

Diamond paste based electrodes for inorganic analysis

by

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Submitted in partial fulfilment of the requirements for the degree

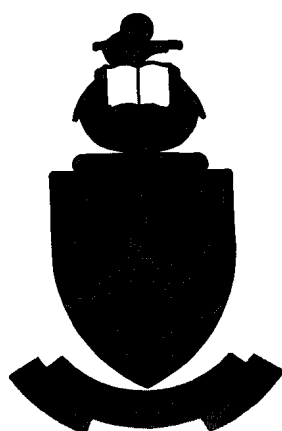
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SYNOPSIS

Differential pulse voltammetry is one of the most widely used analytical polarographic techniques especially for trace inorganic analysis. Up to now mercury electrode and different types of carbon electrodes were used for such analysis. The emphasis of the present dissertation is on the design of a new class of electrodes, namely monocrystalline diamond paste based electrodes, to be used in differential pulse voltammetry for trace analysis of inorganic compounds.

Monocrystalline diamond and boron doped polycrystalline diamond based electrodes exhibit several superior electrochemical properties that are significantly different from those of other carbon allotropes based electrodes, e.g., glassy carbon electrodes, highly oriented pyrolytic graphite based electrodes, which have been widely used for many years. The advantages are: (a) lower background currents and noise signals, which lead to improve S/B and S/N ratios, and lower detection limits; (b) good electrochemical activity (pre-treatment is not necessary); (c) wide electrochemical potential window in aqueous media; (d) very low capacitance; (e) extreme electrochemical stability; and (f) high reproducibility of analytical information. Furthermore, later studies shown the superiority of the monocrystalline diamond as electrode material due to high mobilities measured for electrons and holes.

The design selected for the electrodes is simple, fast and reproducible. The diamond powder was mixed with paraffine oil to give the diamond paste used as electroactive material in the electrodes. The results obtained by employing the diamond paste based electrodes proved a high sensitivity, selectivity, accuracy and high reliability. These characteristics made them suitable to be used for the analysis of different cations (e.g., Fe(II), Fe(III), Cr(III), Cr(VI), Pb(II), Ag(I)) as well as of anions (e.g., iodide) in pharmaceutical, food and environmental matrices.

Diamond pasta elektrodes vir anorganiese analise

deur

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SAMEVATTING

Differensiële puls voltammetrie is een van die mees algemene gebruikte analitiese polarografiese tegnieke veral vir spoor anorganiese analise. Tot hede is die kwikelektrode en verskillende tipes koolstofelektrodes vir sulke analyses gebruik. Die klem van hierdie verhandeling is toegespits op die ontwerp van 'n nuwe klas elektrodes, naamlik monokristallyne diamant pasta elektrodes, wat in differensiële puls voltammetrie vir spooranalise van anorganiese verbindings gebruik kan word.

Monokristallyne diamant en boron ingeïmpregneerde polikristallyne diamant gebaseerde elektrodes vertoon verskeie superieure elektrochemiese eienskappe wat betekenisvol verskillend is van die van ander koolstofallotroop gebaseerde elektrodes byvoorbeeld glasagtige koolstofelektrodes, wat algemeen vir baie jare gebruik is. Die voordele is: (a) laer agtergrond stroom en geraas seine, wat lei tot verbeterde S/B en S/N verhoudings, en laer deteksielimiete; (b) goeie elektrochemiese aktiwiteite (voorafbehandeling is nie nodig nie); (c) 'n wye elektrochemiese potensiaal venster in waterige media; (d) baie lae kapasitansie; (e) ekstrem elektrochemiese stabiliteit; en (f) hoë reproduseerbaarheid van analitiese inligting. Meer onlangse studies toon ook die superieuriteit van die monokristallyne diamant as elektrode materiaal as gevolg van die hoë mobiliteite wat vir elektrone en gate gemeet word.

Die ontwerp van die elektrodes is eenvoudig, vinnig en reproduseerbaar. Die diamantpoeier word met paraffienolie gemeng om die diamant pasta te gee wat as aktiewe materiaal in die elektrodes gebruik word. Die resultate wat verkry word met die diamant pasta elektrodes lewer 'n hoë sensitiwiteit, selektiwiteit, akkuraatheid en hoë betroubaarheid. Hierdie kenmerke maak hulle uiters geskik vir die gebruik in die bepaling van verskillende katione (byvoorbeeld, Fe(II), Fe(III), Cr(III), Cr(VI), Pb(II), Ag(I)) so wel as anione (Byvoorbeeld jodium) in farmaseutiese, voedsel en omgewingsmatryse.

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CHAPTER 1

POLYCRYSTALLINE DIAMOND BASED ELECTROCHEMICAL SENSORS AND THEIR APPLICATIONS IN INORGANIC AND ORGANIC ANALYSIS

1.1 Introduction

Almost all electrochemical studies to date are performed with diamond films prepared by chemical vapor deposition (CVD). Synthetic films often possess a polycrystalline and textured microstructure, with a small volume fraction of non-diamond impurity [1]. The applications for synthetic diamonds, primarily in the area of active electronic components, did not realize to a great extent because of the poor structural quality (i.e., the polycrystalline nature) of most CVD grown films.

Some of the inherent "electrochemically" desirable properties of diamond are hardness, high thermal conductivity, corrosion resistance, chemical inertness, variable conductivity via doping, and electrode geometry patterning using selective growth methods. The resistivity of polycrystalline diamond thin-films made by chemical vapor deposition (CVD) can be decreased by doping with boron [2]. The resulting films can possess either p-type semiconducting or semimetal electronic properties, depending on the doping level. Resistivity as low as 0.01 Ω -cm has been reported for boron doped films, rendering them conductive enough for electrochemical studies.

The electrochemical behavior of diamond electrodes in H_2O_2 solution was reported [3]. The accuracy of the analytical information assured by using boron-doped polycrystalline diamond film electrodes rendered the technique to be used successfully in electroanalysis and electrochemical sensors. The response current is proportional to the square root of the scan rate, reflecting the mass transport controlled by planar diffusion. Excellent stability and reproducibility are attractive properties of the diamond electrode even for the later application.

Boron doped diamond exhibits (BDD) several superior electrochemical properties that are significantly different from those of other carbon allotropes, e.g., glassy carbon (GC), pyrolytic graphite (PG), and highly oriented pyrolytic graphite (HOPG), which have been widely used as electrode materials for many years. Its attractive features include a wide electrochemical potential window in aqueous media, very low capacitance and extreme electrochemical stability. BDD electrodes appear to be relatively free from deactivation problems concerning their sensitivity and stability (e.g., a detection limit of $0.2 \mu\text{mol/L}$ is obtained for ferrocyanide) [4]. The electrodes also show resistance to deactivation even for several weeks of exposure to the laboratory atmosphere. Another interesting feature of BDD films is that its surface is nonpolar as a result of predominant termination of the surface with hydrogen. Thus, the adsorption of polar molecules is suppressed, as demonstrated by Xu et al [5].

High quality polycrystalline diamond electrodes doped with boron are amenable alternatives for a wide range of applications especially in the field of electroanalysis [6] for the following reasons: (i) lower background currents and noise signals, which lead to improved S/B and S/N ratios, and lower detection limits; (ii) good

electrochemical activity without the need for pretreatment; (iii) a chemically inert surface that is resistant to fouling such that a high degree of electrode activity is maintained over time; and (iv) fairly reproducible film properties from batch-to-batch. All these advantages of utilization of this kind of electrode material are illustrated in paragraphs 1.2, 1.3, and 1.4.

1.1.1 Diamond film growth

The diamond films are usually grown on conducting p-Si (100) substrate using a microwave plasma [7,8]. The substrates, $\sim 1 \text{ cm}^2$ and 0.5 mm thick, are first rinsed with ultrapure water, methanol and acetone. They are then hand-polished with 0.1- μm diamond powder for about 5 min on a felt pad. The process seeds the surface with diamond particles, which serve as nucleation sites for film growth. Then it is followed by placement of the substrates in the center of the CVD reactor, atop a boron diffusion source (B_2O_3), and adjacent to a piece of h-BN. The two solid materials served as sources for the boron dopant atoms as the atomic hydrogen in the plasma likely reacts with the solid to form B_2O_6 . The dopant levels are estimated to be $\sim 1 \times 10^{19} \text{ B cm}^{-3}$. The chamber is evacuated to a base pressure of $\sim 20 \text{ mTorr}$ before initiating the growth. Ultra high purity (99.999%) methane and hydrogen are used as the source gases for the growth and the film thicknesses are 1-3 μm .

1.1.2 Boron doping

The use of electrochemically conductive and semiconductive diamond thin-films has only recently been reported [9,10]. Until now, the relationship between the physical,

chemical and electronic properties of the material, and the electrochemical or photo electrochemical performance is not well known. Diamond is one of the nature's best insulators, but when doped with boron, the material can possess semi-conducting electronic properties depending on the doping level. Highly doped, hydrogen terminated diamond films are semimetals, and possess several important and unique properties such as: (i) low and stable voltammetric and amperometric background currents; (ii) wide working potential window in aqueous electrolyte solutions; (iii) reversible to quasi-reversible electron transfer kinetics for several inorganic redox analytes, and enhanced signal-to-background ratios for these analytes due to the low background currents; (iv) morphological and micro structural stability at extreme anodic and cathodic potentials, (v) low adsorption of polar molecules from aqueous solutions like anthraquinone-2,6-disulfonate, and (vi) long-term response stability.

1.1.3 Boron doped diamond background currents and electron transfer reactions

The cyclic voltammetry response of a highly doped diamond film electrode possessing high quality (low non-diamond carbon impurity) were described for two redox analytes [8]. Background current at this high-quality diamond electrode are smaller than those at classical GC by a factor of 10, while the faradaic responses for $\text{Fe}(\text{CN})_6^{3-/4-}$ and $\text{IrCl}_6^{2-/3-}$ are comparable. The diamond electrode is electronically active for these two redox analytes without conventional surface pretreatment, including chemical wet etching [11]. Larger S/B ratios are also observed in voltammetric measurements (made at a high-quality electrode for these two redox couples) than for the freshly polished GC: the S/B ratio is 16 times larger for

$\text{Fe}(\text{CN})_6^{3-/4-}$ and 8 times larger for $\text{IrCl}_6^{2-/3-}$ at diamond compared with those of GC. Atomic force microscopy (AFM) and Raman spectroscopy are used for the structural characterization of the films. Results indicate that the non-diamond carbon impurity is not required for an active diamond electrode, implying that electron transfer reactions do not occur solely through these impurity sites but rather through the doped materials.

1.2 Analysis of organic compounds

1.2.1 Acetaminophen

Cyclic voltammetry and flow injection analyses with amperometric detection are described for the electrochemical analysis of acetaminophen with BDD electrode [12]. The diamond electrode provided a linear dynamic range from 0.1 to 8 mmol/L and a detection limit of 10 $\mu\text{mol/L}$ ($S/B=3$) for the voltammetric measurement. The flow injection analysis results at the diamond electrode indicated a linear dynamic range from 0.5 to 50 $\mu\text{mol/L}$ and a detection limit of 10 $\mu\text{mol/L}$ ($S/N \cong 4$).

1.2.2 Organic acids

Cyclic voltammetric electrooxidation of some organic acids (e.g. citric acid, malic acid, alanine and cysteine) at boron-doped diamond (BDD) electrodes is described [13]. The low background current in the potential region where the oxidation of these compounds occur is an attractive feature of the BDD electrode. For cysteine, the response is nearly ideal due to the reaction taking place on the diamond surface rather

than on sp^2 carbon impurities. The response needs to be improved, however for the other acids.

Cyclic voltammetry and bulk electrolysis electrochemical oxidation of benzoic acid (BA) on acidic medium is presented [14]. Cyclic voltammetric measurements in the potential region of water/supporting electrolyte stability show that BA is oxidized, resulting in electron deactivation due to fouling. Bulk electrolysis of BA in the potential region of water/supporting electrolyte decomposition however results in the inciation of BA with electrogenerated active intermediates. Good agreement between the experimental data and the theoretical model, based on the assumption that the anodic oxidation of BA is diffusion-controlled.

Popa et al. show the selective detection of uric acid (UA) in the presence of high concentrations of ascorbic acid (AA) at electrochemically anodized diamond film electrodes [15]. Uric acid is determined with very good selectivity as the oxidation peak potential for AA approximately 450mV more positive than that for UA at anodized diamond electrodes. Using chronoamperometry technique, the detection limit is found to be as small as 5×10^{-8} mol/L. Hence, the practical utility of the method is demonstrated by the measurement of UA in human urine and serum without any treatment.

1.2.3 Dopamine

Electrochemical oxidation of dopamine at a highly boron-doped thin-film electrodes is examined using cyclic voltammetry and chronoamperometry [16]. One of the main

advantages of the proposed diamond electrode is that dopamine can be reliably assayed in the presence of large excesses of ascorbic acid in acidic medium. A detection limit of 50nmol/L is obtained using chronoamperometry. These studies indicate great promise for the use of diamond film electrodes in biosensor applications.

1.2.4 Histamine

Linear sweep voltammograms for 100 μ mol/L histamine in a 0.1mol/L neutral phosphate buffer at a highly boron-doped diamond electrode were performed [17]. The diamond electrode exhibited a well-defined oxidation peak at 1.4V vs SCE with a potential sweep rate of 100 mVs⁻¹. The background-corrected voltammetric current response is linear ($r = 0.98$) in the concentration range examined (0-100 μ mol/L) with a detection limit of 1 μ mol/L. A detection limit of 0.5 μ mol/L ($S/N = 13.8$) is obtained by using the FIA technique.

1.2.5 3-methylpyridine (3-MP)

Cyclic voltammetry and bulk electrolysis for electrochemical oxidation of 3-methylpyridine (3-MP) at synthetic boron-doped diamond (BDD) thin film electrode in 0.5 mol/L HClO₄ is described [18]. Depending on the applied current density, the BDD based electrode can be used for electroorganic synthesis of nicotinic acid or for combustion of 3-MP. At low current density and low conversion 3-MP is oxidized to nicotinic acid, while at high current density it is directly combusted to CO₂. The theoretical model for the prediction of 3-MP concentration during 3-MP combustion

agree very well with the experimental data. The results demonstrated the application of the technique to electroorganic synthesis and waste water treatment.

1.2.6 NADH

Cyclic voltammograms for the oxidation of NADH at a BDD electrode before and after 1h of exposure to the solution, followed by washing, drying and storage in the laboratory for 19h, are superimposed demonstrating the actual absence of deactivation of the electrode [19]. The concentration range examined is linear between 0-60 $\mu\text{mol/L}$ with a regression factor ($r = 0.999$) up to a sweep rate of 500 mVs^{-1} . Several films are tested and the peak potential for each is $0.58 \pm 0.02 \text{ V}$ with current densities reproducible within 4-5%. An amperometric detection limit is also found to be $\sim 10 \mu\text{mol/L}$ at an S/N ratio of 7 ($n=7$). The response remained stable even for low concentration range indicating the possibility of its applicability for NADH-based sensors.

1.2.7 Pentachlorophenol

Codognoto et al used square wave voltammetry for the determination of pentachlorophenol (PCP) at boron doped diamond electrode [20]. The oxidation occurs at 0.80V vs. Ag/AgCl using a square wave voltammetry. The detection limit for pure water and polluted water taken from the local creek are 5.5 and 15.5 $\mu\text{g/L}$, respectively. The detection limit for later increases because of the degree of contamination of the pure water sample while the recovery efficiencies are close to 100%. Hence, the combination square wave voltammetry and BDD electrode is a

feasible alternative for the analytical determination of PCP and related molecules in either pure water or polluted natural matrices.

1.2.8 Phenol

The electrochemical oxidation of phenol in HClO_4 on synthetic boron-doped diamond thin film electrode (BDD) is reported [21]. Cyclic voltammetry, chronoamperometry and bulk electrolysis are used to obtain complete combustion of phenol to CO_2 or the partial oxidation of phenol to other organic compounds (benzoquinone, hydroquinone, catechol). The theoretical values of phenol concentration and current efficiency during phenol combustion agree very well with the experimental result.

1.2.9 Serotonin

Sweep rate dependent cyclic voltammograms for $10\mu\text{mol/L}$ serotonin in 0.1mol/L phosphate buffer ($\text{pH}=7$) is examined with a potential scan rate of 100 mVs^{-1} [17]. Highly BDD electrode shows an oxidation peak at 0.42V vs SCE indicating the absence of adsorption at the diamond electrode within the experimental time of several hours. An experimental detection limit of 10 vmol/L is obtained with a linear dynamic range from 0.01 to $50\mu\text{mol/L}$.

1.2.10 Sulfur compounds

Cyclic voltammetric electrooxidation of homocysteine, glutathione (GSH), 2-mercapto ethanesulfonic acid and cephalexin at boron-doped diamond (BDD)

electrodes are investigated [22]. Low voltammetric background current in the large positive potential region are obtained without pretreatment of the electrode. Hence, BDD can be a promising electrode material for the electrolysis of other sulfur-containing compounds.

1.2.11 Xanthine and its derivatives

The electrochemical oxidation of xanthine and its naturally occurring N-methyl derivatives (theophylline, theobromine and caffeine) at conductive diamond electrodes are presented [23]. Cyclic voltammograms obtained at BDD electrodes exhibit well-defined voltammograms with high signal to background ratios for all xanthine derivatives. The concentration range is 1 to 400 $\mu\text{mol/L}$ for theophylline, theobromine and caffeine, and of 1 to 100 $\mu\text{mol/L}$ for xanthine. The excellent results obtained for caffeine determination in three commercially available coffee and cola products, with very simple sample preparation, involving only dilution in electrolyte, demonstrates the practical analytical utility of the method.

1.3 Trace metal analysis

1.3.1 Cadmium, lead and zinc

Anodic stripping voltammetry for the detection of trace metal ions like Zn^{2+} , Cd^{2+} and Pb^{2+} is described [24]. All the three analytes are easily resolved and detected in the low to mid nmol/L range. The deposition was accomplished from a 0.1 mol/L acetate buffer, pH 4.2, at a constant potential of -1300 mV versus SCE. The ions are pre-

concentrated on the surface for 3 min under quiescent conditions. Zn^{2+} can easily be detected due the large over potential for hydrogen evolution of the diamond film unlike the glassy carbon where the deposition and stripping occurs at potentials at which hydrogen evolution commences.

1.3.2 Cerium (Ce^{3+})

The electrochemical study of the $\text{Ce}^{3+/4+}$ redox couple at highly boron-doped conductive diamond electrode in aqueous sulfuric acid, nitric acid and perchloric acid is shown [25]. Well-defined cyclic voltammogram indicating quasi-reversible behavior for the $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox couple is derived demonstrating its usefulness for studies of couples with highly positive equilibrium redox potentials. With the use of simple cyclic voltammetric measurements, the diffusion coefficients and electron transfer kinetic parameters can be conventionally determined in a way that is not possible with other types of electrodes. Hence, highly boron-doped diamond is an excellent electrode material for the electrochemical analysis of species with highly positive potentials in aqueous solutions.

1.3.3 Copper (Cu^{2+}) reduction

Nakabayashy et al. investigated the electrochemical reduction of copper (Cu^{2+}) with negligible deposition of the metal on the conductive boron-doped CVD diamond electrode [26]. The copper atoms hardly adsorb on the diamond electrode surface, due to the non-polar nature of hydrogen-terminated surface. Conductive boron-doped

CVD diamond electrodes can be used for the electrochemical reduction of metal ions without electrodeposition.

1.3.4 Lead

Ultrasonically assisted cathodic stripping voltammetry at a boron doped diamond electrode is described for the detection of lead in river sediment [27]. Linear sweep voltammetry for the analytical signal from a cathodic strip of electrodeposited PbO_2 is employed. The linear concentration range is 3-100 $\mu\text{mol/L}$ with 3 $\mu\text{mol/L}$ being the lower detection limit. For the cathodic stripping step square-wave voltammetry is used to lower the detection limit of the technique while retaining the linearity to the order of 10^{-8} mol/L. In combination with an ultrasonically assisted acid digestion, the technique can be used successfully in the analysis of similar contaminated samples, offering a substantial saving of time and cost over currently used techniques.

1.3.5 Lead, mercury and platinum

Awada et al. described the cyclic voltammetry of the electrochemical deposition of Pt, Pb, and Hg on conductive diamond thin-film surface [28]. Results for the three metal ions indicate that electrochemical reduction is a viable approach for metallizing the surface of polycrystalline diamond-thin films demonstrating the development of novel catalytic electrodes, sensors, and detectors using this advanced material.

1.3.6 Manganese (Mn^{2+})

Ultrasonically assisted cathodic stripping voltammetry at a boron-doped diamond electrode for the detection of manganese is described [29]. Differential pulse voltammetry is used to give the analytical signal from a cathodic strip of electrodeposited MnO_2 . For a 2 min deposition the detection limit is 10^{-11} mol/L with a linearity up to 3×10^{-7} mol/L. Both ultrasonic-anodic deposition of MnO_2 and ultrasonic-cathodic stripping are used. The method is successful for the determination of manganese content in two instant tea samples, giving excellent agreement with independent AAS analyses.

1.3.7 Silver

Saterlay et al. described the sonoelectroanalysis of silver at a BDD electrode, using both anodic silver oxide and cathodic silver metal deposition is described [30]. A detection limit for aqueous Ag^+ of 10^{-9} mol/L and a linear range of 10^{-9} - 10^{-7} mol/L is obtained. The analytical benefits of chloride ion complexation of Ag^+ , as an anodic stripping voltammetry (ASV) peak shift-reagent offers the potential to selectively avoid overlapping of contaminants in a complex system. The application of power ultrasound can be used to increase the efficiency of the electrochemistry taking place, allowing trace determinations to be carried out in relatively short times, compared with most silent techniques.

1.3.8 Silver and tin

Boron-doped diamond electrodes and reference substrates comprising Ag and Sn are investigated using abrasive stripping voltammetry [31]. The silver deposited yields an analytically diagnostic signal in stripping voltammetry; tin is found to be extremely dependent on the stripping conditions employed. The initially hydrogenated CVD diamond electrodes become significantly oxidized when employed in this application. The abrasion process produces metallic particulates on the electrode surface, and both the mechanical and electrical contact are sensitively dependent on the abrasive force used.

1.4 Simultaneous analysis

1.4.1 Copper and lead

Simultaneous detection of trace lead and copper at boron-doped diamond is reported [32]. Though both lead and copper appear to be deposited, linear response for both of these metals is found in the range from 2.5×10^{-6} mol/L and 10^{-4} mol/L using anodic stripping voltammetry. SWV is used as a basis for the simultaneous independent detection of Cu and Pb through conventional standard addition methodology.

1.5 Conclusions

Polycrystalline boron-doped diamond electrodes can be used successfully for the assay of inorganic (trace metals) and organic compounds. They demonstrated the best

reliability of the analytical information due to the high stability and attractive electrochemical properties. The advantages of using diamond based electrodes are: the S/N and S/B ratios as increasing; the sensitivity is increasing and the limit of detection is decreasing.

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CHAPTER 2

MODERN POLAROGRAPHIC TECHNIQUES

2.1 Introduction

The study of current-potential relations in an electrolysis cell where the current is determined solely by the rate of diffusion of an electroactive species is called *voltammetry* [1]. A high concentration of an electrochemically inert *background* or *supporting electrolyte* is added to the solution to suppress the migration of electroactive species towards the electrodes by electrostatic attraction. Typically, the cell comprises a mercury or platinum micro-electrode, which is readily polarizable, and a calomel or mercury-pool reference electrode which is non-polarizable. By using a small polarizable electrode, conditions can readily be attained wherein the diffusion current is independent of applied potential and directly proportional to the concentration of electroactive species in the bulk solution. Measurements of such *limiting currents* forms the basis of quantitative analysis. The polarizable micro-electrode is usually made the cathode at which the electroactive species is reduced. The most widely used electrode is the dropping mercury electrode (DME) and the technique involving its use is known as *polarography*. A plot of current flowing in the cell as a function of the applied potential is called a *polarogram* or a *polarographic wave*, Figure 2.1. At small applied potential, only a *residual current* flows in the cell caused by the reduction of trace impurities in the sample solution and by charging of the mercury drops. The charging effect is analogous

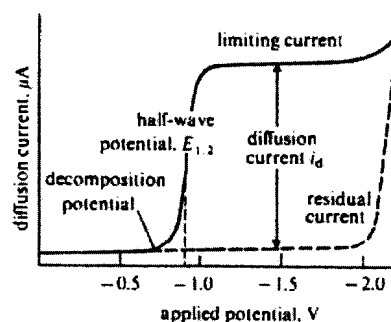


Figure 2.1 Polarographic wave or polarogram [1].

to the behaviour of a condenser. Above the *decomposition potential*, at which point reduction of an electroactive species is initiated, the current increases with applied potential, until it levels off at a limiting value. The difference between the limiting value and the residual current is known as the diffusion current, i_d . If, on increasing the applied potential further, other species in the solution are reduced, additional polarographic waves will be observed. Finally, the current will increase due to reduction of the supporting electrolyte or of the electrode material. In each polarographic wave, the potential at which the diffusion current reaches half the limiting value is known as the half-wave potential $E_{1/2}$ and is characteristic of the particular electroactive species involved. It is therefore useful for qualitative identification.

2.1.1 Diffusion currents

When the potential applied to a polarographic cell exceeds the decomposition potential of an electroactive species, its concentration at the surface of the mercury drop is immediately diminished. A concentration gradient is thereby established and more of that species diffuses from the bulk solution to the electrode surface (Fick's law of diffusion).

The resulting current flow is proportional to the rate of diffusion which in turn is determined by the concentration gradient, i.e.

$$i = k(C - C_o) \quad (1)$$

where C and C_o are the concentrations of the electroactive species in the bulk solution and at the surface of the DME, respectively. By progressively increasing the applied potential, reduction occurs more rapidly, C_o eventually becomes virtually zero, and the concentration gradient reaches a maximum. At this point, the rate of diffusion and therefore the current flowing in the cell reaches a limiting value, i.e.

$$i_d = kC \quad (2)$$

Further increases in the applied potential do not increase the current and the cell is said to be completely polarized or operating under conditions of high overpotential. The diffusion current i_d is hence directly proportional to the bulk concentration of the electroactive species.

2.1.2 Half-wave potentials

Electroactive species are characterized by their $E_{1/2}$ values which are constants related to the standard electrode potentials and given by the equation

$$E_{1/2} = E^\phi - \frac{0.059 \text{ V}}{n} \log \frac{k}{k_r} - E_{\text{reference}} \quad (3)$$

where E^ϕ is the standard electrode potential, $E_{1/2}$ is the half-wave potential, $E_{\text{reference}}$ as the potential of the reference electrode and n is the number of electrons changed per mol of analyte. k and k_r are proportionality constants relating cell current to the rates of diffusion

of oxidized and reduced forms of the electroactive species. Values are independent on the bulk concentration C but depend on the composition of the supporting electrolyte which can affect E^ϕ if complexes are formed. The components of a mixture will give separate polarographic waves if the $E_{1/2}$ values differ by at least 0.1 V. Often, if two waves overlap, by careful choice of a complexing agent, the E^ϕ and hence the $E_{1/2}$ value of one component can be changed by up to a volt or more.

2.1.3 Characteristics of the dropping mercury electrode (DME)

A diagrammatic representation of a DME is shown in Figure 2.2. Mercury from a reservoir is forced through a narrow-bore glass capillary (~ 0.06 mm bore) by gravity. A succession of identical drops is formed which are detached at regular intervals (3 to 8 s), timing and reproducibility of drop dimensions being ensured by electrical control. This characteristics of the DME results in an oscillating cell current, the average of which is given by the Ilkovic equation

$$i_d = AnD^{1/2} m^{2/3} t^{1/6} C \quad (4)$$

where n denotes the number of electrons changed per mol of analyte, D is the diffusion coefficient for the electroactive species, m is the rate of flow of mercury, t is the drop time, C is the concentration in the bulk solution, and A is a constant. The equation is useful in comparing diffusion currents from electrodes with different capillary characteristics, i.e. different values of $m^{2/3} t^{1/6}$. The diffusion coefficient D is temperature sensitive to the extent of about 2.5 % per kelvin; accordingly it is essential to control the cell temperature to ± 0.1 K if the highest precision is required.

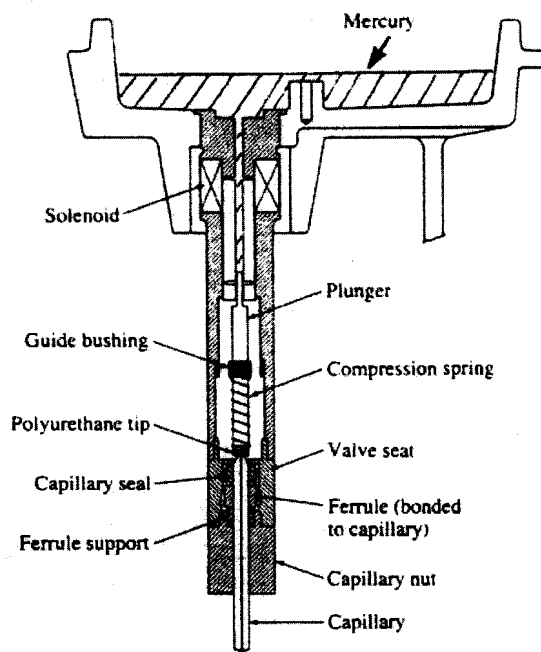


Figure 2.2 Dropping mercury electrode [1].

In practice, a DME has certain advantages over other micro-electrodes:

1. The surface is continually and reproducibly renewed so that its past history is not important.
2. A reproducible average current is produced instantly on changing the applied potential.
3. Mercury has a large activation overpotential for hydrogen formation which facilitates the reduction of many species in acid solution.

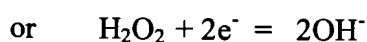
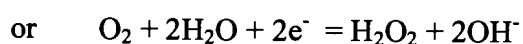
Its use is restricted to the determination of reducible or easily oxidized species at positive applied potentials greater than 0.4 V with respect to the saturated calomel electrode (SCE), mercury dissolves to give an anodic polarographic wave.

2.1.3.1 Current maxima

Polarographic waves often show a peak followed by a sharp fall to the limiting current plateau, the cause of which is related to the streaming of the solution past the mercury drop known as a '*current maximum*', it can be eliminated by adding a surfactant such as gelatin or methyl-red to the sample solution.

2.1.3.2 Oxygen waves

Two waves caused by the reduction of dissolved oxygen can interfere with the waves of other electroactive species unless the solution is purged with nitrogen prior to obtaining the polarogram



The relations have been utilized for the determination of dissolved oxygen or hydrogen peroxide.

2.1.4 Quantitative analysis

For quantitative analysis either calibration graphs prepared from standards or the method of standard addition can be used. For the former, the standards should be as similar as possible in overall chemical composition to that of the samples so that so as to minimize errors caused by the reduction of other species or by variation in diffusion rates. Often, the limiting current for quantitative work is the level of impurities present in the reagents used.

2.2 Pulse polarographic techniques

Pulse polarographic techniques were developed primarily in the general trend towards greater sensitivity in analytical methods as ever lower limits of detection and determination were demanded by the user disciplines [2]. For example, dc polarography was quite suitable in sensitivity for the analysis of electroactive drugs in pharmaceutical preparations, but far too insensitive to determine the same drugs in biological fluids during pharmacological investigations. This was particularly frustrating because polarography showed the ability in many cases to differentiate the drug from its metabolites. Today, pulse techniques are the most widely used methods in analytical polarography.

2.2.1 The limitations of dc polarography

The sensitivity of most instrumental techniques is limited by the signal to noise ratio. The signal to noise ratio, that is the ratio of the Faradaic current (proportional to concentration) to the capacitive current is greatest at the end of the drop lifetime. Classical dc polarography records the mean current during the drop lifetime and thus does not record the maximum Faradaic current. Worse still, it includes an appreciable contribution from the capacitive current. This effectively limits the sensitivity of classical dc technique to a limit of detection of about 5×10^{-5} mol/L.

2.2.2 Normal pulse polarography (NPP)

A great improvement in sensitivity would be possible if electrolysis could be prevented during most of the drop lifetime, that is the potential is kept at a lower voltage until the moment of measurement. This is the basis of normal pulse polarography. The potential is kept as a suitable constant base potential throughout the drop lifetime. The chosen potential signal is imposed as a very short pulse (about 60 ms) near the end of the drop lifetime (Figure 2.3). Thus very little electrolysis and depletion occurs. Typically the Faradaic current from normal pulse polarography is about ten times that from classical dc polarography.

The problem still remains of the capacitive current. When the voltage pulse is imposed a significant capacitive current will be required to produce this potential. However near the end of the drop lifetime the growth of the surface area of the drop has almost ceased,

particularly relative to the short length of the pulse, and the electrode is almost stationary. The current measurement is therefore taken in an even shorter pulse (about 15 ms) near the end of the potential pulse once the capacitive current has decayed to a low steady value.

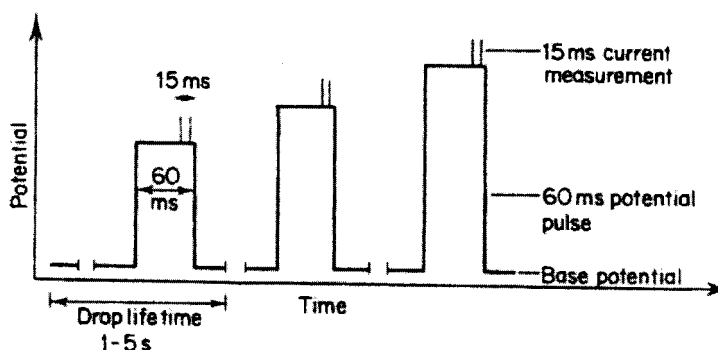


Figure 2.3 The profile of the potential pulse and current measurement in normal pulse polarography [2].

The overall form of the applied voltage signal is of a series of potential pulses, one to each drop, rinsing in a linear ramp with a base potential maintained between the pulses. The current recorded at the end of each pulse is recorded and plotted against the potential of the pulse.

The resulting current/potential curve is similar in form to the classical dc polarography curve with equivalent half wave potential and limiting current (Figure 2.4). In practice the curve is made up of very short flat that segments and is of a clearer, 'cleaner', less noisy form. The height of the pulse polarographic wave, the analytical signal, is about ten times greater than that of the classical wave height, suggesting only a similar increase in sensitivity. However, the noise, i.e. the capacitive current, has also been drastically

reduced. Thus the sensitivity of the technique has been improved by about two orders of magnitude with a limit of detection of about 10^{-7} mol/L.

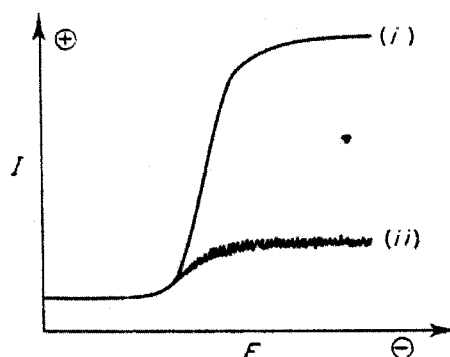


Figure 2.4 Comparison of (i) the normal pulse, and (ii) classical dc polarograms from the same solution at the same recorder and sensitivity [2].

Thus by using more sophisticated electronics and imposition of a more complicated potential signal a much simpler current/potential curve can be obtained with the interferences of depletion and the capacitive current effectively minimized.

2.2.3 Differential pulse polarography (DPP)

This is the most commonly used polarographic technique today. It differs from normal pulse polarography in that after the potential pulse the potential does not return to a constant base value. Instead the potential pulse itself is of a small constant amplitude (10-100 mV) and is superimposed on a conventional rising linear dc voltage ramp. Once again the pulse is imposed for about 60 ms near the end of the drop lifetime when the growth of the drop almost ceased (Figure 2.5). The current is measured in two intervals of about 15 ms, the first immediately prior to the potential pulse and the second during

but towards the end of the potential pulse. The final current signal displayed is in fact the difference of these two current values.

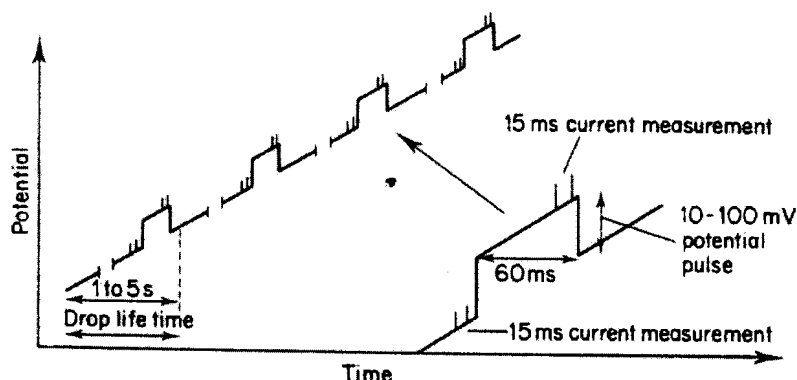


Figure 2.5 The profile of the potential pulse and current measurement in differential pulse polarography [2].

The two current values represent the current at two potential values separated by about 10-100 mV (the pulse amplitude). This difference in current will be greatest on the steep rising part of the polarographic wave around the half wave potential, where a small change in potential produces a large change in current. Thus this technique in fact produces not a wave but a peak with highest current signal at roughly the half wave potential of the classical dc and normal pulse polarography (Figure 2.6). Since the output signal increases with the steepness or slope of the conventional current potential curve, this final curve approximates to a derivative or differential of the classical polarography current potential curve.

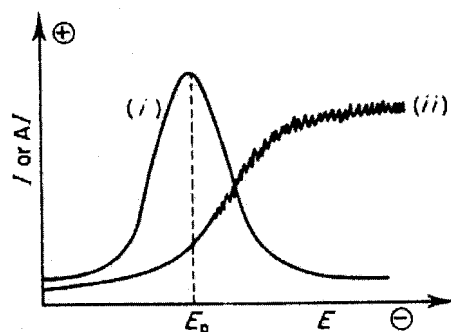


Figure 2.6 Comparison of (i) the differential pulse, and (ii) classical dc polarograms from the same solution at the same recorder and sensitivity [2].

The potential of the peak E_p is indicative of which species is involved. If the reduction (or oxidation) mechanism is diffusion controlled the concentration of the species controls the Faradaic current. Since differential pulse polarography effectively displays the derivative of this current, theoretically it is the area under the peak which is proportional to the concentration. However, provided the shape of the peak does not change, the height of the peak is also proportional to concentration.

Note that the rising linear voltage ramp in differential pulse polarography is exactly similar in form to that of classical dc polarography, except for the superimposed pulses. This means that electrolysis and hence depletion occurs throughout the drop lifetime. Thus in differential pulse polarography the current signal is greatly reduced compared to that in normal pulse polarography and is more similar to that in classical dc polarography. At first glance this would, wrongly, suggest that the differential pulse technique should be inherently less sensitive than normal pulse polarography. In fact, differential pulse polarography is typically an order of magnitude more sensitive than the normal pulse

mode. Typical limits of detection are 10^{-7} - 10^{-8} mol/L for the differential pulse technique and 10^{-6} - 10^{-7} mol/L for the normal pulse technique while for the classical dc it would be only about 0.5×10^{-4} mol/L.

How can there be an increase in sensitivity if the signal has been reduced by depletion? Clearly differential pulse polarography must reduce the noise. It must show better resolution. At low concentration levels the favourable signal to noise ratio of differential pulse polarography gives well-defined peaks where no dc response can be obtained.

Although depletion occurs throughout the drop lifetime, the current measurement is only taken in very brief pulses at the end of the drop lifetime. At the end of the drop lifetime the drop has almost stopped growing and the capacitive current will be reduced to its almost constant and lowest level. The jump of 10-100 mV occurring between the two current measurement pulses will have very little effect on the capacitive current and other non-faradaic sources of noise. On the other hand, the small potential jump will produce a large change in the Faradaic current particularly at the peak potential. It is the change in current, on either side of the potential pulse, which differential pulse polarography records. Thus the differential pulse mode allows the maximum differentiation of the Faradaic or analytical signal from the background signal.

Resolution is in fact a keyword for differential pulse polarography. In classical dc polarography at least 200 mV or more are required between half wave potentials before interfering or overlapping waves can be resolved. With differential pulse polarography overlapping peaks can be usefully resolved for analysis if separated by as little as 50-100

mV. These values are only relative and are larger for broader and less well-formed peaks or waves.

2.2.4 Square-wave polarography

Square-wave polarography is a type of pulse polarography that offers the advantage of great speed and high sensitivity [3]. An entire voltammogram is obtained in less than 10 ms. With a dropping mercury electrode, the scan is performed during the last few milliseconds of the life of a single drop when the charging current is essentially constant. Square-wave voltammetry has also been used with hanging drop electrodes and with chromatographic detectors. Figure 2.7 shows the excitation signal in square-wave voltammetry(c), which is obtained by superimposing the pulse train shown in (b) onto the staircase signal in (a).

The length of each step of the staircase and the period of the pulses (τ) are identical and usually about 5 ms. The potential step of the staircase ΔE_s is typically 10 mV. The magnitude of the pulse $2E_{sw}$ is often 50 mV. Operating under these conditions, which corresponds to a pulse frequency of 200 Hz, a 1-V scan requires 0.5 s. For a reversible reduction reaction, the size of a pulse is great enough so that oxidation of the product formed on the forward pulse occurs during the reverse pulse. Thus as shown in Figure 2.8 [4], the forward pulse produces a cathodic current i_1 , whereas the reverse pulse gives an anodic current i_2 . Usually the difference in these currents Δi is plotted to give voltammograms. This difference is directly proportional to concentration; the potential

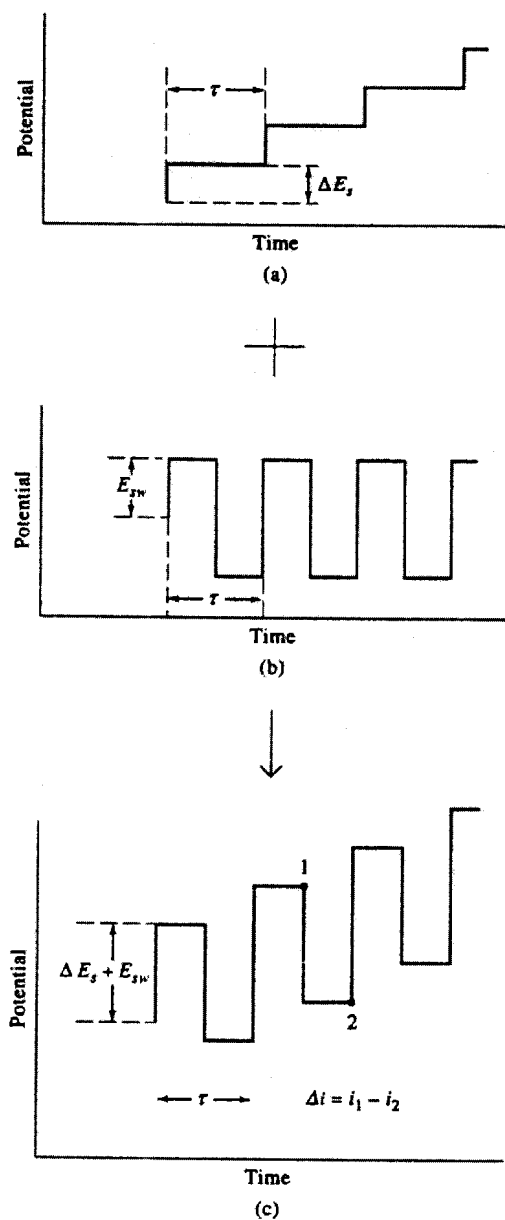


Figure 2.7 Generation of a square-wave voltammetry excitation signals. The staircase signal in (a) is added to the pulse train in (b) to give the square-wave excitation signal in (c). The current response Δi is equal to the current at potential 1 minus the current at potential 2 [3].

of the peak corresponds to the polarographic half-wave potential. Because of the speed of the measurement, it is possible and practical to increase the precision of the analyses by signal-averaging data from voltammogram scans. Detection limits for square-wave voltammetry are reported to be 10^{-7} to 10^{-8} mol/L.

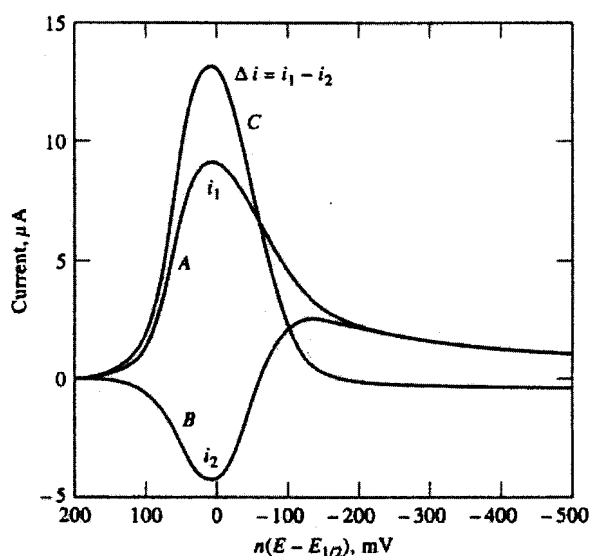


Figure 2.8 Current response for a reversible reaction to excitation signal in Figure 2.6.

A: forward current i_1 . B: reverse current i_2 . C: current difference $i_1 - i_2$ [4].

Commercial instruments for square-wave voltammetry have recently become available from several manufacturers, and as a consequence, it seems likely that this technique will gain considerable use for analysis of inorganic and organic species. It has also been suggested that square-wave voltammetry can be used in detectors for high-performance liquid chromatography.

2.2.5 Choice of parameters in pulse polarography

With the imposition of a more complicated voltage signal in the pulse techniques, some new operating parameters must be set on the instrument in addition to those of classical dc polarography[2]. These are the base potential in normal pulse polarography and the amplitude in differential pulse polarography.

2.2.5.1 Choice of the base potential in normal pulse polarography

Normal pulse polarography is somewhat unwisely neglected today and there is a general tendency to go from classical dc polarography straight to differential pulse polarography. The latter is a little more sensitive than the normal pulse technique (by about one order of magnitude). However the normal pulse mode has some very distinct advantages, and these lie in the choice of the base potential to which the electrode returns between pulses.

Probably the biggest problem in analytical polarography is adsorption of species onto the surface of the electrode. This can be adsorption of the analyte, its electrolysis product, or any other species from the solution. The effect of adsorbed species can be very varied indeed. They can produce the splitting of polarographic waves, the distortion of their shapes, shifting of the half wave potentials, depression or even elimination of the wave heights, etc. The adsorbed forms may produce small waves of their own, known as pre-waves or post-waves, separate from the main diffusion controlled wave. On the other hand some adsorbed species have little or no effect.

If adsorption of the electrode product is likely to cause interference then this can be minimized in normal pulse polarography by setting the base potential to a low value at which no product is formed. A very small amount of electrode product will be formed only during the short duration pulse. This will cause a much smaller interference that would occur in classical dc polarography or in differential pulse polarography, since the later two techniques electrode product is formed throughout the drop lifetime.

As the potential of the electrode changes so the stability of adsorbed forms varies. An individual species can have several adsorbed states each of which occurs only over a particular electrode potential range. As the potential moves out this range, the species is either desorbed completely from the surface, or reorientates into a new adsorbed state.

In some normal pulse polarography equipment the base potential to which the voltage returns between the pulses is simply equal to the initial potential of the potential scan. The initial potential of the scan is the potential imposed during the first pulse. The potential subsequent pulses increases at a regular interval from this initial pulse to form the linear potential scan. In some instruments the initial and base potentials can be set separately. It is possible to scan towards the normal pulse polarographic wave from a base or initial potential either above or below the wave.

Thus it can be seen that normal pulse polarography is potentially the least sensitive to interference from adsorption effects of the common modes of polarography.

2.2.5.2 Choice of parameters in differential pulse voltammetry

2.2.5.2.1 Potential pulse amplitude

Before analysis a choice has to be made of the potential pulse amplitude imposed. With some differential pulse instruments a fixed pulse amplitude of, usually 50 mV, is the only possibility. Others allow a continuous choice from 10 mV to 100 mV.

The peak current I_p for a totally thermodynamically reversible electrode process controlled by diffusion has been derived by Parry and Osteryoung

$$I_p = \frac{n^2 F^2 A c}{4RT} \left(\frac{D}{\pi t} \right)^{1/2} \Delta E \quad (5)$$

where ΔE is the amplitude of the potential pulse

n = Number of electrons changed per mol of analyte

A = The area under the peak

c = the concentration

t = Drop lifetime

R = Proportionality constant, the gas constant

T = Temperature

F = Faraday's number

The Parry-Osteryoung equation shows immediately that the height of the peak is proportional to the concentration as is necessary for analytical use. It also shows that the peak height is proportional to the potential pulse amplitude. That is the higher the amplitude the greater the sensitivity. However increases in pulse amplitude result in broadening of the peaks and subsequent loss of resolution. Two close lying peaks will not be resolved unless the pulse amplitude is significantly smaller than the separation in the two peak potentials.

Thus the choice of potential pulse amplitude must be a compromise between a higher value for increased sensitivity and a lower amplitude for increased resolution. This is particularly true for thermodynamically irreversible process which produces broader, lower and less well formed peaks than do reversible processes.

2.2.5.2.2 The scan rate

The scan rate (mV s^{-1}) must be chosen carefully. The differential pulse peak consists of a series of straight line steps as the pen held stationary (in the current direction) between the pulses. If the scan rate is too high the steps will be too coarse for adequate resolution. The slowest scan rate gives the best results but a reasonable compromise with analysis time may be necessary.

2.2.5.2.3 Peak area and peak height

A choice has to be made for calibration and measurement between the use of peak height or of the area under the peak. Since differential pulse polarography is a differential or derivative technique it is the area under the peak which is proportional to the current of electrolysis and hence to concentration. The measurement of a peak height is much more convenient. However, the relationship between peak height and area is only constant as long as the shape of the peak does not alter. This is probably the case in most analytical problems but it is not always so. Since irreversible processes produce lower broader peaks than reversible processes, any change in the thermodynamic reversibility will alter the relative peak height. The greatest problem is adsorption onto the electrode surface.

Differential pulse polarography is particularly susceptible to surface active phenomena. Adsorbed forms of the analyte and its electrode products can give rise to separate peaks. But even the adsorption of otherwise inactive third species can alter the reversibility and electrode kinetics of the process producing sometimes huge changes in the shape of the peak. The area under the peak will, however, remain constant in most cases. But the height of the peak is of no use. If surfactants are likely to be present it is best to calibrate and measure the area under the peak.

2.2.6 Applications of polarography in inorganic analysis

In the past, linear-scan polarography was used for the quantitative determination of a variety of inorganic and organic species, including molecules of biological and biochemical interest [3]. Currently, pulse methods have substituted the classical method almost completely because of their greater sensitivity, and selectivity.

The polarographic method is widely applicable to the analysis of inorganic substances. Most metallic cations, for example, are reduced at the dropping electrode. Even the alkali and alkaline-earth metals are reducible, provided the supporting electrolyte does not react at the high potentials required; here, the tetraalkyl ammonium halides are useful electrolytes because of their high reduction potentials.

The successful polarographic determination of cations frequently depends upon the supporting electrolyte that is used. The judicious choice of anion often enhances the selectivity of the method. For example, with potassium chloride, as a supporting electrolyte, the waves for iron(III) and copper(II) interfere with one another; in a fluoride medium, however, the half-wave potential of the former is shifted by about -0.5 V, while that for the latter is altered by only a few hundredths of a volt. The presence of fluoride thus results in the appearance of well-separated waves for the two ions.

The polarographic method is also applicable to the analysis of such inorganic anions as bromate, iodate, dichromate, vanadate, selenite, and nitrite. In general, polarograms for these substances are affected by the pH of the solution because the hydrogen ion is a

participant in their reduction. As a consequence, strong buffering to some fixed pH is necessary to obtain reproducible data.

2.3 Stripping voltammetry

Although differential pulse polarography is the most sensitive direct polarographic technique, an even greater sensitivity can be obtained by employing stripping voltammetry [2]. This later technique involves a preconcentration step before the final voltammetric determination. It is the preconcentration step which allows the great sensitivity of stripping voltammetry.

The preconcentration or deposition step consists of the controlled electrodeposition, at fixed potential, of the species of interest onto a stationary electrode. This is followed by the determination step which consists of electrolytically stripping of the deposited species back into the solution.

2.3.1 The deposition step

2.3.1.1 The choice of electrode

The variations possible are concerned with the nature of the electrode and the stripping of the solution. The most common technique is to use a stationary electrode in a stirred solution.

The most popular electrodes are the hanging mercury drop electrode (HMDE), the mercury film electrode (MFE) supported on gold or platinum, and graphite electrode including graphite paste or glassy carbon. The mercury electrodes offer the advantage, in metal ion analysis, that the deposition product, the metal, dissolves in the mercury to form a liquid amalgam. This offers better reproducibility than a solid metal deposit on a solid electrode. In general terms, the mercury film electrode is capable of more sensitive measurements than the hanging mercury drop electrode, but it is less suited to relatively higher trace amounts, since the solubility capacity of a film is less. A general guide would be to use the hanging mercury drop for metal ion levels above 1 ng/mL and the mercury film below this.

2.3.1.2 Stirring effect

Stirring the solution during the deposition step increases the rate at which the analyte reaches the electrode to be deposited. Control of the stirring is vital. The stirring must be uniform and at a rigidly controlled rate. The position of the electrode within the cell and hence in the solution flow pattern must be absolutely reproducible. The stirring must be gentle otherwise unpredictable eddy effects will occur.

Deposition in a still, unstirred solution might appear to offer a much higher reproducibility of conditions but at a cost of a much reduced sensitivity or very much longer deposition times. Unstirred solutions are rarely used except in combination with a

differential pulse stripping technique whose greater sensitivity to some extent offsets this reduced sensitivity.

An alternative to stirring the solution is to rotate the electrode. For this the electrode usually consists of a rod cut to expose a flat disc. The rod is then rotated about its axis. Such an electrode is usually made of glassy graphite, platinum or gold. Sometimes a film of mercury is deposited on the electrode by electrodeposition from a separate solution of mercury(II) ions.

2.3.1.3 The choice of deposition time

A further decision is how to continue the deposition step. The greatest sensitivity would clearly be obtained by carrying on the deposition process until all of the analyte would be deposited on the electrode. Indeed this is sometimes done using a small volume of sample solution. However it is more usual to use a large volume of solution and only deposit a small fraction of the analyte.

It is best to avoid a long deposition time. This often leads to various complications resulting in a loss of proportionality between final signal and the concentration of the analyte. One problem can be reactions of the deposit or changes in its nature over a relatively prolonged time. Too much deposit on the electrode can also cause problems.

In general a good guide is to choose a deposition time so that only about 2 % of the total analyte is deposited from the solution. This allows the nature of the solution to remain essentially unaltered. This avoids changes in the deposition process that occasionally occurs when depletion approaches completion.

2.3.1.4 The choice of deposition potential

The final decision is the choice of constant potential used in the pre-electrolysis or deposition step. Usually a potential is chosen a few hundred millivolts larger than the polarographic half wave potential of the analyte.

The potential chosen allows the improvement of the selectivity. In the analysis of a solution containing a number of metal ions, each metal ion will have its own individual deposition potential. Thus only one metal or a group of metals can be deposited, avoiding the deposition of other metals which might interfere with the stripping step. The higher the potential, the more types of metals will be deposited and the more interference's will occur.

Occasionally it might be possible to differentiate between the oxidation states by choosing a potential at which only one form deposits to the metal. This will only be possible if the higher oxidation state is reduced at a more negative potential than the lower. An example would be arsenic species; arsenic(III) is reduced to elemental arsenic at much lower potentials than is arsenic(V). Dependent on substituents arsenic(V) is

either electroinactive or is reduced at much more negative potentials. However with most metals it is the most negative wave which has the metal as its final product and stripping voltammetry will not differentiate the higher and lower oxidation states.

2.3.2 The stripping step

A number of different stripping procedures have been devised but only two are of great significance – dc or linear sweep stripping voltammetry, and differential pulse stripping voltammetry. These require exactly the same instrumentation as dc polarography and differential pulse polarography.

2.3.2.1 DC or linear sweep stripping voltammetry

Dc or linear sweep stripping voltammetry is the simplest form of stripping voltammetry. This involves the imposition of a simple linear scan on the electrode.

As the potential scan begins no current initially flows. When the re-oxidation potential (or re-reduction potential respectively) is reached the current readily rises. However there was only a fixed amount of material deposited in the deposition step. The current must therefore fall back towards the base line as the last of the deposited material is reoxidized (or reduced). The dc stripping signal thus consists of a peak.

The height of the peak is used to determine the concentration in the original solution. However the peak height is dependent on both the concentration and on the voltage scan rate. It is the area under the peak (in coulombs), which is proportional to the amount deposited in the deposition step. As the scan rate increases the peak becomes narrower and so the peak height will increase. However if the same deposition conditions are used and a fixed scan rate chosen the peak height should be proportional to the concentration of the analyte in the original solution. Linear sweep stripping voltammetry is almost always carried out with a deposition step in a stirred solution.

2.3.2.2 Differential pulse stripping voltammetry

One of the main limitations of dc or linear sweep stripping voltammetry lies in the base line. There is a significant capacitive current as the potential of the electrode is changed. Differential pulse stripping voltammetry offers a much better differentiation of faradaic current signal and noise such as capacitive current.

The voltage sweep is identical to that used in conventional differential polarography. It consists of a linear voltage ramp on which small pulses of 10-100 mV amplitude and about 50 ms duration are imposed at intervals of about 1 s. The current is sampled just before the pulse and almost at the end of the pulse. The final signal is the difference of these two current values.

The two current values measured represent the current at two potential values separated by a few millivolts (the pulse amplitude). At the steeply rising stripping peak this small change in the potential will produce a large change in the electrolysis current whereas the same small change in potential will produce only a very small effect on capacitive current and other sources of noise. As it is the change in the current on either side of the imposition of the pulse which the differential pulse mode records, this mode allows maximum differentiation of the electrolysis current from the background signal.

The much larger sensitivity of the differential pulse stripping step over the simpler linear sweep stripping step allows the use of much shorter pre-electrolysis or deposition times. One can thus avoid the problems associated with prolonged deposition times, such as loss of proportionality.

The greater sensitivity of the differential pulse technique can sometimes even allow the use of pre-electrolysis deposition step in an unstirred solution, thus avoiding the problems of the reproducibility of the stirring. For concentrations below 50 ng/mL stirring is essential but at higher concentrations it can sometimes be avoided.

2.3.3 Suitable analytes for stripping voltammetry

Unfortunately the range of analytes to which stripping voltammetry can be applied is much narrower than for conventional polarography. Several conditions must be met for stripping voltammetry to be possible.

1. The product of the deposition step must be insoluble or soluble in the mercury electrode. If it were soluble it would simply diffuse away back into the solution and no concentration or build up of the product would occur at the electrode. This rules out the majority of all electroactive organic species.
2. If an insoluble product is formed, it must be completely insoluble even at the very high dilutions concerned. It must form a coherent layer on the electrode surface in complete electrical contact. A layer of high electrical resistance must not form.
3. The deposited layer must be capable of re-oxidation (or re-reduction) in order to give a stripping peak. That is, it must be possible to reverse the deposition process, although the reaction need not be strictly thermodynamically reversible.
4. The deposit must be chemically stable and not be attacked by the solution.

There are many insoluble deposition products which are not suitable for stripping analysis.

2.3.3.1 Anodic stripping voltammetry (ASV)

This is concerned almost entirely with trace metal analysis, although a few other applications are known. Metal ions lend themselves particularly well to stripping voltammetry. The metal deposited in the deposition step generally dissolves in the

mercury drop to form an amalgam. This avoids any problem with the nature of an insoluble deposit.

If more than one metal ion is deposited (at the deposition potential), they will in general appear as separate peaks at different potentials in the stripping step and can be determined individually.

However, formation of intermetallic compounds can cause problems. When metals such as copper and zinc are present in solution there is a tendency to form Zn/Cu intermetallic compound when larger amounts are deposited at a mercury electrode. When an intermetallic compound is formed the stripping peaks for the constituent metals may be shifted, severely depressed, or even be absent altogether. When an alloy is formed at a solid electrode its dissolution potentials, in the stripping step, may be quite different to those of the constituent metals.

These interfering effects can be minimized or avoided by reducing the deposition time and the total amount of metal deposited. This would of course mean a loss of sensitivity, but use of differential pulse stripping voltammetry can offset this. The use of a hanging mercury drop electrode with its larger mercury volume offers less intermetallic interference than does the mercury film electrode. Careful choice of a deposition potential can almost sometimes prevent the codeposition of metals forming intermetallic compounds.

2.3.3.2 Cathodic stripping voltammetry (CSV)

The most common species determined by cathodic stripping voltammetry are anions such as halides or sulphide, at a mercury electrode. This involves formation of a film of mercury(I) salts on the electrode in the deposition step. The anodic oxidation process involved in the deposition step is in fact the oxidation of mercury metal to mercury(I) ions. These immediately precipitate insoluble mercury(I) salts with the halide ion etc, on to the surface of the electrode. The anodic deposition potential required depends on the anion concerned. The subsequent cathodic stripping peak for the mercury(I) salt of each anion has at its own individual potential.

Cathodic stripping voltammetry has proved suitable for a number of organic compounds, including drugs and pesticides. These in general contain sulphur and again the deposition step involves anodic (oxidation) formation of an insoluble mercury salt. Clearly this is possible only with a mercury electrode.

A few metal ions such as Mn^{2+} and Pb^{2+} can also be determined by the cathodic stripping of their oxides on carbon or platinum electrodes.

All these cathodic stripping processes involve an initial deposition of an insoluble layer on the surface of the electrode. If too much material is deposited the quality of the stripping peak will deteriorate and the height of the peak will cease to be proportional to

the original concentration. The method is highly sensitive but is suited only to these very low levels.

2.4 References

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CHAPTER 3

DIAMOND PASTE BASED ELECTRODES

3.1 Introduction

Carbon occurs both as the free element (graphite, diamond) and in combined forms (mainly as the carbonates of Ca, Mg and other electropositive elements) [1]. It also occurs as CO₂ a minor but crucially important constituent of the atmosphere.

3.1.1 Occurrence

Diamonds are found in ancient volcanic pipes embedded in a relatively soft, dark coloured basic rock called “blue ground” or “kimberlite”, from the South African town of Kimberly, where such pipes were first discovered in 1870. Diamonds are also found in alluvial gravels and marine terraces to which they have been transported over geological ages by the weathering and erosion of pipes. Diamonds of the kimberlite type are isolated mechanically by crushing, sluicing and passing the material over greased belts to which the diamonds stick.

3.1.2 Crystal structure

In diamond, each carbon atom is tetrahedrally surrounded by four equidistant neighbours at 154.45 pm, and the tetrahedra are arranged to give a cubic unit cell with a_0 356.68 pm as in Figure 3.1.

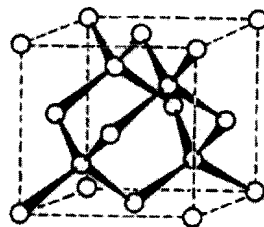


Figure 3.1 Structure of diamond showing the tetrahedral coordination of C; the dashed lines indicate the cubic unit cell containing 8 C atoms [1].

3.1.3 Physical properties

Diamonds have a low density ($d = 3.51 \text{ g/cm}^3$), but they are also the hardest material and the best conductor of heat known. They are transparent to visible light and infrared and ultraviolet radiation. They are electrically insulating but behave as semiconductors with some advantages over silicon.

3.1.4 Diamond synthesis

The high-pressure synthesis of diamonds is expensive, and the diamonds are not entirely pure not crystalline enough for making semiconductor devices. The most promising

method so far seems to be a low-pressure process called “chemical vapor deposition” (CVD). A mixture of hydrogen and a carbon-containing gas such as methane (CH_4) is decomposed by heating to about $2200\text{ }^\circ\text{C}$ (with microwaves or a hot wire). Carbon atoms deposit on a silicon plate or other material in the chamber and slowly build up a film of tiny diamonds.

3.1.5 Monocrystalline diamond

The advances in single-crystal diamond have enabled the development of a wide range of monocrystalline diamond products to meet the exacting requirements of many different applications [2]. Room temperature drift mobilities of $4500\text{ cm}^2/\text{Vs}$ for electrons and $3800\text{ cm}^2/\text{Vs}$ for holes have been measured in high purity single-crystal diamond [3]. These values were determined by using the time-of-flight technique on thick, intrinsic freestanding diamond plates and were verified by current-voltage measurements on p-i junction diodes [3].

3.2 Design of diamond paste based electrodes

Three types of monocrystalline diamond powder were used for the design of the diamond paste electrodes. Namely; natural diamond $1\text{ }\mu$, synthetic diamond $50\text{ }\mu$ (synthetic 1), and synthetic diamond $1\text{ }\mu$ (synthetic 2).

The diamond paste electrode was prepared by mixing 0.1 g of diamond powder with 20 μ L paraffin oil. A portion of the paste was then filled into a plastic pipette tip (3mm). The diameter of the sensing part was 2.3mm. Electric contact was made by inserting a silver wire (0.5mm in diameter) in the diamond paste. Before use, the electrode surface was smoothed by polishing with an alumina paper (polishing strips 30144-001, Orion). When not in use, the diamond paste electrode was stored at room temperature, dry.

3.3 Advantages of using diamond paste based electrodes versus glassy carbon and carbon paste electrodes

Monocrystalline diamond based electrodes are a promising electrode material for electrochemical studies. They exhibit several superior electrochemical properties that are very important than other carbon allotropes based electrodes, e.g. glassy carbon electrodes, highly oriented pyrolytic graphite based electrodes, which have been used for many years [2-4].

The greater sensitivity of using diamond paste based electrodes are wide working concentration range and the relatively low detection limits obtained which proves the sensitivity of the electrode. Typical limits of detection when using the differential pulse are 10^{-8} - 10^{-11} mol/L, glassy carbon and carbon paste would be only about 10^{-4} - 10^{-6} mol/L.

The main problem in any polarographic technique is the adsorption of analytes, its electrolysis product, or any other interference's from the solution. The effect of this

adsorbed species produce the splitting of peaks, distortion of their shapes and shifting of the half-wave potential. Unlike glassy carbon and carbon paste, the use of diamond paste electrodes as an electrode material showed much improvement on adsorption effects. In most of the cases, the resulting peaks are very sharp and do not show any overlapping or shift of half-wave potentials within a specified potential range. It means that, the diamond paste electrodes are potentially less sensitive towards interference's caused from adsorption effects.

Any polarographic wave noise which result from the reduction of dissolved oxygen is minimized by purging the diamond paste electrode with pure nitrogen prior to measurement in order to get a good polarogram.

3.4 References

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CHAPTER 4

DETERMINATION OF Fe(II) USING DIAMOND PASTE BASED ELECTRODES

4.1 Introduction

The advances in single-crystal diamond have enabled the development of a wide range of monocrystalline diamond products to meet the exacting requirements of many different applications [1]. Room temperature drift mobilities of $4500 \text{ cm}^2/\text{Vs}$ for electrons and $3800 \text{ cm}^2/\text{Vs}$ for holes have been measured in high purity single-crystal diamond [2]. These values were determined by using the time-of-flight technique on thick, intrinsic freestanding diamond plates and were verified by current-voltage measurements on p-i junction diodes [2]. The reliability obtained for the electrical properties of single-crystal diamond is encouraging for research in the electrochemical sensors based on monocrystalline diamond. Furthermore, it proves that the doping of this type of diamond is not necessary. That minimizes the time affected for electrodes' construction and also simplifies the steps adopted for the design of such electrodes.

The literature survey shows that up to now, polycrystalline diamond thin film electrodes have been used increasingly in the electrochemical studies due to the low background current, wide potential range, lack of adsorption and high overpotential for oxygen evolution by water oxidation in aqueous electrolyte solution [3-13]. Boron

doped-diamond thin-film electrodes were also used due to their physical and electronic properties such as hardness, chemical inertness, optical transparency, high thermal and electrical conductivity [14,15].

Biologically, iron plays crucial roles in the transport and storage of oxygen and also in electron transport, and it is safe to say that, with only a few possible exceptions in the bacterial world, there would be no life without iron [16]. Pure iron is produced on a small scale by the reduction of the pure oxide or hydroxide with hydrogen, or by the carbonyl process in which iron is heated with carbon monoxide under pressure and the $\text{Fe}(\text{CO})_5$ so formed decomposed at 250°C to give the powdered metal. However, it is not in the pure state but in the form of an enormous variety of steels that iron finds its most widespread uses, the annual world production being of the order of 700 million tones.

Iron(II) is necessary for haemoglobin production and iron deficiency results in small red blood cells with insufficient haemoglobin (microcytic hypochromic anemia). Iron(II) is essential to periods of human growth and so its quantitative determination has biological interest. The administration of iron preparations is needed in iron deficiency, which may be due to chronic blood loss, pregnancy (the fetus takes iron from the mother), various abnormalities of the gut (iron absorption may be reduced), or premature birth (such babies are born with very low iron stores). Iron must be in the ferrous form for absorption, which occurs by active transport. In plasma, iron is transported bound to transferrin, a β -globulin [17].

Up to now, different electrodes were proposed for the assay of Fe(II) in environmental or clinical matrices, using direct analysis [18-20] and indirect analysis (titration) [21,22]. The electrodes proposed for the assay of Fe(II) were also used as detectors in flow injection analysis systems, [23] and in chromatography [24].

In this chapter a new class of diamond electrodes is described for the assay of Fe(II). A diamond paste similar with the carbon paste was preferred for the electrodes design, since the carbon paste based electrodes proved high reliable construction and response characteristics [25]. Three types of diamonds were used for the design of the diamond paste: a natural diamond and two types of synthetic diamond. Differential pulse voltammetry (DPV) was used for the calibration of the electrodes as well as for the uniformity content test of Fe(II) in four types of vitamins.

4.2 Experimental section

4.2.1 Diamond paste electrode design

All diamond paste electrodes were prepared by mixing of 0.1g of each diamond powder with 20 μ L of paraffin oil. A portion of the paste was then filled into a plastic pipette tip (3mm). The diameter of the sensing part was 2.3mm. Electric contact was made by inserting a silver wire (0.5mm in diameter) in the diamond paste. Before each use the electrode surface was smoothed by polishing with an alumina paper (polishing strips 30144-001, Orion). When not in use, the diamond paste electrode was stored at room temperature.

4.2.2 Apparatus

A663VA Stand (Metrohm, Herisau, Switzerland) in combination with a PGSTAT 20 and software (Ecochemie version 4.8) were used for all measurements. A Pt electrode and an Ag/AgCl electrode served as the counter and reference electrodes in the cell.

4.2.3 Reagent and materials

All chemicals were analytical grade. All solutions were prepared by using de-ionised water. Phosphate buffer (pH 1-10) were prepared by mixing 0.67 mol/L KH_2PO_4 (SAARCHM-HOLPRO ANALYTIC) solution with 0.67 mol/L Na_2HPO_4 (Chemical Suppliers) solution in different ratios. All solutions of Fe(II) were freshly prepared everyday by dissolving the required amount of ammonium ferrous sulphate in de-ionised water. Monocrystalline natural 1μ and synthetic diamond: 50μ (synthetic-1) and 1μ (synthetic-2) powders were purchased from Aldrich (Milwaukee, WI, USA) while the paraffin oil was purchased from Fluka (Buchs, Switzerland). Vitaforce 21-PlusBPR protectavite was supplied by Pharma Natura (Pty) Ltd, Sandton, South Africa. Vital multi-vitamin & mineral with iron was supplied by Vital Health Foods (Pty) Ltd, Kuils River, South Africa. Weigh-Less daily multi-vitamin with antioxidants was supplied by Weigh-Less S.A. (Pty) Ltd, Hout Bay, South Africa. Bettaway iron extra was supplied by Better Nutrition (Pty) Ltd, Sandton, South Africa.

4.2.4 Recommended procedures

4.2.4.1 Cyclic voltammetry

For the optimisation procedure, cyclic voltammetry scans were performed using the new diamond paste based electrodes as working electrodes together with a reference electrode (Ag/AgCl), and an auxiliary platinum electrode. The voltammetric scan rate was adjusted to 10 mV/sec. All solutions were deoxygenated prior to use by degassing with N₂.

4.2.4.2 Direct DPV assay

The technique used for the direct voltammetric assay was differential pulse voltammetry with the applied potential pulse amplitude of 25 mV vs. Ag/AgCl. All measurements were performed at 25°C. The diamond paste electrode together with the reference and auxiliary electrodes were dipped into a cell containing phosphate buffer (pH 9.0) and sodium pyrophosphate as supporting electrolyte in a ratio of 3.5:1. All solutions were deoxygenated before the measurements with N₂. The peak height measured at 75 mV was plotted versus the concentration of Fe(II). The unknown concentrations of Fe(II) were determined from the calibration graphs.

4.2.4.3 Content uniformity assay of four vitamin tablets

Ten tablets from Iron Extra (Sample 1) and ten tablets from Vital multi-vitamin & mineral with iron (Sample 2) are individually placed in ten 100 mL calibrated flasks,

and dissolved in de-ionised water. Ten tablets from Weigh –Less daily multi-vitamin with antioxidants (Sample 3) and ten tablets from Vitaforce 21-PlusBPR protectavite (Sample 4) are individually placed in ten 50 mL calibrated flasks, and dissolved in distilled water. The direct DPV method was used for the assay of Fe(II) content in each of the vitamin solution.

4.3 Results and discussions

4.3.1 Optimisation of working conditions

In order to optimise the working conditions cyclic voltammograms for different electrolytes solutions and pHs (phosphate buffer with the pH between 1 and 10) were recorded before and after adding different aliquots of Fe(II) solution. Five different supporting electrolytes (0.05 mol/L KCl, 0.1mol/L KNO₃, 0.1mol/L NaNO₃, 0.1mol/L NaCl and 0.1mol/L Na₄P₂O₇) were tested. Figure 4.1. A, B and C shows the effect of pH and supporting electrolyte on the peak height.

The peaks measured at pH 9.0 (phosphate buffer) in a 0.1mol/L of Na₄P₂O₇ were higher than the peaks recorded for the rest of the electrolytes at different pHs with the exception of the ones obtained using the electrode based on synthetic-2. The shape of the peaks was also contributing to the selection of the optimum electrolyte and pH. The shape of the peaks recorded for the three electrodes was the best at pH 9.0, in the presence of Na₄P₂O₇ solution. Therefore, the optimum working pH was established to be 9.0 (phosphate buffer), in 0.1mol/L Na₄P₂O₇ supporting electrolyte.

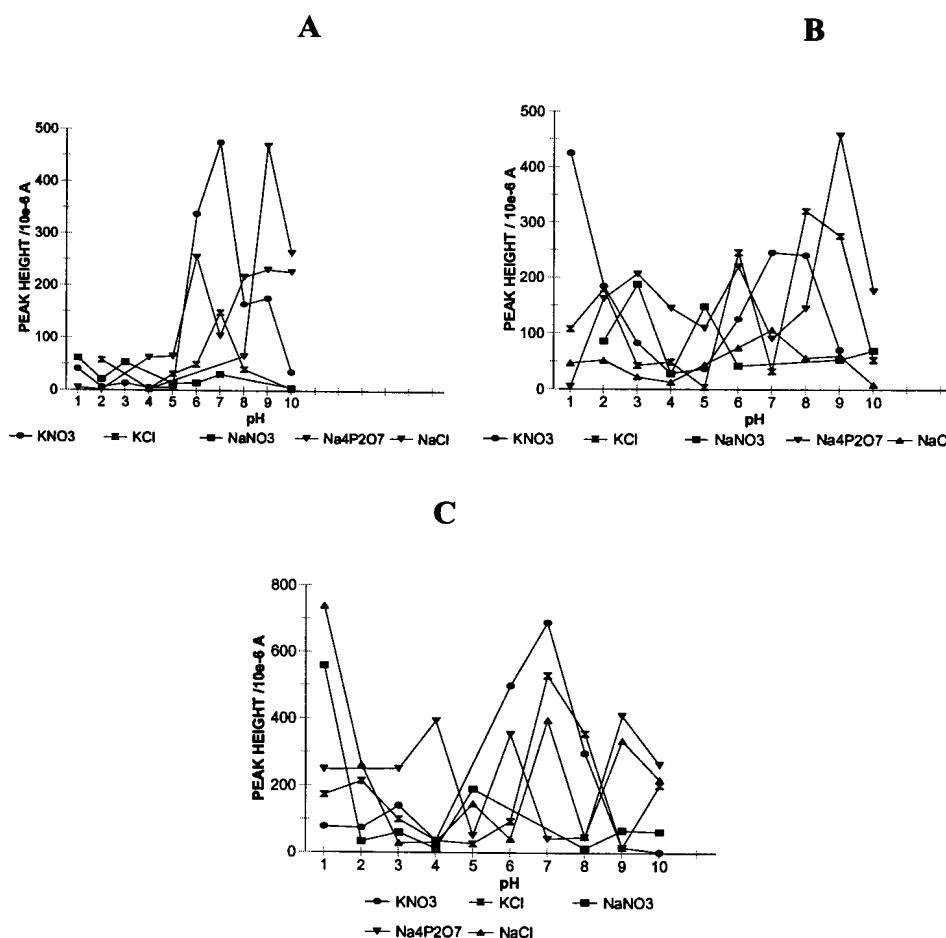


Figure 4.1 The effect of electrolyte and pH on the peak height for a concentration of Fe(II) solution of 10^{-4} mol/L. A. Natural diamond; B. Synthetic-1; C-Synthetic-2.

4.3.2 Response of the diamond paste electrodes

The responses of the electrodes to different Fe(II) concentrations were linear over wide concentration ranges and can be described by the following equations of calibration: a. (natural diamond); b. (synthetic-1) and c. (synthetic-2):

a. $H = 0.37 + 6.11 C$; $r = 0.9707$

b. $H = 7.50 + 5.30 C$; $r = 0.9543$

c. $H = 1.84 + 969.15 C$; $r = 0.9983$

where H is the peak height (μA), C is the concentration of Fe(II) (mmol/L) and r is the regression coefficient. The peaks height for natural diamond and synthetic diamond-2 were proportional with the Fe(II) concentration between 10^{-8} and 10^{-4} mol/L with detection limits of 10^{-10} and 10^{-9} mol/L , respectively. For the synthetic diamond-1, the linear concentration range is between 10^{-7} and 10^{-3} mol/L with a detection limit of 10^{-8} mol/L . The peak profiles for the assay of two different concentrations of Fe(II) with the three electrodes are shown in Figure 4.2A, 4.2B, and 4.2C. The signal to background ratio is very high. The reproducibility of peak current was good as proved by the values of relative standard deviation ($\text{RSD} < 1\%$).

4.3.3 Selectivity of the diamond paste electrodes

The effect of various ions on the peak height of Fe(II) was examined for all diamond paste electrodes. Mixed and separate solution methods were used in order to determine the amperometric selectivity coefficients [25]. The ratio between iron(II) and the possible interferent was 1:10 (mol/mol). The results obtained for the amperometric selectivity coefficients using the mixed solution method (Table 4.1) indicate that all ions investigated: Mg^{2+} , Cr^{3+} , Mn^{2+} , Cu^{2+} and Zn^{2+} do not interfere with the determination of Fe^{2+} .

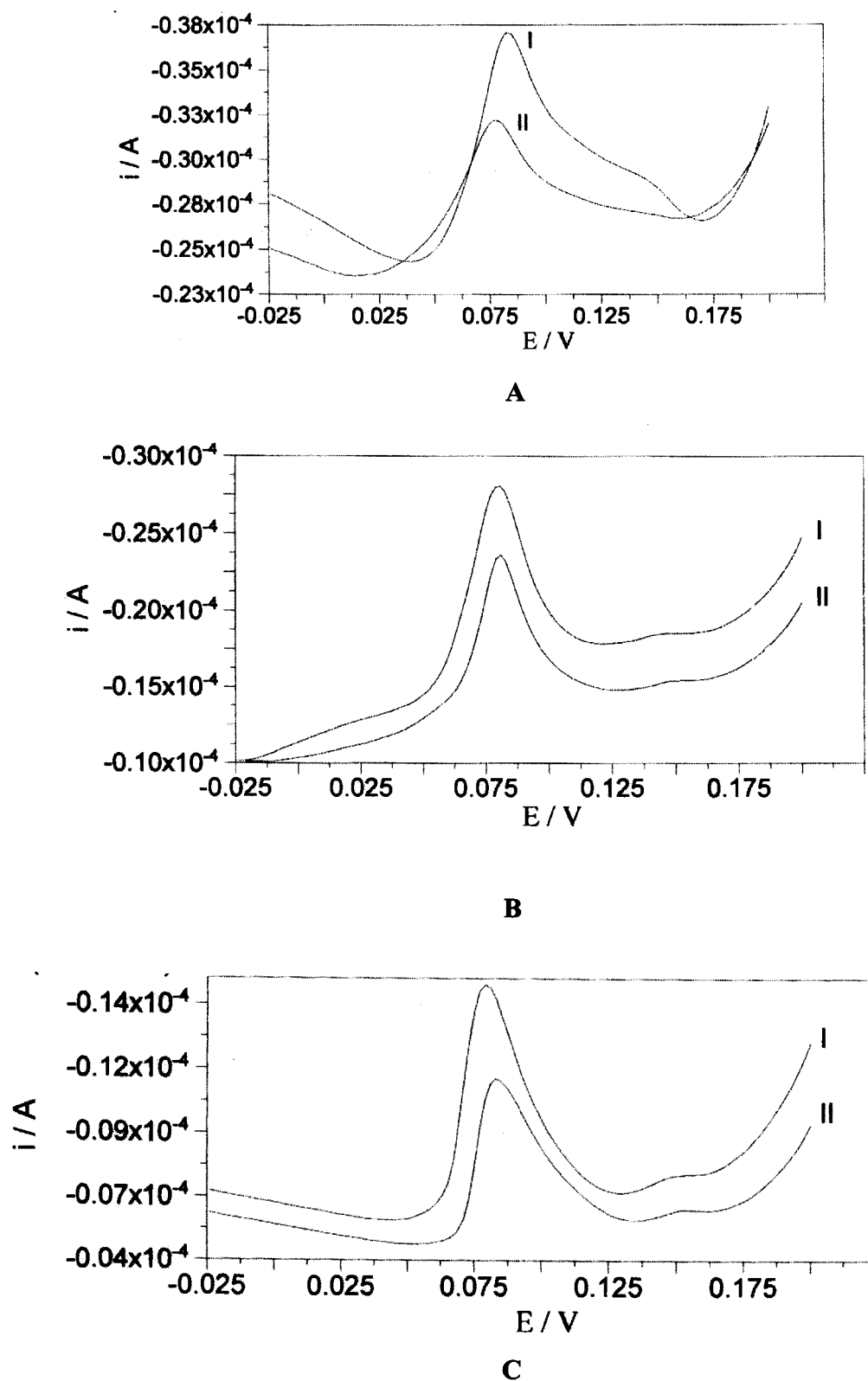


Figure 4.2 Peak profiles for DPV measurements when the electrodes based on: **A.** Natural diamond (I $C_{\text{Fe(II)}} = 10^{-4} \text{ mol/L}$; II $C_{\text{Fe(II)}} = 10^{-6} \text{ mol/L}$); **B.** Synthetic-1 (I $C_{\text{Fe(II)}} = 10^{-3} \text{ mol/L}$; II $C_{\text{Fe(II)}} = 10^{-4} \text{ mol/L}$); **C.** Synthetic-2 (I $C_{\text{Fe(II)}} = 10^{-5} \text{ mol/L}$; II $C_{\text{Fe(II)}} = 10^{-6} \text{ mol/L}$) are used.

Table 4.1 Amperometric selectivity coefficients. All measurements were made at 25°C all values are the average of ten determinations

Interfering species (J)	Electrode based on		
	Natural diamond	Synthetic-1	Synthetic-2
Mg ²⁺	1.20 x 10 ⁻³	3.50 x 10 ⁻³	1.10 x 10 ⁻³
Cr ³⁺	2.10 x 10 ⁻³	3.26 x 10 ⁻³	1.25 x 10 ⁻³
Mn ²⁺	2.30 x 10 ⁻³	8.29 x 10 ⁻³	1.18 x 10 ⁻³
Cu ²⁺	6.67 x 10 ⁻⁴	4.78 x 10 ⁻³	8.14 x 10 ⁻⁴
Zn ²⁺	1.91 x 10 ⁻³	1.00 x 10 ⁻³	3.36 x 10 ⁻³

4.3.4 Analytical applications

The response characteristics as well as the selectivity of the diamond paste electrodes made them suitable for the determination of Fe(II) in pharmaceutical products. The recovery tests performed for Fe(II) solution using DPV, were higher than 99.00% with RSD (%) values less than 1% (N=10). The results obtained for the uniformity content test of four different vitamin tablets are shown in Table 4.2. Fe(II) can be reliably assayed from the tablets with a high average recovery and low RSD% values. All the values for the recovery (%) of Fe(II) fall within labeled amount of 90-110% required by the USP XXV [26]. The advantage of the proposed method is the simplicity and also high precision due to the lower values of the RSD (%).

Table 4.2 Uniformity content test for vitamins. All measurements were made at 25°C; all values are the average of ten determinations.

Average recovery, Fe(II)mg/tablet		
Sample No.	mg Fe(II)/ tablet	Electrode based on natural diamond
1	13	12.94 ± 0.12
2	18	17.82 ± 0.22
3	7.5	7.18 ± 0.08
4	5.0	4.87 ± 0.04
Average recovery, Fe(II)mg/tablet		
Sample No.	mg Fe(II)/ tablet	Electrode based on synthetic-1
1	13	12.93 ± 0.14
2	18	17.83 ± 0.21
3	7.5	7.17 ± 0.08
4	5.0	4.86 ± 0.05
Average recovery, Fe(II)mg/tablet		
Sample No.	mg Fe(II)/ tablet	Electrode based on synthetic-2
1	13	12.94 ± 0.13
2	18	17.84 ± 0.21
3	7.5	7.18 ± 0.08
4	5.0	4.86 ± 0.04

4.3.5 Statistical comparison between the results obtained for the uniformity content test of vitamins tablets using the diamond paste based electrodes

Mathematical calculations and statistical treatment of analytical data were performed for all the vitamins samples using the paired t-test approach [27]. The idea was to examine whether the different diamond paste based electrodes gave results that differed significantly at the 95% confidence level (N=10). $t_{\text{calculated}}$ (t_{calc}) was computed using the following formula [27]:

$$t_{\text{calc}} = \left| \bar{X}_1 - \bar{X}_2 \right| \sqrt{\frac{N(N-1)}{\sum (d_i - \bar{d})^2}}$$

where $\bar{X}_1$ and $\bar{X}_2$ are the average recoveries of Fe(II) for each sample, N is the number of measurements, $\bar{d}$ is the mean of d_i values and d_i is the individual difference between the two methods for each sample. As it can be seen from Table 4.3, all the t_{calc} values, at the 95% confidence level, are less than the tabulated theoretical value: 2.262. It follows that there is no statistically significant difference between the results obtained for the uniformity content test of Fe(II) using the proposed diamond paste based electrodes.

Table 4.3 Statistic evaluation of the uniformity content test performed with the proposed diamond paste based electrodes.

Electrodes based on			
Sample	Natural diamond vs synthetic-1	Synthetic-1 vs synthetic-2	Natural diamond vs synthetic-2
	$t_{calc.}$		
1	1.04	1.13	-
2	0.39	0.58	0.89
3	0.28	1.44	-
4	1.55	-	1.92

4.4 Conclusions

The new class of diamond electrodes, namely, diamond paste based electrodes provides excellent features for the detection of Fe(II) in pharmaceutical products, biological fluids, food and water. The design of the diamond paste based electrode is simple, fast and reproducible. The reliability of the analytical information is assured by the low RSD (< 5%) values obtained in the recovery tests, by the fast response of the differential pulse voltammetry (DPV), and by its large working concentration range. The proposed new diamond paste electrode has got high sensitivity and stability. By utilization of diamond paste based electrodes, the noise is reduced considerably. The signal/noise ratio increased if one compare with the values obtained when a carbon paste or glassy carbon electrodes are used for the same measurements.

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CHAPTER 5

DETERMINATION OF Fe(III) USING DIAMOND PASTE BASED ELECTRODES

5.1 Introduction

Monocrystalline diamond and boron doped polycrystalline diamond based electrodes exhibit several superior electrochemical properties that are significantly different from those of other carbon allotropes based electrodes, e.g., glassy carbon electrodes, highly oriented pyrolytic graphite based electrodes, which have been widely used for many years [1-3]: (a) lower background currents and noise signals, which lead to improve S/B and S/N ratios, and lower detection limits; (b) good electrochemical activity (the pre-treatment is not necessary); (c) wide electrochemical potential window in aqueous media; (d) very low capacitance; (e) extreme electrochemical stability; and (f) high reproducibility of analytical information. Furthermore, later studies shown the superiority of the monocrystalline diamond as electrode material due to high drift mobilities measured for electrons and holes [2].

Iron is lustrous and silvery in colour [4]. Iron when pure is fairly soft, and readily worked. The structure of the solid is typically metallic, being bcc for iron at room temperature. The magnetic properties of iron are dependent on purity and heat treatment. Up to 768°C pure iron is ferromagnetic as a result of extensive magnetic interactions between unpaired electrons on adjacent atoms, which cause the electron spins to be aligned in the same direction, so producing so exceedingly high magnetic

susceptibilities and the characteristic ferromagnetic properties of “saturation” and “hysteresis”.

Iron is a usual constituent of hundreds of mineral species, ground water and acid rain drainage. Henceforth, its chemistry is very important for its quantitative determination in environmental, industrial, metallurgical and geological context [5]. The following voltammetric techniques were proposed for the assay of Fe(III) from diverse matrices: stripping voltammetry, [6,7] square wave voltammetry, [8] and differential pulse voltammetry [9]. Ion-selective electrodes [10] and potentiometric titrations [11] were also used for the assay of Fe(III). Some of the voltammetric and spectrometric methods proposed for the assay of Fe(III) were automated: a flow injection analysis using a glassy carbon as detector [12] and a sequential injection analysis with spectrometric detection [13].

In this chapter monocrystalline based diamond paste electrodes are proposed for the assay of Fe(III). A diamond paste similar with the carbon paste was preferred for electrodes design, since the carbon paste based electrodes proved high reliable construction and response characteristics [14]. Three types of diamonds were used for the design of the diamond paste: a natural diamond and two types of synthetic diamond. Differential pulse voltammetry (DPV) was used for the calibration of the electrodes as well as for the recovery of Fe(III) in water samples.

5.2 Experimental

5.2.1 Diamond paste electrode design

The diamond paste electrode was prepared by mixing 0.1g of diamond powder with 20 μ L of paraffin oil. A portion of the paste was then filled into a plastic pipette tip (3mm). The diameter of the sensing part was 2.3mm. Electric contact was made by inserting a silver wire (0.5mm in diameter) in the diamond paste. Before use, the electrode surface was smoothed by polishing with an alumina paper (polishing strips 30144-001, Orion). When not in use, the diamond paste electrode was stored at room temperature.

5.2.2 Reagent and materials

All chemicals were analytical grade. All solutions were prepared by using de-ionised water. All Fe(III) solutions were freshly prepared everyday by dissolving the required amount of Fe(III) ammonium sulphate in de-ionised water prior to use. Monocrystalline natural 1 μ and synthetic diamond: 50 μ (synthetic-1) and 1 μ (synthetic-2) powders were purchased from Aldrich (Milwaukee, WI, USA) while the paraffin oil was purchased from Fluka (Buchs, Switzerland). Phosphate buffer (pH=9.00) was prepared from KH_2PO_4 (SAARCHM-HOLPRO ANALYTIC) and Na_2HPO_4 (Chemical Suppliers). 0.1 mol/L pyrophosphate solution was used as supporting electrolyte.

Different aliquots from four water samples collected from stream effluents were individually placed in 100mL calibrated flasks and a mixture of phosphate buffer (pH=9.00) and pyrophosphate solution (0.1 mol/L) in a ratio of 3.5:1 was added up to the mark.

5.2.3 Apparatus

Differential pulse voltammograms were performed with a 663 VA Stand (Metrohm, Herisau, Switzerland) connected to a PGSTAT 20 and a Ecochemie Software Version 4.8. A platinum electrode and a Ag/AgCl (0.1mol/l KCl) electrode served as counter and reference electrode in the cell respectively. The operating conditions were: Applied potential pulse amplitude of 25mV/sec; temperature 25°C; potential range +200 to +400 mV.

5.2.4 Recommended procedures: Direct DPV assay

The technique used for the direct voltammetric assay was differential pulse voltammetry with the applied potential pulse amplitude of 25mV vs. Ag/AgCl. All measurements were performed at 25°C. The diamond paste electrode together with the reference and auxiliary electrodes were dipped into a cell containing phosphate buffer (pH=9.0) and sodium pyrophosphate as supporting electrolyte in a ratio of 3.5:1. All solutions were deoxygenated for 5 min before the measurements with N₂. The peak height measured at 300 mV vs Ag/AgCl was plotted versus the concentration of Fe(III). The unknown concentrations of Fe(III) were determined from the calibration graphs.

5.3 Results and discussions

5.3.1 Equation of calibration

The current responses to different Fe(III) concentrations employing the proposed diamond paste electrodes were linear over a wide concentration range and can be described by the following equations of calibration (a. natural diamond; b. synthetic-1 and c. synthetic-2):

a. $H = 2.14 + 6.87 C$; $r = 0.9612$

b. $H = 15.20 + 210.00 C$; $r = 0.9943$

c. $H = 0.88 + 138.17 C$; $r = 0.9817$

where H is the peak height (μA), C is the concentration of Fe(III) (nmol/l), and r is the regression coefficient. The linear concentration ranges for the proposed electrodes are the following: for natural diamond between 10^{-12} and 10^{-9} mol/L with detection limit of 10^{-13} mol/L, for synthetic-1 between 10^{-7} and 10^{-5} mol/L with detection limit of 10^{-8} mol/L, and for synthetic-2 between 10^{-11} and 10^{-5} mol/L with a detection limit of 10^{-12} mol/L. The peaks' profiles recorded for the assay of Fe(III) with the three electrodes are shown in Figure 5.1. The signal to background ratio is very high when compared to classical glassy carbon (GC) and carbon paste electrodes. The reproducibility of peak current was excellent (RSD% values recorded were less than 1%).

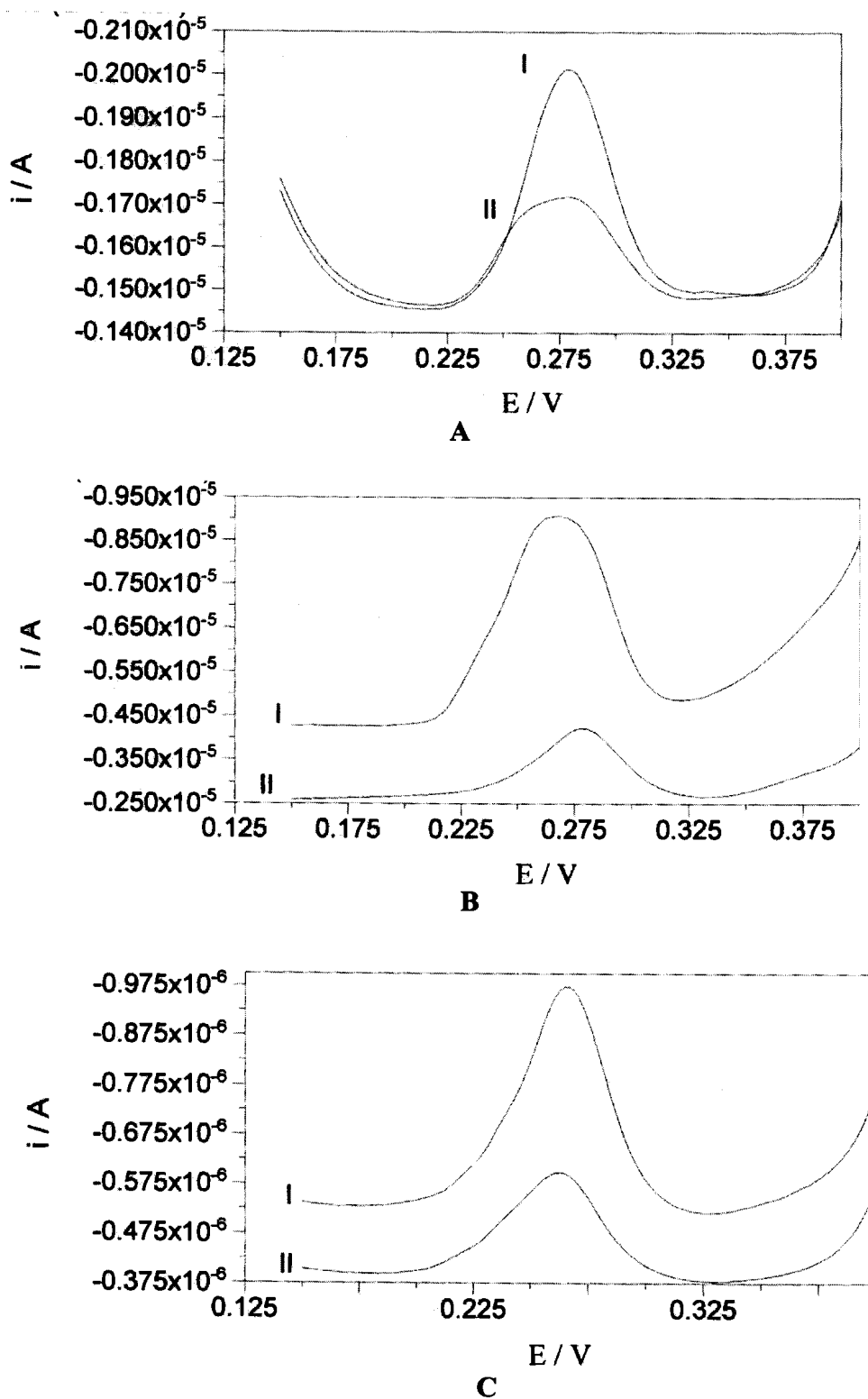


Figure 5.1 Peak profiles for DPV measurements when the electrodes based on: A. Natural diamond (I $C_{\text{Fe(III)}} = 10^{-9}$ mol/L; II $C_{\text{Fe(III)}} = 10^{-10}$ mol/L); B. Synthetic-1 (I $C_{\text{Fe(III)}} = 10^{-5}$ mol/L ; II $C_{\text{Fe(III)}} = 10^{-6}$ mol/L) ; C. Synthetic-2 (I $C_{\text{Fe(III)}} = 10^{-6}$ mol/L ; II $C_{\text{Fe(III)}} = 10^{-9}$ mol/L) are used.

5.3.2 Selectivity studies

The effect of various ions on a differential pulse voltammogram peak current was examined for all diamond paste electrode types using mixed solutions method. The ratio between Fe(III) and the possible interferent was 1:10 (mol/mol). The amperometric selectivity coefficients were calculated accordingly with the method proposed by Wang [15]. The values obtained for amperometric selectivity coefficients (Table 5.1) indicate that all the ions investigated: Mg^{2+} , Cr^{3+} , Mn^{2+} , Cu^{2+} , Zn^{2+} and Fe^{2+} did not interfere with the determination of Fe(III).

Table 5.1 Amperometric selectivity coefficients. All measurements were done at 25°C; all values are the average of ten determinations.

Interfering species (J^{z+})	Natural diamond	Synthetic-1	Synthetic-2
		$K_{\text{sel}}^{\text{amp}}$	
Fe^{2+}	9.90×10^{-4}	9.00×10^{-4}	5.90×10^{-4}
Mg^{2+}	9.20×10^{-3}	4.56×10^{-3}	8.88×10^{-3}
Cr^{3+}	3.40×10^{-4}	5.85×10^{-3}	5.41×10^{-3}
Mn^{2+}	9.15×10^{-3}	7.10×10^{-3}	6.91×10^{-3}
Cu^{2+}	8.90×10^{-3}	2.30×10^{-3}	7.48×10^{-3}
Zn^{2+}	6.01×10^{-3}	6.91×10^{-3}	8.33×10^{-3}

5.3.3 Analytical applications

The response characteristics as well as the selectivity of the diamond paste electrodes made them suitable for the determination of Fe(III) in water samples. The RSD (%) values obtained for the recovery tests performed for determination of Fe(III) in water samples were less than 1% ($n=10$) (Table 5.2). As it can be seen from Table 5.2, it is a good correlation between the results obtained for the assay of Fe(III), by using the

proposed diamond paste based electrodes. The advantage of the proposed method is the simplicity and also higher precision due to the lower values of the RSD(%).

Table 5.2 Recovery of Fe(III) in water samples. All measurements were done at 25°C; all values are the average of ten determinations.

Sample No.	Recovery of Fe(III), mol/L		
	Natural Diamond	Synthetic-1	Synthetic-2
1	20.86 ± 0.20	20.95 ± 0.25	21.12 ± 0.10
2	22.41 ± 0.21	22.95 ± 0.15	23.30 ± 0.10
3	4.79 ± 0.10	5.00 ± 0.30	4.80 ± 0.20
4	22.01 ± 0.30	21.20 ± 0.29	23.90 ± 0.09

5.4 Conclusion

The diamond paste electrodes presented in this paper provides excellent features for the detection of Fe (III) in pharmaceutical products, biological fluids, food and water samples. The design of the diamond paste based electrode is simple, fast and reproducible. The reliability of the analytical information is assured by the low RSD % values obtained in the recovery tests, low limits of detection and large working concentration range, and high selectivity. The proposed new diamond based paste electrodes are also very stable in time.

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CHAPTER 6

DIAMOND PASTE BASED ELECTRODES FOR THE DETERMINATION OF Cr(III) IN VITAMINS

6.1 Introduction

Diamond thin film electrode is a promising material for electrochemical application due to diamond's attractive properties such as hardness, high thermal conductivity, corrosion resistance, chemical inertness, variable conductivity via doping, electrode geometry patterning using selective growth methods and superior microstructural stability [1-5]. However, recent studies shown the superiority of monocrystalline diamond as a possible alternative for the polycrystalline material due to its special properties, such as improved holes and electrons mobilities [6,7].

Chromium, 122 ng/mL of the earth's crustal rocks and is well known by the variety of colours found in its compounds [8]. The only chromium ore having commercial importance is ferrous chromite, $\text{Fe}(\text{Cr}_2\text{O}_4)$, which is produced in huge amount in USSR and the Southern Africa. The main use of chromium metal is in the production of non-ferrous alloys, its use being limited because of its low ductility at ordinary temperatures.

Chromium(III) is used in the leather tanning industry, the manufacture of catalysts, pigments and paints, fungicides, the ceramic, glass and pharmaceutical industry, in

photography, for chrome alloy and chromium metal production, chrome plating, and corrosion control. Methods for the determination of chromium in biological and environmental samples are developing rapidly. Ion chromatography inductively coupled plasma mass spectrometry (IC-ICP MS) [9] is successfully applied for the determination of Cr(III) in solid samples. High performance liquid chromatographic method with diode array detection (HPLC-DAD) [10] is used in environmental analysis. Speciation of chromium using resin functionalised as applied prior to flame atomic absorption spectroscopy (AAS) [11] for trace Cr(III) and total chromium determination has been exploited. Solid phase adsorption followed by thin layer X-ray fluorescence spectrometric method [12] is applied for the determination of Cr(III) at low ng/mL levels in water.

In this paper, a new class of electrodes based on monocrystalline diamond powder is described for Cr(III) determination in two different vitamin tablets at trace concentration levels. Since the carbon paste based electrodes proved high reliable construction and response characteristics [13], a diamond paste similar with the carbon paste was preferred for electrodes design. Three types of diamonds were used for the design of the diamond paste: a natural diamond and two types of synthetic diamond. Differential pulse voltammetry (DPV) was used for the calibration of the electrodes and for the recovery tests of Cr(III) in vitamin tablets.

6.2 Experimental

6.2.1 Reagents and solutions

All chemicals were analytical grade. All solutions were prepared by using deionised water. Phosphate buffer (pH=8.00) was prepared from KH_2PO_4 (SAARCHM-HOLPRO ANALYTIC) and Na_2HPO_4 (Chemical Suppliers). 0.1 mol/L pyrophosphate solution was used as supporting electrolyte.

All the solutions of Cr(III) were prepared by dissolving the required amount of $\text{Cr}_4(\text{SO}_4)_5(\text{OH})_2$ (SAARCHM-HOLPRO ANALYTIC) in de-ionised water. The monocrystalline diamond powder Synthetic-1, synthetic-2 and natural diamond with particle sizes ca.50 μ , ca.1 μ , and ca.1 μ , respectively, were purchased from Aldrich while the paraffin oil was purchased from Fluka. Bettaway iron extra was purchased from Better Nutrition (Pty) Ltd, Sandton, South Africa. Vital multi-vitamin & mineral with iron was purchased from Vital Health Foods (Pty) Ltd, Kuils River, South Africa.

6.2.2 Recommended procedure: Direct DPV assay

The technique used for the direct voltammetric assay was differential pulse voltammetry with the applied potential pulse amplitude of 25mV vs. Ag/AgCl. The diamond paste electrode together with the reference and auxiliary electrodes were dipped into a cell containing phosphate buffer (pH=8.0) and sodium pyrophosphate as supporting

electrolyte in a ratio of 3.5:1. All solutions were deoxygenated for 5 min before the measurements with N_2 . The peak height measured at 275 mV vs Ag/AgCl was plotted versus the concentration of Cr(III). The unknown concentrations of Cr(III) were determined from the calibration graphs.

6.2.3 Uniformity content tests

Ten tablets from Daily Multi-Vitamin (100 μ g) and ten tablets from Vitaforce 21-PlusBPR protectavite (125 μ g) are individually placed in ten 100 mL calibrated flasks, dissolved and diluted with de-ionised water to the mark. The direct DPV method was used for the assay of Cr(III) content in each of the vitamin solution.

6.2.4 Electrode design

All diamond paste electrodes were prepared by mixing 0.1 g of each diamond powder with 20 μ L paraffin oil. A portion of the paste was then filled into a plastic pipette tip. The diameter of the sensing part was 2.3mm. Electric contact was made by inserting a silver wire in the diamond paste. Before each use the electrode surface was smoothed out by polishing with an alumina paper (polishing strips 30144-001, Orion). When not in use, the diamond paste electrode was stored at room temperature.

6.2.5 Instrumentation

Differential pulse voltammograms were performed with a 663 VA Stand (Metrohm, Herisau, Switzerland) connected to a PGSTAT 20 and a Ecochemie Software Version 4.8. A platinum electrode and a Ag/AgCl (0.1mol/l KCl) electrode served as counter and reference electrode in the cell respectively. The operating conditions were: applied potential pulse amplitude of 25mV/sec; potential range +200 to +400 mV vs Ag/AgCl electrode; equilibration time, 5 s; step potential 1.95 mV.

6.3 Results and discussions

6.3.1 Electrode response

All solutions are thoroughly deoxygenated by degassing with N₂ until no further decrease in background current could be produced for about 5 min. The current responses to different Cr(III) concentrations employing all the three diamond paste electrodes were linear over a wide concentration range and can be read from the following equations of calibration: **a.** natural diamond ; **b.** synthetic-1 and **c.** synthetic-2

a. $H = 7.64 + 740.81 C ; r = 0.9998$

b. $H = 3.64 + 25.14 C ; r = 0.9430$

c. $H = 0.44 + 36.45 C ; r = 0.9986$

where **H** is the peak height (μA), **C** is the concentration of Cr(III) ($\mu\text{mol/L}$) and **r** is the regression coefficient. The DPV peak currents were proportional with the concentration of Cr(III) in wide concentration ranges: natural diamond, 10^{-10} to 10^{-8} mol/L with detection limit of 10^{-12} mol/L; synthetic-1, 10^{-9} to 10^{-7} mol/L with detection limit of 10^{-12} mol/L and synthetic-2, 10^{-10} to 10^{-8} mol/L with a detection limit of 10^{-11} mol/L. Figure 6.1 shows some peak profiles obtained using DPV technique. The reproducibility of the peak currents were excellent for all three electrodes, when the measurements were done every day for a period longer than 6 months ($\text{RSD} < 0.1\%$).

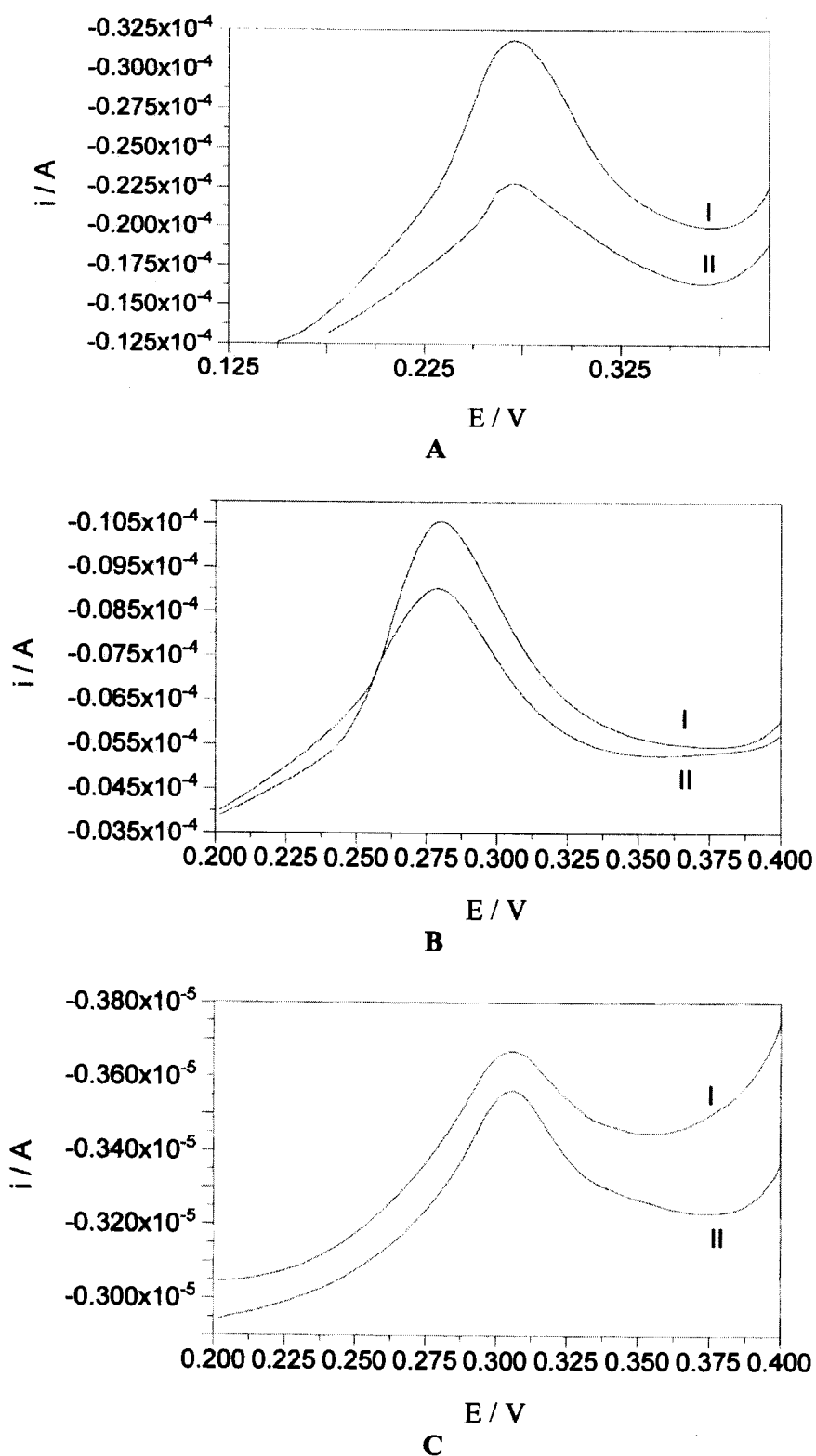


Figure 6.1 Peak profiles obtained using DPV with: **A.** Natural diamond (I $C_{Cr(III)} = 10^{-8}$ mol/L; II $C_{Cr(III)} = 10^{-10}$ mol/L); **B.** Synthetic-1 (I $C_{Cr(III)} = 10^{-7}$ mol/L; II $C_{Cr(III)} = 10^{-8}$ mol/L); and **C.** Synthetic-2 (I $C_{Cr(III)} = 10^{-9}$ mol/L ; II $C_{Cr(III)} = 10^{-10}$ mol/L) based electrodes.

6.3.2 Selectivity of the diamond paste

The most significant advantage of using diamond paste based electrodes is that the analyte interaction gives greatly enhanced selectivity. Because of the high selectivity of the diamond paste electrodes towards an analyte in a given working potential range, a number of metal ions have no or little effect on the determination of Cr(III) as tabulated in Table 6.1. It was found that 1×10^{-5} mol/L metal ions such as Fe^{2+} , Mg^{2+} , Cr^{6+} , Mn^{2+} , Cu^{2+} and Zn^{2+} do not interfere in the determination of 1×10^{-6} mol/L Cr(III).

Table 6.1 Amperometric selectivity coefficients. All values are the average of ten determinations.

Interfering Species (J)	K_{amp}		
	Natural Diamond	Synthetic Diamond-1	Synthetic Diamond-2
Fe^{2+}	3.96×10^{-4}	8.52×10^{-4}	1.76×10^{-3}
Mg^{2+}	3.30×10^{-4}	2.06×10^{-3}	4.93×10^{-5}
Cr^{6+}	8.38×10^{-6}	6.08×10^{-4}	1.09×10^{-3}
Mn^{2+}	6.23×10^{-4}	2.82×10^{-3}	4.34×10^{-4}
Cu^{2+}	3.79×10^{-4}	1.07×10^{-3}	5.53×10^{-4}
Zn^{2+}	7.54×10^{-5}	2.50×10^{-4}	1.85×10^{-3}

6.3.3 Analytical applications

The average recovery of Cr(III) in synthetic samples was $99.80 \pm 0.10\%$, $99.98 \pm 0.09\%$ and $99.92 \pm 0.12\%$ when natural diamond, synthetic-1 and synthetic-2 are used for the design of the electrodes. The diamond paste based electrodes were used for determination

of Cr(III) in two different vitamin tablets. The results of the uniformity content tests are shown in Table 6.2. They indicate that the recoveries are quite comparable when using different diamond electrodes. Cr(III) was determined from the vitamin tablets at trace concentration levels. The advantages of the proposed method are the possibility of direct assay of Cr(III) without any prior separation from the vitamin tablets, the enhanced selectivity at a given working potential, simplicity of the method and also the higher precision as evidenced by the lower values of the RSD(%).

Table 6.2 Determination of Cr(III) in vitamin tablets using the three diamond paste electrodes. All values are the average of ten determinations.

Sample No.	Average Recovery, % Cr(III)/tablet		
	Natural Diamond	Synthetic Diamond-1	Synthetic Diamond-2
1	98.35 $\pm$ 0.01	98.23 $\pm$ 0.07	98.28 $\pm$ 0.05
2	97.48 $\pm$ 0.10	97.46 $\pm$ 0.17	97.41 $\pm$ 0.09

6.4 Conclusions

All diamond paste based electrodes presented in this work provides excellent reproducibility for the detection of Cr(III) in vitamins. Using all the three electrodes; characteristic peak currents appeared to be at about $+0.275 \pm 0.015$ V vs. Ag/AgCl. The design of the monocrystalline diamond paste based electrode is simple, fast, reproducible and robust. The reproducibility of the analytical information is assured by the low RSD values obtained in the recovery tests. The proposed new class of electrodes has got enhanced sensitivity and the required stability for applications in various analyses.

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CHAPTER 7

DIAMOND PASTE BASED ELECTRODES FOR THE DETERMINATION OF Cr(VI) AT TRACE LEVELS

7.1 Introduction

Electroanalysis is one field that can benefit much from the attractive properties of diamond as electrode material. Up to now, only polycrystalline diamond was used for the design of the electrochemical sensors [1-5]. Monocrystalline diamond proved to be a good alternative for the polycrystalline material due to its special properties, such as improved holes and electrons mobilities [6,7].

Chromium is a common constituent of many materials, especially irons and steels and methods for its determination are of considerable importance. The hexavalent chromium has a strong oxidizing properties and are frequently used in organic chemistry [8]. CrO_3 is a strong acid and is commonly called “chromic acid”. It is generally prepared by the addition of concentrated H_2SO_4 to a saturated aqueous solution of a dichromate.

Chromium as Cr(VI) is considered very hazardous for humans and its environmental monitoring has found great application in the field of science. Spectrophotometry [9-12] is the most common technique for the determination of Cr(VI) in alloy steel, high purity nickel, certified ores, water, sediments and soil. Kinetic spectrophotometric methods

[13,14] were also applied for its determination in electroplating waste water. Spectrophotometric detection for trace Cr(VI) with [15] and without FIA [16,17] were proposed. Electrothermal atomic absorption spectrometry (ETAAS) [18,19] is proposed for the assay of Cr(VI) in mineral, natural, potable and waste waters.

In this chapter, a new class of electrodes based on monocrystalline diamond paste is described for Cr(VI) determination - as impurity - in four different vitamin tablets at trace concentration levels. Since the carbon paste based electrodes proved high reliable construction and response characteristics [20], a diamond paste similar with the carbon paste was preferred for electrodes' design. Three types of diamonds were used for the design of the diamond paste: a natural diamond and two types of synthetic diamond. Differential pulse voltammetry (DPV) was used for the calibration of the electrodes and for the recovery of Cr(VI) in the vitamin tablets.

7.2 Experimental

7.2.1 Reagents and solutions

All chemicals were of analytical grade. All solutions were prepared by using de-ionised water. Phosphate buffer (pH=8.00) was prepared from KH_2PO_4 (SAARCHEM-HOLPRO ANALYTIC) and Na_2HPO_4 (Chemical Suppliers). 0.1 mol/L pyrophosphate solution was used as supporting electrolyte.

All the solutions of Cr(VI) were prepared by dissolving the required amount of potassium chromate (SAARCHM-HOLPRO ANALYTIC) in phosphate buffer prior to use. The monocrystalline diamond powder Synthetic-1, synthetic-2 and natural diamond with particle sizes ca.50 μ , ca.1 μ , and ca.1 μ , respectively, were purchased from Aldrich while the paraffin oil was purchased from Fluka. Bettaway iron extra was purchased from Better Nutrition (Pty) Ltd, Sandton, South Africa. Vital multi-vitamin & mineral with iron was purchased from Vital Health Foods (Pty) Ltd, Kuils River, South Africa. Bettaway iron extra was purchased from Better Nutrition (Pty) Ltd, Sandton, South Africa. Vital multi-vitamin & mineral with iron was purchased from Vital Health Foods (Pty) Ltd, Kuils River, South Africa. Weigh-Less daily multi-vitamin with antioxidants was purchased from Weigh-Less S.A. (Pty) Ltd, Hout Bay, South Africa. Vitaforce 21 plusBPR protectavite was purchased from Pharma Natura (Pty) Ltd, Sandton, South Africa.

7.2.2 Calibration plot preparation

0.1mol/L potassium chromate (K_2CrO_4) stock solution was prepared using 0.1 mol/L H_2SO_4 solution. From this stock solution, working solutions ranging between 10^{-2} to 10^{-12} mol/L were prepared using phosphate buffer pH 8.00 and 0.1 mol/L supporting electrolyte in the ratio 3.5:1.

7.2.3 Preparation vitamin solutions

Ten tablets from Iron Extra (sample 1) and ten tablets from Vital multi-vitamin & mineral with iron (sample 2) are individually placed in ten 100 mL calibrated flasks, and dissolved in de-ionised water. Ten tablets from Weigh-Less daily multi-vitamin with antioxidants (sample 3) and ten tablets from Vitaforce 21 PlusBPR (sample 4) are individually placed in ten 50 mL calibrated flasks, and dissolved in distilled water. The direct DPV method was used for the assay of Cr(VI) content in each of the vitamin solution.

7.2.4 Electrode construction

All diamond paste electrodes were prepared by mixing 0.1 g of each diamond powder with 20 μ L paraffin oil. A portion of the paste was then filled into a plastic pipette tip. The diameter of the sensing part was 2.3mm. Electric contact was made by inserting a silver wire in the diamond paste. Before each use the electrode surface was smoothed out by polishing with an alumina paper (polishing strips 30144-001, Orion). When not in use, the diamond paste electrode was stored at room temperature.

7.2.5 Recommended procedures: Direct DPV assay

The technique used for the direct voltammetric assay was differential pulse voltammetry with the applied potential pulse amplitude of 25 mV vs. Ag/AgCl. The diamond paste

electrode together with the reference and auxiliary electrodes were dipped into a cell containing phosphate buffer (pH=8.0) and sodium pyrophosphate as supporting electrolyte in a ratio of 3.5:1. All solutions were deoxygenated for 5 min before the measurements with N₂. The peak height measured at 290 mV vs Ag/AgCl was plotted versus the concentration of Cr(VI). The unknown concentrations of Cr(VI) were determined from the calibration graphs.

7.2.6 Instrumentation

Differential pulse voltammograms were performed with a 663 VA Stand (Metrohm, Herisau, Switzerland) connected to a PGSTAT 20 and a Ecochemie Software Version 4.8. A platinum electrode and a Ag/AgCl (0.1mol/l KCl) electrode served as counter and reference electrode in the cell respectively. The operating conditions were: applied potential pulse amplitude, 25 mV/sec; potential range, +425 to +150 mV (vs Ag/AgCl); equilibration time, 5sec; step potential, 1.95 mV.

7.3 Results and discussion

7.3.1 Electrode response

All solutions are thoroughly deoxygenated by degassing with N₂ until no further decrease in background current could be produced for about 5 min. The current responses to different Cr(VI) concentrations employing all the three diamond paste electrodes were

linear over a wide concentration range and can be read from the following equations of calibration: **a.** natural diamond ; **b.** synthetic-1 and **c.** synthetic-2

a. $H = 4.44 + 0.007 C$; $r = 0.9940$

b. $H = 4.27 + 571.91 C$; $r = 0.9950$

c. $H = 3.12 + 4.97 \times 10^3 C$; $r = 0.9999$

where **H** is the peak height (μA), **C** is the concentration of Cr(VI) ($\mu mol/L$) and **r** is the regression coefficient. The DPV peak height were proportional for a wide concentration range: natural diamond, 10^{-11} to 10^{-9} mol/L with detection limit of 10^{-12} mol/L; synthetic-1, 10^{-10} to 5×10^{-7} mol/L with detection limit of 10^{-11} mol/L and synthetic-2, 10^{-6} to 10^{-3} mol/L with a detection limit of 10^{-8} mol/L. Figure 7.1 shows some peak profiles obtained using DPV for different concentrations of Cr(VI). The reproducibility of the peak currents were excellent ($RSD < 0.1\%$) for a period longer than 6 months.

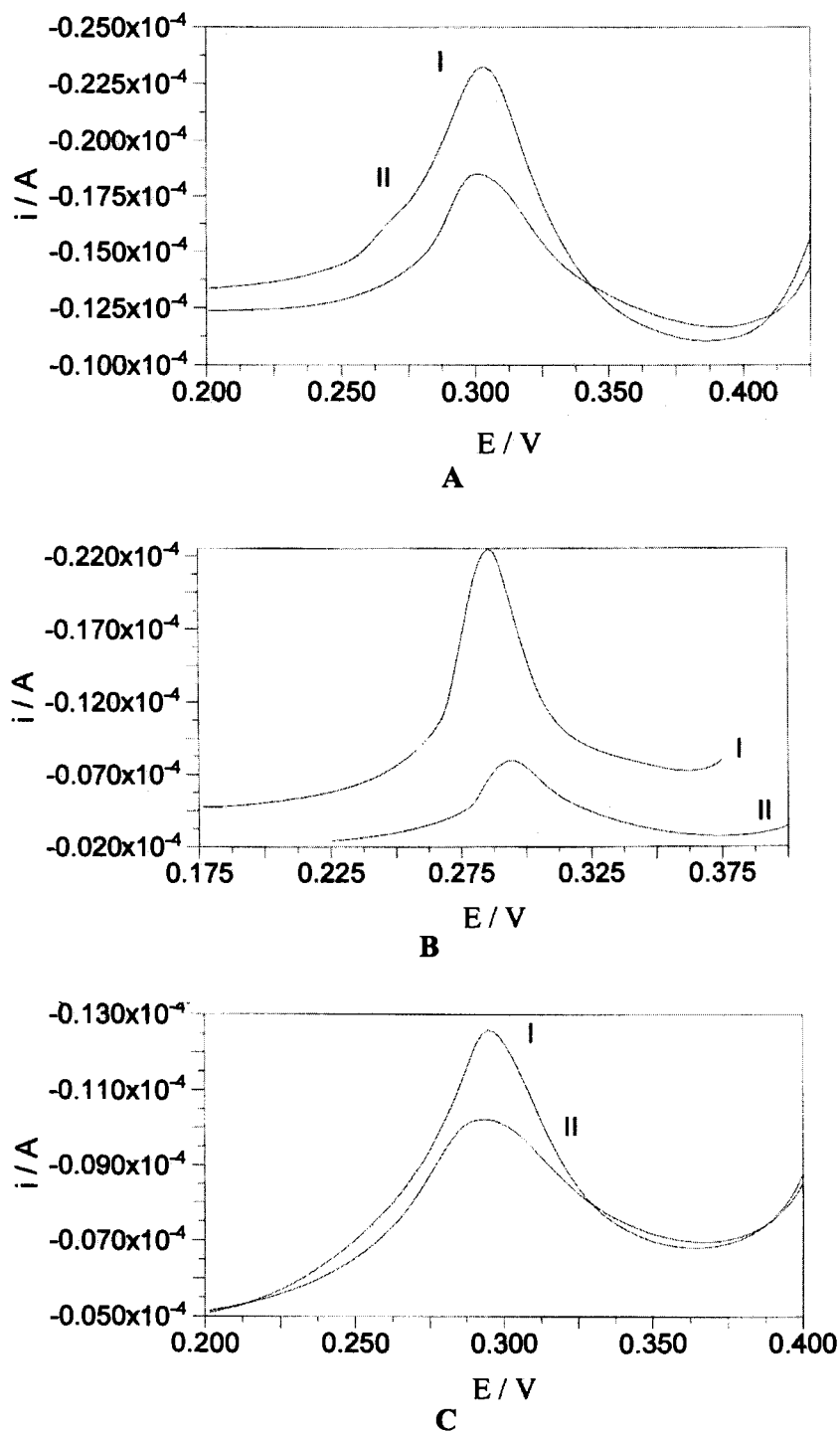


Figure 7.1 Peak profiles obtained using DPV with the electrodes based on: **A.** Natural diamond (I $C_{Cr(VI)} = 10^{-9}$ mol/L; II $C_{Cr(VI)} = 10^{-10}$ mol/L); **B.** Synthetic-1 (I $C_{Cr(VI)} = 10^{-7}$ mol/L; II $C_{Cr(VI)} = 10^{-9}$ mol/L); and **C.** Synthetic-2 (I $C_{Cr(VI)} = 10^{-3}$ mol/L ; II $C_{Cr(VI)} = 10^{-4}$ mol/L).

7.3.2 Selectivity of the diamond paste based electrodes

The most significant advantage of using diamond paste based electrodes is that the analyte interaction gives greatly enhanced selectivity. Because of the high selectivity of the diamond paste electrodes towards an analyte in a given working potential range, a number of metal ions have no or little effect on the determination of Cr(VI) as tabulated in Table 7.1. It was found that 1×10^{-5} mol/L metal ions such as Fe^{2+} , Mg^{2+} , Cr^{3+} , Mn^{2+} , Cu^{2+} and Zn^{2+} do not interfere in the determination of 1×10^{-6} mol/L Cr(VI).

Table 7.1 Amperometric selectivity coefficients. All values are the average of ten determinations.

Interfering Species (J)	K_{amp}		
	Natural Diamond	Synthetic Diamond-1	Synthetic Diamond-2
Fe^{2+}	1.66×10^{-3}	6.64×10^{-5}	1.46×10^{-3}
Mg^{2+}	8.40×10^{-4}	6.24×10^{-4}	5.76×10^{-5}
Cr^{3+}	1.21×10^{-3}	3.68×10^{-4}	3.21×10^{-3}
Mn^{2+}	4.42×10^{-4}	4.19×10^{-4}	7.80×10^{-5}
Cu^{2+}	2.81×10^{-5}	3.13×10^{-4}	4.35×10^{-4}
Zn^{2+}	2.81×10^{-4}	1.55×10^{-4}	1.97×10^{-3}

7.3.3 Analytical applications

The response procedures were applied to the determination of Cr(VI) in four different vitamin tablets by using direct DPV method. Table 7.2 shows the recoveries obtained for the vitamin tablets. The results indicate that the recoveries are quite comparable when

using different diamond paste electrodes. Cr(VI) was determined from the vitamin tablets at very low concentration level (ng Cr(VI)/tablet). The advantages of the proposed method are the possibility of direct determination of Cr(VI) in vitamin tablets without any prior separation, the enhanced selectivity at a given working potential, simplicity of the method and also higher precision as evidenced by the lower values of the RSD(%).

Table 7.2 Determination of Cr(VI) in vitamins. All the values are the average of ten determinations.

Sample No.	Average Recovery, ng Cr(VI)/tablet		
	Natural Diamond	Synthetic Diamond-1	Synthetic Diamond-2
1	28.00 ± 0.11	27.05 ± 0.20	28.05 ± 0.15
2	66.00 ± 0.01	66.57 ± 0.10	66.50 ± 0.08
3	22.00 ± 0.05	21.90 ± 0.10	21.83 ± 0.08
4	17.00 ± 0.27	16.81 ± 0.19	16.53 ± 0.23

7.4 Conclusions

All diamond paste based electrodes presented in this work provides excellent reproducibility for the detection of Cr(VI) in some pharmaceutical products. The design of the monocrystalline diamond paste based electrode is simple, fast, highly reproducible and robust. The reproducibility and robustness of the analytical information can be assured by the low RSD values obtained in the recovery tests. Attractive response characteristics and enhanced selectivity of the electrodes made them suitable for the determination of Cr(VI) at trace concentration levels.

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CHAPTER 8

DIAMOND PASTE BASED ELECTRODES FOR THE DETERMINATION OF Pb(II) AT TRACE CONCENTRATION LEVELS

8.1 Introduction

Electroanalysis is one field that can benefit much from the attractive properties of diamond as electrode material. Polycrystalline diamond based electrodes have been used in the electrochemical studies because of their properties, especially low background current, wide potential range and lack of adsorption [1-13]. Monocrystalline diamond proved to be a good alternative for the polycrystalline material due to its special properties, such as improved holes and electrons mobilities [14,15].

Lead (13 ng/mL) is by far the most abundant of the heavy elements [16]. This abundance is related to the fact that 3 of the 4 naturally occurring isotopes of lead (206, 207, and 208) arise primarily as the stable end products of the naturally radioactive series. The most important Pb ore is the heavy black mineral galena, PbS. Other ore minerals are anglesite (PbSO₄), cerussite (PbCO₃), pyromorphite (Pb₅(PO₄)₃Cl), and mimetesite (Pb₅(AsO₄)₃Cl). Lead is normally obtained from PbS. This is first concentrated from low-grade ores by froth flotation and then roasted in a limited supply of air to give PbO, which is then mixed with coke and a flux such as limestone and reduced in a blast furnace.

Lead is recognised as a poisoning heavy metal. It acts by complexation with oxo-groups in enzymes and affects virtually all steps in the process of haeme synthesis and porphyrin metabolism [17-19]. It also inhibits acetylcholine-esterase, acid phosphatase, ATPase, carbonic anhydrase, etc. Typical symptoms of lead poisoning are cholic, anaemia, headaches, convulsions, chronic nephritis of the kidneys, brain damage, and central nervous system disorders. As a result, quantitative determination of lead at trace concentration levels has its own biological importance and requires great consideration.

The determination of trace lead in water samples, blood, drugs and food additives have biological importance. ICP-MS [20-22] is the most powerful technique but the cost of the required instrumentation is very high and cannot be tolerated for use in most of the laboratories. Graphite furnace atomic absorption spectrometry [23] and flame atomic absorption spectrometry [24] are another alternative for the determination of lead in drugs, food and water. Electroanalytical techniques were also proposed for the assay of lead in different matrices [25-27].

In this chapter, a new class of electrodes based on monocrystalline diamond paste is described for Pb(II) determination in water and food. A diamond paste similar with the carbon paste was preferred for electrodes design, since the carbon paste based electrodes proved high reliable construction and response characteristics [28]. Three types of diamonds were used for the design of the diamond paste: a natural diamond and two types of synthetic diamonds. Differential pulse voltammetry (DPV) was used for the calibration of the electrodes and for the recovery tests of Pb(II) in water and tea samples.

8.2 Experimental

8.2.1 Diamond paste electrodes design

Each diamond paste electrode was prepared by mixing 0.1 gram of diamond powder with 20 μ L paraffin oil. A portion of the paste was then filled into a plastic pipette tip. The diameter of the sensing part was 2.3 mm. The electric contact was made by inserting a silver wire in the diamond paste. Before use the electrode surface was smoothed out by polishing with an alumina paper (polishing strips 30144-001, Orion). When not in use, the diamond paste electrode was stored at room temperature, dry.

8.2.2 Reagents and materials

All chemicals were of analytical grade. All solutions were prepared by using doubly deionised water. Phosphate buffer (pH=8.00) was prepared from KH_2PO_4 (SAARCHM-HOLPRO ANALYTIC) and Na_2HPO_4 (Chemical Suppliers). 0.1 mol/L pyrophosphate (Merck) solution was used as supporting electrolyte.

All the solutions of Pb(II) were freshly prepared everyday by dissolving the required amount of lead nitrate (General Purpose Reagent) in de-ionised water prior to use. High purity monocrystalline diamond powder: natural diamond 1 μ , synthetic diamond 50 μ (synthetic-1), and synthetic diamond 1 μ (synthetic-2) were purchased from Aldrich, while the paraffin oil was purchased from Fluka (Buchs, Switzerland). All solutions were deoxygenated prior to use by thorough degassing with high purity N_2 .

Five Roses Quality Tea (South Africa), Four Red Fruits Tea (England) and Chinese green tea were used for the assay of Pb(II).

8.2.2.1 Preparation of water samples for analysis

Two water samples were brought for analysis. 10 mL of each sample are individually placed in two 100 mL calibrated flasks. A mixture of phosphate buffer (pH=8.0) and 0.1mol/L of the pyrophosphate (supporting electrolyte) solution in a ratio of 3.5 to 1 is added to the water samples up to the mark.

8.2.2.2 Preparation of tea samples for analysis

The preparation of tea samples was done accordingly with the method proposed by Jing et al [29]. 1.00 g of the tea sample was transferred to a porcelain crucible. The sample was carbonized on a gas lamp. Then the carbonized sample was transferred into a muffle furnace and heated at 550°C for 4 h. After the sample was taken out from the furnace and cooled to room temperature, 2 mL conc. HNO₃ was added to the ash. Then the sample was heated to dryness on the gas lamp. The sample was transferred into the muffle furnace again and heated at 550°C for another hour. When the sample was taken out from the furnace and cooled to room temperature, 2 mL 6 mol/L HCl and two drops of 30% H₂O₂ was added to the sample ash. Then the sample was heated to dryness on the gas lamp again. At last, 2.5 mL 6 mol/L HCl was added and the sample was diluted to 25 mL with water. The analysis of the sample was then performed using standard addition method.

8.2.2.3 Direct DPV assay

The technique used for the direct voltammetric assay was differential pulse voltammetry. All measurements were performed at 25°C. The diamond paste electrode together with the reference and auxiliary electrodes were dipped into a cell containing phosphate buffer (pH=8.0) and sodium pyrophosphate as supporting electrolyte in a ratio of 3.5:1. All solutions were deoxygenated before the measurements with N₂. The peak height measured at 300 mV vs Ag/AgCl was plotted versus the concentration of Pb(II). The unknown concentrations of Pb(II) were determined from the calibration graphs.

8.2.2.4 Apparatus

Differential pulse voltammograms (DPV) were recorded using a 663 VA Stand (Metrohm, Herisau, Switzerland) connected to a PGSTAT 20 and an Ecochemie Software Version 4.8. A platinum electrode and a Ag/AgCl (0.1mol/l KCl) electrode served as counter and reference electrode in the cell. The operating conditions were: applied potential pulse amplitude, 25mV/s; potential range, +0.4 to +0.2 V (vs Ag/AgCl); equilibration time 5s; step potential 1.95 mV.

8.3 Results and discussion

8.3.1 Calibration equations

The dependency between the peak height and the concentration of Pb(II) was linear over a wide concentration range and can be read from the following equations of calibration: a. natural diamond; b. synthetic-1 and c. synthetic-2:

a. $H = 2.75 + 13.45 C$; $r = 0.9895$; $\langle C \rangle = \mu\text{mol/L}$

b. $H = 0.40 + 118.50 C$; $r = 0.9990$; $\langle C \rangle = \mu\text{mol/L}$

c. $H = 2.96 + 0.71 C$; $r = 0.9999$; $\langle C \rangle = \text{nmol/L}$

where H is the height of the peak (μA), C is the concentration of Pb(II) and r is the regression coefficient. For natural diamond, the linear concentration range is between 10^{-9} and 10^{-6} mol/L with detection limit of 10^{-10} mol/L; while for synthetic-1 is between 10^{-10} and 10^{-7} mol/L with detection limit of 10^{-11} mol/L and for synthetic-2 is between 10^{-10} and 10^{-8} mol/L with a detection limit of 10^{-11} mol/L. The reproducibility of the peak currents were good (RSD less than 1%, $n=10$).

8.3.2 Selectivity studies

Several ions were tested as possible interfering species in the determination of Pb(II) using mixed solutions method. The ratio between the possible interfering ion and Pb(II) was 10:1. Amperometric selectivity coefficients were determined for each

possible interfering ion (Table 8.1), and they proved that Fe^{2+} , Mg^{2+} , Cr^{3+} , Mn^{2+} , Cu^{2+} and Zn^{2+} do not interfere in the determination of Pb(II) .

Table 8.1 Amperometric selectivity coefficients. All values are the average of ten determinations.

Interfering Species (J^{z+})	K_{amp}		
	Natural Diamond	Synthetic-1	Synthetic-2
Fe^{2+}	4.20×10^{-4}	5.00×10^{-4}	7.83×10^{-4}
Mg^{2+}	3.10×10^{-3}	1.98×10^{-3}	4.55×10^{-4}
Cr^{2+}	4.69×10^{-5}	5.64×10^{-4}	1.27×10^{-4}
Mn^{2+}	2.27×10^{-3}	1.72×10^{-3}	2.80×10^{-3}
Cu^{2+}	1.44×10^{-3}	9.10×10^{-4}	3.86×10^{-3}
Zn^{2+}	1.11×10^{-3}	1.70×10^{-3}	1.43×10^{-3}

8.3.3 Analytical applications

The most significant advantage of using diamond paste based electrodes is the higher selectivity of the diamond paste based electrodes. Accordingly, Pb(II) can be determined at trace concentration level in different kinds of food, pharmaceuticals as well as in biological fluids.

The DPV method was used for the recovery of Pb(II) in tea and water samples. For the tea samples, a standard addition method was employed. Peak profiles obtained for the assay of lead in tea samples are shown in Figure 8.1. Tables 8.2 and 8.3 show the recovery values of Pb(II) in water and tea samples, respectively. DPV results indicate that the recoveries are comparable when using different diamond electrodes. Pb(II) was determined from the tea samples at very low concentration level (ng Pb(II)/g tea).

Table 8.2 Recovery of Pb(II) in water samples. All values are the average of ten determinations.

Sample No.	Average Recovery, mg/L		
	Natural Diamond	Synthetic-1	Synthetic-2
1	15.17 ± 0.07	15.58 ± 0.04	14.90 ± 0.05
2	27.43 ± 0.06	26.92 ± 0.04	27.17 ± 0.08

Table 8.3 Recovery of Pb(II) in tea samples. All values are the average of ten determinations.

Tea Samples	Average recovery, ng Pb ²⁺ /g tea		
	Natural Diamond	Synthetic-1	Synthetic-2
4 Red fruits	140.20 ± 0.2	139.90 ± 0.1	145.00 ± 0.2
Five roses	169.20 ± 0.3	165.80 ± 0.2	165.80 ± 0.1
Green tea	70.00 ± 0.3	71.80 ± 0.2	69.40 ± 0.2

8.4 Conclusions

The design of the monocrystalline diamond paste based electrode is simple, fast, highly reproducible and robust. The proposed new class of electrodes has got enhanced sensitivity and the required stability for sensor application. The attractive response characteristics as well as the high selectivity of the electrodes made them suitable for determination of Pb(II) at trace concentration levels from various water and food samples.

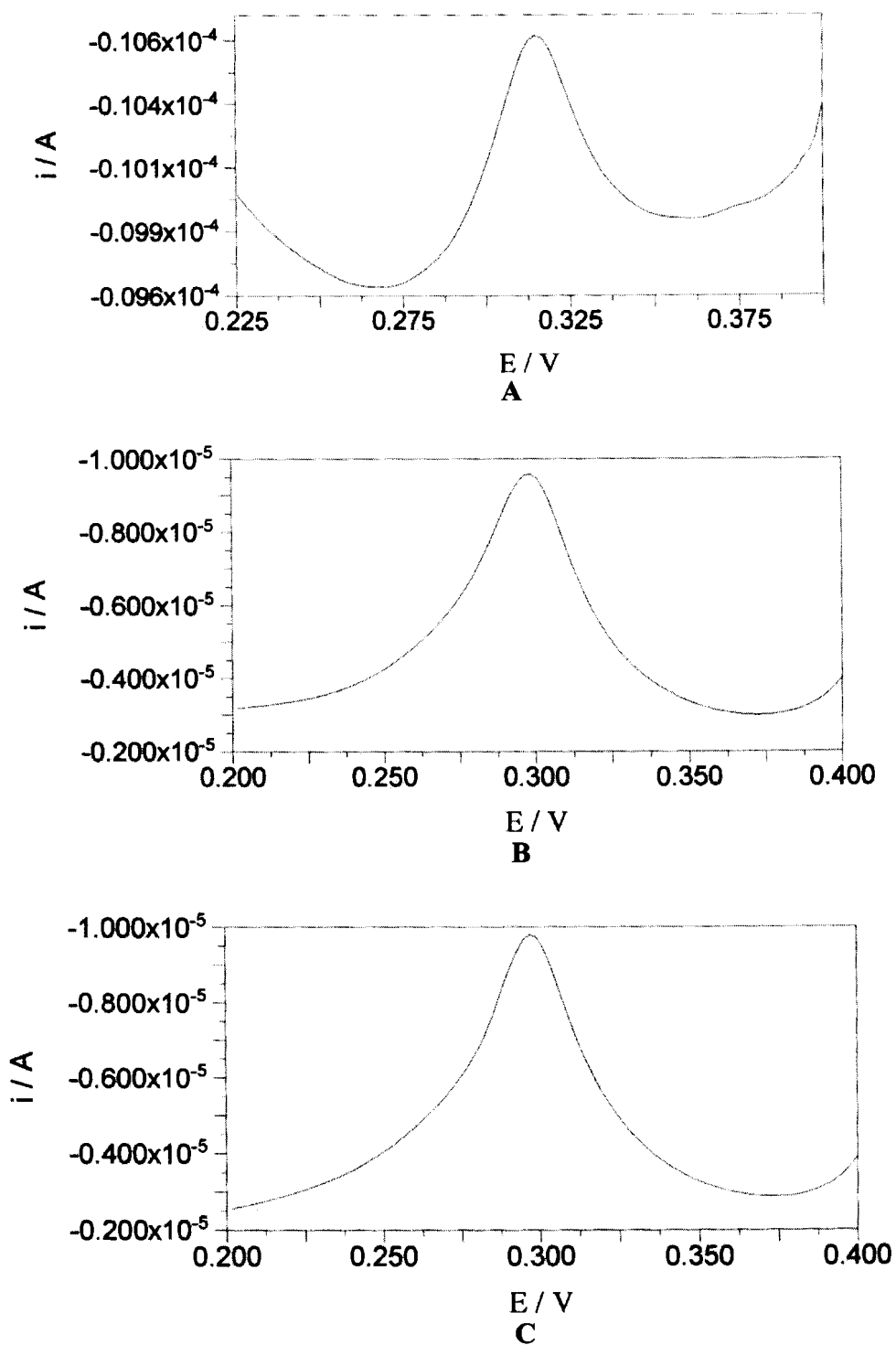


Figure 8.1 Peak profiles obtained using the electrode based on: **A.** Natural diamond; **B.** Synthetic-1; and **C.** Synthetic-2 for the assay of Pb(II) in tea samples.

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CHAPTER 9

DIAMOND PASTE BASED ELECTRODES FOR THE DETERMINATION OF Ag (I)

9.1 Introduction

Polycrystalline diamond thin film electrodes have been used up to now in the electrochemical sensors design due to its superior physical and electronic properties such as hardness, chemical inertness, optical transparency, high thermal and electrical conductivity, low background current, wide potential range, lack of adsorption, and high overpotential for oxygen evolution by water oxidation in aqueous electrolyte solution [1-5]. Monocrystalline diamond proved to be a good alternative for the polycrystalline material due to its special properties, such as improved holes and electrons mobilities [6,7]. The reliability obtained for the electrical properties of these single-crystal diamond is encouraging for research in electrochemical sensors based on high quality monocrystalline diamond.

Silver occurs native and widely distributed in sulfide ores of which silver glance (argentite) are the most important [8]. Native silver is sometimes associated with these ores as a result of their chemical reduction, while the action of salt water is probably responsible for their conversion into "horn silver", AgCl, which is found in Chile and New South Wales. The fire assay [9-11] method is the most commonly used for the determination of silver and gold in ores and ore dressing products. Among the other well known alternatives are atomic absorption spectrometry (AAS) [12,13] and wet

chemical analysis [14,15] of the lead assay button in ores and concentrates of these two precious metals. Recently, cathodic and anodic stripping voltammetry [16] based on the introduction of power ultrasound at a highly boron doped diamond (BDD) electrode was developed as a sensitive technique for the analysis of trace silver ions. The chemistry of silver is very important for its quantitative determination because of its use in photography, silverware, jewellery, electricity, silvering mirrors and as dental amalgam [8].

In this chapter, a diamond paste electrode and its utilization for the assay of Ag(I) in residual waters is described.

9.2 Experimental

9.2.1 Diamond paste electrode design

The diamond paste electrode was prepared by mixing 0.1g of diamond powder with 20 μ L of paraffin oil. A portion of the paste was then filled into a plastic pipette tip (3mm). The diameter of the sensing part was 2.3mm. Electric contact was made by inserting a silver wire (0.5mm in diameter) in the diamond paste. Before use, the electrode surface was smoothed by polishing with an alumina paper (polishing strips 30144-001, Orion). When not in use, the diamond paste electrode was stored at room temperature.

9.2.2 Reagents and materials

All chemicals were of analytical grade. All solutions were prepared by using de-ionised water. Phosphate buffer (pH=9.00) was prepared from KH_2PO_4 (SAARCHM-HOLPRO ANALYTIC) and Na_2HPO_4 (Chemical Suppliers). 0.1mol/L pyrophosphate solution was used as supporting electrolyte.

All the solutions of Ag(I) were freshly prepared everyday from silver nitrate. Monocrystalline natural 1μ and synthetic diamond: 50 μ (synthetic-1) and 1μ (synthetic-2) powders were purchased from Aldrich (Milwaukee, WI, USA) while the paraffin oil was purchased from Fluka (Buchs, Switzerland).

9.2.3 Apparatus

Differential pulse voltammograms were performed with a 663 VA Stand (Metrohm, Herisau, Switzerland) connected to a PGSTAT 20 and a Ecochemie Software Version 4.8. A platinum electrode and a Ag/AgCl (0.1mol/l KCl) electrode served as counter and reference electrode in the cell respectively.

9.2.4 Recommended procedures: Direct differential pulse voltammetry (DPV)

The technique used for the direct voltammetric assay was differential pulse voltammetry with an applied potential pulse amplitude of 25 mV vs. Ag/AgCl. The diamond paste as a working electrode together with the reference electrode (Ag/AgCl), and an auxiliary platinum electrode were dipped into a cell containing

phosphate buffer (pH=9.0) and sodium pyrophosphate solution 0.1 mol/L as supporting electrolyte in a ratio 3.5:1. All solutions were deoxygenated for 5 min before the commence of the measurements with high purity N₂. The peak height measured at 80mV vs Ag/AgCl was plotted versus the concentration of Ag(I). The unknown concentrations of Ag(I) were determined from the calibration graph.

9.3 Results and discussion

9.3.1 Equation of calibration

The relationship between the peak height and the concentration of Ag(I) was linear over a wide concentration range using all the diamond electrodes and can be described by the following equations of calibration: **a.** natural diamond ; **b.** synthetic diamond-1 and **c.** synthetic diamond-2

$$\mathbf{a. \quad H = 4.55 + 5.53 \, C ; \quad r = 0.9887}$$

$$\mathbf{b. \quad H = 1.97 + 3.67 \, C ; \quad r = 0.9999}$$

$$\mathbf{c. \quad H = 2.52 + 27.30 \, C ; \quad r = 0.9964}$$

where **H** is the peak height (μA), **C** is the concentration of Ag(I) (μmol/L) and **r** is the regression coefficient. The DPV peak currents were proportional for a wide concentration range: natural diamond, 10⁻⁹ to 10⁻⁶ mol/L with detection limit of 10⁻¹¹ mol/L; synthetic-1, 5x10⁻⁹ to 10⁻⁶ mol/l with detection limit of 10⁻¹⁰ mol/L and synthetic-2, 10⁻⁹ to 10⁻⁷ mol/L with a detection limit of 10⁻¹⁰ mol/L. The peaks

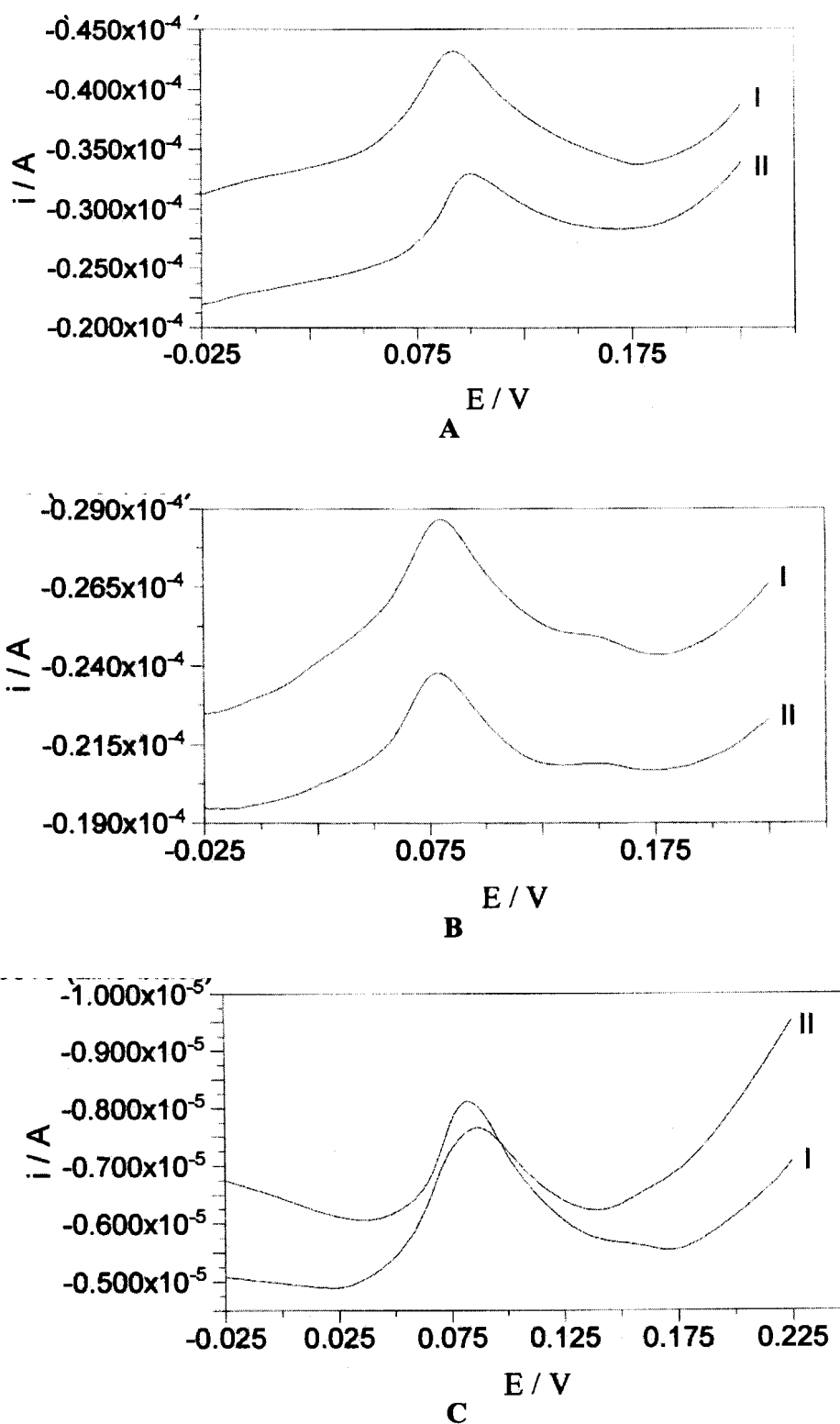


Figure 9.1 DPV peak currents measured using all the electrodes based on: **A.** Natural diamond (I $C_{Ag(I)} = 10^{-6}$ mol/L; II $C_{Ag(I)} = 10^{-7}$ mol/L); **B.** Synthetic-1 (I $C_{Ag(I)} = 10^{-8}$ mol/L; II $C_{Ag(I)} = 10^{-9}$ mol/L); and **C.** Synthetic-2 (I $C_{Ag(I)} = 10^{-7}$ mol/L ; II $C_{Ag(I)} = 10^{-8}$ mol/L) are used in a phosphate buffer (pH=9) and $Na_4P_2O_7$ as a supporting electrolyte.

recorded for the assay of Ag(I) with the three electrodes are also shown in Figure 9.1.

In all cases the reproducibility of peak currents were good (RSD less than 1%, n=10).

9.3.2 Selectivity studies

The effect of various ions on a differential pulse voltammogram peak current of 1×10^{-6} mol/L Ag(I) was examined for all diamond paste electrode types using mixed solutions method. The amperometric selectivity coefficients were calculated accordingly with the method proposed by Wang [17]. The concentration of the possible interfering ions was 1×10^{-5} mol/L. The results obtained for the amperometric selectivity coefficient (Table 9.1) indicate that all the ions investigated, such as Fe^{2+} , Mg^{2+} , Cr^{3+} , Mn^{2+} , Cu^{2+} , Zn^{2+} , Cr^{6+} , Pb^{2+} and Fe^{3+} did not interfere with the determination Ag(I).

Table 9.1 Amperometric selectivity coefficients. All values are the average of ten determinations.

Interfering Species (J)	K_{amp}		
	Natural Diamond	Synthetic Diamond-1	Synthetic Diamond-2
Fe^{2+}	1.79×10^{-3}	6.02×10^{-3}	4.58×10^{-3}
Mg^{2+}	3.30×10^{-3}	4.60×10^{-3}	4.54×10^{-3}
Cr^{3+}	5.67×10^{-3}	7.75×10^{-4}	4.16×10^{-3}
Mn^{2+}	2.83×10^{-3}	8.91×10^{-3}	3.43×10^{-3}
Cu^{2+}	3.00×10^{-4}	9.28×10^{-4}	3.68×10^{-3}
Zn^{2+}	6.93×10^{-3}	4.95×10^{-3}	5.17×10^{-3}
Cr^{6+}	1.09×10^{-3}	6.48×10^{-3}	2.03×10^{-3}
Pb^{2+}	6.34×10^{-3}	2.61×10^{-3}	2.35×10^{-3}
Fe^{3+}	1.81×10^{-3}	5.04×10^{-3}	2.62×10^{-3}

9.3.3 Analytical applications

The response characteristics as well as the selectivity of the diamond paste electrode for silver at a predetermined potential range made it suitable for the determination of Ag(I) in residual water samples. The results obtained for the quantitative determination of silver in five water samples are shown in Table 9.2. Ag(I) proved to be reliably assayed from these samples with a high average recovery and low RSD% values ($< 1\%$).

Table 9.2 Determination of Ag(I) in residual samples using the three paste electrodes of diamond and a standard method. All values are the average of ten determinations.

Standard method Average Recovery, $\mu\text{g Ag(I)/L}$	Average Recovery, $\mu\text{g Ag(I)/L}$		
	Natural Diamond	Synthetic Diamond-1	Synthetic Diamond-2
0.539	0.538 ± 0.06	0.528 ± 0.06	0.530 ± 0.07
1.29	1.27 ± 0.07	1.21 ± 0.08	1.26 ± 0.06
5.39	5.33 ± 0.06	5.25 ± 0.08	5.30 ± 0.06
1.29	1.19 ± 0.07	1.24 ± 0.09	1.28 ± 0.07
1.83	1.78 ± 0.07	1.76 ± 0.08	1.76 ± 0.08

9.4 Conclusions

The diamond paste electrodes presented in this paper provides excellent features for the detection of Ag(I) in geological and environmental samples. The design of the diamond paste based electrode is simple, fast and reproducible. The reproducibility of the analytical information is assured by the low RSD % values obtained in the recovery tests, by the fast response of the DPV response, and by its large working

concentration range. The proposed new diamond paste electrode has got the necessary high sensitivity and stability for different application.

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CHAPTER 10

DIAMOND PASTE BASED ELECTRODES FOR THE DETERMINATION OF IODIDE IN VITAMINS AND TABLE SALT

10.1 Introduction

Polycrystalline diamond thin film electrodes were extensively used for inorganic analysis due to special properties of the diamond material such as hardness, high thermal conductivity, corrosion resistance, chemical inertness, variable conductivity via doping, electrode geometry patterning using selective growth methods and superior microstructural stability [1-5]. However, recent studies shown the superiority of monocrystalline diamond as a possible alternative for the polycrystalline material due to its improved holes and electrons mobilities [6,7].

Iodine is a volatile halogen, diatomic element [8]. Compared to the lighter halogens, iodine is considerably less abundant in the earth's crust and in the hydrosphere. Rarely, it occurs as iodide minerals and commercial deposits are usually as iodates. Iodine is a lustrous, black, crystalline solid, mp 113.6°C, which sublimates readily and boils at 185.2°C. Iodine which contains iodine, is used internally in medicine [9]. A solution of KI and iodine in alcohol is used as a disinfectant for external wounds. The deep blue colour in starch solution is a sign of the free element. Iodine is also added to table salt for nutrition purposes, to stop goitres (Derbyshire neck) which is an iodine deficiency

disease due to lack of iodine in the water supply. The general use of iodized salt in goitrous areas was shown to be effective in preventing simple endemic goiter. But unfavourable symptoms of iodism were frequent owing to over use and overdose of iodine. Hence, much attention has been taken to the determination of iodide in medicinal and environmental chemistry.

Different techniques are used for the separation as well as analysis of inorganic ions such as iodate, iodide, bromate etc. Some of the most commonly used techniques are: ion-chromatography separations [10,11], ion-chromatography separation with ICP MS detection [12], capillary electrochromatography (CEC) [13], anion-exchange separation [14], adsorption chromatography [15], spectrophotometric determination [16], flow-injection amperometry [17], and amperometric detection [18].

In this chapter, diamond paste based electrodes are proposed for the iodide determination. Since the carbon paste based electrodes proved high reliable construction and response characteristics [19], a diamond paste similar with the carbon paste was preferred for electrodes design. Three types of diamonds were used for the design of the diamond paste: a natural diamond and two types of synthetic diamond. DPV was used for the calibration of the electrodes and for the recovery tests of iodide in vitamins and table salt.

10.2 Experimental

10.2.1 Reagents and solutions

All chemicals were of analytical grade. All solutions were prepared by using de-ionised water. Phosphate buffer (pH=2.00) were prepared by mixing potassium dihydrogen phosphate (SAARCHM-HOLPRO ANALYTIC City, Country) solution and sodium hydrogen phosphate (Chemical Suppliers) solution. Sodium pyrophosphate (MERCK) solution 0.1 mol/L acts as supporting electrolyte through out the experiment.

All the solutions of iodide were freshly prepared by using potassium iodide (PAL Chemicals). Monocrystalline natural 1 μ and synthetic diamond: 50 μ (synthetic-1) and 1 μ (synthetic-2) powders were purchased from Aldrich (Milwaukee, WI, USA) while the paraffin oil was purchased from Fluka (Buchs, Switzerland). Vital multi-vitamin & mineral with iron was purchased from Vital Health Foods (Pty) Ltd, Kuils River, South Africa. Cerebos iodated table salt was purchased from National Brands Limited, Rivonia (NBL).

10.2.2 Uniformity content test

Ten tablets from Vital multi-vitamin & mineral with iron (150 μ g iodide/tablet) are individually placed in ten 100 mL calibrated flasks, and dissolved in de-ionised water. Different aliquots from this solution were placed into a 100 ml calibrated flasks and filled

up to the mark with a solution of phosphate buffer (pH=2.00) and supporting electrolyte in 3.5:1 ratio. The direct DPV method was used for the assay of iodine content in this solutions and furthermore in vitamins tablets.

10.2.3 Sample preparation for table salt

1 g of table salt was dissolved in 100 mL de-ionised water. Different aliquots from this solution were placed into 100 ml calibrated flasks and filled up to the mark with a solution of phosphate buffer (pH=2.00) and supporting electrolyte in 3.5:1 ratio. The direct differential pulse voltammetry (DPV) method was used for the assay of iodine content in this solutions and furthermore in the table salt.

10.2.4 Electrode design

All diamond paste electrodes were prepared mixing 0.1 g of each diamond powder with 20 μ L paraffin oil. A portion of the paste was then filled into a plastic pipette tip. The diameter of the sensing part was 2.3mm. Electric contact was made by inserting a silver wire in the diamond paste. Before each use the electrode surface was smoothed out by polishing with an alumina paper (polishing strips 30144-001, Orion). When not in use, the diamond paste electrode was stored at room temperature.

10.2.5 Instrumentation

Differential pulse voltammograms (DPV) were performed with a 663 VA Stand (Metrohm, Herisau, Switzerland) connected to a PGSTAT 20 and a Software Version 4.8. A platinum electrode and a Ag/AgCl (0.1mol/l KCl) electrode served as counter and reference electrode in the cell respectively. The operating conditions were: applied potential pulse amplitude, 25mV/sec; potential range, +0.5 to -0.7 V (vs Ag/AgCl); equilibration time, 5sec; step potential, 1.95mV.

10.3 Results and discussion

10.3.1 Electrode response

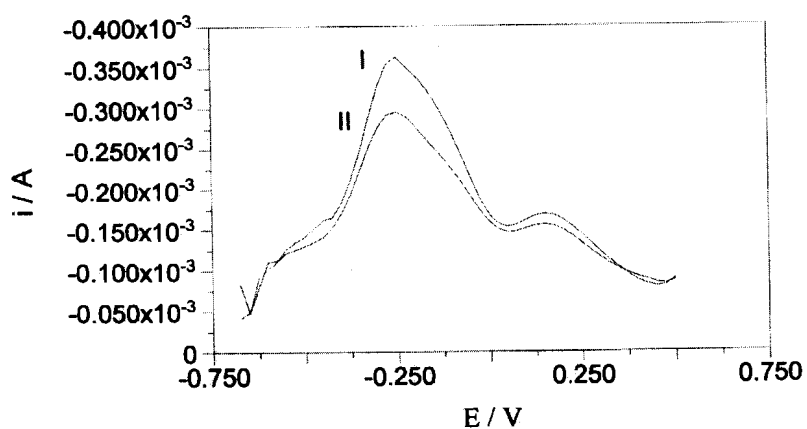
All solutions are thoroughly deoxygenated by degassing with N₂ until no further decrease in background current could be produced for about 5 min. The current responses to different iodide concentrations employing all the three diamond paste electrodes were linear over a wide concentration range and can be read from the following equations of calibration: **a.** natural diamond ; **b.** synthetic diamond-1 and **c.** synthetic diamond-2

a. $H = 249.05 + 32.98 C ; r = 0.9784$

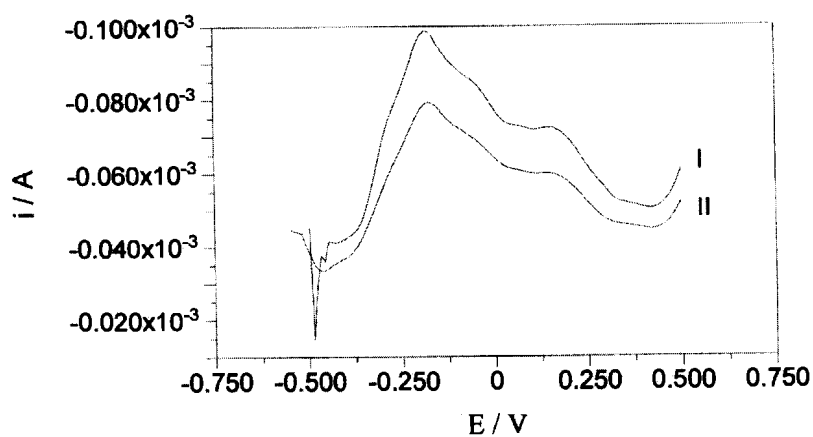
b. $H = 40.88 + 193.754 C ; r = 0.9876$

c. $H = 1.789 + 42.69 C ; r = 0.9594$

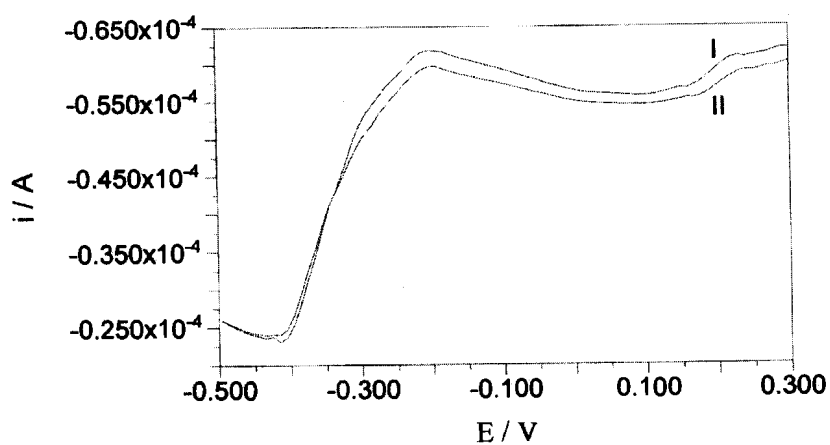
where **H** is the peak height (μA), **C** is the concentration of I^- (nmol/L) and **r** is the regression coefficient. The DPV peak currents were proportional for a wide concentration range: natural diamond, 10^{-6} to 10^{-3} mol/L with detection limit of 10^{-7} mol/L ; synthetic-1 and synthetic-2, 10^{-12} to 10^{-10} mol/L with detection limit of 10^{-13} mol/L . Figure 10.1 shows some of the peak profiles obtained using DPV with the proposed diamond paste based electrodes. The reproducibility of the response characteristics were very good ($\text{RSD} < 1\%$, $n=10$).



A



B



C

Figure 10.1 Peak profiles obtained using DPV with the proposed electrodes based on:

A. Natural diamond (I $C_I^- = 10^{-3}$ mol/L; II $C_I^- = 10^{-4}$ mol/L); **B.** Synthetic-1 (I $C_I^- = 10^{-10}$ mol/L; II $C_I^- = 10^{-11}$ mol/L); and **C.** Synthetic-2 (I $C_I^- = 10^{-10}$ mol/L ; II $C_I^- = 10^{-11}$ mol/L).

10.3.2 Selectivity of the diamond paste based electrodes

The most significant advantage of using diamond paste based electrodes is that the analyte interaction gives greatly enhanced selectivity. Bromide and chloride do not interfere in the determination of I^- as tabulated in Table 10.1. The ratio between the concentration of the iodide and of bromide or chloride was 1:10.

Table 10.1 Amperometric selectivity coefficients. All values are the average of ten determinations.

Interfering Species (J)	K_{amp}		
	Natural Diamond	Synthetic Diamond-1	Synthetic Diamond-2
Br^-	9.07×10^{-4}	3.02×10^{-4}	2.91×10^{-5}
Cl^-	2.01×10^{-3}	1.85×10^{-3}	1.17×10^{-3}

10.3.3 Analytical applications

The response characteristics of the proposed diamond paste based electrodes as well as their selectivity made them suitable for the uniformity content tests of vitamin tablets as well as for the determination of iodide content in table salt. Tables 10.2 shows the results of the uniformity content test performed for vitamin tablets. The results indicate that the recoveries are quite comparable when using different diamond electrodes. I^- was determined from the table salt at very low concentration level (ng I^- /g table salt) (Table 10.2). The advantage of the proposed method is the enhanced selectivity at a given

working potential, simplicity of the method and also higher precision as evidenced by the lower values of the RSD(%).

Table 10.2 Determination of iodide in vitamin tablets and table salt. All values are the average of ten determinations.

Sample	Average Recovery, %		
	Natural Diamond	Synthetic Diamond-1	Synthetic Diamond-2
Vitamin	97.79 ± 0.42	97.88 ± 0.49	97.90 ± 0.46
	Average Recovery, ng I/g salt		
	Natural Diamond	Synthetic Diamond-1	Synthetic Diamond-2
Table salt	380.01 ± 0.03	382.27 ± 0.02	383.00 ± 0.02

10.4 Conclusions

All diamond paste based electrodes presented in this work provides excellent reproducibility for the detection of I⁻ in some pharmaceutical products and table salt. Using all the three electrodes; characteristic peak currents appeared to be at about +0.2 ± 0.05V vs. Ag/AgCl. The design of the monocrystalline diamond paste based electrode is simple, fast, highly reproducible and robust. The reproducibility and robustness of the analytical information can be assured by the low RSD values obtained in the recovery tests. The proposed new class of electrodes has got enhanced sensitivity and the required stability for different application.

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CHAPTER 11

CONCLUSIONS

The reliability obtained for the electrical properties of single-crystal diamond is encouraging for research in the electrochemical sensors based on the monocrystalline diamond. The utilization of diamond paste based electrodes for the determination of various ions such as Fe(II), Fe(III), Pb(II), Cr(III), Cr(VI), Ag(I), and iodide ion has been investigated. The results obtained in this work confirm the need to use diamond paste based electrodes to assess the content of inorganic ions in food, water, soils, and pharmaceutical products.

Cyclic voltammetry measurements were run to examine various electrolytes and phosphate buffer solutions (pH 1-10) for use in differential pulse voltammetric measurements. The use of phosphate buffer (pH=9) and sodium pyrophosphate as a supporting electrolyte proved to be the best, yielding sharpest peaks and good sensitivity.

The best signal/background ratio and high sensitivity can be obtained with 25 mV versus Ag/AgCl pulse amplitude. Therefore, it is used in all the differential pulse voltammetric measurements.

Selection of the potential range for optimum detection performance represented a compromise between maximizing the signal current obtained and minimizing the

background current contribution from oxygen reduction. Moreover, purging the solution prior to measurements is a necessary condition for reducing the noise.

Compared to glassy carbon and carbon paste electrodes, the diamond paste electrodes yielded relatively larger linearity of the calibration curve, covering 10^{-3} – 10^{-11} mol/L range. Detection limits of 10^{-8} – 10^{-13} mol/L are also proof of sensitivity of the method.

The most significant potential advantage of using diamond paste electrodes in electroanalytical chemistry is the opportunity that the analyte interaction affords for greatly improved sensitivity and selectivity. Because of this high selectivity towards the target analyte, a number of ions have little effect on its determination.

Due to the accuracy of the analytical information assured by using the diamond paste electrodes, and the characteristic biocompatibility of the diamond, they can be used successfully for the assay of pharmaceutical products, as well as in clinical analysis. The reliability of the proposed diamond paste electrodes makes them suitable for utilization as detectors in flow system (e.g., flow injection analysis, sequential injection analysis).

APPENDIX

APPENDIX A

PUBLICATIONS

1. *Polycrystalline diamond based electrochemical sensors and their applications in inorganic and organic analysis*
R.I. Stefan, S.G. Bairu and J.F. van Staden
Crit.Rev.Anal.Chem., In Press.
2. *Monocrystalline diamond paste based electrodes and their applications for the determination of Fe(II) in vitamins*
R.I. Stefan and S.G. Bairu
Anal.Chem., Submitted
3. *Determination of Fe(III) in water samples using diamond paste based electrodes*
R.I. Stefan, S.G. Bairu and J.F. van Staden
Electroanalysis, Submitted
4. *Diamond paste based electrodes for the determination of Pb(II) at trace concentration levels*
R.I. Stefan and S.G. Bairu
J.Electroanal.Chem., Submitted

5. *Diamond paste based electrodes for the determination of Ag(I)*
R.I. Stefan, S.G. Bairu and J.F. van Staden
Anal.Chim.Acta, Submitted
6. *Diamond paste based electrodes for the determination of iodide in vitamins and table salt*
R.I. Stefan, S.G. Bairu and J.F. van Staden
Anal.Lett., In Press.
7. *Diamond paste based electrodes for the determination of Cr(III) in pharmaceutical compounds*
R.I. Stefan, S.G. Bairu and J.F. van Staden
Anal.Bioanal.Chem., Submitted
8. *Diamond paste based electrodes for the determination of Cr(VI) at trace levels*
R.I. Stefan and S.G. Bairu
Instrum.Sci. & Technol., Submitted

APPENDIX B

PRESENTATIONS

1. *Diamond paste based electrodes for the determination of Fe(II)*

R.I. Stefan, S.G. Bairu and J.F. van Staden

EUROANALYSIS 12, Dortmund, Germany, September, 2002.

2. *Diamond paste based electrodes for the determination of Fe(II)*

R.I. Stefan, S.G. Bairu and J.F. van Staden

Analitika 2002, Stellenbosch, South Africa, December, 2002.