



Review

Fabrications of electrochemical sensors based on carbon paste electrode for vitamin detection in real samples

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Received: February 26, 2022; Accepted: April 24, 2022; Published: May 4, 2022

Abstract

This review article examines some advancements in electrochemical sensors for vitamin detection in the past few decades. Vitamins are micronutrients found in natural foods essential for maintaining good health. Most vitamins cannot be synthesized by a body and must be obtained externally from natural food. Vitamins make a class of organic chemicals that shortage can cause various ailments and diseases, and consumption can become harmful if it exceeds the usually needed level. Because of these factors, vitamin detection has become highly significant and sparked interest over the past few decades. The electrochemical sensors function on the concept of electrochemical activity of practically all vitamins. This implies that concentrations of vitamins in the electrolyte may be detected by measuring the amounts of current generated at certain potentials by their oxidation and reduction at the working electrode surface. Voltammetric methods are superior to other methods because they are cheaper and show sharp sensitivity with faster analysis speed. The carbon-based electrodes, in particular carbon paste electrodes (CPE), have significant advantages like easier catalyst incorporation, surface renewability, and expanded potential windows with lower ohmic resistance. This review goes into detail about several electrochemical sensors involving CPE as the working electrode and its utilization to detect water- and fat-soluble vitamins.

Keywords

Water-soluble vitamins; fat-soluble vitamins; redox reactions; voltammetry; modifiers

Introduction

Vitamins are a collection of complex chemical molecules that a human body needs in small amounts to maintain optimum health. In general, vitamins are not synthesized by the human body (apart from vitamins B₃, D, and K) and must be obtained from the diet. Vitamins aid in maintaining cells, tissue, and organ growth and act as an immune system booster. Another important role of vitamins is to act as cofactors (co-enzymes) in enzymatic reactions [1-5]. Table 1 provides the daily

allowance of vitamins by normal male and female adults and the diseases caused due to their deficiency.

Table 1. Required amounts of vitamins for adults (males and females) and related diseases due to their deficiency

Vitamin	Common name	Required daily amounts, mg		Deficiency diseases
		Male	Female	
A	Retinol	0.90	0.70	Night blindness
B ₁	Thiamine	1.2	1.1	Beri-beri
B ₂	Riboflavin	1.3	1.1	Ariboflavinosis
B ₃	Niacin, Niacin amide	16	14	Pellagra
B ₅	Pantothenic acid	5	5	Paresthesia
B ₆	Pyridoxine	1.3	1.3	Anemia
B ₇	Biotin	0.030	0.030	Dermatitis, enteritis
B ₉	Folic acid	0.400	0.400	Megaloblastic anemia
B ₁₂	Cobalamin	0.0024	0.0024	Megaloblastic anemia
C	Citric acid	90	75	Scurvy
D	Calciferol, Ergosterol	0.015	0.020	Rickets, osteomalacia
E	Alfa-Tocopherol	15	15	Less fertility
K	Menadione	0.120	0.090	Non-clotting of blood

Vitamins also aid in converting food into energy, lowering the risk of sickness, and encouraging a healthy way of life. The human body requires enough vitamins and any deviation from the appropriate amount might indicate a problem. Therefore, widespread research has been done to detect vitamins in the human body and real samples.

Depending on the solubility properties, vitamins can be divided into two broad categories, water-soluble vitamins, and fat-soluble vitamins. Fat-soluble vitamins include A, D, E, and K. Fat-soluble vitamins can be stored in adipose tissue. Water-soluble vitamins, such as those of the B group and vitamin C, cannot be kept in human bodies since they travel with the water and are extracted through the urine, so they must be consumed regularly by our body.

Vitamins may be detected using a variety of techniques, including high-performance liquid chromatography, immuno-affinity columns, fluorescence, ultraviolet spectroscopy, and capillary electrophoresis. Although these approaches offer many benefits, such as high selectivity and sensitivity, they have significant drawbacks, including long analysis time, difficult sample preparation, huge sample amounts, expensive apparatus, and the need for highly skilled workers. Electrochemical sensors are viable alternatives to these technologies because of their simplicity, cost-effectiveness, high sensitivity, ease of downsizing, dependability, and repeatability. So far, electrochemical sensors have found widespread use in a variety of disciplines, including pharmaceutical, food, and clinical analyses [6-8].

Electrochemical sensors record the concentration of analyte (here vitamins) in the electrolyte solution by measuring the current at the working electrode, which is based on the electrochemical redox (oxidation/reduction) process of an analyte. The current response is typically proportional to the analyte concentration. At present, amperometry and voltammetry are the most used electrochemical methods. Cyclic voltammetry (CV) and linear scan voltammetry (LSV) are the two simplest voltammetry procedures. With the tuning of different parameters, square wave voltammetry (SWV) and differential pulse voltammetry (DPV) are two approaches that can give improved sensitivity [1].

The selection of the working electrode is crucial in electrochemical analysis. Carbon paste electrode (CPE) has several advantages over other typical carbon working electrodes, including ease

of preparation, rapid surface renewal, consistent response, and, most importantly, decreased ohmic resistance. In this review, some advancements in vitamin detection accomplished by the utilization of CPE will be presented and discussed.

Electrochemical sensors for water-soluble vitamins

Water-soluble vitamins are commonly present in a variety of foods, including milk powder, drinks, and supplements. Water-soluble vitamins cannot be kept in the human body for lengthy periods because they are promptly eliminated by the urine. Insufficiency of water-soluble vitamins has a detrimental impact on human health and is frequently linked to illness. As a result, maintaining the proper operation of the human body needs a regular and sufficient dietary intake of water-soluble vitamins.

Electrochemical sensors based on the carbon paste electrodes are a typical tool for examining redox characteristics of water-soluble vitamins since each water-soluble vitamin is made up of distinct molecules that may transfer electrons in an aqueous electrolyte. Electrochemical sensors for the detection of water-soluble vitamins have become quite popular over the past few decades.

Electrochemical sensors for vitamin B₁

Vitamin B₁ (VB₁) is one of eight vitamins that make up the vitamin B complex, a potent group of nutrients. It is extremely important for both physical and mental wellness and necessary for the human body's regular metabolism, particularly in the neurological system. Deficiency of VB₁ is linked to several illnesses, including beriberi and neurological problems. It is important to note that VB₁ are electrochemically active redox moieties and therefore, it is possible to detect them using voltammetric methods.

The electrochemical response of VB₁ in an alkaline medium at a carbon paste electrode (CPE) is discussed by J. Oni *et al.* [2], who used CV for the determination of VB₁ at a carbon paste electrode (CPE) modified with manganese phthalocyanine (MnPc). For the detection of VB₁, a pH 10 buffer solution was selected. MnPc modified CPE showed catalytic activity towards the oxidation of VB₁ by considerably increasing the oxidation current compared to the unmodified electrode. The detection limit for VB₁ at the MnPc-CPE was 14.6 $\mu\text{mol dm}^{-3}$. The real sample analysis was done using commercial VB₁ tablets [2]. For the detection of VB₁, Muppuriqoh *et al.* [3] developed a CPE modified by a molecularly imprinted polymer (MIP) based on polypyrrole. The authors also used CV for sensing purposes in potassium chloride (KCl) tris buffer supporting electrolyte of pH 10. The limit of detection (LOD) was found to be 0.069 mmol L^{-1} [3]. P. K. Brahman *et al.* [4] developed a simple methodology for the determination of VB₁. The method is based on the interaction of VB₁ with DNA using a multi-walled carbon nanotube paste electrode (PMWCNTPE) and the DPV method. Under the optimum conditions, LOD was found to be 0.44 mg mL^{-1} at ds-DNA modified PMWCNTPE. The analysis for serum, plasma, and urine samples suggested that the proposed electrode is promising for VB₁ analysis in real samples [4].

Electrochemical sensors for vitamin B₂

Vitamin B₂ (VB₂) (chemical name: 7,8-dimethyl-10-ribityl-isoalloxazine), also known as riboflavin, is a water-soluble vitamin found in several foods. VB₂ plays an important part in human physiological activities like the breakdown of fats and carbohydrates, thereby playing a major role in maintaining the human body's energy supply. Unfortunately, the human body cannot synthesize VB₂, and it must be received from the food from sources such as liver, cheese, milk, pork, eggs, wines, and tea. The

deficiency of VB₂ is linked to eye lesions and skin illnesses. It is possible to detect VB₂ using voltammetric methods.

E. Mehmeti *et al.* [5] developed MnO₂ modified CPE (MnO₂MCPE) to sense VB₂ using the DPV method. The MnO₂MCPE showed higher redox peak currents when compared to unmodified CPE because of the higher active surface area obtained from MnO₂. The found LOD value was 15 nM. The authors also used the developed sensor to determine VB₂ in pharmaceutical formulations [5]. A. Nezamzadeh-Ejhi *et al.* [9] modified CPE with Co²⁺-Y zeolite. Using CV, the authors showed that the presence of Co²⁺ ions lowers the oxidation potential (for around 200 mV) and increases the peak currents of VB₂. which shows that Co²⁺ ions improve CPE sensing properties for VB₂ detection. The authors checked the analytical utility of the prepared sensor electrode for analysis of VB₂ in pharmaceutical products with the fluorometric method evidence [9].

Electrochemical sensors for vitamin B₆

Vitamin B₆ (VB₆) (pyridoxine) is included in a variety of products, including multivitamin supplements and enhanced foods. It is essential for both mental and physical well-being. Also, VB₆ is required for over 100 enzymes involved in protein metabolism and producing hemoglobin (which transports oxygen to tissues).

M. F. S. Teixeira *et al.* [10] have studied the redox behaviour of VB₆ using CPE modified with N, N-ethylene-bis(salicylideneiminato)oxovanadium (IV) complex. The redox nature of the modified CPE and the electrooxidation of VB₆ were analysed using CV. After the modification, CPE showed a LOD value of 37 μmol L⁻¹. The concentrations of VB₆ in commercial drugs were also tested by cross verifying results with the spectrophotometric method. Obtained results were satisfactory and within an acceptable range of errors [10]. In another work, M. F. S Teixeira *et al.* [11] modified CPE using copper (II) hexacyanoferrate (III) (CuHCF) for the determination of VB₆ using CV. CuHCF modified CPE showed a LOD value of 0.41 μmol L⁻¹. The authors tested the analytical utility of prepared electrodes by testing VB₆ concentration in different pharmaceutical samples [11].

Electrochemical sensors for vitamin B₉

Vitamin B₉ (VB₉) is also known as folate (folic acid), which is required to produce white and red blood cells in the bone marrow and produce RNA and DNA. It also plays a crucial role in the conversion of carbohydrates into energy. Therefore, it is extremely critical to get enough folate, especially during periods of fast growth, such as infancy, puberty, and pregnancy.

Khaleghi *et al.* [12] developed a sensitive voltammetric sensor by modifying CPE with 1,3-dipropylimidazolium bromide (1,3-DIBr) and ZnO/CNTs nanocomposite, forming (1,3-DIBr/ZnO/CNTs/CPE) as an electrocatalyst. The modified CPE showed a negative shift of oxidation potential for 95 mV when compared to CPE, and LOD was found to be 0.05 μM. The proposed electrode was also tested to detect VB₉ in real samples like (tablets and food samples) with a 95% confidence level [12]. S. Cheraghi *et al.* [13] measured curcumin in the presence of VB₉, using a new sensor, which was built with cadmium oxide nanoparticles-ionic liquid (1,3-dipropylimidazolium bromide as a binder) modified CPE (CdO-IL-MCPE). It was found that curcumin and VB₉ oxidation signals are separated, appearing at roughly 0.41 and 0.73 V vs. Ag/AgCl at pH 7.0, respectively. Curcumin and VB₉ concentrations were altered concurrently for this purpose, and SWVs were measured. The sensitivity of the CdO-IL-MCPE to curcumin in the absence and presence of VB₉ was nearly identical, indicating that the oxidation processes of curcumin and VB₉ on the sensor are independent of one another, allowing thus a simultaneous or independent determination of curcumin and VB₉.

Electrochemical sensors for vitamin B₁₂

Vitamin B₁₂ (VB₁₂) is one of the significant vitamins of B family members, which is commonly known as cobalamin. Vitamin B₁₂ is the most massive and structurally complex of all vitamins. It is found naturally in animal products such as meat and eggs and can also be manufactured by bacterial fermentation synthesis. Its presence in mammals will help a proper RBC synthesis and brain functions like nerve tissue health. When the concentration of VB₁₂ is below a certain concentration, it may lead to severe symptoms like brain disorders.

S. Karastogianni and S. Girousi [14] constructed the CPE modified with manganese complex (thiophene-2-carboxylic acid and triethanolamine as ligands) and used SWV for the characterization of sensing properties of the modified CPE. The authors confirmed VB₁₂ interaction with modified CPE by observing reduction peaks (positive shift of 48 mV). This unique method helps to confirm the presence of VB₁₂ in an electrolyte solution. However, the authors did not report LOD values of modified CPE towards cobalamin. Later, the authors extended their procedure to detect VB₁₂ in real samples like commercial drugs. The obtained values were in very good agreement with the prescribed concentration of cobalamin in tablets [14]. R. G. Compton's research group also modified CPE with trans-1,2- dibromocyclohexane for VB₁₂ detection using SWV [15]. A LOD value of 0.85 nmol dm⁻³ was obtained at modified CPE and also, VB₁₂ was successfully detected in pharmaceutical products and biological matrix media [15].

Electrochemical sensors for vitamin C

Vitamin C (VC), commonly known as ascorbic acid, is required to repair, develop, and grow human tissues. VC is also engaged in a variety of human body activities, including collagen creation, iron absorption, immune system function, wound healing, cartilage, bone, and tooth maintenance. Another important VC duty is to act as an antioxidant to protect healthy cell lines from free radicals, hazardous chemicals, and pollutants like cigarette smoke attacks. Therefore, it is important to monitor VC concentrations in the human body. Electrochemical voltammetric methods are very promising for detecting VC in real samples. Here, some important works on developing sensors to detect VC in real samples using modified CPE will be presented [16-19].

G.K. Jayaprakash *et al.* [16] used the cetylpyridinium modified CPE (CPMCPE) to sense VC using CV. First, the authors compared the effects of different cationic surfactants on the CPE and found that the active surface area of the electrode is higher when CPE is modified by cetylpyridinium surfactant. Later, the authors compared the bare CPE and CPMCPE behaviour for the detection of VC in phosphate buffer solution. Bare CPE showed a broad CV peak at 0.342 mV vs. SCE, while CPMCPE showed a sharp oxidation peak at -0.084 mV vs. SCE with an increased oxidation peak current value. Therefore, the authors concluded that using a cetylpyridinium modifier of CPE is beneficial for the detection of VC. The authors also used the proposed electrode to detect the VC in urine samples without any pre-treatment and the proposed electrode detected VC with about 107 % recovery. The authors did not check the LOD of CPMCPE for the detection of VC [16]. A. Baghizadeh *et al.* [17] applied ZrO₂ nanoparticle/ionic liquids modified CPE for the determination of VC in the presence of VB₆. The formed ZrO₂/Nps/IL/CPE detected VC in the presence of VB₆ with the LOD value of 0.009 µM. The authors performed the real sample analysis using tablets, urine, fruit juice, and injection, obtaining satisfactory results [17]. S. Gheibi *et al.* [18] determined VC amounts using p-aminophenol modified carbon nanotubes paste electrode (CNTPE) using the CV method. At the modified CPE electrode, APMCNTPE, the oxidation peak potential of VC was shifted negatively, and therefore, the authors concluded that the proposed electrode is suitable for the detection of

VC, showing LOD value of 80 nM. The analytical application of the electrode was tested using fruit juices and fresh vegetable juice [18].

A summary of CPE-based electrochemical sensors developed for the detection of water-soluble vitamins (B₁, B₂, B₆, B₉, B₁₂, and C) is presented in Table 2.

Table 2. Summary of CPE based electrochemical sensors for detection of water-soluble vitamins

Vitamin	Modifier	Method	LOD	Real sample analysis	Ref.
VB ₁	MnPc	CV	14.6 mmol dm ⁻³	commercial VB1 tablets	[2]
VB ₁	Polypyrrole	CV	0.069 mmol L ⁻¹	NA	[3]
VB ₁	ds-DNA	DPV	0.44 mg mL ⁻¹	serum, plasma, urine	[4]
VB ₂	MnO ₂ MCPE	DPV	15 nM	pharmaceutical formulations	[5]
VB ₂	Co ²⁺ Y zeolite	CV	-	pharmaceutical products	[9]
VB ₂	Poly-arginine	DCV	93 nM	human blood serum, b-complex capsule	[20]
VB ₆	N,N-ethylene-bis(salicylideneiminato) oxovanadium(IV) complex	CV	37 mmol L ⁻¹	pharmaceutical formulations	[10]
VB ₆	(CuHCF)	CV	0.41 mmol L ⁻¹	pharmaceutical formulations	[11]
VB ₉	(1,3-DIBr) & (ZnO/CNTs) nanocomposite	CV	0.05 μM	drugs	[12]
VB ₉	cadmium oxide nanoparticles-IL	SWV	0.08 μM	food samples	[13]
VB ₉	(Pt:Co/ RTIL)	SWV	40 nM	food samples	[14]
VB ₁₂	manganese complex			drugs	[15]
VB ₁₂	trans-1,2- dibromo-cyclohexane	SWV	0.85 nmol dm ⁻³	pharmaceutical products, plasma	[15]
VC	cetylpyridinium	CV	--		[16]
VC	ZrO ₂ nanoparticle/ionic liquids		0.009 μM	tablet, urine, fruit juice, injection	[17]
VC	p-aminophenol		80 nM	food sample	[18]

Electrochemical sensors for fat-soluble vitamins

A, D, E, and K are fat-soluble vitamins and hence, they are absorbed in the lymph, transported in the blood *via* carrier proteins, and can be stored in the liver and fatty tissues. These vitamins do not dissolve in water and are present in foods containing fats. The human body absorbs these vitamins as dietary fats do. All these vitamins are physically similar in featuring a five-carbon isoprene segment as a fundamental structural unit of the molecule.

Electrochemical sensors for vitamin A

Vitamin A (VA) is a group of unsaturated fat-soluble organic compounds called retinoids which include retinol, retinal, and retinyl esters. VA is critical for vision and is involved in immune function, reproduction, and cellular communication. The deficiency of VA may lead to many serious diseases like night blindness. In the human diet, VA is available in two forms: preformed vitamin A (retinol and retinyl esters) found in animal food, including dairy products, fish, meat, etc. Provitamin A is plant pigments that are consumed through vegetables and fruits.

X. Lv *et al.* [21] used SWV for determining VA concentrations in vegetables (cabbage) and drugs, utilizing a CPE modified with nano-alloy (Pt:Co) room temperature ionic liquid (Pt:Co/IL). The

prepared Pt:Co/IL/CPE was compared with bare CPE (BCPE), ionic liquid (IL) modified CPE, and Pt:Co modified CPE. Based on the results, Pt:Co/IL/CPE showed maximum sensitivity and electrochemical reversibility for the VA detection in phosphate buffer solution (PBS), pH 9, as the supporting electrolyte. For Pt:Co/IL/CPE, the highest oxidation peak current and the lowest oxidation peak potential were observed compared to other electrodes. Therefore authors concluded that the modification of CPE with Pt:Co/IL is beneficial for sensing VA. The Pt:Co/IL/CPE showed LOD of 0.04 μM and the authors also analysed the electrode utility using cabbage and tablet specimens [21]. S. Žabčíková *et al.* [22] used CV to investigate the oxidation mechanism of all-trans retinol and their esters in non-aqueous, aqueous organic mixture, and pure aqueous media. Their most sensitive oxidation peak appearing at +0.8 V vs. Ag/AgCl was used for the development of a new direct voltammetric method based on DPV for the determination of retinol at carbon paste. The results showed that modification of CPE using 30 % (by mass) sodium dodecyl sulphate (SDS) has optimal sensitivity. In comparison to the regularly used glassy carbon electrode (GCE), the CPE/SDS demonstrated remarkable progress in retinol electroanalysis, yielding a LOD of 1.3 μM [22].

Electrochemical sensors for vitamin D₃

Also called cholecalciferol, vitamin D₃ (VD₃) is a fat-soluble secosteroid responsible for increasing the absorption of calcium, magnesium, and phosphate in the intestine and maintaining their level in blood and cardiovascular health and preventing infections. VD₃ helps to strengthen bones and muscles, and its deficiency may lead to serious diseases like rickets, osteoporosis, osteomalacia, autoimmune disorders, cardiovascular disease, cancer, *etc.*

A hybrid imprinted polymer-based electrochemical sensor was set up by Kia *et al.* [23], which was found to be highly sensitive to VD₃ and applied successfully in real samples. The modified carbon paste electrode was constructed by mixing graphite powder and n-eicosane (binder) with a molecularly imprinted polymer synthesized in the presence of multi-walled carbon nanotubes, forming MIP/ MWCNT/ CPE. SWV was employed to study the oxidation of VD₃ using a mixture of perchloric acid and 70 % methanol as an electrolyte at pH 3. The linear range was observed between 0.05 and 7 μM and LOD was found to be 3×10^{-8} M [23].

Electrochemical sensors for vitamin E

Vitamin E refers to a group of eight different compounds: α , β , γ , and δ tocopherols and corresponding four tocotrienols, among which α - tocopherol is biologically most active as it is transported and used by the liver. It is one of the major antioxidants which protect cells, tissues, and organs from free radicals and maintains immune and neurological health. Therefore, VE needs to be consumed in proper amounts through diet.

Sýs *et al.* [24] introduced a silicone oil-modified glassy carbon paste electrode (SO/GCPE) for the detection of VE in portions of margarine and edible oils. To obtain the results with the highest efficiency, 60 % aqueous-acetone solution was used. Square wave anodic stripping voltammetry (SWASV) was carried out after VE accumulation on SO/GCPE at pH 9.0, using HNO₃ as the supporting electrolyte. After 5 minutes of accumulation, the linear range was 0.5–40 mol L⁻¹, with an LOD of 0.1 mol L⁻¹. After 15 minutes of accumulation, however, the linear range was 0.05–10 mol L⁻¹ with an LOD of 3.3 nmol L⁻¹ [24].

Electrochemical sensors for vitamin K

Vitamin K (VK) is a fat-soluble vitamin that may be found in two forms: vitamin K₁ (VK₁) also called phyloquinone and vitamin K₂ (VK₂) menaquinone. VK₂ is found in plants and leafy green vegetables

but also in cheeses, eggs, meat, and a variety of fermented foods. In blood coagulation and bone calcification, VK plays a critical function. VK insufficiency produces a drop in prothrombin and clotting factors in the blood, which causes hemorrhagic and profuse bleeding.

For detecting VK₁, J. P. Hart *et al.* [24] built up carbon paste electrodes made with various kinds of graphite, and pasting agents were studied using linear sweep voltammetry (LSV). The vitamin was shown to accumulate strongly but dependent on the graphite type and pasting agent utilized. Then using adsorptive stripping voltammetry (ADSV), a carbon paste electrode comprising Nujol-Ultra Carbon Ultra Superior Purity graphite provided the maximum sensitivity where the optimal accumulation time was 15 minutes at the open circuit potential. To remove vitamin K₁ from plasma before adsorptive stripping analysis, several techniques were tested. The vitamin levels in the blood were measured throughout these procedures. The best recovery (91 %) and LOD of 180 ng ml⁻¹ in the supporting electrolyte and 450 ng mL⁻¹ in plasma were obtained utilizing a solvent extraction approach employing hexane and ethanol. However, by deproteinizing the plasma with ethanol and measuring the resultant supernatant directly, the analysis time might be cut in half (at the cost of some sensitivity) [25].

A summary of CPE-based electrochemical sensors developed to detect fat-soluble vitamins (A, D₃, E, and K₁) is given in Table 3.

Table 3. Summary of electrochemical sensors for detection of fat-soluble vitamins

Vitamin	Modifier	Method	LOD	Real sample analysis	Ref.
VA	Pt:Co/IL/CPE	SWV	0.04 μM		[21]
VA	SDS/CPE	DCV	1.3×10 ⁻⁶ M	cabbage and drugs	[22]
VD ₃	MIP/ MWCNT/ CPE	SWV	3 ×10 ⁻⁸ M		[23]
VE	SO/GCPE	SWASV	5 min: 10 ⁻⁷ mol L ⁻¹ 15 min: 3.3×10 ⁻⁹ mol L ⁻¹	margarine and edible oils	[24]
VK ₁		LSW	180 ng mL ⁻¹	human blood and plasm	[25]

Conclusion

The advances in the field of electrochemistry have demonstrated good results on carbon paste electrodes (CPE) used as electrochemical sensors, which generated a great deal of attention. This is also due to exceptional features of CPE like cost-effectiveness, repeatability, dependability, and sensitivity. Although there has been a significant improvement in electrochemical sensors used for vitamin detection, many elements, such as improving sensitivity, remain a hot issue for researchers. Up to now, it is also not possible to identify the presence of both fat-soluble and water-soluble vitamins at the same time. This review attempted to thoroughly discuss several electrochemical approaches employing CPE for the detection of fat- and water-soluble vitamins. The electrical conductivity, active surface area, and stability of the CPE are poor compared to the other electrodes for detecting fat and water-soluble vitamins. Therefore, different types of modifiers such as redox mediators (MnPc, MnO₂, bis(salicylideneiminato)oxovanadium (IV) complex), nanomaterials (ZrO₂, MWCNT), polymers, and surfactants (CPB, CTAB, TX-100) were used to sense vitamins in real samples. After modifications, CPE showed excellent activity towards sensing vitamins in real samples like vegetables, oils, human serum, and drugs.

Acknowledgment: V.S. is very thankful to Arundhati Sharma, B. A. Hons, Semester-I, Delhi University, India, for proofreading the article.

References

- [1] L. Huang, S. Tian, W. Zhao, K. Liu, J. Guo, *Talanta* **222** (2021) 121645. <https://doi.org/10.1016/j.talanta.2020.121645>
- [2] J. Oni, P. Westbroek, T. Nyokong, *Electroanalysis* **14(17)** (2002) 1165-1168. [https://doi.org/10.1002/1521-4109\(200209\)14:17%3C1165::AID-ELAN1165%3E3.0.CO;2-S3](https://doi.org/10.1002/1521-4109(200209)14:17%3C1165::AID-ELAN1165%3E3.0.CO;2-S3).
- [3] N. M. Muppariqoh, W. T. Wahyuni, B. R. Putra, *IOP Conference Series: Earth and Environmental Science* **58** (2017) 012050. <https://doi.org/10.1088/1755-1315/58/1/012050>
- [4] P. K. Brahman, R. A. Dar, K. S. Pitre, *Sensors and Actuators B: Chemical* **177** (2013) 807-812. <https://doi.org/10.1016/j.snb.2012.11.073>
- [5] E. Mehmeti, D. M. Stanković, S. Chaiyo, L. Švorc, K. Kalcher, *Microchimica Acta* **183** (2016) 1619-1624. <https://doi.org/10.1007/s00604-016-1789-4>
- [6] G. Tigari, J. G. Manjunatha, H. Nagarajappa, N. S. Prinith, *Journal of Electrochemical Science and Engineering* **12(1)** (2022) 3-23. <https://doi.org/10.5599/jese.1094>
- [7] P. A. Pushpanjali, J. G. Manjunatha, N. Hareesha, *Journal of Electrochemical Science and Engineering* **11(3)** (2021) 161-177. <https://doi.org/10.5599/jese.999>
- [8] B. Ferreira, L. O. Duarte, É. N. Oiyé, M. F. M. Ribeiro, J. M. T. Katayama, P. H. B. Oliva, M. F. de Oliveira, *Journal of Electrochemical Science and Engineering* **10(4)** (2020) 361-371. <https://doi.org/10.5599/jese.849>
- [9] A. Nezamzadeh-Ejhieh, P. Pouladsaz, *Journal of Industrial and Engineering Chemistry* **20(4)** (2014) 2146-2152. <https://doi.org/10.1016/j.jiec.2013.09.044>
- [10] M. F. Teixeira, G. Marino, E. R. Dockal, É. T. Cavalheiro, *Analytica Chimica Acta* **508(1)** (2004) 79-85. <https://doi.org/10.1016/j.aca.2003.11.046>
- [11] M. F. Teixeira, A. Segnini, F. C. Moraes, L. H. Marcolino-Júnior, O. Fatibello-Filho, É. T. Cavalheiro, *Journal of the Brazilian Chemical Society* **14(2)** (2003) 316-321. <https://doi.org/10.1590/S0103-50532003000200021>
- [12] F. Khaleghi, A. E. Irai, R. Sadeghi, V. K. Gupta, Y. Wen, *Sensors* **16(6)** (2016) 747. <https://doi.org/10.3390/s16060747>
- [13] S. Cheraghi, M. A. Taher, H. Karimi-Maleh, *Electroanalysis* **28(10)** (2016) 2590-2597. <https://doi.org/10.1002/elan.201600252>
- [14] S. Karastogianni, S. Girousi, *Analytical Letters* **55(3)** (2021) 399-410. <https://doi.org/10.1080/00032719.2021.1937195>
- [15] P. Tomčík, C. E. Banks, T. J. Davies, R. G. Compton, *Analytical Chemistry* **76(1)** (2004) 161-165. <https://doi.org/10.1021/ac030308j>
- [16] G. K. Jayaprakash, B. E. K. Swamy, S. Rajendrachari, S. C. Sharma, R. Flores-Moreno, *Journal of Molecular Liquids* **334** (2021) 116348. <https://doi.org/10.1016/j.molliq.2021.116348>
- [17] A. Baghizadeh, H. Karimi-Maleh, Z. Khoshnama, A. Hassankhan, M. Abbasghorbani, *Food Analytical Methods* **8** (2015) 549-557. <https://doi.org/10.1007/s12161-014-9926-3>
- [18] S. Gheibi, H. Karimi-Maleh, M. A. Khalilzadeh, H. Bagheri, *Journal of Food Science and Technology* **52** (2015) 276-284. <https://doi.org/10.1007/s13197-013-1026-7>
- [19] G. Tiris, Y. Khoshnavaz, E. N. Öven, M. Mehmandoust, N. Erk, *Journal of Electrochemical Science and Engineering* **12(1)** (2022) <https://doi.org/10.5599/jese.1153>
- [20] G. Tigari, J. G. Manjunatha, D. K. Ravishankar, G. Siddaraju, *Methods and Objects of Chemical Analysis* **14(4)** (2019) 216-223.
- [21] X. Lv, J. Zhao, X. Dong, H. Tian, S. Qi, Y. Jiang, Y. Ping, *International Journal of Electrochemical Science* **12** (2017) 8457-8466. <https://doi.org/10.20964/2017.09.23>
- [22] S. Žabčíková, T. Mikysek, L. Červenka, M. Sýs, *Food Technology and Biotechnology* **56(3)** (2018) 337-343. <https://doi.org/10.17113/ftb.56.03.18.5618>

- [23] S. Kia, *A new Voltametric sensor, based on molecularly imprinted polymer (MIP) for vitamin D3 Detection*, in *2019 International Conference on Biomedical Innovations and Applications (BIA)*, Varna, Bulgaria, 2019, 1-4. <https://doi.org/10.1109/BIA48344.2019.8967459>
- [24] M. Sýs, B. Švecová, I. Švancara, R. Metelka, *Food Chemistry* **229** (2017) 621-627. <https://doi.org/10.1016/j.foodchem.2017.02.068>
- [25] J. P. Hart, S. A. Wring, I. C. Morgan, *Analyst* **114(8)** (1989) 933-937. <https://doi.org/10.1039/AN9891400933>