Review Article

A Review on the Application of Voltammetry in the Determination of Various Substances in Fruit Juices

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Abstract
Voltammetry is preferred amongst other detection techniques for vitamins and antioxidants because of its selectivity, sensitivity, ease of access, and inexpensive instrumentation. This study aims to assess and evaluate existing studies revolving around the voltammetric determination of vitamins and antioxidants of fruit juices, seeing as they are a rich source of vitamins and antioxidants, to find commonalities and trends over the years. Literature studies found differential pulse voltammetry (DPV) and square wave voltammetry (SWV) to be the most utilized determination method for vitamins and antioxidants, respectively. Electrode performance was also compared between bare and modified electrodes by comparing the limit of detection and recovery rate of each sample. Bare electrodes are found to be suitable for the detection of vitamins by having a high level of detection (LOD) values, but modified electrodes seemed to display enhanced performance when compared to the bare electrode. The optimal pH value of the supporting electrolyte in vitamins is $5.0 \leq pH \leq 7.0$, while it was found that the optimal pH value for antioxidants was $2.0 \leq pH \leq 6.0$. Voltammetric determination is highly dependent on the combination of the method, the material used in making the electrode, and the pH of the supporting electrolyte solution.

Keywords: Electrochemical detection, Electrodes, Food components, Fruit juices, Voltammetry

1 Introduction

Food analysis is essential in ensuring the quality, safety, and nutrition of the food products distributed to the public. Specifically, this field of research plays a major role in the food industry whose responsibility is to maintain public health and nutrition by overseeing the preparation, production, preservation, and distribution of various food products. Analytical chemists have developed a variety of electroanalytical techniques over the years to assist in food component detection, which includes the earliest techniques, namely spectroscopic and chromatographic techniques [1]. Spectroscopic methods involve molecular spectroscopy, ultraviolet-visible spectroscopy, infrared spectroscopy, and Raman spectroscopy. They provide relatively fast detection time, but are unable to simultaneously determine substances and exhibit subpar selectivity. Meanwhile, chromatographic techniques, such as liquid chromatography and gas chromatography allow researchers to better examine the chemical composition of food [2]. These methods display high selectivity and sensitivity albeit is considered to be a time-consuming process, both of which have become less preferred over time due to its expensive instrumentation that requires trained personnel in order to operate.

To address the aforementioned issues, voltammetric methods have been introduced as an alternative.

Voltammetry is an electrochemical technique used in both gathering data quantitatively and qualitatively. It can quantify the concentration and diffusion coefficient of a substance in a solution, as well as observe the various reduction-oxidation processes occurring in it [3]. Its adaptability in data gathering allows it to be applied in various fields e.g. analytical chemistry, environmental science, pharmaceutical analysis, and mainly, in the food industry, where it is used to assess the safety and quality of foods. Recently, voltammetry has become the favored method in food analysis due to its cheap instrumentation, excellent sensitivity, rapid analysis, and simultaneous determination of analytes [4]. Additionally, it does not require any laborious sample preparations and can be easily operated by individuals. Using this method, information of the analyte's properties can be obtained by observing the current as the potential is varied. With that, voltammetric methods are able to successfully quantify active species, proving itself to be advantageous in analyzing a wide range of compounds found in foods and beverages, such as quercetin, rutin, and catechin [5]. Aside from the mere detection of components in foods, these methods are also used to study and determine different interactions between chemical components, which enables the food industry to determine whether or not certain combinations of substances are suitable for production. These components often consist of antioxidants, vitamins, and contaminants.

Figure 1 shows a schematic representation of a three-electrode system, showing the working electrode that is used in the detection and quantification of the analyte, the counter or auxiliary electrode that serves to complete the circuit allowing the charge to flow through the cell, and the reference electrode, which is used in measuring and controlling the working electrode potential.

Aside from the naturally occurring antioxidants and vitamins, fruit juices are also most likely to contain contaminants that could have been acquired during the cultivation stage. These potentially harmful contaminants can induce diseases thereby putting human health at risk when consumed in excess, thus, quantification is important to ensure the safety of the public. As a result, several studies have investigated the determination of metals that can be potentially toxic, such as lead, cadmium, and zinc with Anodic Stripping Voltammetry (ASV) and Square Wave Voltammetry (SWV) [6], [7], and detection of additives applied to foodstuff to elongate food shelf lifes, such as colorants and preservatives with Cyclic Voltammetry (CV) [8], [9]; and analysis of pesticide contents used in controlling weeds and insect infestation, such as ethion with Linear Sweep Voltammetry (LSV) [10]. Voltammetric methods are versatile when they are applied to the determination of various contaminants present in foods. Therefore, having available studies about voltammetric techniques to study various kinds of components found in fruit juices is highly convenient for the food industry. These resources should be able to help and guide them in applying the right voltammetric technique with its suitable type of electrode and appropriate experimental conditions to study fruit juices. With the presence of numerous studies that provide relevant information about the determination of fruit juice components using electrochemical techniques, this study examined various references on the application of different voltammetric techniques in fruit juice components.

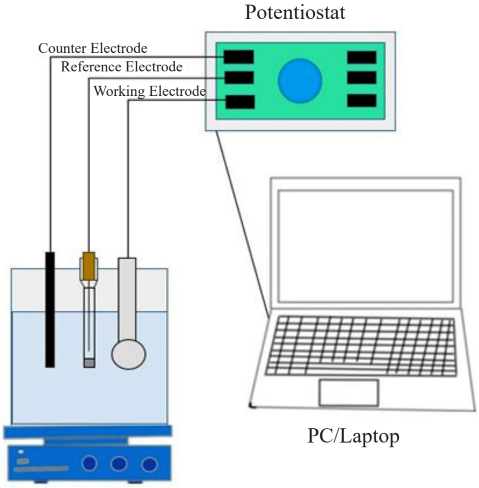

Figure 1: Schematic representation of a three-electrode system that is used in the quantification and detection of components in fruit juice using voltammetry.

2 Electrochemical Detection of Vitamins and Antioxidants

Electrochemical techniques of vitamin and antioxidant determination for food analysis are becoming more widely used due to their practical advantages over standard methods, such as GCMS [11], [12]. Among the distribution trend exhibited by the pool of included articles, the prevalence of studies directed to the determination of vitamins and antioxidants in fruit juices have been the most studied. This can be highly attributed to the fact that these beverages are known as rich sources of vitamins and antioxidants [13]. Specifically, all of the studies have focused on the determination of vitamin C or ascorbic acid (AA). On the other hand, there has not been a prevailing component for antioxidants, however, commonly investigated antioxidants were found to be gallic acid (GA), rutin, quercetin, and other organic acids.

2.1 *Method of determination*

Differential pulse voltammetry (DPV) is the most commonly employed technique for the determination of vitamins, such as ascorbic acid (AA) because of its accuracy, excellent sensitivity and fast detection [14]. In DPV, an amplitude potential pulse is superponated to a linear ramp potential. The current signal is the difference between the current measured before and after the application of the pulse. The applied pulse reduces the effect of capacitive current and enhances the signal associated with the faradaic current. In order to verify the results obtained using voltammetry, most studies carried out the standard analysis and checked the literature to validate the results. Several studies obtained AA contents that were in agreement with data obtained from standard titration methods; hence, proving the effectiveness of DPV in the determination of vitamins in fruit juices [15], [16].

Other methods used for vitamin determination in the reviewed literature also included CV and Adsorptive Stripping Voltammetry (AdSV). Despite not being as prominent, AdSV was found to be effective not only in determining levels of AA, but also of vitamins B_1 and B_2 as well. This was applied by Baś *et al.* [17] in mixed fruit juices to test a modified electrode where results were reported to be similar to the declared amounts. As for CV, the method was noted for its simplicity and sensitivity across its usage in various studies. Pisoschi *et al.* [18] and Tadese *et al.* [19] used this technique for AA quantification where the obtained data corresponded to the reference data and showed satisfactory reliability in AA analysis. Table 1 shows a list of various voltammetric techniques used in determining the various components of fruit juices.

Moreover, a comparative study between CV and DPV by Pisoschi *et al.* [20] concluded the former to have the better sensitivity based on their calibration graphs. The previous study, however, was found to contradict the findings obtained in the majority of other studies. In most studies, DPV was observed to perform better in measuring faradaic currents. It can detect micromolar amounts of chemical components, making it convenient for detection of low concentration samples [21]. This is further supported by Gopalakrishnan *et al.* [15] who stated that DPV verifies a lower limit of detection (LOD) than CV, making it more dependable in the detection of components. Its other advantages were shown when several studies chose DPV over CV due to its higher current sensitivity, better resolution and capability to eliminate capacitive charging currents [16], [22].

Table 1: Voltammetric techniques used in the determination of elements. The limits of detection are rough estimates which could be higher or lower in some cases [23]

Voltammetric Technique	Advantages	Limitations	Elements	Detection Limit
Cyclic Voltammetry (CV)	- fast and simple	- applicable for electroactive compounds	Cd, Cu, Zn, Bi, V, Pb, Sn	down to 10^{-5} mol/L
Differential Pulse Voltammetry (DPV)	- enhance faradaic current, minimize capacitive current	- applicable for electroactive compounds	Tl, Ag, Hg, Pb, Zn, Bi,Cd, Sn, Cu	down to 10^{-11} mol/L
Linear Sweep Voltammetry (LSV)	- fast and simple	- applicable for electroactive compounds	Cd, Cu, Zn, Bi, V, Mo, Pb, Sn, Ti, Fe, Ga, As, Se, Br, I, In	down to 10^{-5} mol/L
Adsorptive Stripping Voltammetry (AdSV)	- effective for hydrophobic and amphiphilic compounds (metal complexes with organic ligand)	- requires preconcentration step	Al, Ni, Co, Pd, Pt, Cr, Fe, Si	down to 10^{-11} mol/L
Square Wave Voltammetry (SWV)	- enhance signal to noise ratio	- applicable for electroactive compounds	S, Se, Te, Cl, Br, I Fe, W, Mo, Cd, Cu	down to 10^{-11} mol/L

The CV method, which was demonstrated by Bordonaba & Terry [24] as the usual method choice in antioxidant analysis, was utilized in examining phenolic compounds in various berry juices, such as grape and blueberry [25], [26]. Comparison of standard results and CV shows agreement in values, hence, CV could be applied as an alternative to standard methods in antioxidant determination. On the other hand, the method DPV was found to be useful in detecting organic acids. Simultaneous determination of these acids without any interference and sensitivity reduction was concluded to be possible with DPV [27]. Aside from this, the method was capable of detecting flavonoids and phenolic acids in fruit juices [28]. These studies acquired promising results, hence, DPV can be used as an excellent alternative to standard antioxidant analysis methods. Similarly, AdSV was capable of detecting quercetin, which could be a good alternative analytical technique. Its satisfactory selectivity and sensitivity were proved in its interference test and low LOD. Additionally, the method Anodic Stripping Differential Pulse Voltammetry (ASDPV) was also used to investigate quercetin in blackcurrant and cranberry juice samples using a pretreated electrode [27]. Despite these studies utilizing DPV, AdSV, and ASDPV, these methods are not commonly used.

SWV is the most popular in antioxidant determination among the reviewed articles. Compared to the conventional antioxidant determination methods, square wave voltammetry (SWV) is more selective, faster and cheaper. In SWV, a square-wave pulse is superponated to a staircase wave. In this technique, the applied pulse duration is equal to the length of staircase. Half of the staircase length corresponds to the forward pulse and the other half to the return square wave pulse. The current signal is the difference between the current at the ends of the forward and returns square-wave pulse. This technique was developed to increase the signal to noise ratio by amplifying Faradaic current and reducing parasitic charging current [29]. SWV gives sharper and defined peaks since the timing is frequency dependent, an increase in frequency increases in faradaic current as the time constant is decreased [30]. This was demonstrated in multiple studies, such as those of Abdel-Hamid & Newair [28], Cuartero *et al.* [31], and Silva *et al.* [32] where SWV was compared with the colorimetric method and high performance liquid chromatography (HPLC) in determining antioxidant substances in juices. Simultaneous determination of four organic acids, such as citric acid (CA), lactic acid (LA), malic acid (MA) and tartaric acid (TA), was carried out using SWV [32]. Aside from exhibiting improved detection compared to traditional methods, SWV was observed to remain superior and more favorable as compared to CV for antioxidant assays due to more defined detection peaks associated with the better signal to noise ratio. It is said to have the best characteristics of several voltammetric methods which, aside from sharing similar advantages with CV, include easy detection of reversible oxidation reaction during scanning and determination of oxidation and reduction peaks [20]. These findings substantiate the effectiveness of SWV as the most favored method for antioxidant determination.

2.2 *Comparison of electrode performance*

The utilization of carbon electrodes, particularly carbon paste electrode (CPE), has been the most exploited type of WE especially for older studies published from 2004 to the 2011 [19]. Hence, there is a large potential for further exploration and development of modified electrodes to bring forth numerous new benefits for voltammetry in vitamins and antioxidant determination. These effects of electrode modification on electrode performance were further investigated through the comparison of limit of detection (LOD) and the recovery rate (RR) obtained from voltammetric determination of various kinds fruit juices spiked with a specific component as seen in Figure 2. Among the studies which have utilized the conventional CPE for ascorbic acid (AA) determination, a lowest LOD value of 2.2×10^{-11} M with a 99.4% average RR was acquired from the study.

In contrast to AA determination, there is a significant difference in electrode performance between the bare GCE and modified electrodes, specifically for modified CPEs. Despite the modified GCE showing a slightly higher LOD as compared to the bare electrode, the $CoFe_2O_4$ NPs/ILs/CPE was employed for rutin determination and a LOD value of 3.0×10^{-11} M and average recovery rate of 99.8%, as shown in Figure 3 [33]. This was performed using SWV, and has exhibited the most exemplary electrode performance among all electrodes utilized for antioxidant detection, specifically for rutin. Furthermore, it can also be observed that for

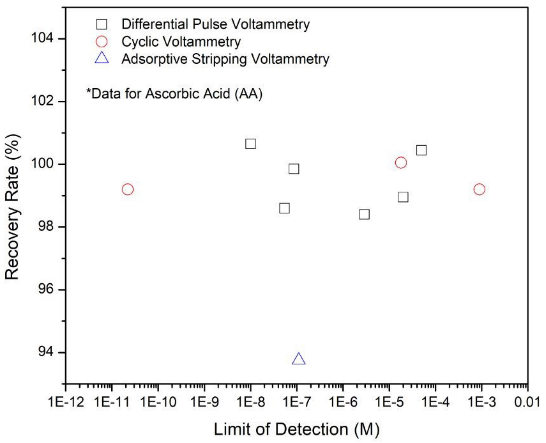

Figure 2: Detection limit and recovery rate for the determination of ascorbic acid in juices using DPV, CV, AdSV, SWV and ASDPV voltammetric techniques.

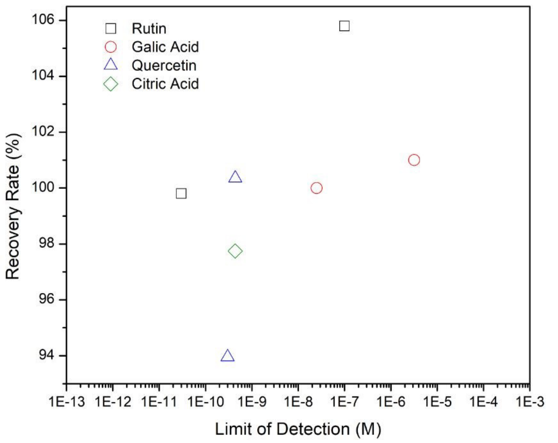

Figure 3: Detection limit and recovery rate for the determination of rutin, GA, quercetin and CA in juices using DPV, CV, AdSV, SWV and ASDPV voltammetric techniques.

the determination of GA, the ZrO_2/ChCl/AuNPs/CPE has also performed better than the PGA/MWCNT/GCE with a lower LOD of 2.5×10^{-8} M and an acceptable RR of 97.9–102.1% [24].

CPEs perform better as compared to GCEs, modified or bare, for antioxidant determination in general. Further studies are recommended to provide absolute certainty to this conclusion. Overall, these still validate the effect of modification on the increase of electrode performance. However, it can be speculated that electrode-method relationships could be a factor that brings the slight discrepancy and ambiguity in the determination of AA.

However, due to the numerous options brought forth by electrodes and electrode modifications, it must also be expected that pretreatments will differ based on the chosen option. With that, further studies must explore the corresponding pretreatment that will work best with the chosen electrode.

2.3 Parametric study on electrochemical detection

The reviewed studies observed various parameters in investigating the electrode performance to detect antioxidants and vitamins. The majority of the studies considered the pH value as a contributing factor in electrochemical detection (Table 2). In a study conducted by Tadese *et al.* [16], the pH value was optimized to obtain the electrocatalytic oxidation of AA and observed that its electrochemical behavior is dependent on the pH value of the electrolyte. The effect of pH was then investigated using CV where the optimal pH value obtained was pH 5.0.

Table 2: Obtained optimal pH values for AA and antioxidant determination

Method	Component	Working Electrode	pH	Ref.
Cyclic Voltammetry (CV)	Ascorbic acid	APMCNTPE	7.0	[16]
Cyclic Voltammetry (CV)	Ascorbic acid	CPE	5.0	[19]
Differential Pulse Voltammetry (DPV)	Ascorbic acid	AuSNPS/CeO/SNGC	7.0	[21]
Cyclic Voltammetry (CV)	Phenols	Pt Strip	3.0	[26]
Differentail Pulse Voltammetry (DPV)	Gallic acid	ZrO_2/ChCl/AuNPs/CPE	3.0	[27]
Adsorptive Stripping Voltammetry (AdSV)	Quercetin	BDDE	2.0–5.0	[31]
Anodic Stripping Differential Pulse Voltammetry (ASDVP)	Quercetin	PGE	6.0	[32]
Square Wave Voltammetry (SWV)	Gallic acid	PGA/MWCNT/GCE	2.6	[33]
Square Wave Voltammetry (SWV)	CA, LA, MA, TA	CoPC/CPE	4.5	[34]
Square Wave Voltammetry (SWV)	Rutin	CoFe2O4 NPs/ILs/CPE	6.0	[35]
Differentail Pulse Voltammetry (DPV)	Ascorbic acid	GCE	3.5	[36]

*APMCNTPE - p-aminophenol-modified CN paste electrode; CoPC/CPE - cobalt phthalocyanine-modified carbon paste electrode

Meanwhile, Gheibi *et al.* [13] assessed the effect of pH on peak currents and peak potentials in the AA determination using p-aminophenol modified carbon nanotubes paste electrode (APMCNTPE), obtaining a rather neutral optimal value with a pH level of 7.0. Thus, establishing an optimal condition for the electrocatalytic oxidation of AA at the electrode surface. Both studies were able to determine the optimal pH value in AA determination with a modified electrode; although their findings do not exactly align with each other. The AA determination using voltammetry can also make use of any supporting electrolyte with very acidic pH levels that are as acidic as pH 1.5–3.5 [37], [11].

It was found that the height of the peak increased as the pH was also increased, with the current observed only within the range of pH 2.0–5.0. In a study conducted by Abdullah *et al.* [26], the redox behavior of quercetin was investigated using AdSV with a BDDE. Additionally, the optimal value obtained for polyphenol contents and organic acids (citric acid (CA), lactic acid (LA), malic acid (MA), and tartaric acid (TA)) were pH 2.6 and pH 4.5, respectively [28], [32].

3 Electrochemical Detection of Trace Metals

Although trace metals can be inherently exhibited by food products and are able to bring forth health benefits to humans, they can be harmful when excessive levels are consumed. Oftentimes, the substantial amounts of these metals are due to the processing and manufacturing of these fruit juices, soil cultivation and other agricultural factors. Research on this aspect can be attributed to the need for regulation and monitoring to avoid concentration falling beyond the safe limit. Metals, such as Sn^{2+}, Cu^{2+}, Pb^{2+}, and Hg^{2+} have been determined in previous studies, however, Cd^{2+} and Pb^{2+} are the most frequently examined metals across the reviewed studies. Both of which are heavy metals that can potentially pose serious threats to the consumer' healths when consumed at excessive levels, and were also found to be highly prevalent among fruit juices [34].

The commonly used analytical methods to measure trace metals are atomic absorption spectroscopy (AAS), inductively-coupled plasma mass spectrometry (ICP-MS) and inductively-coupled plasma atomic emission spectrometry (ICP-AES). However, these techniques are expensive, time consuming and require trained personnel to operate compared with voltammetric methods. Figure 4 shows the detection limit of various heavy metals present in juices using various voltammetric techniques.

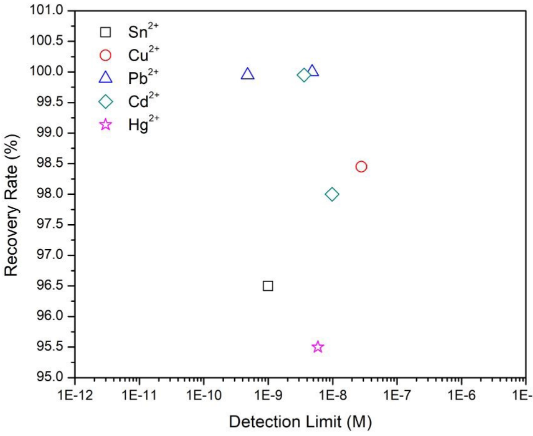

Figure 4: Detection limit and recovery rate of various heavy metals present in fruit juices.

ASV is considered to be one of the efficient methods in quantifying metal contaminants [35]. This claim is substantiated by several reviewed literatures that have successfully utilized ASV method in trace metal analysis. Sobhanardakani *et al.* [36] used ASV in the quantification of tin using a modified electrode, where spiked fruit juice samples showed good recoveries. Likewise, different variations of ASV, such as square wave anodic stripping voltammetry (SWASV) and differential pulse anodic stripping voltammetry (DPASV) showed satisfactory performance in terms of sensitivity and selectivity in determining Pb^{2+}, Cd^{2+}, and Cu^{2+} ions respectively [38]–[40]. On the other hand, a study made by Zhang *et al.* [41] utilized differential pulse stripping voltammetry (DPSV) in making a smartphone-based platform that can determine metals in liquid products. Results of the Cd^{2+}, Pb^{2+}, and Hg^{2+} levels show agreement with results from standard technique, such as atomic absorption spectroscopy (AAS), hence, it shows that DPSV method could be used as an alternative to detect these trace metals. Furthermore, this study can be compared to that of Malakootian *et al.* [39], given that both studies used apple juice for sample analysis in Pb^{2+} and Cd^{2+} detection. Although both methods exhibited great performance in determining the concentration of the two metals, a comparison of the average recovery values reveal that the method SWASV is more selective than DPSV. However, the electrodes used, as well as the parameters, in both studies should be taken into account as these may also imply significant effects on the selectivity of the voltammetric technique.

Meanwhile, a unique method, competitive ligand exchange-adsorptive stripping voltammetry (CLEAdSV) was used by Magnier *et al.* [42] to investigate aluminum speciation in orange and tomato juices. Despite being reported to be time- consuming due to its reliance on titration curves, it was said to allow simultaneous determination of electroactive aluminum fraction and complexing capacity of the samples [42]. The flexibility of the different variations of stripping voltammetry is advantageous for various electrodes used in detecting trace metals.

In the modification of electrodes, cupferron was a common substance in the studies conducted by Sobhanardakani *et al.* [43] and Magnier *et al.* [42] to modify an MWCNT and a ligand onto HMDE. Cupferron is an ammonium salt of N-nitroso-N-phenylhydroxylamine. The addition of cupferron to MWCNT was found to provide a wide linear dynamic range for tin determination. Another study that used modified electrodes as an organic sensor to detect Cu^{2+} in pomegranate juices by introducing INID to a bare GCE, resulted in a higher electron-transfer resistance and lower surface-active area [40]. Its selectivity increased which enabled it to specifically determine Cu^{2+} despite the presence of other metal ions.

Similar to other studies, these electrodes were also tested by measuring a variety of spiked fruit juices in order to test their performance, the extracted data are presented in Table 3. Among collated values, it can be observed that the limit of detection (LOD) values appear in close precision with no datum higher than 2.8×10^{-8} M. It signifies that all developed electrodes had relatively high levels of sensitivity. The Eu^{3+} doped NiP/CPE used by a similar study when coupled with SWASV exhibited superior performance for Pb^{2+} determination with the lowest LOD and average RR value of 4.8×10^{-10} M and 99.95%, respectively [39].

The close precision of LOD and RR values also signify the high sensitivity, selectivity, and general performance of the modified electrodes, especially given their low LODs and acceptable RR ranges. This affirms the positive enhancements brought by modifications, specifically on the use of the polymers and organic compounds, emphasizing the great potential of these substances possess for future research on trace metal analysis.

4 Electrochemical Detection of Trace Additives

Additives are common components in the food industry, they have been profoundly researched when it came to a variety of foods. However, they seemed to be in a minority components of fruit juices. These are most often present in processed foods to fulfill purposes, such as aesthetic (i.e. dyes) or flavoring enhancements, and fruit juices, especially commercialized variants, are of no exception. Once present in excessive amounts, these substances can pose harmful effects to humans, hence, requiring the need for analysis of additives in food products.

Table 3: Performance of electrodes in the determination of trace metals in fruit juices

Method	Component	Working Electrode	Limit of Detection	Recovery Rate	Ref.
SWASV	Cd^{2+}	Eu^{3+}/NiO/CPE	3.6×10^{-9}	96.7–103.2	[39]
SWASV	Pb^{2+}	Eu^{3+}/NiO/CPE	4.8×10^{-10}	96.7–103.2	[39]
ASV	Sn	Cupferron/MWCNT	1.0×10^{-9}	93.5–99.5	[43]
DPASV	Cu^{2+}	INID/GCE	2.8×10^{-8}	95.0–101.9	[40]
DPSV	Cd^{2+}	AuNPs/ME	9.8×10^{-9}	99.0–102.0 (orange) 94.0–96.0 (apple)	[41]
DPSV	Pb^{2+}	AuNPs/ME	4.8×10^{-9}	96.0–98.0 (orange) 101.0–104.0 (apple)	[41]
DPSV	Hg^{2+}	AuNPs/ME	5.9×10^{-9}	95.0–96.0 (orange) 95.0–96.0 (apple)	[41]
CLE - AdSV	Al	Ligand cupferron/HMDE	5.0×10^{-8} to 1.0×10^{-7}	-	[42]

*Cupferron/MWCNT - cupferron modified multiwalled carbon nanotubes; INID/GCE - indenoindole modified glass carbon electrode ; Eu^{3+}/NiO/CPE - europium doped nickel oxide modified carbon paste electrode; AuNPS/ME - gold nanoparticles modified microdisc electrode; ligand cupferron/HMDE - ligand cupferron onto hanging mercury drop electrode.

However, only three articles have been classified to focus on additive determination, all of which focus on different additives in fruit juices. Thus, it is evident that this specific field in food analysis is yet to be explored and investigated further.

Among the existing literature at present, the determination of additives in fruit juices has been carried out using both SWV and DPV. The latter method was utilized for the determination of rhodamine B (RhB) and salicylic acid (SA), respectively. The process bears its benefits in the fact that it did not require complicated and time-consuming steps to have a successful determination of the aforementioned substances [44], [45]. DPV was further characterized by low cost and portable equipment, making it suitable for onsite analysis [44]. Recovery studies were done using DPV and revealed the method to be sensitive and reliable in both RhB and SA analysis. Given the advantages brought forth by this method, its effectiveness also entails a high potential for it to exhibit great potential in the determination of additives in general.

On the other hand, Silva *et al.* [46] chose SWV over DPV in sulfite determination for the reason that it allows faster measurements. No interference was reported in pineapple juice, unlike red grape juice where a peak was observed to be almost identical to the sulfite reduction potential. Despite this strong interference in a singular juice sample, the method was found to produce results of close congruence with standard methods, therefore implying SWV to still be selective to a certain extent depending on the sample being observed. These studies prove the two mentioned voltammetric methods to be effective in this field of component detection.

To test the efficiency of the listed electrodes and methods, fruit juice samples spiked with various kinds of additives were examined. The results from electrochemical detection have been tabulated in Table 4. Similar to AA determination, the table shows that a bare GCE has prevailed above the other two electrodes for RhB detection when paired with DPV, obtaining LOD and average RR values of 6.1 × 10^{-9} M and 99.2%, respectively [44]. This showed a remarkable difference in electrode performance, especially in terms of sensitivity, as compared to the other two with higher LOD values. Despite proving the excellent selectivity exhibited by the MWCNT/CPE with SWV having the most accurate RR with a range of 96.0–100% with spiked pineapple juice [46], the obtained LOD value was still relatively higher as compared to the aforementioned bare electrode.

Although a favorable electrode-method combination exhibited promising results when it came to additive determination, it is still recommended for future researchers to conduct more studies to affirm its effectiveness when compared to a wider scope of electrodes employed for the same objective. Additives found in fruit juices, namely SO_2, SA, and RhB, were all successfully determined with buffer solutions of pH 1.0, pH 2.0, and pH 4.0, respectively [44]–[46]. Although it is still subject to further research and exploration, all studies commonly used carbon electrodes as voltammetric sensors.

5 Electrochemical Detection of Pesticides and Herbicides

Evidently, fruit juices are derived from fruits that often have the possibility of being exposed to toxic chemicals, which constitute herbicides and pesticides used in agriculture. Despite being beneficial for the prevention of weeds and pests which may infestate crops, there is a high possibility for remains of such substances to bring forth negative effects upon consumption. Voltammetry has been an effective tool that has been used for the detection of these pesticides and herbicides, which further poses its functionality in attaining food safety. There is no specific variant of these substances that have been repetitively determined across the reviewed articles. However, these variations also prove their versatility and efficiency in the determination of pesticides and herbicides in fruit juices.

Table 4: Performance of electrodes in determination of additives in fruit juices

Method	Component	Working Electrode	Limit of Detection (M)	Recovery Rate (%)	pH	Ref.
DPV	RhB	GCE	6.1 × 10^{-9}	95.5–102.9	4.0	[44]
DPV	Salicylic Acid (SA)	SPCE	1.6 × 10^{-5}	84.1	2.0	[45]
SWV	SO_2	MWCNT/CPE	1.6 × 10^{-5}	96.0–100.0	1.0	[46]

Aside from their capability to determine vitamins, antioxidants and additive components, DPV and SWV were also found to be useful in determining pesticides. These electrochemical methods were observed to be more advantageous, because unlike conventional techniques, they provide an inexpensive, simple and quick alternative that has high sensitivity and selectivity [47]–[49]. Similar to vitamin determination, the prominent method used in determining pesticides is DPV. Rapini *et al.* [50] and Maximiano *et al.* [51] used this method in determining the pesticides thiram (THI) and carbendazim (MBC), and acetamiprid, respectively. Both studies relied on HPLC in obtaining reference data which showed good correspondence with the DPV results, indicating effectiveness and accuracy. DPV was also utilized in detecting diphenylamine (DPA) in apple juice where satisfactory recovery values were obtained, implying compatibility with the proposed sensor and excellent practicability to DPA detection [48]. These successful studies using DPV demonstrate the reliability and usefulness of the method in pesticide determination. Figure 5 shows the detection limit and recovery rate of these pesticides in various electrodes.

Tefera *et al.* [47] and De Souza & Machado [48] were successful in applying SWV in determining the pesticides paraquat and phenothrin in fruit juices, respectively. Reference data for paraquat determination were acquired through CV and were found to be aligned with the SWV results. Consequently, the usage of CV as the method of obtaining reference data implies that this voltammetric method can also be applied for paraquat determination and can be possibly used for detecting pesticides in general. However, more studies focusing on this method are needed in order to prove its properties and usefulness.

Meanwhile, a study by Thriveni *et al.* [49] used DPAdSV to determine the pesticide oryzalin in spiked grape juice. The proposed method acquired a satisfactory recovery range where high accuracy and reproducibility were observed. However, due to the lack of application like CV, further research and more information are needed to gauge its application in the field of pesticide determination.

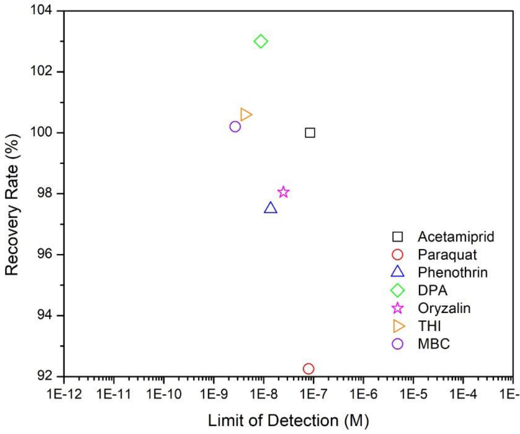

Figure 5: Detection limit and recovery rate of various pesticides and herbicides in fruit juices.

It was observed that the majority of the studies opted to modify their electrodes with a substance that increased its conductivity, which appeared to be associated with an improved sensitivity due to higher electroanalytical activity. Rapini *et al.* [50] developed a modified GSPE by electroplating the electrode with polyaniline film (PANI) and gold nanoparticles (AuNPs). Conductivity notably increased, consequently improving the sensitivity of the sensor due to a smoother electron transfer process. The charge transfer resistance of the electrode also increased upon the addition of PANI and AuNPs compared to its bare GSPE. As seen in Table 5, the modified electrode worked best with apricot juice with a RR of 90–110%, which is the closest to the optimal value of 100%. Similarly, a study by Sakthievel *et al.* [52] made use of adding Eu^{3+} to the commonly used $MoSe_2$ to create a $EuMoSe_2$/GCE in the determination of DPA. Eu^{3+} itself already exhibits high electrocatalytic activity. With the combination of the high electrical conductivity of $MoSe_2$, the modified electrode displayed an enhancement in electron transfer kinetics, which is evident in the values listed in Table 5. Meanwhile, the addition of thermally activated zeolite alongside sodium dodecyl sulfate (SDS) to CPE to create a ZMCPE increased the electrochemical processes occurring in the surface of the electrode, consequently increasing the electron transfer speed [51]. This is due to the adsorption of the surfactants on the surface, forming layers of it on the working electrode, which increased the value of the peak current and peak potential, indicating the better sensitivity and the better selectivity, respectively. Further studies regarding the effects of surfactants in electrode modifications can be explored by using cationic and nonionic surfactants and by varying their quantities.

The ZMCPE has exhibited superior performance

Table 5: Performance of electrodes in determination of pesticides and herbicides in fruit juices

Method	Component	Working Electrode	Limit of Detection (M)	Recovery Rate (%)	pH	Ref.
SWV	Phenothrin	GO/PPy/GCE	1.38×10^{-8}	90.0–105.0	6.5	[47]
SWV	Paraquat	Au microelectrodes	8×10^{-8}	89.5–95	5.0	[48]
DP - AdSV	Oryzalin	HMDE	2.5×10^{-8}	97.8–98.3	6.0	[49]
DPV	Acetamiprid	PANI/AuNPs/GSPE	8.6×10^{-8}	90–110	-	[50]
DPV	DPA	EuMoSe2/GCE	8.8×10^{-9}	99.0–107.0	7.0	[52]
DPV	THI	ZMCPE	4.2×10^{-9}	99.3–101.9	5.0	[51]
DPV	MBC	ZMCPE	2.7×10^{-9}	98.6–101.8	5.0	[51]

*PANI/AuNPs/GSPE - polyaniline film and gold nanoparticles modified graphite screen-printed electrode; GO/PPy/GCE graphene-oxide polypyrrole modified glassy carbon electrode; HMDE- ZMCPE - zeolite modified carbon paste electrode.

with high sensitivity and selectivity, making it an accurate electrode-method combination with a great potential for the determination of pesticides and herbicides in general. This further confirms the positive enhancements in terms of sensitivity and selectivity brought by the added surfactants onto a bare GCE. The performance of DPV for pesticide and herbicide determination is further asserted given its compatibility and effectiveness, even when used with a variety of modified electrodes.

6 Conclusions

Voltammetry has proven to be an effective technique for the electrochemical determination of various food components in fruit juices. The technique is highly dependent on the specific voltammetric method, electrode, and the parameters, such as pH of the analyte and scan rate. The voltammetric methods that displayed superior performance in the determination of the reviewed compounds were SV for trace metals; DPV for vitamins and pesticides; SWV for antioxidants; and both DPV and SWV for additives. Recent studies showed that electrode modifications improve the efficiency of the method with lower LOD values and better recovery rates due to its altered properties that allowed it to overcome common problems in electrochemistry, such as polymeric film formation and passivation. The optimal pH of the electrolytes ranges from low to neutral (1.0 to 7.5). Scan rate values did not observe any quantitative trend. However, the relationship of most scan rates to the peak currents indicated the electrochemical process involved. Therefore, the performance of voltammetry in detecting components in fruit juices may be further improved by ascertaining the compatibility of the method, electrode, and parameters.

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