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The Role of Voltammetric Analysis in the Wine Industry †

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Abstract: Voltammetry has been used in many industries and has been a popular method of food analysis in recent years. Its high sensitivity, rapid analysis, availability in the wide variety of concentrations and temperature posed positive potential in the wine industry. With standardized methods of food analysis bulky and time-consuming for the fast market demand, the main purpose of this study is to gain an understanding of the possible benefits of voltammetry can provide to the wine industry. The review paper focused its discussion on the different voltammetric methods, parametric conditions, and electrochemical behavior of detected compounds wherein wine was the main substance of origin. Particularly, the limit of detection (LOD), initial voltage peak, pH levels, working electrodes, and their respective reagents were taken into account to determine the applicable methods that can be utilized in the wine industry. The study could serve as a point of reference for future research into the topic.

Keywords: Voltammetry; wine industry; electrode; electrochemical detection

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1. Introduction

Voltammetry is the analytical method that gives us information about "analyte through electrical currents obtained from a potential variation" [1]. This was first brought about in the 1920s by an experiment conducted by Heyrovský, which measures the surface tension of mercury that provided the information about the nature of the liquid-metal interface. This capillary electrometer could also serve as a sensitive null-point detector for balancing potentiometric bridges [2].

Today Voltammetry has expanded to greater variations such as linear sweep, hydrodynamic, stripping, pulse and cyclic voltammetry (CV). The most common voltammetry methods used by the food industry are cyclic and pulse voltammetry. Cyclic voltammetry is an electrochemical technique which measures the current that develops in an electrochemical cell under conditions where voltage is in excess of that predicted by the Nernst equation. On the other hand, pulse voltammetry utilizes a regularly increasing pulse height that is applied at periodic intervals. These methods have been utilized to locate and accurately measure substances like polyphenols characterization and determination of polyphenols content in wine products [3]. Food analysis has used systems that were put into operation for the guarantee, standardization, and safety of its consumers. There were two (2) prominent methods of food analysis namely gas (GC) and liquid (HPLC) chromatography used alongside statistical tools to examine the correlation between samples. Although both GC and HPLC techniques are widely used in wine analysis which are based on traditional separations frequently coupled online with other analytical devices, the main drawback is its non-reliability in analyzing non-volatile substances [4]. Recent advance technique like capillary electrophoresis and supercritical fluid chromatography have also been used for wine determinations, but they are still in an early stage of application [5].

The recent demand for voltammetry in the food industry is largely due to the demand for faster and more efficient systems providing faster and more precise results from a higher sensitivity to environmental monitoring as the world moves forward in technological advancements [5]. Aside from its usage in the food industry, voltammetry has also been seen being used in analytical chemistry and industrial processes such as pharmaceuticals.

The numerous methods of voltammetric analysis have sparked a large number of studies to be conducted with different samples, commonly food substances. Polyphenols and antioxidants that are commonly found in wines have been the subject of research, as wines also possess potentially harmful chemicals such as sulfides which are used to preserve the freshness and taste of red wines [6]. Other properties such as oxidation states and oxygen consumption can be monitored by voltammetry [7]. Due to the flexible nature and low cost of common voltammetric set-ups, the system of determination has many advantages in the wine industry. This study benefits to those that will utilize the findings to further the investigation of the study of Voltammetry as it would allow researchers an overview of the past and present trends of voltammetry, serving as a point of reference for future research.

As the paper will only cover voltammetry in the wine industry, its possible uses, effects, and outcome; studies that use voltammetry for industries excluding the wine industry, papers that do not utilize wine as the main substance for determination, and those in which their full text cannot be accessed by the public will be deemed ineligible for review. Research papers cited will have published dates that are from the year 2000-to 2021, to ensure the relevance and trends of the subject are accurate and objective. Studies in which wine is not the main component for review will not be included for review.

2. Methodology

The systematic literature review adapted by Okili and Schabram (2015) [8] was utilized in the collection and screening of eligible literature as seen in Figure 1. With four (4) main steps being Planning, Selection, Extraction, and Execution, all papers included are extensively reviewed for inclusion in the study. Planning begins by determining the proper keywords factors to be extracted from the paper, this includes the publishing date to fit into the given timeframe. The selection of papers was done automatically through technology-based databases, then papers were manually selected as they fit the criteria of the systematic review. Extraction of information was then conducted manually for each paper and cross-referenced to ensure information was accurate and aligned with the objectives of the paper. Execution of the systematic literature review was then conducted with the data retrieved from papers, highlighting trends and common factors seen.

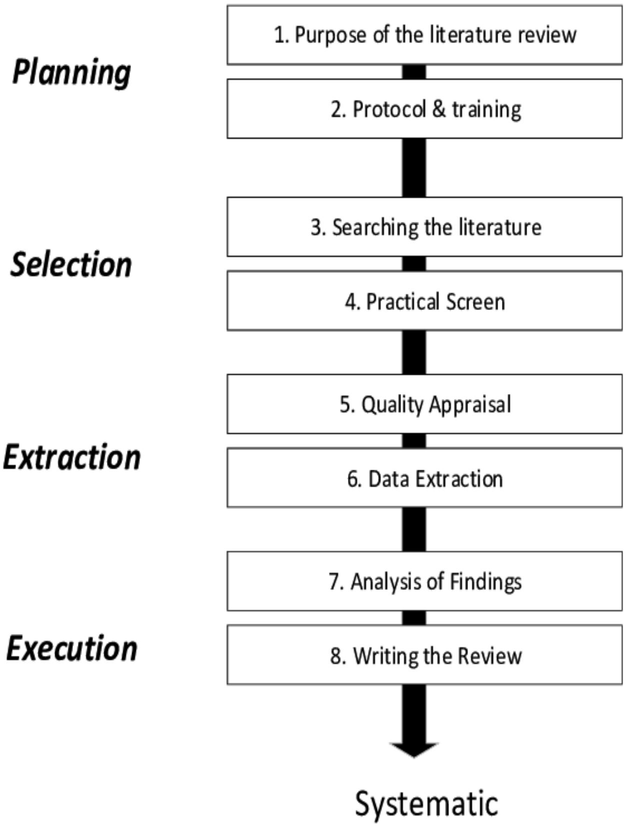

Figure 1. Adapted Systematic Literature Review from Okili and Schabram (2015) [8].

The Preferred Reporting Items for Systematic reviews and Meta-Analyses (PRISMA) guidelines were also observed for the data collection procedure of the study, with the final version seen in Figure 2. The extensive screening was done to ensure only relevant and important papers were used in this study; sixty-nine (69) papers were identified from online records. Initial screening was accomplished using the keywords of 'voltammetry', 'wine', 'substances', 'sensor' and 'electrode'; duplicate papers were manually removed from the database alongside papers that do not possess relevant information towards the given topic. Once the papers have passed the initial screening they are retrieved for further analysis, only one paper was excluded from the retrieval process (n=1). The final screening for eligibility was done by individually reading abstracts of screened papers, four (4) papers were excluded from eligibility. This is due to the fact that two (2) papers did not explicitly use voltammetry to identify the compound, another paper (1) did not use wine as the main substance to identify components, and the final paper was excluded since the paper solely focused on oxidation levels, instead of tangible substances. To determine the most suitable method of determination for each compound, factors such as voltametric methods, working electrodes, the limit of detection (LOD), and pH levels were reviewed from each paper.

3. Results and Discussion

3.1. Electrochemical Detection of Components

According to Cordova and Sumpio (2009) [6], a generic bottle of red wine is composed of approximately 1.8 g/L of total polyphenols (TP) which is an important component of wine products that needs to be detected to ensure quality, while a bottle of commercial white wine consists of only about 0.2 g/L to 0.3 g/L of TP. Thus, a glass of red wine would contain around 200 mg of polyphenol, and 30 mg in a glass of white wine. In red wine, the majority of the phenols are composed of flavonoids.

2,4,6-trichloroanisole (TCA) is a low threshold sensory metabolite originating from the family of chlorophenols usually by means of natural fungal strains in cork. As cork stoppers are widely used by a plethora of wine companies, 'cork taint' is a common defect associated with the spread of TCA throughout the bottle, on average, costing the wine industry over 10 billion USD in losses worldwide [9].

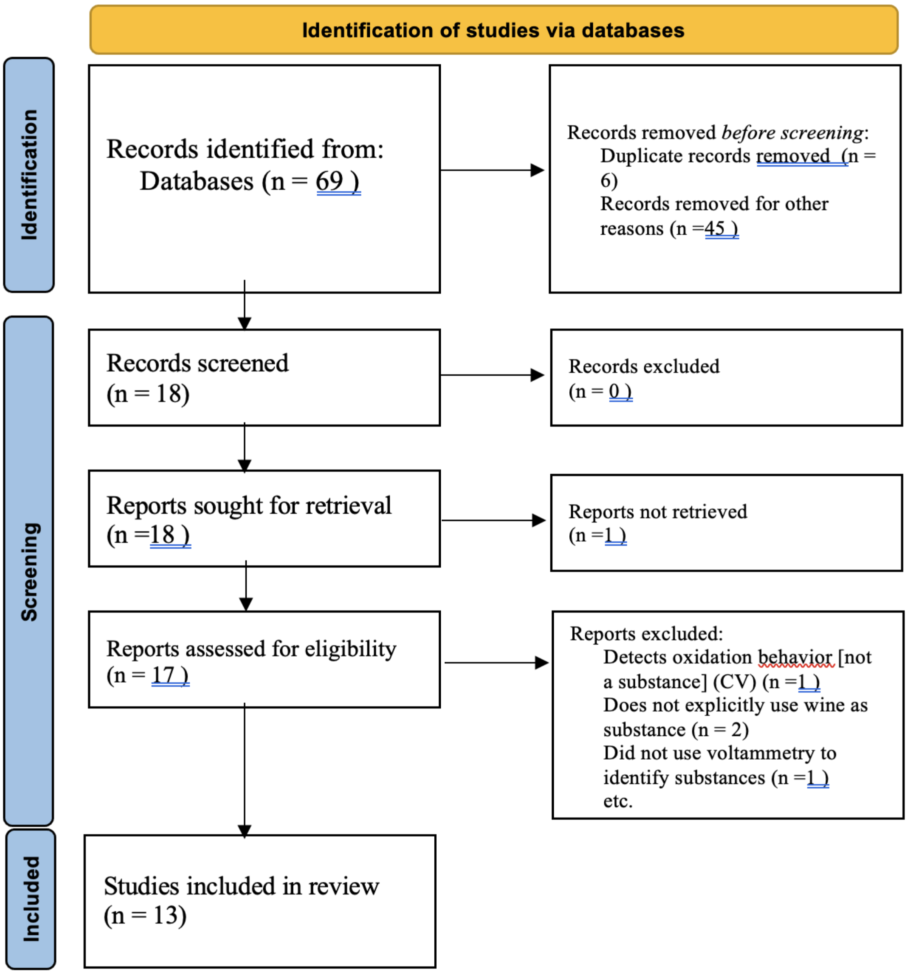

Figure 2. Adapted PRISMA Diagram used in the study.

Sulfur dioxide (SO_2) is one of the most common compounds found in wine. Wines that contain more than 10 mg/L of SO_2 should not be consumed on a regular basis, as too much SO_2 may cause adverse side effects. Much like voltammetry, SO_2 can be easily influenced by pH levels, as the pH in wine increases, there is a higher percentage of SO_2 content and vice versa [10]. Trace minerals and metals are low in number in wines, with the most prominent trace mineral found being manganese. Manganese (II) concentrations range from 0.4 to 7.8 mg/L for red wines, while white wines have, on average, 1.3 mg/L [11].

3.2. Method of Determination

Of the thirteen (13) studies reviewed for wine components, a total of six (6) studies made use of cyclic voltammetry, two (2) for differential pulse, four (4) for square wave, and one (1) for stripping voltammetry, as seen in Figure 3.

In determining the polyphenol content of wine, cyclic voltammetry (CV) was used most frequently. However, Vilas-Boas et al. (2019) [12] claimed that differential pulse voltammetry (DPV) is a better voltammetric method to use between DPV and CV because it has a lower sensitivity of 64% to sulfur dioxide - which may interfere with results for polyphenol activity [12] compared to the 141% of CV.

For metal detection, such as manganese (II), stripping voltammetry (SV) was utilized as the voltammetric method. Sulfur content and sulfur dioxide were utilized in three (3) studies, two of which used square wave voltammetry (SWV) and the others used CV. Ascorbic acid was found in two (2) studies using both CV and SWV. Lastly, 2,4,6-trichloroanisole (TCA) was found in one study with CV as its method of choice.

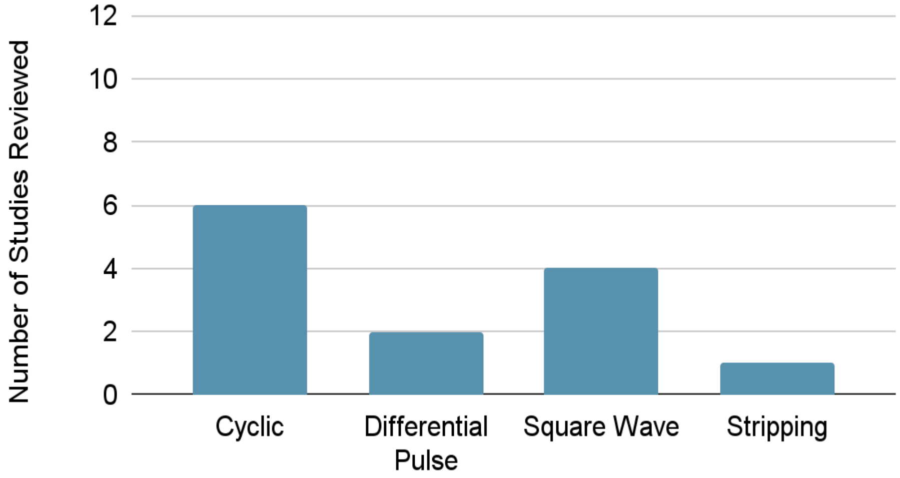

Figure 3. Wine component determination.

3.3. Comparison of Electrode Performance

As seen in Table 1, the pH levels for sulphides were reported to be >1.0 by Ramos et al. (2016) [13] which is relatively low, while total sulphur dioxide was recorded at pH 3.3 by Makhitkina and Kilmartin (2010) [14] who also recorded peak voltages at 1120 mV using CV. The limit of determination (LOD) for free and total sulphur dioxide was recorded at 3 mg/L, while sulphides were recorded at 0.4 mg/L showing how flexible SWV can be. Both studies have noted that their respective LODs can be easily increased or decreased depending on the extraction time utilized [15].

All pH levels for and flavonoids and polyphenols Table 2, on the other hand, were reported to be between 3.4 and 3.76. Catechins show a common cathodic peak at around 400-500 mV using CV and increased to around 730-750 mV when DPV and SWV are employed. The LOD was lowest at 1. 77 mg/L with DPV [16-17]. With the DPV voltammograms having narrower potential ranges, it can be inferred that CV is less efficient than DPV to differentiate wines with diverse compositions; DPV is not susceptible to residual current, while cyclic is sensitive to it [12].

Ascorbic acid (AA) Table 3 was determined using CV and SWV. Despite identical LOD and pH levels which were 4.14 mg/L and 7.0 respectively, CV displayed a higher first peak at 596 mV, while SWV at 450 mV [18-19]. Manganese (II) content was determined through SV, showing a peak of 550 mV with a low LOD of 0.6 mg/L.

4. Conclusion

Different methods and factors are optimal when used to determine certain components and in varying situations. Working electrodes, reagents, LOD, and methods of voltammetry all play important roles in the determination of components and should be analyzed further in future studies. Lead (Pb) and gold (Au) both have impressive electrocatalytic ability but have lower oxidation peaks and also serve the chance to contaminate the sample by oxidation and/or reduction. The most common working electrode is a glassy carbon electrode (GEC) due to the fact that it possesses the widest electrochemical window. CV is most suitable for polyphenols because of its accessibility to researchers and parameters of detection, while DPV may be better suited if the situation calls for a higher degree of sensitivity or flexibility.

Table 1. Performance of electrodes in the determination Metals and Sulfur based compounds found in wine.

Working Electrode	Component	Method	Peak	LOD	pH	Reference
AgCl/Ag (3M 78 KCl)	Free and Total sulfides	SWV	n.r,	3 mg/L	n.d.	[20]
Glassy-carbon (GC) electrode	Free sulfur dioxide	CV	1120 mV	n.r,	3.3	[14]
Graphite Electrode	Manganese (II)	SV	550 mV	0.6 mg/L	5-5.2	[17]
screen printed carbon	Sulphides	SWV	n.r,	0.4 mg L	>1.0	[13]

Table 2. Performance of electrodes in the determination of Polyphenols and Flavoniods found in wine.

Working Electrode	Component	Method	Peak	LOD	pH	Reference
Ag (Silver)	2,4,6-trichloroanisole	CV	n.r,	0.08-0.16 mg/L	n.d.	[9]
Glassy/ screen-printed carbon electrode	Catechin	CV	151mV	n.r	3.6	[19]
Glassy-carbon (GC) electrode	Catechins	DPV	750 mV	1.77 mg/L	n.r.	[16]
Glassy-carbon (GC) electrode	Polyphenols	CV	450 mV	n.r,	3.3	[14]
Glassy-carbon (GC) electrode	polyphenols	SWV	395 and 730 mV	n.r,	3.46-3.74	[15]
Glassy-carbon (GC) electrode	r total polyphenols (TP) content,	DPV	440-475 mV	1.77 mg/L	3.6	[21]

Table 3. Performance of electrodes in the determination of Ascorbic Acid (AA) found in wine.

Working Electrode	Component	Method	Peak	LOD	pH	Reference
Glassy-carbon (GC) electrode	AA	CV	596 mV	4.14 mg/L	7	[18]
Glassy-carbon (GC) electrode	AA	SWV	450 mV	4.14 mg/L	7	[18]

With this information in mind, future studies and research should be able to utilize a wider spectrum of voltammetric methods to identify different common wine components more efficiently. Finally, pulse techniques, such as DPV, is more advantageous since it is more sensitive than the linear sweep methods because there is minimization of the capacitive current.

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