

Vitamin Analysis Using Electroanalytical Techniques

Subjects: Chemistry, Analytical

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Vitamins comprise a group of organic chemical compounds that contribute significantly to the normal functioning of living organisms. Although they are biosynthesized in living organisms, some are also obtained from the diet to meet the needs of organisms, which is why they are characterized as essential chemical compounds. The lack, or low concentrations, of vitamins in the human body causes the development of metabolic dysfunctions, and for this reason their daily intake with food or as supplements, as well as the control of their levels, are necessary. The determination of vitamins is mainly accomplished by using analytical methods, such as chromatographic, spectroscopic, and spectrometric methods, while studies are carried out to develop new and faster methodologies and techniques for their analysis such as electroanalytical methods, the most common of which are voltammetry methods.

Keywords: vitamins ; nanomaterials ; voltammetry technique ; carbon paste electrode

1. Fat-Soluble Vitamins

1.1. Vitamin A

The determination of vitamin A in foods has been studied by using square-wave pulse voltammetry that uses carbon paste electrode (CPE) molded with Pt:C nanoalloy in ionic liquid (IL). This technique exhibits good sensitivity with a linear response between 0.1–100 M and with an LOD equal to 0.04 M [1]. The electrochemical determination of retinol has also been done by using differential pulse voltammetry with carbon paste electrode molded with sodium dodecyl sulfate surfactant (CPE/SDS). The method has turned out to be linear with low detection limits (up to 4.6×10^{-7} M) [2]. A simultaneous determination of retinol and Vitamin E in CH_3CN has also been done with cyclic voltammetry with glassy carbon electrode (GCE) molded with the synthetic nanomaterial MWCNT [3].

1.2. Vitamin D

The determination of vitamin D2 has been done with a combination of cyclic voltammetry and differential pulse voltammetry using a glassy carbon electrode coated with a thin synthetic indium-titanium oxide (ITO; CD-CH) layer [3]. In order to determine vitamin D3, this electrode was combined with polyacrylonitrile nanofibers (PANnFs) and nanoparticles (NPs) of magnetite (Fe_3O_4) and studied with differential pulse voltammetry. PANnFs are very soluble and have thermal and mechanical stability, while magnetite nanoparticles are biocompatible and non-toxic [4]. A better determination of D3 was done with the glassy ITO electrode, molded with a gadolinium oxide sensor NRs ($\text{Gd}_2\text{O}_3\text{NRs}$), combined with aspartic acid (Asp- $\text{Gd}_2\text{O}_3\text{NRs}$) and with differential pulse voltammetry analysis [5]. In **Figure 1** are shown cyclic voltammograms of vitamin D₃.

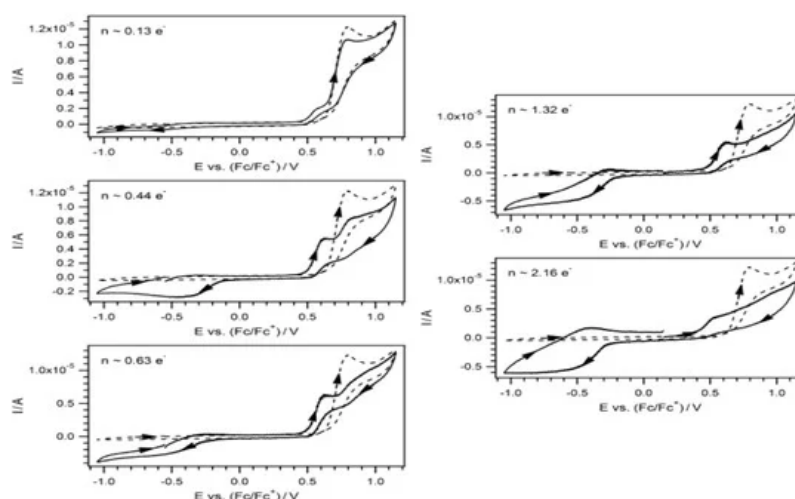


Figure 1. Cyclic voltammograms of vitamin D₃ [5].

Vitamin D₃ has also been determined in pharmaceutical samples with a combination of cyclic voltammetry and differential pulse voltammetry using glassy carbon electrode molded with Ni(OH)₂ particles in an inorganic SiO₂/graphene oxide matrix. This method exhibited great selectivity and sensitivity, while the limit of detection was very low [6]. In analysis of blood samples, the detection of vitamin D was done with cyclic voltammetry using a glassy carbon electrode molded with an electrochemical sensor consisting of a synthetic film of bimetallic nanoparticles Cu-Ni and fullerene-C₆₀. The method proved quite effective and showed good sensitivity [7]. Another technique for detecting vitamin D in human plasma samples has recently been developed by means of a reconstructive adsorbent voltammetry using a screen-printed carbon paste electrode (SPCE) coated with a polymer (MIP) combined with p-phenylenediamine resorcinol [8]. Another recent combination study of cyclic voltammetry and differential pulse voltammetry used a cerium (IV) oxide immunonanosenor (nCeO₂/CC), which was prepared in carbon fabric (CC) by electrophoretic deposition of the nanomaterial (nCeO₂). The method was applied to biological samples with good repeatability and high sensitivity [9].

1.3. Vitamin E

Differential pulse voltammetry experiments on Pt microelectrodes to quantify vitamin E in solutions of vegetable oils and fats in N-methyl-2-pyrrolidine (NMP) solution with 0.2 M electrolyte nBu₄NPF₆ gave a potential of +1.04 V versus the standard Ag|AgCl electrode [10]. In another study, a combination of cyclic voltammetry and differential pulse voltammetry was applied to analyze simultaneously vitamins E and K in dietary supplements using Au electrodes molded with polyaniline (PAn) and γ -aluminium oxide (c-Al₂O₃), forming the nanomaterial PAn/c-Al₂O₃ [11]. On the other hand, to determine the active forms of E and K (quinones and tocopherols) in dietary supplements, adsorptive stripping square-wave voltammetry was applied to a glassy carbon electrode. The method had excellent sensitivity while being a low-cost and simple technique [12]. In another quantification study of α -, γ - and δ -tocopherols in oil samples, a square-wave pulse voltammetry was applied to a CF UME in Bz/ EtOH disk (1: 2) with 0.1 mol/L H₂SO₄ [13]. The results were processed using chemometric methods with two multivariate calibration models, MCR-ALS (multivariate curve resolution-alternating least squares) [14], and SandANNs (artificial neural networks (ANNs)) [15]. The advantages of these chemometric methods are their ability to obtain quantitative information from overlapping signals through mathematical models and the fact that no prior pretreatment of the sample is required. However, a disadvantage that can arise in the application of electroanalytical techniques is the lack of selectivity.

A recent study conducted a simultaneous identification of vitamins E and K in dietary supplements. The method involved a glassy carbon electrode in which an ex situ accumulation of the vitamins on the electrode surface was first performed. The vitamins were then detected by using adsorptive stripping square-wave voltammetry in a solution of 0.01 mol/L HNO₃ containing 0.1 mol/L KCl at pH = 2.08. Both vitamins were detected in the anode, while the method turned out to be quite selective and highly sensitive [12].

1.4. Vitamin K

For the study of the reduction of phyloquinone with cyclic voltammetry a glassy carbon electrode has been used on which a reversible adsorption reaction takes place [16]. In plant foods, vitamin K₁ has been detected with a square wave adsorptive stripping voltammetry, preceded by the adsorption of the vitamin on the surface of the solid glassy carbon electrode. This method turned out to be quite sensitive and effective [17]. Additionally, the analysis of vitamin K₂ in pharmaceutical preparations samples and foods has been done with cyclic voltammetry with a glassy carbon electrode, bare and modified [16][18]. The polyelectrode Pt, modified with a liquid amalgam film (RAgLAFm-E), has also been used for the quantification of K₂. In recent years, many electrochemical sensors have also been developed to detect K, triggering the study of the manufacture of optical fiber sensors, which have a fairly low cost but very high sensitivity [19]. In blood plasma, vitamin K₁ has been detected with cyclic voltammetry using pencil graphite electrode (PGE) modified with Ag nanoparticles and 2-amino-5-chlorobenzophenone (2-A-5-CBP), which were deposited by electro deposition on the surface of the PGE [20]. Additionally, for the determination of vitamin K₃ in animal pharmaceuticals, a sensor consisting of a glassy carbon electrode molded with an imprinted poly(3,4-ethylenedioxythiophene) film (PEDOT) has been used [21]. The method has been applied with a combination of cyclic voltammetry and linear sweeping voltammetry, and has had very good sensitivity and detected K₃ in traces. Additionally, an attempt has been made to simultaneously determine all four vitamins—A, D, E and K—by using square-wave adsorptive stripping voltammetry with a glassy carbon electrode. However, because all four vitamins are deposited on the surface of the electrode, the method has not shown selectivity and has not been able to separate them from each other. This is notably the case for vitamin D₃. The simultaneous determination can be achieved by modifying the electrode with carbon nanomaterials [22].

2. Water-Soluble Vitamins

2.1. Vitamin C

A recent study carried out the determination of vitamin C in fruit juices and creams with a combination of cyclic voltammetry and differential pulse voltammetry using a Hydroxyapatite-ZnO-Pd NPs modified carbon paste electrode (HAP-ZnO-Pd NPs/CPE) [23]. The voltammetric determination of ascorbic acid was also done using a disposable printed carbon electrode, bare and molded with a synthetic ZnO/Al₂O₃ nanosensor, which showed high selectivity, repeatability, and sensitivity. The anodic peak potential for the oxidation of ascorbic acid with the ZnO/Al₂O₃/SPE sensor is approximately 335 mV compared to 370 mV for the bare SPE. This shows that ZnO/Al₂O₃ nanomaterial improves the oxidation signal of ascorbic acid [24].

Differential pulse voltammetry with a graphene-molded carbon paste electrode has been successfully applied to determine ascorbic acid. Graphene greatly enhances the intensity of the current of a redox reaction as it is a good conductor. In this way the sensitivity of the method has been increased [25]. Differential pulse voltammetry has also been applied to pharmaceutical analysis using molded carbon paste electrodes with porphyrins. This combination has given low detection limits to the method (up to 1.1×10^{-14} mol/L) [26].

The successful determination of ascorbic acid with high sensitivity has also been done with cyclic voltammetry with a glassy carbon electrode molded with a polymeric film of poly [bromocresol purple], which enhances the signal of the generated current [27]. With cyclic voltammetry, a formed hyaline carbon electrode with a polymeric film (3-(5-chloro-2-hydroxyphenylazo)-4,5-dihydroxynaphthalene-2,7-disulfonic acid) has also been used in a solution with pH = 4, where a successful detection of ascorbic acid in a mixture of substances has been done [28]. The glassy carbon electrode has also been successfully modified with multi-wall carbon nanotubes and synthetic carbon nanotubes with [poly] xanthurenic acid. The formation with carbon nanotubes leads to great stability of the electrode at various pH values, low detection limits, and very good sensitivity [29][30]. Cyclic voltammetry with iodine-coated Pt electrode in 0.1 M KCL solution has been successfully applied for the selective determination of ascorbic acid in multivitamin pharmaceutical products (B1, B6, B12, B9, and C). The oxidation peak of ascorbic acid has occurred at 0.28 V, while the detection limits have been quite low [31]. Pharmaceutical formulations and foods have been studied with a combination of cyclic voltammetry and differential pulse voltammetry, with a carbon paste electrode molded with multi-walled carbon nanotubes and graphite in acidic solution with pH = 2 [32]. The successful determination of ascorbic acid in commercial samples has also been done with cyclic voltammetry, using bare carbon paste electrodes (PCPEs) and molded carbon paste electrodes (MCPEs) with calixarenes, such as p-tert-butylcalix(4)arene, in ammonium acetate (pH = 5) containing Pb²⁺ ions [33]. MCPEs have displayed better electrocatalytic activity. The greater catalytic action of MCPE can be explained by considering that the Pb²⁺ ion is strongly held in the p-tert-butylcalix(4)arene cavity, acting as an electron transport bridge, allowing it to interact with the ascorbic acid in the solution while oxidizing it. As the oxidation of ascorbic acid depends on pH, with its increase, there is a shift in the potential towards less positive values. This is also true in the case of any bare electrode, such as Au. For the MCPEI electrode, at low pH values, peak heights are low, and this can be attributed to an absence or reduced complexation of Pb²⁺ on the electrode surface while the mechanism is assumed to occur through diffusion [33].

Several voltammetric studies have been performed to concurrently determine ascorbic acid, uric acid, and dopamine. Studies of cyclic voltammetry using carbon paste electrode with formers such as 2,2'-(1,8-octanediylbisnitriloethylidene)-bis-hydroquinone and tetrabromo-p-benzoquinone have been used effectively [34][35]. The molded electrode enhances the production of current, contributing to the efficient detection of ascorbic acid in the mixture. The same sample has been studied by using cyclic voltammetry with a glassy carbon electrode molded with 0.1 mol/L H₂SO₄ solution in phosphate solution. The results have showed that the molded electrode interacts with H₂SO₄ to form a redox pair, resulting in active groups that reduce the oxidation potential when compared to the interactions of the non-molded electrode. The detection of all three compounds has been successful [36]. A simultaneous identification of all three compounds was also carried out with a molded glassy carbon electrode with LaFeO₃ nanoparticles [37]. A combination of cyclic voltammetry and differential pulse voltammetry with a glassy carbon electrode molded with graphene/Pt nanoparticles was performed in the same sample [38]. In a bovine embryonic serum sample, the three compounds were detected by using differential pulse voltammetry with a glassy carbon electrode molded with helical carbon nanotubes. This method proved quite effective and showed great sensitivity [39]. Another study of this mixture used square-wave pulse voltammetry and molded glassy carbon electrode with Ni-poly(1,5-diaminonaphthalene) nanoparticles in NaOH 0.1 mol/L [40].

Ascorbic acid was successfully detected in a mixture with tryptophan and paracetamol by using square-wave pulse voltammetry and with a carbon paste electrode molded with multi-walled carbon nanotubes. A selective assay of ascorbic acid was carried out with this method [41]. By using square-wave pulse voltammetry, ascorbic acid was also determined in

a mixture with rutin, using a carbon paste electrode molded with a carbon-chitosan nanotube film [42]. The simultaneous determination of ascorbic acid and dopamine in pharmaceutical products was conducted via the application of cyclic voltammetry with a glassy carbon electrode molded with a polymerized (poly)caffeic acid film. The polymerized film enhanced the rate of electron transfer at the electrode, resulting in the increased selectivity of the method [43]. On the other hand, the simultaneous determination of ascorbic acid and paracetamol was done by using differential pulse voltammetry with glassy carbon electrodes molded with carbon nanotubes [44].

Another study with differential pulse voltammetry was applied for the simultaneous determination of ascorbic acid and uric acid using a carbon paste electrode the surface of which was modified by adsorption of the surfactant chitosan-cetylpyridinium bromide. Both compounds were selectively identified by this method [45]. The same mixture was also studied by using linear sweeping voltammetry using a molded copper electrode with dimercaptiothiadiazole, which effectively separated the peaks of the two substances [46]. In another cyclic voltammetry study to detect ascorbic acid and dopamine in pharmaceuticals and foods, the carbon paste electrode was successfully modified with a copper binuclear complex, which effectively reduced the potentials of redox reactions [47]. The mixture of ascorbic acid and dopamine was also successfully studied with differential pulse voltammetry, with an Au electrode molded with Au nanoparticles, where an effective separation of the peaks of the two substances took place [48].

In another study, a combination of differential pulse voltammetry and cyclic voltammetry was applied for the simultaneous determination of ascorbic acid, uric acid, and epinephrine. A glassy carbon electrode molded with a film of carbon nanotubes was used, thanks to which low detection limits were obtained [49]. These two techniques were also combined with a $\text{SiO}_2/\text{Nb}_2\text{O}_5$ -coated carbon electrode, which improved the electron transfer from ascorbic acid to the electrode surface. Covalent bonds may develop between ascorbic acid and Nb_2O_5 , increasing the rate of oxidation. Nb_2O_5 helped to reduce the oxidation potential of ascorbic acid, which shifted to smaller values. The use of this electrode proved quite effective in determining ascorbic acid [50].

Many studies have been done to determine ascorbic acid in juices with various combinations of techniques and electrodes. Cyclic voltammetry has been applied in combination with carbon paste electrodes, while for low concentrations of ascorbic acid, modified graphite electrodes with manganese dioxide have been used in phosphate buffers (pH = 7.2) [51]. Linear sweeping voltammetry using an Au electrode has also been applied. Differential pulse voltammetry has been applied to juices and wines using glassy carbon electrode and Pt microelectrodes molded with polyvinyl sulfonium and polystyrene sulfonium film, which increased the functionality of the electrode [52][53][54]. The effective quantification of ascorbic acid has also been done in plants of the Rosa family via application of differential pulse voltammetry and square-wave pulse voltammetry with hyaline carbon electrodes [55]. In a recent study done to determine ascorbic acid in the Rosa canina plant, a square-wave pulse voltammetry was applied with a graphene oxide paste electrode molded with a film of Mn(II) complex. The method was effective, and no interference from the presence of other substances in the sample was detected. The detection limits were low ($1.2888 \mu\text{g/mL}$) and the determination of ascorbic acid was successful [56]. Another study conducted a cyclic voltammetric study of ascorbic acid using a polymelamine/gold nanoparticle modified carbon paste electrode (PM/AuNPs/CPE) in phosphate buffer solution of pH = 7.0. The electrode favored the oxidation of ascorbic acid and significantly increased the peak current, while the oxidation potential shifted to more negative potentials [57]. In a recent study, a combination of cyclic voltammetry and square-wave pulse voltammetry was applied, with a microelectrode made from pyrolytic graphite sheet (PGS), to quantify ascorbic acid in real samples. The method proved to be quite sensitive, showing low sensitivity thresholds and a linear response across a wide range of concentrations [58].

2.2. Vitamin B1 (Thiamine)

The determination of thiamine in pharmaceuticals and juices has been studied by adsorptive stripping voltammetry at a glassy carbon electrode naked and molded with Pb^{2+} film, in acetate buffer of 0.05 mol/L and pH = 5.6. On the molded electrode a reduction peak with a potential of -1.25 V versus the Ag/AgCl electrode appeared, while on the bare electrode no peak was observed. This showed the effectiveness of Pb^{2+} film as a formator. One possible mechanism indicates that thiamine is likely adsorbed to the Pb^{2+} film but not to the electrode. At Pb^{2+} concentration of between 1×10^{-4} – 1.5×10^{-4} mol/L, the maximum reduction of thiamine was observed [59].

In another study, the electrochemical behavior of thiamine was studied by using square-wave voltammetry at a Cys/SAM shaped Au electrode (Cys/SAM/Au) in an alkaline environment (pH = 11.0). The results showed that the Cys/SAM/Au molded electrode had electrocatalytic activity with versus thiamine and that the process was controlled by adsorption. With an increase in pH (from 7.4 to 11.9) the anodic peak shifted to more negative values. This method was a simple, fast, and

selective high-precision technique for determining thiamine in the presence of other vitamins in pharmaceutical formulations, and could be applied in clinical analysis and drug analysis [60].

The successful determination of vitamin B1 in a mixture of vitamins B2 and C was also achieved by using adsorptive stripping voltammetry with a glassy carbon electrode molded with solid silver amalgam film (AgLAF-AgSAE), which caused very good separation of the peaks of vitamin B1 and C and showed satisfying detection limits [61]. The use of DNA/MWCNT-molded carbon paste electrode also appeared effective [62].

2.3. Vitamin B2 (Riboflavin)

The determination of riboflavin in pharmaceutical formulations has been done by using cyclic voltammetry using an optical sensor made of cyclodextrin wherein riboflavin is encapsulated in cyclodextrin [63]. The determination of riboflavin in real samples has been mainly done by adsorptive stripping voltammetry with an Hg electrode at basic conditions (a bare glassy carbon electrode has also been used), in H₂SO₄ buffer of 0.5 M. The mechanism has showed the reversible reduction of two electrons and two protons in the solution while a small amount of riboflavin has been adsorbed to the bare electrode [64]. This electrode has also been used to determine riboflavin in breast milk [65]. Riboflavin has also been studied with a pretreated glassy carbon electrode (PGCE). In one such study, the described mechanism showed a reversible reduction of riboflavin to quinone on the carbon surface with a potential of +0.4 V. Riboflavin and its reduction product adsorbed much more readily to the activated electrode than to the untreated electrode [63]. The mechanism of adsorption of vitamin B2 on the hanging Hg drop electrode in an aqueous mean is due to the redox reaction of $2e^-/2H^+$ of the flavin portion, accompanied by strong adsorption on the electrode surface of both the redox form of quinone and the hydroquinone of vitamin B2. In addition to conventional square-wave pulse voltammetry, the mechanism of electrodes has been investigated in more detail with cyclic square-wave voltammetry (CSWV) [66]. Voltammetric parameters are affected by vitamin B2 concentration, pH, and accumulation time. With an increase in the concentration of the adsorbed materials on the electrode surface, the peaks shift to less negative potentials. This demonstrates that interactions between the adsorbed species take place. With an increase in pH the transfer of electrons becomes faster, and the adsorption of riboflavin becomes stronger, than at a lower pH. The increase in accumulation time forms a solid film on the surface of the electrode, allowing it to require higher energy for the redox reaction, thus shifting the potential towards negative values. However, by increasing the surface concentration, repulsive interactions between adsorbed molecules become important [66].

The determination of riboflavin has also been studied by using adsorptive voltammetry with hyaline carbon electrode molded with nanomaterials which enhance the catalytic action of riboflavin. Such nanomaterials include polythiophene nanotubes, metal nanocrystals, oleylamine nanoparticles (OLA), Cr/SnO nanoparticles, NiO/MWCNTs, and poly(3,4-ethylenedioxythiophene)/zirconia (PEDOT/ZrO₂NPs) [67]. Additionally, a study was conducted using differential pulse voltammetry with carbon paste electrodes molded with Co-Y zeolites. The Co-Y zeolite interacted with riboflavin, resulting in increased electrode selectivity and sensitivity [68]. Recently, a sensor based on the transition nanocomposite materials made of metal binary oxide (ZnO-MnO) was synthesized with a CSNs shell core on the surface of a glassy carbon electrode. This sensor was used to determine riboflavin with cyclic voltammetry, differential pulse voltammetry, and linear sweeping voltammetry with excellent stability, repeatability, selectivity, and sensitivity [69].

2.4. Vitamin B3 (Nicotinic Acid/Niacin)

The determination of vitamin B3 in biological samples, food, and pharmaceutical tablets has been an object of much interest. The use of electrochemical sensors on a carbon paste electrode is a very good method of determining vitamin B3 in pharmaceutical products due to their simplicity, selectivity, high sensitivity, and low cost. A study that used cyclic voltammetry to determine vitamin B3 in syrup samples used CoTMPP-molded graphite paste microelectrode (CoTMPP/Nafion/GPE), which enhanced the electrocatalytic response of the vitamin's reduction current. The corresponding cyclic voltammograms were recorded in 0.1 mol/L NaNO₃ solution, pH = 3.9, using GPE, CoTMPP/GPE, and CoTMPP/Nafion/GPE at a scan rate of 0.1 V/s. The utilized method proved too sensitive and simple for the selective determination of nicotinic acid [70]. The determination of nicotinic acid in pharmaceutical products was also done using an Au electrode and the application of cyclic voltammetry, while in food, an Au electrode molded with thioglycolic acid and an adsorptive stripping voltammetry was applied [71][72].

2.5. Vitamin B5 (Pantothenic Acid)

The detection of D-Panthenol in a urine sample was done by using square-wave pulse voltammetry with a glassy carbon electrode at pH = 4.2. The method proved to be quite sensitive and with low limits of detection (5.0×10^{-7} M) [69].

2.6. Vitamin B6 (Pyridoxine)

The determination of vitamin B6 in pharmaceutical products has been carried out with applications of cyclic voltammetry and differential pulse voltammetry using molded glassy carbon electrodes with materials such as vanady(IV)-salen complex, carbon nanotube, $\text{Ru}(\text{bpy})_3^{3+}$ with diamond-boron complex, Prussian blue, poly-methylene blue, and graphite-modified carbon paste electrode. A study conducted with differential pulse voltammetry for the simultaneous determination of vitamins B6 and C used a carbon paste electrode molded with ZnO/Cuo nanocomposites with 2-[ferrocenylethynyl]fluorine-9-one, ZnO/Cuo in an ionic liquid, 2FE/ZC/IL/CPE. The results showed good sensitivity and competent separation of the peaks [73]. On the other hand, in other differential pulse voltammetric studies, Au electrodes fused with carbon nanotubes and Au-CuO molded carbon nanotubes have also been effectively used. In foods (energy drinks and cereals) and dietary supplements (multivitamins), B6 has been determined by using differential pulse voltammetry with printed disposable silk electrodes. This method proved to be quite effective, selective, repeatable, and with low sensitivity limits ($1.5 \times 10^{-6} \text{ M}$) [74].

2.7. Vitamin B7 (Biotin)

In food, the electroanalytical study of biotin has been done by using differential pulse voltammetry with a film biosensor that was synthesized from ionic liquid-chitin and modified with Pd-Fe-Ni nanoparticles [75]. In another study, the determination of biotin in blood plasma was performed using a boron-doped diamond electrode (BDD) on the surface of which a Nafion layer had formed. The detection limit of the method was quite low (up to 5 nM), and it has been quite an effective method in clinical analyses [76].

2.8. Vitamin B9 (Folic Acid)

The detection of vitamin B9 in pharmaceuticals and foods has been done primarily with square-wave voltammetry, differential pulse voltammetry, and cyclic voltammetry, but also with a combination of these. In each case, different working electrodes are used. In studies with square-wave pulse voltammetry, carbon paste electrodes molded with Pt:Co nanomaterials have been used [77]. In studies that have combined square-wave pulse voltammetry and cyclic voltammetry, carbon paste electrodes molded with complexed carbon nanotubes with $\text{Ru}(\text{II})\text{ZnO}$ have been used [78]. In studies combining square-wave and differential pulse voltammetry, carbon paste electrodes modified with nanomaterials have been used [79][80]. In differential pulse voltammetry studies, carbon paste electrodes molded with polymer films, TiO_2 nanomaterials, and magnetite nanoparticles have been used, and Au electrodes molded with nanomaterials have also been used [81][82][83][84]. In studies combining differential pulse voltammetry and cyclic voltammetry, carbon paste electrodes molded with carbon nanotubes have been used [85]. Additionally, the determination of folic acid in food has also been studied by using adsorptive voltammetry with film-Bi-molded Au electrodes, Ag amalgams, or Hg [76][86][87]. In a recent study involving pharmaceutical tablets, the detection of vitamin B9 was done using a combination of cyclic voltammetry and differential pulse voltammetry in a phosphate buffer (pH = 7), using as a sensor an electrochemically polymerized tyrosine film on a graphite substrate. This method turned out to be quite sensitive and repeatable [88].

Additionally, the simultaneous determination of folic acid and riboflavin has been done by using cyclic voltammetry using Hg electrodes [89]. The results have showed that both vitamins are strongly adsorbed on the surface of the electrodes, and that this is due to the presence of the aromatic rings. Adsorbed molecules can then be measured by using the technique of adsorptive stripping voltammetry, which has been found to be quite effective for the simultaneous determination of folic acid and riboflavin, in the presence of excess electroactive substances in solution with great precision and selectivity. In another study, the successful determination of folic acid in a mixture with ascorbic acid and riboflavin was performed by using adsorptive stripping voltammetry involving glassy carbon electrodes molded with Pb^{2+} [90].

2.9. Vitamin B12 (Cobalamin)

The determination of vitamin B12 in blood plasma and urine has been studied by using differential pulse voltammetry with an electrochemical sensor, molded with polypyrrole, which is prepared with carbon fiber paper, and then by applying the electro deposition of palladium-gold nanoparticles (PdAu). A study on this has showed good selectivity in the presence of other substances [91]. Similarly, vitamin B12 has been detected in foods with ferromagnetic nanoparticles from triazine dendrimers (FMNPs@TD) using a combination of cyclic voltammetry and differential pulse voltammetry techniques [11]. The selective detection of B12 in injectable drugs has also been performed by using cyclic voltammetry with glassy carbon electrodes, molded with fluorescent nanosensors without labeled carbon. The fluorescence intensity of CD charts decreases as the concentration of vitamin B12 increases, showing a linear relationship in the range from 0 to 60 M [92]. In another recent study, the electrochemical determination of cyanocobalamin with square-wave pulse voltammetry was applied using an electrode of a carbon paste molded with a Mg complex film with thiophene-2-carboxylic acid and

triethanolamine substituents in KCl. The method proved to be selective, as the resulting interference did not affect the detection of cyanocobalamin, had low detection limits and low cost, and was effectively applied to pharmaceutical tablets and dietary supplements [93]. In another study, the determination of cyanocobalamin was performed in human urine samples by using a combination of cyclic voltammetry and adsorptive transfer square wave voltammetry, using a DNA electrochemical biosensor and a modified carbon paste electrode. The electrode was modified with an electrochemically produced polymer (Mn(thiophenyl-2-carboxylic acid)₂(triethylenamine)), while cyanocobalamin was immobilized onto the modified electrode. The method proved to be simple, fast, selective, and with low detection limits (1210 µg/L) [94].

The determination of B12 in pharmaceuticals has been done by using cyclic voltammetry, with an Au electrode modified with mercaptoacetic acid at 0.01 mol/L HCl. The corresponding voltammogram has showed three reduction peaks with potentials of 0.21 V, 0.16 V, and -0.41 V, with a total exchange of two electrons. The main form of Co³⁺ is directly reduced to 0.21 V via transfer of an electron by CN⁻ cleavage into the cyanocob(II)alamin. The detection limit of this method is quite low (1.0×10^{-9} mol/L) [95]. In previous studies on the determination of vitamin B12 in pharmaceuticals, anodic adsorptive voltammetry was applied with disposable graphite screen-printed electrodes that had been modified with Bismuth film [96]. Square-wave voltammetry using a disposable pencil graphite electrode modified with peptide nanotubes was also effective [97]. Additionally, a successful combination of cyclic voltammetry and square-wave voltammetry with a disposable pencil graphite electrode modified with carbon-chitosan nanotubes has been applied [98]. In a study of dietary supplements, the determination of vitamin B12 was done through the application of cyclic voltammetry with a boron-doped diamond electrode wherein the determination of the redox pair Co⁺ → Co²⁺ was monitored. The corresponding voltammogram obtained at pH = 5.0 showed two oxidation peaks for the pairs Co⁺ → Co²⁺ and Co²⁺ → Co³⁺ with potentials -0.74 V and +0.18 V, respectively, and two reduction peaks for the pairs Co³⁺ → Co²⁺ και Co²⁺ → Co⁺ with potentials -0.12 V and -0.75 V, respectively [99]. All relevant analytical figures of merit are being summarized in **Table 1**.

Table 1. Aggregated results from the voltammetric studies of vitamins (fat/water-soluble) in samples.

Vitamin	Voltammetric Technique [ab.]	Working Electrode	Sample	Reference
Vitamin A	CV	Glassy carbon	Retinol/Vitamin E	[100]
	SWV	Carbon paste modified with Pt: Co nanoalloy	Foods	[1]
	DPV	Carbon paste modified with surfactant sodium dodecyl sulfate [CPE/SDS]	-	[2]
	SWV	Boron Doped Diamond Electrode	-	[101]
	CV	Glassy carbon	-	[5][10][102][103]
Vitamin D	CV, DPV	Glassy carbon modified thin synthetic indium-titanium oxide	D2	[3]
	DPV	Glassy carbon modified with PANnFs and NPsFe ₃ O ₄	D3	[4]
	DPV	Glassy carbon ITO, modified with Asp-Gd ₂ O ₃ NRs sensor	D3	[5]
	CV, DPV	Glassy carbon modified with Ni[OH] ₂ particles in SiO ₂ / graphene oxide organic-inorganic matrix	Pharmaceutical	[6]
	CV	Glassy carbon modified with nanosensor employing fullerene-C60 and bimetallic nanoparticles composite film	Blood	[7]
	AdSV	Screen-printed carbon coated with MIP and p-phenylenediamine-resorcinol	Real samples	[8]
	CV, DPV	nCeO ₂ /CC immunosensor	Biological samples	[9]

Vitamin	Voltammetric Technique [ab.]	Working Electrode	Sample	Reference
Vitamin E	DPV	Planar Pt	Vegetable oils and fats	[10]
	CV, DPV	Au modified with Pan/c-Al ₂ O ₃	Food supplements	[11]
	SWAdSV	Glassy carbon	Vitamins E και K	[12]
	SWV	CF disk UME in Bz/EtOH [1:2]	α-, β-, γ-, δ-tocopherols in oil samples	[13]
	SWAdSV	Glassy carbon	Vitamins E and K in food supplements	[17]
	CV	Glassy carbon	-	[17]
Vitamin K	SWAdSV	Glassy carbon	Plant based foods	[18]
	CV	Glassy carbon	Pharmaceutical Products and Foods	[17][19]
	CV	Pencil graphite modified with silver nanoparticles and 2-amino-5-chloro benzophenone	Blood plasma	[20]
	CV, LSV	Glassy carbon modified with PEDOT	Poultry drugs	[21]
	SWAdSV	Glassy carbon	Vitamins A, D, E, K	[22]

Vitamin	Voltammetric Technique [ab.]	Working Electrode	Sample	Reference
Vitamin C	SWV	Carbon paste modified with Fe[III]-Y	-	[104]
	CV	Carbon paste modified with p-tert-butylcalix ^[105] arene	Commercial Samples	[33]
	CV, DPV	Carbon paste coated with NPsZnO-Pd	Fruit Juices, creams	[23]
	CV, DPV	Printed carbon electrode bare and modified with ZnO/Al ₂ O ₃	Real samples	[24]
	DPV	Carbon paste modified with graphene	Pharmaceutical Products	[25]
	DPV	Carbon paste modified with porphyrins	Pharmaceutical Products	[26]
	CV	Glassy carbon modified with poly[bromocresol purple] film	-	[27]
	CV	Glassy carbon modified with poly [3-[5-chloro-2-hydroxyphenylazo]-4, 5-dihydroxynaphthalene-2, 7-disulfonic acid] film	Ascorbic acid in a mixture of substances	[28]
	CV	Pt coated with iodine	MultiVitamins [B1, B6, B9, B12, C]	[31]
	CV, DPV	Carbon paste modified with multi-wall carbon nanotubes and graphite	Pharmaceutical formulations και Foods	[32]
	CV	Carbon paste modified with 2,2'-[1,8-octanediylbisnitriloethylidene]-bis-hydroquinone and tetrabromo-p-benzoquinone	Mixture of ascorbic acid, uric acid and dopamine	[34][35]
	CV	Glassy carbon modified with H ₂ SO ₄	-	[36]
	CV	Glassy carbon modified with LaFeO ₃ nanoparticles	-	[37]
	CV, DPV	Glassy carbon modified with graphene/Pt nanoparticles	-	[38]
	SWV	Glassy carbon modified with Ni-poly [1,5-diaminonaphthalene] nanoparticles	-	[40]
	DPV	Glassy carbon modified with helical carbon nanotubes	Ascorbic acid, uric acid and dopamine in a bovine foetal serum sample	[39]
	SWV	Carbon paste modified with multi-wall carbon nanotube	Ascorbic acid, tryptophan, paracetamol	[41]
	SWV	Carbon paste modified with multi-walled carbon nanotubes–chitosan composite film	Ascorbic acid-Rutin	[42]
	CV	Glassy carbon modified with poly [caffeic acid]	Ascorbic acid and dopamine in Pharmaceutical Products	[43]
	DPV	Glassy carbon modified with carbon nanotubes	Ascorbic acid, paracetamol	[44]
	DPV	Carbon paste modified with cetosan-cetylpyridinium bromide	Ascorbic acid and uric acid	[45]
	LSV	Au modified with dimercaptotriadiazole	-	[46]
	CV	Carbon paste modified with novel bicopper complex	Ascorbic acid and dopamine in Pharmaceutical Products και Foods	[47]
	DPV	Au modified with self-assembled Au nanoparticles	Ascorbic acid abd dopamine	[48]
	DPV, CV	Glassy carbon modified with multiwall carbon nanotubes with nafion	Ascorbic acid, uric acid, epinephrine	[49]
	DPV, CV	Carbon coated with SiO ₂ /Nb ₂ O ₅	-	[50]

Vitamin	Voltammetric Technique [ab.]	Working Electrode	Sample	Reference
	CV	Carbon paste	Juices	[51]
	CV	Graphite modified with Manganese dioxide	Juices	[51]
	LSV	Gold	Juices	[51]
	DPV	Glassy carbon	Juices and wines	[47][48][49][50] [51][52][53][54]
	DPV	Pt microelectrodes modified with polyvinyl sulfonium and polystyrene sulfonium film	Juices and wines	[52][53][54]
	DPV, SWV	Glassy carbon	Plants of the <i>Rosa</i> family	[55]
	SWV	Graphene oxide paste modified with manganese[II] complex	<i>Rosa canina</i>	[56]
	CV	Carbon paste modified with PM/AuNPs	-	[57]
	CV, SWV	Microelectrode made from pyrolytic graphite sheet [PGS]	Real samples	[58]
	DPV	Glassy carbon modified with MXene powder (titanium carbide)	Human urine samples	[106]
	AdSV	Carbon paste	-	[107]
	CV	Carbon paste modified with MnPC	-	[107]
	CV	Platinum	Thiamine Pyrophosphate	[108]
Vitamin B ₁	AdSV	Glassy carbon modified with Pb ²⁺ film	Pharmaceutical Products and Juices	[59]
	SWV	Au modified with Cys/SAM	Pharmaceutical formulations	[60]
	AdSV	Glassy carbon modified with AgLAF-AgSAE	Mixture vitamins B1, B2, C	[61]
	AdSV	Carbon paste modified with DNA/MWCNT	-	[62]
	CV	Optical sensor made of cyclodextrin	Pharmaceutical formulations	[63]
	AdSv	Hg/Bare glassy carbon	Real samples	[64]
Vitamin B ₂	AdSV	Bare Glassy carbon	Breast milk	[65]
	ASV	Glassy carbon modified with nanomaterials	-	[66]
	DPV	Carbon paste modified with Co zeolites	-	[68]
	CV, DPV, LSV	Glassy carbon modified with ZnO-MnO/CSNs	-	[69]
	DPV	Glassy carbon	-	[10]
	CV	Hg/Dropping Hg/Pt	-	[10]
Vitamin B ₃	CV	Microelectrode graphite paste modified with CoTMPP/Nafion	Syrup	[70]
	CV	Gold	Pharmaceutical Products	[71][72]
	ASV	Au modified with thioglycolic acid	Foods	[71][72]
Vitamin B ₅	CV, DPV, LSV	Carbon paste modified with cobalt[II]oxide catalyst	D-panthenol	[10]
	SWV	Glassy carbon	Urine	[69]

Vitamin	Voltammetric Technique [ab.]	Working Electrode	Sample	Reference
Vitamin B ₆	SWV	Carbon paste modified with ZnO/Cuo	Mixture of vitamins C and B6	[73]
	DPV	Au modified with carbon nanotubes	-	[73]
	DPV	Glassy carbon modified with dsDNA	-	[73]
Vitamin B ₇	DPV	Disposable printed silk	Foods (Energy drinks, cereals), multivitamins	[74]
	SWV	Film biosensor modified with Pd-Fe-Ni NPs	Foods	[75]
	CV, DPV	Diamond with mixture of boron/Nafion	Blood plasma	[76]
	CV	Au modified with MBT/SAM film	-	[10]
	CV	Dropping Hg	-	[10]
Vitamin B ₉	CV	Au modified. with multi-wall carbon nanotube Au/NPs,	-	[109]
	CV, AdSV	Hg electrode	Folic acid, riboflavin	[89]
	ASV	Glassy carbon modified. with Pb ²⁺ film	Mixture of ascorbic acid and riboflavin	[90]
	SWV	Carbon paste modified. with Pt:Co nanomaterials	Pharmaceutical Products, Foods	[77]
	SWV, CV	Carbon paste modified. with Ru[II]ZnO complex carbon nanotubes	Pharmaceutical Products, Foods	[78]
	SWV, DPV	Carbon paste modified. with nanomaterials	Pharmaceutical Products, Foods	[79][80]
	DPV	Carbon paste modified. with polymeric film, TiO ₂ nanomaterials, magnetite nanoparticles/Au modified with nanomaterials	Pharmaceutical Products, Foods	[81][82][83][84]
	DPV, CV	Carbon paste modified with carbon nanotubes	Pharmaceutical Products, Foods	[85]
	ASV	Au modified. with Bi-film, Ag or Hg amalgams	Foods	[84][86][87]
	CV, DPV	Polymerized tyrosine film on graphite substrate	Pharmaceutical tablets	[88]
Vitamin B ₁₂	DPV	Electrochemical sensor modified. with polypyrrole and PdAu NPs	Blood plasma, Urine	[91]
	CV, DPV	Ferromagnetic nanoparticles from triazine dendrimers [FMNPs@TD]	Foods	[11]
	CV	Glassy carbon	Injectable Drugs	[92]
	SWV	Carbon paste modified. with Mg complex film with thiophene-2-carboxylic acid and triethanolamine substituents	Pharmaceutical tablets, Food supplements	[93]
	AdSV	Carbon paste modified. with [Mn (thiophenyl-2-carboxylic acid)-2 [triethylonamine] polymer and DNA biosensor	Urine samples	[94]
	CV	Au modified. with mercaptoacetic acid	Pharmaceutical Products	[95]
	ASV	Disposable carbon mesh modified with bismuth film	Pharmaceutical Products	[96]
	SWV	Graphite modified with peptide nanotubes	Pharmaceutical Products	[97]
	SWV	Pencil Graphite modified with carbon nanotube-chitosan	Pharmaceutical Products	[98]
	CV	Diamond with boron admixture	Food supplements	[99]

CV; cyclic voltammetry, SWV; square wave voltammetry, ASV anodic stripping voltammetry, AdSV adsorptive voltammetry, DPV; Differential pulse voltammetry.

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