^{-6} mol L⁻¹, with the detection limits of 2.3×10^{-7} g mL⁻¹.

The adsorptive and electrochemical behavior of norfloxacin on a glassy carbon electrode was investigated by cyclic and square-wave voltammetry [70]. In acetate buffer of pH 5.0, norfloxacin gave a sensitive adsorptive oxidative peak at 0.9 V. Applicability to measurement of norfloxacin at submicromolar levels in urine samples was illustrated. The peak current was linear with the norfloxacin concentration in the range 5-50 $\mu\text{g mL}^{-1}$ urine. The detection limit was $1.1 \mu\text{g mL}^{-1}$ urine.

Square-wave adsorptive anodic stripping voltammetric procedure was described to assay of both the rifampicin (RIF) and isoniazid (INH) drugs separately or combined in pharmaceutical formulations and human serum has been investigated at a carbon paste electrode [71]. The proposed procedure was also successfully applied to simultaneous assay of rifampicin and isoniazid drugs combined in pharmaceutical formulations. Moreover, the proposed procedure was successfully applied to simultaneous assay of both drugs in human serum samples with limits of detection and quantitation of 5×10^{-8} and 1.7×10^{-7} M for RIF and 6.1×10^{-8} and 2×10^{-7} M for INH.

A systematic study of the adsorption and association of the cancerostatic drug actinomycin-C₁ (ACT) at a hanging mercury drop electrode has been conducted using phase-sensitive a.c. voltammetry and cyclic voltammetry [72]. Also, Adsorptive accumulation in stripping voltammetry has been applied for trace measurements of the ACT [73]. Accumulation is achieved by controlled adsorption of ACT film on the hanging mercury drop electrode (HMDE). The limit of detection after 5 minutes preconcentration is 8×10^{-10} M.

Cephalosporins (such as rocephin and cefobid), were determined by several voltammetric techniques [74-82]. Sulfadiazine was determined in artificial gastric and intestinal juices using differential pulse voltammetry [83]. Indirect differential pulse voltammetry was used for the determination of sulfonamide [84]. This procedure depend diazotization and coupling occurs between 1-naphthol and sulfonamide in alkaline medium.

Different antibacterial drugs were determined in dosage forms, plasma and urine by several voltammetric and polarographic methods using hanging mercury drop electrode (HMDE) and membrane selective electrode (MSE) [85-91].

Voltammetric behavior of chloroquine was investigated using cyclic voltammetry and differential pulse voltammetry [92]. DNA-modified carbon paste electrode was used in this study. Voltammogram obtained show linearity range of 1×10^{-7} - 1×10^{-5} mol L⁻¹ with detection limit 3×10^{-8} mol L⁻¹.

Dc-polarography, cyclic voltammetry, controlled-potential coulometry and square-wave adsorptive stripping voltammetry techniques were used to study the electrochemical behavior of cefazolin sodium (CFZ) in Britton-Robinson buffer (pH 2-11) at the mercury electrode [93]. Square-

wave adsorptive cathodic stripping voltammetric procedure was described for the trace determination of CFZ in bulk form up to limits of detection and quantitation of 2.6×10^{-10} M and 8.6×10^{-10} M, respectively. The method was successfully applied for determination of CFZ in pharmaceutical preparation.

Different types of electrodes namely: dropping mercury electrode (DME), static mercury drop electrode (SMDE), glassy carbon electrode (GCE), carbon paste electrode (CPE), and modified carbon paste electrode (MCPE) were used to investigate the electrochemical behavior of the monobactam antibiotic aztreonam at different electrodes and in biological fluids [94]. Differential pulse stripping voltammetry (DPSV) and Osteryoung square-wave stripping voltammetry (OSWSV) were utilized for the drug determination in either aqueous medium or in urine samples. Detection limits of 2×10^{-8} M and 8×10^{-8} M aztreonam were achieved in aqueous and urine samples, respectively.

2.1.3. Antineoplastic drugs:

Modified carbon paste electrode was used for electrochemical studying of interaction between mitoxantrone and double-standard DNA (dsDNA) and single-standard DNA (ssDNA) [95]. This study was carried out using DNA-modified carbon paste electrode in combination with cyclic voltammetry and differential pulse voltammetry.

5-Fluorouracil was determined using cathodic stripping voltammetry in presence of trace concentrations of Cu(II) [96]. Linearity range of 5×10^{-9} - 6×10^{-8} mol dm⁻³ of 5-fluorouracil with detection limit 4.6×10^{-10} mol dm⁻³ was obtained. Another method for the determination of 5-fluorouracil was suggested utilizing flow injection system with voltammetric detection [97].

Carboplatin was determined by differential pulse voltammetry using DNA-modified glassy carbon electrode [98]. This method was applied for determination in serum. Also, it was applied to pharmacokinetic studies on patients receiving carboplatin treatment.

The electrochemical oxidation and reduction behavior of adsorbed species of tarabine PFS at an in situ-mercury film electrode is studied using cyclic voltammetry and Osteryoung square-wave stripping voltammetry (OSWSV) [99]. The drug is easily detected as 0.134 ng mL^{-1} .

A sensitive procedure for trace measurement of tamoxifen is described [100]. The method is based on controlled adsorptive accumulation of the drug at an electrochemically treated glassy carbon electrode, followed by chronopotential-metric measurement of the surface species.

A carbon paste electrode modified by hydrophobic molecules of hydroxypropyl β -cyclodextrin to form enantioselective membrane sensor was used for the enantioseparation of racemic methotrexate [101]. Also, determination of its enantiomeric purity in some pharmaceuticals is suggested.

Trace measurements of 2-thiouracil and 4-thiouridine in presence of Cu(II) is described [102]. In this method the adsorption and redox behavior occurs on hanging mercury drop electrode, and the reduction current of the accumulated complex is measured by cathodic stripping voltammetry.

2.1.4. Cardiovascular drugs:

Indapamide was determined by an adsorptive stripping method using carbon paste electrode modified by castor oil [103]. Utilizing anodic stripping differential pulse voltammetry procedure, the

calibration plot was linear in the range 18.3-36.5 ng mL⁻¹ indapamide with detection limit of 1.8 ng mL⁻¹. The method was applied for the determination of indapamide in spiked serum.

Analytical method based on the adsorptive accumulation of Cu(II)-indapamide complex followed by the reduction of the complexed copper was developed for the indapamide determination [104]. Under the optimal experimental conditions, a linear calibration graph in the range 20-200 nmol L⁻¹ and detection limit of 5 nmol L⁻¹ were calculated.

1,4-Dihydropyridine derivatives such as nitrendipine, nifedipine, dehydro- nifedipine and other calcium antagonist members were determined by different voltammetric techniques [105-114].

Differential-pulse voltammetric method was developed for the determination of amlodipine based on the oxidation of the dihydropyridine group on the surface of glassy carbon electrode under stationary and rotating conditions [115]. The limit of detection (LOD) and the limit of quantitative (LOQ) for the rotating and stationary techniques were found to be 0.004 and 0.0072 mg mL⁻¹ (for $S/N = 3.3$) and (LOQ) 0.012 and 0.022 mg mL⁻¹ (for $S/N = 10$), respectively. The proposed method was applied to the tablets containing amlodipine and according to the statistical evaluations acceptable results were obtained at the 95 % probability level.

Captopril was subjected for different voltammetric techniques. The voltammetric behavior was studied [116, 117]. Carbon-paste electrode modified with cobalt-5-nitrosalophen was used as a sensitive voltammetric sensor for detection of captopril [118]. Captopril was determined using adsorptive cathodic differential pulse stripping voltammetry with the HMDE [119]. Square-wave voltammetric determination of captopril also was suggested [120, 121]. Quite fast and inexpensive voltammetric method was suggested for the determination of captopril using differential pulse polarography in presence of oxygen [122]. Adsorptive cathodic stripping voltammetry is used for the determination of trace levels of captopril in phosphoric acid (pH 2.3) [123]. The method was applied to determine the mentioned drug in pharmaceutical formulations, urine and blood-serum. The limit of detection was 0.019 ng/ml

Cyclic voltammetry, direct current polarography, differential pulse polarography and alternating current polarography were used to study the voltammetric behavior of ramipril [124]. Verapamil was determined by adsorptive stripping voltammetry [125]. The suggested procedure shows linearity range of 1×10^{-8} - 1×10^{-6} M with detection limit 5×10^{-10} M. This procedure was successfully applied for the determination of verapamil in urine and in dosage forms

Diltiazem as an antihypertensive agent was determined in capsules and urine using adsorptive stripping voltammetry [126]. The calculated detection limit of diltiazem in aqueous solution in 2.7 ng mL⁻¹.

The square-wave adsorptive cathodic stripping voltammogram of terazosin exhibited a single well-defined two-electron irreversible cathodic peak which may be attributed to the reduction of C=O double bond of the drug molecule [127]. The described procedure was suitable for the determination of terazosin in bulk form, tablets and human serum. Limits of detection (LOD) and quantitation (LOQ) of 1.5×10^{-11} and 5×10^{-11} M bulk terazosin were achieved, respectively. The proposed procedure was successfully applied to determination of the drug in tablets and human serum samples.

DC polarography and the determination of doxazosin employing different polarographic techniques are described in this study [128]. Since the sensitivity of suggested procedure was higher

than the others, the determination of doxazosin was performed in filtered and unfiltered tablet solutions containing 4 mg active material.

Square wave voltammetry of antihypertensive doxazosin at nafion modified carbon paste electrode has been carried out [129]. The detection limit reached using square wave voltammetry was 2.33×10^{-11} M and the variation coefficient at 2.0×10^{-9} M level was 3.54%. The suggested procedure can be used to determine the drug at trace level in human urine samples with good recoveries.

A polarographic procedure of sufficient sensitivity for the determination of bulk amiloride drug in Britton–Robinson buffer at pH 2 using mercury electrodes is described [130]. The calibration graph was obtained over the concentration range 2.5×10^{-5} – 2.5×10^{-4} M amiloride. The limits of detection (LOD) and quantitation (LOQ) of the procedure were 1×10^{-5} and 3.3×10^{-4} M bulk amiloride, respectively. Moreover, a differential-pulse adsorptive cathodic stripping voltammetric procedure has been described to assay of the drug at lower concentration levels. The calibration graph was obtained over the concentration range 2×10^{-8} – 1×10^{-6} M for bulk amiloride. Both procedures were successfully applied to the determination of amiloride in tablets.

2.1.5. Anesthetic drugs:

Anodic adsorptive stripping voltammetric determination of methohexital sodium was proposed [131]. This procedure is based on the formation of insoluble mercury salt on a hanging mercury drop electrode after preaccumulation by adsorption. The detection limit was found to be 2×10^{-7} M with 180-s accumulation time. The application of this method was tested in the determination of methohexital in spiked urine samples.

Cathodic stripping voltammetric method is described for the determination of thiopentone-sodium [132]. The method is based generally on the formation of a slightly soluble mercury salt of thiopentone-sodium with Hg onto HMDE surface. The proposed method was applied for the determination of the drug in pure pharmaceutical dosage form, urine, and human serum samples.

Ghandour *et al* [133] have been proposed a sensitive and simple voltammetric method for the trace determination of muscle relaxant gallamine triethiodide (flaxedil).

2.1.6. Flavonoids:

Characterization of voltammetric behavior and antioxidative activity for selected four flavonoids (quercetin, rutin, catechin and epigallocatechin gallate) was suggested using carbon paste electrode modified with dsDNA [134].

Square wave anodic stripping voltammetry was used for the determination of quercetin is investigated [135]. Under the optimal experimental conditions, the linear concentration ranged from 67.66 to 338.3 ppb quercetin. The detection limit of 6.77 ppb quercetin at 15 s accumulation time.

Electrochemical behavior of quercetin was studied in detail by field emission scanning electron microscope (FE-SEM), UV-spectroelectrochemical and various electrochemical methods [136]. A highly sensitive adsorptive stripping voltammetric measurement (AdSV) for quercetin was also shown

at multi-wall carbon nanotubes-modified paraffin-impregnated graphite electrode, the adsorptive stripping response of the peak was proportional to the concentration in a range of 9×10^{-9} to 4×10^{-5} M with a detection limit of 4.8×10^{-9} M.

2.1.7. Vitamins:

Water soluble vitamins (thiamine, riboflavin, pyridoxine and ascorbic acid) were determined by linear sweep voltammetry at carbon paste electrode [137]. Thiamine (vitamin B₁) was determined by different voltammetric methods [138-140]. Also, riboflavin was determined by square wave adsorptive stripping voltammetry at mercury film electrode [141-143].

Ascorbic acid was determined using different voltammetric techniques. Using modified carbon paste electrode to study the electrocatalytic determination of ascorbic acid in aqueous solution [144]. Also, ascorbic acid was determined in fruits and vegetables [145, 146]. Differential pulse voltammetric determination of ascorbic acid has been realized on the carbon paste electrode (CPE) [147]. The developed method has been applied to the direct determination of vitamin C in pharmaceutical tablets and in different types of fruit juices. Limits of determination are 1.5×10^{-7} M, 8×10^{-7} M and 1×10^{-5} M for tablets, dehydrated and liquid juices, respectively.

Ascorbic acid is simultaneously determined by voltammetric techniques; with uric acid [148, 149], with epinephrine [150] and with dopamine [151, 152]. Simultaneous determination of dopamine, ascorbic acid and uric acid at modified glassy carbon electrode is suggested [153]. Also, ascorbic acid, epinephrine and uric acid were determined at glassy carbon electrode modified with caffeic acid [154].

2.1.8. Antifungal agents:

The electrochemical behavior of tinidazole was studied by normal and reverse pulse polarography [155]. According to electrochemical reduction peak obtained from tinidazole [156, 157], it could be determined easily in pharmaceutical preparations.

Clotrimazole as an example of weak bases with α -tocopherol, was determined by linear sweep voltammetry [158]. This method depends on the oxidation prepeak resulting from the oxidation of α -tocopherol. Clotrimazole can be determined by cathodic stripping voltammetry at 50 ng mL^{-1} level when pre-accumulated for 3 min at an accumulation potential of -0.20 V [159]. The proposed method is applied successfully for the determination of clotrimazole in a commercial formulation.

Two procedures, based on differential pulse polarography (DPP) and adsorptive differential pulse voltammetry (AdS-DPV) in aqueous medium were developed for the determination of ketoconazole in a gel formulation and spiked urine samples, respectively [160].

2.1.9. Antidepressant drugs:

Imipramine-HCl, trimipramine and thioridazine were determined using carbon paste electrode modified with β -cyclodextrin [160]. Amitriptyline-HCl and imipramine-HCl were determined by

voltammetry using polymer modified carbon paste electrode [162], fatty acid carbon paste electrode [163], platinum and activated glassy carbon electrode [164]. At lipid-coated glassy carbon electrode and lipid-coated carbon paste electrode, the desipramine, imipramine and trimipramine were determined by voltammetry [165].

Electrochemical behavior of trazodone-HCl was investigated using carbon paste electrode [166] and platinum electrode [167]. Also, direct current (DC_v), differential pulse (DPP) and alternating current (AC_v) polarography were used to study the voltammetric behavior of trazodone-HCl [168].

The electrochemical oxidation of tryptophan at graphite electrodes has been studied in aqueous solutions [169]. A simple, fast and sensitive method is proposed for tryptophan determination in pharmaceutical formulations containing other non-electroactive amino acids, vitamins and hydroxycobalamines was suggested using carbon paste electrode [170].

2.2. Electroanalytical application for the trace determination of metals:

Modern electroanalytical methods show a remarkable sensitivity, broad scope and very low quantitation limit. Different electroanalytical methods, especially stripping analysis, widely used for the trace metals determination in environmental, industrial and in biological samples. Various stripping techniques were used for the determination of 30 trace elements [23].

2.2.1. Industrial Samples:

A highly sensitive and selective stripping voltammetric procedure for the determination of uranium (VI) based on the adsorption properties of dioxouranium (II)-phthalate complexes onto hanging mercury drop electrode was developed [171]. The reduction current of adsorbed complex ions of U(VI) was measured by both linear sweep (LSCSV) and differential pulse cathodic stripping voltammetry (DPCSV). As low as 2×10^{-9} mol dm⁻³ (0.5 ug/L) and 2×10^{-8} mol dm⁻³ (4.8 ug/L) with accumulation time 240 and 120 s using DPCSV and LSCSV, respectively, have been determined successfully. The application of this method was tested in the determination of uranium in super-phosphate fertilizer.

Application of orthogonal functions to differential pulse voltammetric analysis was suggested [172]. The study was extended to differential pulse cathodic stripping voltammetry (DPCSV) for the simultaneous determination of tin and lead. The stripping voltammetric analysis data processed by orthogonal functions and the first-derivative (1D) methods were successfully applied to the simultaneous determination of both metals in canned soft drinks.

Differential pulse cathodic stripping voltammetry (DPCSV) was used to determine ultra trace platinum in gasoline after wick bold combustion and subsequent UV digestion [173].

Cathodic stripping voltammetry combined with the Osteryoung square-wave mode at the glassy carbon electrode gave rise to both sensitivity and selectivity of the determination of manganese in some industrial samples [174]. The detection limit with 5 min accumulation is 0.022 ug/L. Simultaneous determination of manganese in presence of Cu(II), Pb(II) and Zn(II) could be easily done using anodic stripping voltammetry at pH 4.

Bismuth film electrodes were prepared ex-situ by pulsed potential electrodeposition. The analytical performances of these electrodes for adsorptive cathodic stripping voltammetry of nickel were evaluated in nonde-aerated solutions using dimethylglyoxime as complexing agent [175]. Linear calibration curves were obtained for Ni^{+2} concentrations ranging from 1×10^{-8} - 1×10^{-7} mol L⁻¹ and from 1×10^{-7} - 1×10^{-6} mol L⁻¹ with relative standard deviations of 5% (n = 15) at 1×10^{-7} mol L⁻¹ level. The analytical methodology was successfully applied to monitor Ni^{+2} content in industrial electrolytic baths, ground water and tap water.

Differential pulse cathodic stripping voltammetry (DPCSV) and linear sweep cathodic stripping voltammetry (LSCSV) were used for the determination of trace amounts Cr(VI) ions in neutral phosphate media [176]. Detection limit was 5×10^{-9} mol L⁻¹ and 1×10^{-9} mol L⁻¹ using LSCSV and DPCSV, respectively.

Differential pulse cathodic and anodic stripping voltammetry were applied for the determination of trace ions Cd(II), Co(II), Cu(II), Pb(II), Mn(II), Ni(II) and Zn(II) which are found in different grades of common salt as contaminants [177].

A procedure for the determination of lead in paints by differential-pulse anodic-stripping voltammetry is presented [178].

Differential pulse anodic stripping voltammetry with a hanging mercury drop electrode has been used for the determination of trace amounts of Cu(II), Cd(II), Pb(II) and Zn(II) ions in white cane sugar [179, 180].

Trace amounts of Zn(II), Cd(II) and Pb(II) were determined in refined beet sugar by differential pulse anodic stripping voltammetry (DPASV) at a hanging mercury drop electrode [181]. The procedure was applied to the determination of toxic elements in commercial beet sugar samples and levels of metals below 35 mg kg⁻¹ Pb(II), 80 mg kg⁻¹ Zn(II) and 10 mg kg⁻¹ Cd(II) were found.

Determination of heavy metals (Cu(II), Cd(II), Pb(II) and Zn(II)) in concentrated refined sugar and raw syrups with differential pulse polarography and anodic stripping voltammetry was described [182]. Using differential pulse polarography, trace determinations down to 10^{-7} M were measured. But using anodic stripping voltammetry at a mercury film electrode, it was found that the refined sugar of alimentary grade contained: 57 Cu(II), 34 Zn(II), 1 Cd(II), and 6 Pb(II) µg/kg of dry sugar.

Anodic stripping voltammetry with a hanging mercury drop electrode was used for the determination of trace amounts of Zn(II), Pb(II) and Cu(II) in sugar cane spirit from different sources: commercial, oak-cask matured and home-made [183].

Experiments have been carried out to assess the potential of differential pulse voltammetry and potential stripping analysis for determining Pb(II), Cu(II) and Cd(II) directly in dissolved honey samples [184].

Se(IV) is determined by differential pulse anodic stripping voltammetry using gold electrodes [185]. A wide linear response range 0.5-291 ng mL⁻¹, was obtained using a 5.0 mm diameter gold electrode.

Mo(VI) is determined by anodic stripping voltammetry using a carbon paste electrode modified in situ with cetyltrimethylammonium bromide (CTAB) [186]. Differential pulse anodic stripping voltammetry exploiting the reoxidation signal is used for the determination of trace levels of molybdenum(VI). Linearity between current and concentration exists for a range of 0.5-500 µg L⁻¹

Mo(VI) with proper preconcentration times; the limit of detection is $0.04 \mu\text{g L}^{-1}$ with an accumulation period of 10 min.

A chemically modified carbon paste electrode was developed for the determination of silver by incorporating the strong acid ion-exchanger into a conventional graphite-Nujol oil paste using by square wave anodic stripping voltammetry [187]. For 5 min of accumulation, the linear range was from $1.62 \mu\text{g L}^{-1}$ to 0.8 mg L^{-1} with a detection limit of $0.27 \mu\text{g L}^{-1}$. Another type of chemically modified carbon paste electrode was suggested for the determination of silver [188]. Using differential pulse stripping voltammetry, the appropriate calibration graph for Ag(I) was obtained between $5 \times 10^{-7} \text{ M}$ and $1.5 \times 10^{-6} \text{ M}$ and detection limit was $2 \times 10^{-7} \text{ M}$.

Determination of lead and antimony in firearm discharge residues on hands by anodic stripping voltammetry using a mercury-coated graphite electrode are established [189].

Anodic stripping voltammetric determination of trace amounts of titanium has been studied using glassy carbon electrode modified with thymol blue (TB) [190]. The method has been successfully applied to determine titanium in two standard reference material Portland cement samples, then to Portland cement and cement clinker.

A voltammetric method has been used for the determination of the contents of toxic heavy metals in domestic waste and in compost produced from it [191]. Cu(II), Pb(II), Zn(II) and Cd(II) were determined in wet-digested samples of domestic waste, compost produced of that waste and in compost mixed with sewage sludge by anodic stripping voltammetry.

An indirect voltammetric method is described for determination of cyanide ions and hydrogen cyanide, using the effect of cyanide on cathodic adsorptive stripping peak height of Cu-adenine using mercury electrode [192]. The detection limit was obtained as $1 \times 10^{-8} \text{ M}$ for 60 s accumulation time. The method was applied to the determination of cyanide in various industrial waste waters such as electroplating waste water and also for determination of hydrogen cyanide in air samples.

Simultaneous determination of Cu(II), Zn(II) and Pb(II) by adsorptive stripping voltammetry in the presence of Morin was suggested [193]. With an accumulation time of 60 s, the peak currents are proportional to the concentration of copper, lead and zinc over the 1-60, 0.3-80 and 1-70 ng/mL range with detection limits of 0.06, 0.08 and 0.06 ng/mL, respectively. The procedure was applied to the simultaneous determination of Cu(II), Zn(II) and Pb(II) in some real and synthetic artificial real samples.

Ni(II) and Co(II) have been determined simultaneously by means of adsorptive cathodic stripping voltammetry (AdCSV) in a computerized flow injection system [194]. The selectivity of the method was demonstrated for the analysis of high purity iron.

A voltammetric method is presented for the determination of trace levels of Cr(VI) in the presence of cupferron as ligand [195]. This method based on using square wave adsorptive stripping voltammetry (SWAdSV) in conjunction with the electrochemical batch injection analysis technique at mercury thin-film electrodes. An analytical method has been developed for the determination of dissolved chromium at concentrations less than $2 \mu\text{g/L}$ in PWR coolant by differential-pulse adsorptive stripping voltammetry at a hanging mercury drop electrode [196].

Mo(VI) has been determined by differential-pulse adsorptive stripping voltammetry in a pH 2 phosphate buffer utilising the strong adsorption of 12-molybdophosphoric acid at a hanging mercury

drop electrode [197]. Calibration graphs are rectilinear up to the 7×10^{-7} M Mo(VI). A clearly defined stripping peak was observed at the 5.6×10^{-9} M level with 2 min accumulation.

Adsorptive stripping voltammetry at a static mercury drop electrode for the determination of Al(III) and Fe(III) in Portland cement has been employed [198].

An analytical procedure for the determination of Fe(III) and total iron in wines based on adsorptive stripping voltammetry is described [199]. Fe(III) was determined by using Solochrome Violet Red as chelating agent while catechol was used for the determination of the total iron content.

A sensitive stripping voltammetric procedure for quantifying thorium is described [200]. The chelate of thorium with the azo dye mordant blue 9 is adsorbed on the hanging mercury drop electrode. The detection limit is 4×10^{-10} M (4-min accumulation), a linear current-concentration relationship is observed up to 1.3×10^{-7} M.

Square wave adsorptive stripping voltammetric method for the determination of Ti(IV) is described [201]. The method is based on Ti(IV) complexed with hydroxynaphthol blue (HNB) at the static mercury drop electrode. The limit of detection was found to be $0.18 \mu\text{g/L}$ and the limit of determination to be $1.09 \mu\text{g/L}$, both using 30 s of preconcentration time.

Simultaneous determination of tin and lead by differential pulse polarography with addition of hyamine-2389 is described [202]. Calibration plots are linear up to 5×10^{-5} M for tin and 1.3×10^{-4} M for lead, with detection limits of 8.4×10^{-7} M and 2.4×10^{-7} M, respectively. Simple methods are proposed for the determination of tin in solders and canned fruit juices.

Traces of Fe(III) were determined by differential pulse polarography in solar-grade silicon [203]. Differential pulse polarography provides a detection limit of about $0.15 \mu\text{g g}^{-1}$ with a precision of 1-2% and linear calibration graphs up to $0.5 \mu\text{g mL}^{-1}$ Fe(III).

Differential pulse polarographic determination of Cr(VI) in semiconductor gallium arsenide based on the catalytic current produced by nitrate in the electrolytic reduction of the Cr(VI)-diethylenetriaminepentaacetate complex [204]. This method is suitable for determinations of Cr(VI) at levels as low as about $1 \mu\text{g g}^{-1}$ with about 50 mg of sample.

Mo(VI) was determined in steel by differential-pulse polarography [205]. The method is applicable to the determination of molybdenum in the 0.001-5% of Mo(VI) range and good agreement is reported for a number of certified British Chemical Standard and commercial steels.

Ternary mixtures of metals can be resolved by using the ratio derivative polarography without the need for any pre-separation step [206]. The method is based on the simultaneous use of the first derivative of ratios of polarograms and measurements of zero-crossing potentials. The method has been successfully applied for resolving ternary mixtures of Cu(II), Cd(II) and Ni(II), which have overlapped polarograms. The concentration ranges to be determined are $0.30\text{-}1.40 \text{ mg L}^{-1}$ for Cu(II), $0.90\text{-}4.50 \text{ mg L}^{-1}$ for Cd(II) and $0.20\text{-}1.20 \text{ mg L}^{-1}$ for Ni(II).

An electrochemical method for the quantitative determination of boron in minerals and ceramic materials is described [207]. It is based on the abrasive attachment of mixtures of ZnO plus sample to modified graphite electrodes.

A method for determining trace level of V(V) has been developed [208]. The reaction is the polarographic reduction of the bromate, catalyzed by this metal ion, in the presence of cupferron. A linear current-concentration relationship is observed between 2×10^{-8} and 3×10^{-7} M, with a detection

limit of 6×10^{-9} M. The procedure is very selective and has been successfully applied to a certified steel sample.

Voltammetric determination of the iodide ion with a quinine copper(II) complex modified carbon paste electrode employing linear sweep and differential pulse voltammetry [209]. Using linear sweep voltammetry, a calibration curve was attained over the concentration ranges 1×10^{-4} – 2.5×10^{-6} M of the iodide ion at deposition time of 10 min, with the detection limit 1×10^{-6} M. Using differential pulse voltammetry, linear response range for the iodide ion was between 10^{-6} and 10^{-8} M, and the detection limit was 1×10^{-8} M. This method was evaluated by analyzing the iodide ion content in a commercial disinfectant.

2.2.2. Biological Samples:

Determination of trace Al(III) in foods by stripping voltammetry was presented [210]. The method based on study of electrochemical behavior of Al(III)–cupferron complex. This complex absorbed in hanging mercury drop electrode (HMDE) and creates a sensitive peak current. The peak current and concentration of Al(III) accorded with linear relationship in the range of 4×10^{-8} – 2×10^{-9} g/mL. This method has been used to determine trace aluminum in foods and water.

The electrochemical behavior of Cu(II)-2-[2,3,5-triazolylazo]-5-dimethyl-aninobenzonic [Cu(II)–TZAMB] complex was studied [211]. This complex has adsorptive characteristics on hanging mercury drop electrode (HMDE) and can be reduced in an irreversible reduction step. The calibration graph for Cu(II) was linear over the concentration range 9.5×10^{-9} mol L⁻¹– 4.7×10^{-7} mol L⁻¹, the detection limit of the method was 9.5×10^{-9} mol L⁻¹. The method was found suitable for the determination of Cu(II) in rice and vegetables.

A polarographic method for the determination of nitrate in vegetables is illustrated [212]. The method is based on the reduction of nitrate to nitric oxide which reacts in solution with Co(II) and thiocyanate ions forming an electroactive complex that is reduced at the dropping mercury electrode. The calibration graph was linear in the range of 2 – 12×10^{-6} mol nitrate.

Differential-pulse cathodic stripping voltammetric determination of Se(IV) in food supplements is presented [213]. Se(IV) was determined by cathodic stripping voltammetry in a 1 mol L⁻¹ HCl acid solution containing added Cu(II). In this medium, Se(IV) was preconcentrated on the hanging mercury drop electrode and stripped cathodically in differential-pulse mode.

Pulse-polarographic determination of tin, lead and molybdenum were investigated [214]. Total tin in shipyard waters was determined at pH 5. The same method was also applied to the determination of tin in canned food.

Determination of Cd(II) in Some foodstuffs by anodic stripping pulse voltammetry (ASPV) using glassy carbon electrode was suggested [215]. Linear calibration curves were obtained in the concentration range between 1.5×10^{-9} – 2×10^{-10} M. This method was successfully applied to the determination of Cd(II) in some foodstuffs (wheat and its products, vegetables) after acid digestion.

Performance of a bismuth coated carbon microdisk electrode for the determination of trace heavy metals by anodic stripping voltammetry (ASV) was studied [216]. Measurements were

performed on synthetic solutions containing Cd(II), Pb(II), and Cu(II) as target ions. In particular, linear calibration curves over the range 5×10^{-8} – 1×10^{-6} M for Cd(II) and Pb(II), detection limits of 7.8 and 2.9 nM for Cd(II) and Pb(II), respectively. This method was applying for the determination of Pb(II) and Cu(II) in drinking water, wine, and tomato sauce.

An analytical procedure regarding the determination of Cu(II), Pb(II), Cd(II), Zn(II) and Sb(III) in matrices involved in foods and food chain as wholemeal, wheat and maize meal is proposed [217]. Differential pulse anodic stripping voltammetry (DPASV) was employed for simultaneously determining all the elements. The limits of detection were in the range 0.009–0.096 $\mu\text{g/g}$

A method for the determination of Pb(II) in soft drinks and fruit juices by potentiometric stripping analysis is described [218].

Trace levels of tin can be determined by voltammetry after controlled adsorptive preconcentration of the tin-tropolone complex on a hanging mercury drop electrode [219]. For a 8-min preconcentration period, the detection limit is 2.3×10^{-10} M. The method was applied for the determination of tin in orange-juice samples.

The application of potentiometric stripping analysis (PSA) to simultaneous determination of lead and tin has been investigated using a continuous flow system [220]. The suggested procedure was applied for the determination of lead and tin in fruit juices and soft drinks are also described.

A square wave adsorptive stripping voltammetric (SWAdSV) method for the indirect determination of trace amounts of Mg(II) with thiopentone sodium (TPS) as an electroactive ligand, at carbon paste mercury film electrode (CP-MFE) is proposed [221]. A linear relation in the range 6×10^{-9} to 9×10^{-8} M Mg(II) (0.14–2.16 ppb), at 60 s deposition time, is obtained. The detection limit of Mg(II) is 0.14 ppb for 60 s deposition time.

The complex formation between uric acid and Zn(II), Cd(II) and Pb(II) has been investigated using differential pulse polarography [222]. A sensitive voltammetric method is developed for the quantitative determination of uric acid. This method is based on controlled adsorptive preconcentration of uric acid on the hanging mercury drop electrode (HMDE), followed by tracing the voltammogram in the cathodic going potential scan. The modes used are direct current stripping voltammetry (DCSV) and differential pulse stripping voltammetry (DPSV). The detection limits found were 8×10^{-9} M (quiescent period 15 sec) by DPSV and 1.6×10^{-8} M by DCSV.

Controlled adsorptive accumulation of Mo(VI)-2-benzylideneiminobenzo hydroxamic acid (BIBH) at the hanging mercury drop electrode (HMDE) provides the basis for the direct stripping measurement of Mo(VI) in nanomolar concentration [223]. A differential pulse cathodic stripping voltammetric method for the determination of Mo(VI) with 2-BIBH in urine is proposed.

The modified carbon paste electrode (CPE) responding simultaneously to Pb(II), Cu(II), and Hg(II) ions has been constructed by incorporating humic acid (HA) into the graphite powder with Nujol oil [224]. Here, the detection limit for Pb(II), Cu(II), and Hg(II) ions were 5×10^{-9} M, 8×10^{-9} M, and 8×10^{-9} M, respectively, for 20 minutes of deposition time. Satisfactory results were acquired for the determination of the test metal ions in certified standard urine.

Determination of traces of thallium in urine by anodic stripping AC voltammetry [225]. Determination of thallium by measuring the current peak which results from the fundamental harmonic ac stripping voltammogram recorded.

Concentrations of heavy metals such as Pb(II), Cd(II), Cu(II), and Zn(II) have been determined by using differential pulse anodic stripping voltammetry (DPASV) in air particulates, diet, and children's blood residing [226]. The determination of Zn(II) in human eye tissues by anodic stripping voltammetry was introduced [227].

Arsenic was determined in ancient bone samples was determined using a gold tipped rotating disc electrode and differential pulse anodic stripping voltammetry [228]. For a deposition time of 120 sec, the lowest detection limit (LOD) for arsenic was 1.078 $\mu\text{g/L}$.

Differential-pulse adsorption voltammetry for the simultaneous determination of nickel and cobalt in bovine liver [229]. The limits of detection obtained under the conditions of this study were 0.01 $\mu\text{g g}^{-1}$ and 0.02 $\mu\text{g g}^{-1}$ for cobalt and nickel, respectively,

Application of stripping voltammetry to trace Pb(II) analysis in intermediates and final products of syntheses of pharmaceuticals [230]. The method showed a good linearity up to 50-100 ppm Pb(II) with a detection limit less than 10 ppb.

The determination of Pb(II) and Cd(II) biological materials was carried out by potentiometric stripping analysis [231]. The method was applied to different standard reference materials (leaves, needles, hair).

Differential pulse cathodic stripping voltammetry (DPCSV) have been used for the determination of selenium in plants[232]. The selenium content in capsules and in seeds was evaluated; the seed contains $\approx 5000 \text{ mg kg}^{-1}$ as total selenium, of which almost 50% is soluble in solvents.

Simultaneous determination of Cd(II), Cu(II), Pb(II) and Zn(II) in amino acid parenteral nutrition solutions by anodic stripping voltammetry and sample digestion by UV irradiation [233]. The metal concentrations ranged between 1.3-4.4 for Cd(II), 2.9-40.8 for Cu(II), 4.4-16.8 for Pb(II), and 1.4-208.5 for Zn(II).

Bismuth film electrode is presented as a promising alternative to mercury electrodes for the simultaneous determination of trace Co(II) and Ni(II) in non-deoxygenated solutions [234]. This method show low detection limits of 0.08 $\mu\text{g L}^{-1}$ for Co(II) and 0.26 $\mu\text{g L}^{-1}$ for Ni(II) employing a deposition time of 60 s.

Square wave stripping voltammetry of Pb(II), Cu(II), and Hg(II) was performed on the modified gold electrode [235]. The detection limits of 0.16, 0.15, and 0.14 ppb for Pb(II), Cu(II) and Hg(II) were obtained, respectively.

2.2.3. Environmental Samples:

Square-wave voltammetric determination of eight elements viz. Cd(II), Pb(II), Cu(II), Zn(II), Co(II), Ni(II), Cr(VI), and Mo(VI) in soil and indoor-airborne particulate matter has been examined and optimized [236]. It was found that the square-wave anodic stripping voltammetry is the conventional technique for the determination of Zn(II), Cd(II), Pb(II), and Cu(II), but square wave adsorptive cathodic stripping voltammetric method is used for the determination of Co(II), Ni(II),

Mo(VI) and Cr(VI). The detection limits of these metal ions were 0.03, 0.4, 0.04, 0.1, 0.15, 0.05, 0.2, and 3.2 $\mu\text{g}/\text{kg}$ for Cd(II), Pb(II), Cu(II), Zn(II), Co(II), Ni(II), Cr(VI), and Mo(VI), respectively

A method was described for the determination of selenium in soils and plants by differential pulse cathodic-stripping voltammetry (DPCSV) at a hanging mercury-drop electrode [237].

An ultrasensitive adsorptive catalytic stripping (voltammetric and potentiometric) procedure for determining trace levels of chromium in the presence of cupferron is described [238]. A preconcentration time of 1 min results in a detection limit of 1.0 ng L^{-1} . The stripping potentiometric scheme allows convenient measurements of chromium in the presence of dissolved oxygen. The identical stripping response for Cr(III) and Cr(VI) solutions makes the method applicable to the measurement of the total chromium content. The simultaneous determination of chromium and uranium is illustrated. The merits of the proposed procedure are demonstrated by the analysis of soil and groundwater samples.

A differential pulse stripping voltammetry method for the trace determination of Mo(VI) in water and soil has been developed [239]. The suggested procedure can be used for determining Mo(VI) in the range 5×10^{-10} to $7 \times 10^{-9} \text{ M}$, with a detection limit of $1 \times 10^{-10} \text{ M}$ (4 min accumulation).

Direct and simultaneous voltammetric analysis of heavy metals in tap water samples at Assiut city was developed [240]. Tap water samples are analyzed to determine the total content of Cd(II), Cu(II), Pb(II) and Zn(II) by differential pulse anodic stripping voltammetry (DPASV) while Ni(II) and Co(II) are determined by a new simple differential pulse adsorptive stripping voltammetry (DPAdSV), using dimethylglyoxime (DMG) as the complexing agent. This method uses sodium sulfite as the supporting electrolyte, which facilitates the removal of oxygen interference without the traditional necessity of purging with inert gas

Graphite Electrodes Modified by 8-hydroxyquinolines exhibited an affinity to chelating Cu(II) forming a Cu(II) complex, which was employed for Cu(II) trace analysis [241]. A differential pulse voltammetry, combined with a preconcentrating-stripping process and a standard addition method was used for the analysis. A detection limit for trace copper determination in water, such as $5.1 \times 10^{-9} \text{ mol L}^{-1}$, was obtained.

Catalytic adsorptive stripping voltammetry determination of ultra trace amount of Mo(VI) is proposed [242]. The method is based on adsorptive accumulation of the Mo(VI)-pyrocatechol violet (PCV) complex on to a hanging mercury drop electrode, followed by reduction of the adsorbed species by voltammetric scan using differential pulse modulation Mo(VI) can be determined in the range 1×10^{-3} - 100.0 ng mL^{-1} with a limit of detection of 0.2 pg mL^{-1} . The procedure was applied to the determination of Mo(VI) in mineral water and some analytical grade substances with satisfactory results.

Differential pulse adsorptive cathodic stripping voltammetric method has been developed for trace determination of Mo(VI) in presence of alizarin red S as complexing agent [243]. The peak current is proportional to the concentration of Mo(VI) over the concentration range of 1-25 ppb with a detection limit of 0.25 ppb. The method has been applied to the determination of Mo(VI) in water samples.

Carbon paste electrode modified with diacetyldioxime used for the simultaneous determination of Pb(II) and Cd(II) [244]. Calibration graphs were linear in the concentration ranges of 1.0×10^{-7} -

1.5×10^{-5} mol/L (Pb(II)) and 2.5×10^{-7} - 2.5×10^{-5} mol/L (Cd(II)), respectively. For 5 min preconcentration, detection limits of 1×10^{-8} mol/L (Pb(II)) and 4×10^{-8} mol/L (Cd(II)) were obtained. The diacetyldioxime modified carbon paste electrode was applied to the determination of Pb(II) and Cd(II) in water samples.

Electrochemical method is described for the determination of inorganic arsenic in water at the $\mu\text{g/L}$ level, applicable in the laboratory and in the field, based on differential pulse cathodic stripping voltammetry [245]. Determination of total As is performed by reducing As(V) to As(III) using sodium meta-bisulfite/sodium thiosulfate reagent stabilized with ascorbic acid. As(V) is quantified by difference. The detection limit was $0.5 \mu\text{g/L}$ with a linear range from 4.5 to $180 \mu\text{g/L}$.

Adsorptive stripping voltammetric determination of Pb(II) in presence of 2,2'-dipyridyl-2,4-dioxybenzoic acid molecular complex was proposed [246]. The compounds formed by Pb(II) and 2,2'-dipyridyl-2,4-dioxybenzoic acid molecular complex (DDOB) are adsorbed on the mercury electrode. Linear dependence between the current and Pb(II) concentration in the solution was observed in the range 1.2×10^{-8} - 3.5×10^{-7} M Pb(II), for accumulation time 60 s and stationary diffusion. This method was applied for the determination of the Pb(II) in the natural waters.

Anodic stripping voltammetric method with a mercury thin film electrode is reported for the establishment of baseline concentrations of Cd(II), Pb(II) and Cu(II) in natural waters [247].

A voltammetric method based on chelate adsorption at the hanging mercury electrode is described for the simultaneous determination of Cu(II), Pb(II), Cd(II), Ni(II) and Co(II) by adsorptive stripping voltammetry using quercetin as complexing agent [248]. The method was applied successfully for the simultaneous determination of the five metals in tap water samples.

Differential pulse anodic stripping voltammetry was used for the determination of Zn(II), Cd(II), Pb(II) and Cu(II) in the underground water [249]. The trace elements levels found are in the ranges 0.01-0.37, 1.27-49.5, 0.41-29.8 and 0.13-98.09 $\mu\text{g/L}$ for Cd(II), Cu(II), Pb(II) and Zn(II), respectively. The method was applied with satisfactory results for the determination of these metals in underground water samples.

Adsorptive cathodic stripping voltammetric determination of Mo(VI) in synthetic solutions and environmental samples was proposed [250]. This method is based on controlled adsorptive preconcentration of Mo(VI) species on the hanging mercury drop electrode (HMDE) using mixtures of nitrate and phosphate as supporting electrolytes. The method used is cathodic linear sweep stripping voltammetry (CLSSV). The detection limit found was 1×10^{-8} M using 120 s. as accumulation time. This method has been applied for the determination of Mo(VI) in environmental samples; e.g., soil, natural water and indoor airborne particulate.

Determination of iron in seawater using cathodic stripping voltammetry preceded by adsorptive collection with the hanging mercury drop electrode [251]. The detection limit for the determination of iron in seawater of pH 6.9 was 6×10^{-10} M in the presence of 4×10^{-4} M catechol and after a collection period of 3 min. The peak current increased linearly with the metal concentration up to about 5×10^{-8} M, but the linear range could be increased by using a shorter collection period.

Direct determination of sub-nanomolar levels of Zn(II) in seawater by cathodic stripping voltammetry is presented [252]. The zinc complex with ammonium pyrrolidine dithiocarbamate is adsorbed on a hanging mercury drop electrode and the reduction current of zinc is measured by voltammetry. The detection limit for Zn(II) is 3×10^{-11} M, with 10-min collection time.

Dissolved Al(III) in seawater and freshwater is determined by cathodic stripping voltammetry preceded by adsorptive collection of complex ions with 1,2-dihydroxyanthraquinone-3-sulphonic acid (DASA) on the hanging mercury drop electrode [253].

Direct determination of dissolved Co(II) and Ni(II) in seawater by differential pulse cathodic stripping voltammetry preceded by adsorptive collection of cyclohexane-1,2-dione dioxime complexes [254]. Detection limit for Co(II) and Ni(II) depend upon reagent blanks and are 6 pM and 0.45 nM, respectively, for 15-min adsorption periods.

Complex ions of Mo(VI) with 8-hydroxyquinoline (oxine) are shown to adsorb onto the hanging mercury drop electrode [255]. This property forms the basis of a sensitive electrochemical technique by which dissolved Mo(VI) in seawater can be determined directly. The peak current-Mo(VI) concentration relationship is linear up to 3×10^{-7} M; the detection limit is 4 nM.

Procedures are presented to determine simultaneously Cu(II), Pb(II) and Cd(II) in seawater by differential pulse cathodic stripping voltammetry preceded by adsorptive collection of complexes with 8-hydroxyquinoline (oxine) onto a hanging mercury drop electrode (HMDE) [256]. The limits of detection for a 1 min stirred adsorption time are 0.12 nM Cd(II), 0.3 nM Pb(II) and 0.24 nM Cu(II).

A sensitive stripping voltammetric procedure for determining titanium is described [257]. There is a linear relationship between the preconcentration time and peak height at low surface coverages. With a 5 min preconcentration period the detection limit is 7×10^{-10} M. The merits of the described procedure are demonstrated in the analysis of sea, river and rain waters.

Ti(IV) dissolved in sea water can be determined using adsorptive cathodic stripping voltammetry in the presence of mandelic acid [258]. The sensitivity of the voltammetric technique was thus improved by a factor of 20, and the limit of detection was lowered to 7 pM with 60 s adsorption, sufficiently low to determine Ti(IV) in water of oceanic origin.

Direct electrochemical determination of dissolved vanadium in seawater by cathodic stripping voltammetry with the hanging mercury drop electrode [259]. Polarographic measurements showed that catechol complexes of V(V) adsorb onto the hanging mercury drop electrode. This property forms the basis of a sensitive electrochemical technique by which dissolved vanadium in sea-water can be determined directly. The limit of detection is 0.3 nM vanadium after a 2-min collection with a stirred solution, which is decreased further to 0.1 nM after a 15-min collection.

A procedure for the direct determination of iodide in seawater is described [260]. Using cathodic stripping square wave voltammetry, it is possible to determine low and subnanomolar levels of iodide in seawater, freshwater, and brackish water. The minimum detection limit is 0.1-0.2 nM (12 parts per trillion) at a 180-s deposition time.

3. CONCLUSION:

The previous survey shows that the number of publications dealing with the application of some selected modern electrochemical techniques (voltammetric techniques) to determine pharmaceuticals and metals in different samples. The importance of such applications increased steadily, and this due to the following advantages:

- 1- Voltammetric methods have been very popular and have made valuable contributions to trace elements speciation because they combine the requirements of accuracy and sensitivity.
- 2- The sensitivity is sufficiently high and can be increased more by modifications of classical voltammetric techniques (modified microelectrodes and ultramicroelectrodes) that enhance significantly sensitivity and selectivity of the method.
- 3- Voltammetry coupled with different separation methods such as (HPLC, Flow Injection (FI) and Capillary Electrophoresis (CE)) enhancing the analytical properties for complex mixtures in different compounds.
- 4- Turbid and colored solutions, which are a problem with other methods, can be easily analyzed. The separation of the excipients, in pharmaceutical analysis, is in many cases not necessary and this simplified the preparation of samples.
- 5- Only small volumes of samples are necessary.
- 6- Modern voltammetry also continues to be a potent tool used by various kinds of chemists interested in studying oxidation and reduction process in various media, adsorption process on surfaces and electron transfer mechanism at chemically modified electrodes surfaces.
- 7- Electroanalytical stripping procedures have been developed for the measuring down to sub- $\mu\text{g/L}$ level.
- 8- Also, these techniques combine low maintenance costs with high sensitivity and selectivity that allows the determination of low levels of analytes with out prior treatments of the samples.
- 9- These techniques have been developed for various cations, anions and organic molecules.
- 10- Electroanalytical techniques (specially stripping analysis) are well known as excellent procedures for the determination of trace chemical species.
- 11- The developed stripping voltammetric methods are simple, time saving, selective and more sensitive for the simultaneous determination of trace substances.
- 12- Electroanalytical methods especially square wave voltammetry is a very sensitive and rapid analytical method due to it is high scan rate in all cases where the reacting species is accumulated by adsorption on the electrode surface.
- 13- The short analysis time in these methods makes it very attractive for routine determination of the analytes in different samples.

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