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Review Article

The Role of Voltammetric Methods in Determination of Metals in Alcoholic Beverages: A Critical Review

CrossMark

دور طرق القياس الفولتومترية في تحديد المعادن في المشروبات الكحولية : مراجعة نقدية

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Abstract

Sources of metals in alcoholic beverages can be classified into primary and secondary sources. High concentrations of metals may lead to potential toxicity in cases of overconsumption over a long period of time. Metal content in alcoholic beverages may be used to ascertain their authenticity and geographic origin. Therefore, determination of metals in alcoholic beverages becomes a matter of utmost importance to forensic agencies.

Many analytical techniques are available for qualitative and quantitative estimation of metals. Stripping methods can be used, and anodic stripping voltammetry proves to be a cheap, sensitive, reliable and less time-consuming method. With advancements in the field of electrodes, the sensitivity of voltammetry has greatly increased, making it an ideal analytical technique for the analysis of metals in wines and other alcoholic beverages.

In the present review, an attempt has been made to critically review the various aspects of voltammetry with particular attention to stripping methods along with their application in determination of metal content in various alcoholic beverages.

Keywords: *Forensic Science, Voltammetric Methods, Authentication, Geographic Origin, Metal Content, Alcoholic Beverages.*

المستخلص

تلعب المعادن دورًا مهمًا في طعم وإدراك الخمور والمشروبات الكحولية الأخرى. ويمكن تصنيف مصادر المعادن في المشروبات الكحولية إلى مصادر أولية وثانوية. وقد يؤدي التركيز العالي للمعادن في المشروبات الكحولية إلى سمية محتملة في حالات الاستهلاك الزائد على مدى فترة زمنية طويلة. ومن جانب آخر فإن محتوى المشروبات الكحولية من المعادن يسهم في التأكد من موثوقيتها وأصلها الجغرافي. لذلك، يصبح تحديد المعادن في المشروبات الكحولية مسألة بالغة الأهمية لكل من صناعة النبيذ ووكالات الأدلة الجنائية.

هناك العديد من التقنيات التحليلية المتاحة للتقدير الكمي والنوعي للمعادن. ومع ذلك، أثبتت طرق التحليل الفولتامتري النزعي ولا سيما نزع القطب الموجب أنها وسيلة رخيصة، وحساسة وموثوقة وأقل استهلاكاً للوقت. ومع التقدم في مجال الأقطاب الكهربائية المتاحة، زادت حساسية القياسات الفولتاميترية لعدة أضعاف ما يجعلها تقنية تحليلية مثالية لتحليل المعادن في الخمور والمشروبات الكحولية الأخرى.

في هذه المراجعة العلمية، تمت محاولة إجراء مراجعة نقدية لجوانب مختلفة من القياس الفولتومتري مع إيلاء اهتمام خاص لطرق نزع الأقطاب جنباً إلى جنب مع تطبيقها في تحديد محتوى المعادن في مختلف المشروبات الكحولية.

الكلمات المفتاحية: علوم الأدلة الجنائية، الأساليب الفولتميترية، الموثوقية، المنشأ الجغرافي، محتوى المعادن، المشروبات الكحولية.

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1. Introduction

The analysis of wine and alcoholic beverages has developed vastly in the last few decades. Quality maintenance of wines and alcoholic beverages has become a primary concern for analytical chemists in the food industry [1]. The composition of alcoholic beverages primarily depends on various factors which are related to the specific area of production, including substrate used, raw materials, soil, climate, culture, variety of yeast, liquor manufacturing process, transport, and storage. The concentration of metals in many alcoholic beverages is an important factor, which can affect their conservation and therefore, their consumption. Minerals can find their way into alcoholic beverages through different sources during different processing procedures [2]. Sources of elements in alcoholic beverages (wines) can be classified into primary and secondary sources. Primary mineral content may vary due to the type of soil, the raw material used and climatic condition. The concentration of primary metals is characteristic and compromises the largest part of the metal content in wine. Secondary mineral content is based upon contamination due to the use of pesticides and fertilizers. Such contaminations are termed as geogenic contaminations, that is, originating from the soil and include factors related to crop growing practices and environmental pollution in the region [3]. Various endogenous and exogenous factors influencing the concentration of metals in wines and other alcoholic beverages have increasingly become the subject of investigation in order to prevent undesirable contamination [4–6].

1.1. Forensic Significance

Four aspects contribute to the forensic importance of the metal content in wines and beverages. These are 1) Characterization and differentiation of wines and other alcoholic beverages, 2) Toxicity due to high metal contents, 3) Authenticity of wines and other alcoholic beverages, and 4) Geographical origin of wines and other alcoholic beverages.

1.1.1 Characterization and differentiation of wines and other alcoholic beverages

One of the most important aspects of wine analysis is characterization and differentiation. To use metal concentration as a source of authentication, the concentration of a number of metals, including trace elements to major elements, must be determined. The distribution of the elements is determined in groups or classes having features, according to processing methods, or any other discriminating scheme. Using pattern recognition methods, a comparison should be made to characterize and discriminate the wines and beverages. Traceability of alcoholic beverages is based on comparison of different samples produced in the same production chain. For this purpose, isotopic analysis is often used, which involves isotopic fingerprinting of the samples of alcoholic beverages [7]. Camean et al. used atomic absorption spectroscopy to determine the metal content in twenty samples of Sherry brandies and twelve samples of Penedes brandies. The data of metal content was then subjected to principal component analysis (PCA) and other pattern recognition classification methods such as least discriminant analysis (LDA), and partial least square – disriminant analysis (PLS-DA). Fe, Mg, Cu, and Ca were found to be the most significant variables out of the eleven elements taken into consideration [8].

1.1.2 Toxicity due to high metal content

The concentration of metals in alcoholic beverages has a significant influence on their taste as well as the related metal toxicity [9]. Alcoholic beverages, especially wine, may be a source of metals for humans, if consumed in moderate quantities. Many elements such as Cu and Zn are essential to humans in low concentrations but potentially harmful in high concentrations. Many heavy metals such as Arsenic (As), Cadmium (Cd), Mercury (Hg), and Lead (Pb) have no nutritional value but may accumulate over time in the body and cause toxicity even in low concentrations [10]. Death may result due to the bioaccumulation of such heavy metals [11]. Metals are present in form of complexes which are attached to phenolic compounds in wine;

however, at low gastric pH, the metal ions are released for absorption. Once absorbed, these metal ions cause toxicity in the body [10].

1.1.3 Authenticity of wines and other alcoholic beverages

Often, the content declared on the product label does not match the contents present inside the bottle. In such cases, it becomes important to verify the contents present. This process of matching is known as authentication. Authentication of alcoholic beverages is of extreme importance in fraud cases, where liquor of low quality and unknown origin is used [12]. In the past, only organic ingredients were used to establish the authenticity of wines and beverages [13]. Adam et al. used concentrations of copper and other metals as indicators of the authenticity of scotch whiskeys. Copper content of malt and grain whiskeys were also compared. Malt whiskeys are produced in traditional copper stills, whereas grain whiskeys are produced using more industrial style patent stills. It was observed that whisky spirits contain copper in significantly greater quantities than other distilled spirits. Therefore, copper content can be used to differentiate malt whiskeys from blended scotch whiskeys and pure grain whiskeys [13]. However, more and more studies on different types of alcoholic beverages are required to accept or refute the role of metal content in establishing the authenticity of wines and beverages[14].

1.1.4 Geographical origin of wines and other alcoholic beverages

One of the main interests of analytical scientists related to food is the use of mineral content to characterize wines and beverages on the basis of their geographical origin, taking into account the relationship between the metallic content in the samples and soil composition [15]. Particular patterns of trace metals in alcoholic beverages act as territory markers and are often used for classifying alcoholic beverages based on the geographic origin of the raw material used. In contrast to metal patterns, which are known as primary geographic indicators, organic parameters such as volatile components, polyphenols, etc. are known as secondary geographic indicators[7]. Medina argues that the best way to identify the geographical origin due to their direct correlation with soil composition is through the study of patterns of metal composition [4].

2. Voltammetry

Due to the profound scope of wine and beverage analysis, there is an increased demand for knowledge of the metallic content of the wine and beverage. There has been a growing prerequisite to introduce more accurate, reproducible and objective procedures for evaluation of quality of wine and beverages in place of the old-fashioned, slow and relative inadequate methods. Many analytical techniques such as atomic absorption spectroscopy [9, 11, 12, 16, 17], capillary electrophoresis [18], inductively coupled plasma – atomic emission spectrometry (ICP-AES) [19, 20], and inductively coupled plasma – mass spectrometry (ICP-MS) [21–23] have been used for the qualitative and quantitative determination of metals in alcoholic beverages; however, voltammetric methods have gained popularity in the food industry. Table-1 illustrates the concentrations of different metals as reported in studies on various alcoholic beverages using voltammetric methods along with a summary of various parameters involved in the analysis of metals in alcoholic beverages. Table-02 gives an overview of the alcoholic beverages analyzed by voltammetric methods.

Voltammetric methods generally play an important role in analysis of metals. They refer to those interfacial electrochemical methods in which information is acquired about the analytes by measuring current in an electrochemical cell as a function of applied potential [24]. The electrothermal cell contains three electrodes i.e. the working electrode (WE), the reference electrode (RE), and the counter electrode (CE) (also called auxiliary electrode) immersed in a solution of analyte and non-reactive electrolyte known as supporting electrolyte. In this arrangement, the electrochemical potential of the polarizable WE is determined by an electronic instrument, the potentiostat. A polarized electrode is one to which an electrochemical potential more than that predicted by the Nernst equation is applied to cause oxidation or reduction to occur. To enhance polariza-

Table 1- *Concentration of various metals reported in literature*.

S.No	Type of Alcoholic Beverage	Metal analyzed	Concentration	Year	Reference
1	Wine	Cadmium	0.1 – 0.5 ppb	1979	[53]
2	Wine	Copper	2.0 – 7.5 ppb	1979	[53]
3	Wine	Lead	0.8 – 5.1 ppb	1979	[53]
4	Wine	Lead	43.5 – 62.5 ng/mL	1979	[52]
5	Beer	Copper	83 μg L^{-1}	1980	[35]
6	Beer	Lead	100 μg L^{-1}	1980	[35]
7	Wine	Copper	52 – 770 ng mL $^{-1}$	1986	[30]
8	Wine	Lead	68.4 – 209 μg L^{-1}	1992	[54]
9	Wine	Cadmium	0.12 – 0.42 ng/mL	1997	[52]
10	Rum	Copper	3 – 45 μg L^{-1}	1997	[47]
11	White wine	Copper	5.13 – 197.49 mg/L	1997	[55]
12	Wine	Copper	0.23 – 0.67 mg L^{-1}	1997	[74]
13	Wine	Copper	121 – 270 ng/mL	1997	[52]
14	Rum	Lead	23 – 65 μg L^{-1}	1997	[47]
15	Rum	Zinc	44 – 69 μg L^{-1}	1997	[47]
16	Whisky	Copper	39 – 120 μg L^{-1}	1998	[43]
17	Wine	Lead	4.1 – 36 μg L^{-1}	1998	[43]
18	Wine	Zinc	6.4 – 58 μg L^{-1}	1998	[43]
19	Distilled beverages	Copper	47 – 1110 μg L^{-1}	1999	[45]
20	Wine	Zinc	0.05 – 3.71 mg L^{-1}	1999	[49]
21	White wine	Copper	0.33 - 0.352 μg mL^{-1}	2000	[42]
22	Port wine	Copper	40 – 453 μg L^{-1}	2000	[56]
23	Port wine	Lead	0.086 – 1.58 mg L^{-1}	2000	[56]
24	Sugarcane spirits	Copper	0.035 – 3.20 mg L^{-1}	2001	[78]
25	Wine	Cadmium	0.11 – 0.52 μg L^{-1}	2004	[46]
26	White wine	Copper	1.82 – 3.64 μM	2004	[63]
27	Wine	Copper	49.3 – 114 μg L^{-1}	2004	[34]
28	Wine	Copper	25 – 175 μg L^{-1}	2004	[46]
29	Wine	Lead	16 – 40 μg L^{-1}	2004	[46]
30	Wine	Copper	0.18 – 41 mg L^{-1}	2005	[38]

Table 1- *Continued*.

S.No	Type of Alcoholic Beverage	Metal analyzed	Concentration	Year	Reference
31	Wine	Lead	0.032 – 0.15 mg L^{-1}	2005	[38]
32	Wine	Zinc	0.24 – 0.41 mg L^{-1}	2005	[38]
33	White wine	Copper	0.04 – 0.42 mg L^{-1}	2006	[37]
34	Tequila	Copper	0.38 – 11.80 mg L^{-1}	2008	[62]
35	Alcoholic beverages	Lead	112 – 280 µg L^{-1}	2012	[28]
36	Wine	Cadmium	0.041 – 0.087 µg L^{-1}	2013	[41]
37	Wine	Copper	7.3 – 15 µg L^{-1}	2013	[41]
38	Wine	Lead	3.3 – 10.2 µg L^{-1}	2013	[41]
39	Wine	Cadmium	0.097 µmol L^{-1}	2014	[79]
40	Wine	Copper	1.57 µmol L^{-1}	2014	[79]
41	Wine	Iron	0.12 – 0.17 mg L^{-1}	2014	[59]
42	Wine	Lead	0.009 µmol L^{-1}	2014	[79]
43	Spirit Drinks	Copper	2 – 82 × 10-7 µg L^{-1}	2015	[60]
44	Chardonnay (White) wine	Copper	0.015 0.200 mgL^{-1}	2016	[61]

Table 2- *List of Alcoholic beverages analysed along with the type of electrode and technique used.*

S.No	Alcoholic Beverage (Matrix)	Sample preparation technique	Analytes analysed	Electrode Used	Technique Used	LOD	Year	Reference
1	Distilled Beverages	Direct analysis	Copper	Hanging drop mercury electrode	Anodic stripping voltammetry	5µg/L	1999	[45]
2	Sugarcane spirits	Direct analysis	Zinc, Lead, Copper	Hanging drop mercury electrode	Anodic stripping voltammetry	Pb- 2 µg/L Zn-5 µg/L Cu-5 µg/L	1995	[80]
3	Whiskey samples	Direct analysis	Zinc, Lead, Copper	Hanging mercury drop electrode	Anodic stripping voltammetry	Pb- 2 µg/L Zn - 5 µg/L Cu - 5 µg/L	1998	[43]
4	Alcoholic beverages	Dry and wet digestion	Lead	Bismuth film electrode	Square wave anodic stripping voltammetry	0.27 µg/L	2012	[28]
5	Spirit drinks	Direct analysis	Copper	Biochar modified electrode	Adsorptive stripping voltammetry	4 × 10^{-7} mol/L	2015	[60]
6	Distilled alcoholic beverages	Direct analysis	Trace metals	Graphite pencil electrode	Cyclic voltammetry	0.6 µg/L	2013	[32]
7	Wine	Direct analysis	Copper	Mercury electrode (film and drop)	Square wave anodic stripping voltammetry	<0.06 µg/L	2004	[34]

Table 2- *Continued*.

S.No	Alcoholic Beverage (Matrix)	Sample preparation technique	Analytes analysed	Electrode Used	Technique Used	LOD	Year	Reference
8	Wine	Oxidative UV photolysis	Copper, Cadmium, Lead, Zinc, Nickel, Cobalt	Multimode electrode	Differential pulse anodic and cathodic voltammetry	Cu - 10 μg/L Cd - 5 μg/L Pb - 10 μg/L Zn - 20 μg/L Ni - 5 μg/L Co - 10 μg/L	1999	[31]
9	Wine	Direct analysis	Zinc	Multimode electrode	Absence of gradient and Nernstian equilibrium stripping (AGNES) voltammetry	-	2008	[50]
10	Wine	UV photo oxidative digestion	Cadmium, Lead, Copper	Thin mercury film electrode	Square wave anodic stripping voltammetry	Cd – 7ng/L Pb – 1.2ng/L Cu – 6.6ng/L	2013	[41]
11	Wine	Direct analysis	Copper	Mercury film screen printed carbon electrode	Medium exchange stripping voltammetry	0.0001 mg/L	2016	[61]
12	Rum	Direct analysis	Zinc, Lead, Copper	Hanging mercury drop electrode	Anodic stripping voltammetry	Zn< 0.02 mg/L Pb < 0.2mg/L Cu < 0,09mg/L	1997	[47]
13	Wines	Acid treatment to regulate pH	Cadmium, Copper, Lead, Zinc	Glassy carbon electrode	Derivative anodic stripping voltammetry	Cd –0.05 μg/L Cu -0.07 μg/L Pb -0.05 μg/L Zn -0.07 μg/L	2005	[39]
14	Wine	Direct analysis	Iron	Ruthenium oxide hexacyanoferrate modified microelectrode	Amperometric titration	0.22 μmol/L	2014	[59]
15	Wine	Wet digestion	Lead	Multimode mercury electrode	Square wave cyclic voltammetry	.5 μmol/L	2000	[81]
16	Sugarcane spirits	Direct analysis	Copper	Compact disc gold electrodes	Potentiometric stripping	30 ng/L	2001	[78]
17	Wine	Direct analysis	Copper, Lead, Zinc	Thick film graphite containing electrode	Stripping voltammetry	-	2005	[38]

tion, WEs in voltammetry have a very small surface area, in order of few square mm or less[25].

The potential of the WE is measured against the potential of the RE, whose potential remains constant, whereas the current flows between WE and CE. CEs are often a coil of platinum wire or a pool of mercury. A voltammogram is the plot of the current between WE and CE as the function of the potential between WE and RE. [26]. A special form of voltammetry is the polarography with a dropping mercury electrode as the WE.

2.1. Sample Preparation

Samples can be analyzed directly without any sample pretreatment, or samples can treated using wet and dry ashing methods. Sensitivity in cases where sample pretreatment is not done is limited, because of interferences due to organic matter which makes it difficult to determine total metal concentration. These methods have been explained by Ghanjari et al. [27]. In the wet ashing method, 25ml of sample is mixed with 5ml of HNO_3 (67%) and 3% H_2O_2 (37%). The mixture is heated until all the organic matter is digested. The final solution is transferred to a 50ml volumetric flask. After that, 5ml of acetate buffer (1M) and 2.5ml of bismuth solution (10000 μg/L) are added. In the dry ashing method, liquid parts of the sample are removed by heating reflux for 40min under 120°C. After that, 5 ± 0.5 g of the solid residue is placed in a crucible. The furnace temperature is increased from room temperature to 550°C in 1hr. The residues were dissolved in 5% HNO_3 (25% v/v) and the mixture was heated when necessary. The dry ashing method was found to be the most effective for wine digestion and is recognized as the best method for digestion of organic mass in alcoholic beverages. It can be successfully used for simultaneous decomposition of alcohols, sugars, acids, and phenolic compounds [28].

McKinnon and Scollary [29] used three methods for digestion of organic matter in wines: adjustment of pH only using 0.1M HCl, heat pretreatment with HCl, and heat pretreatment with HNO_3. It was observed that the pretreatment with HNO_3 produced the best results with maximum discrepancy of 3%. The other two methods were not able to release complete copper ion from its conjugated state. Furthermore, when an equal volume of wine is boiled with 0.2M HCl, a precipitate is formed which leads to a concentration decrease of detectable copper to zero.

Organic matrix present in alcoholic beverages can also be degraded by oxidative UV photolysis by maintaining the temperature at 85 ± 5 °C by a system of a high pressure mercury lamp and a combined air/water cooling system [30]. This method results in degradation of most organic wine constituents in less than an hour, keeping the concentration of metals unchanged. This method cannot be used for manganese, the concentration of which is affected by the use of ultraviolet radiation.

2.2. Electrodes

Voltammetric methods involve measuring the current which flows across the working electrode once the potential perturbation is achieved; therefore, the electrode may be regarded as the heart of the experiment[24]. Electrodes are available in a variety of shapes and forms. The redox process at the working electrode is crucial for the qualitative and quantitative analysis. The dimensions of the working electrode are kept small to enhance polarization. Working electrodes may be made of different materials and in different shapes. A reference electrode helps to monitor the potential of the working electrode. Ag/AgCl/ 3M KOH reference electrodes are often used. To complete the electrochemical cell, an additional auxiliary electrode or counter electrode is used. The current between the working and auxiliary electrodes are adjusted by the potentiostat in a manner as to maintain the desired potential at the working electrode. Platinum wire is the most common auxiliary electrode used. Ly et al. used graphite pencils in place of traditional reference and counter electrodes to counter the expensive nature of the former [31]. Analyte and reference electrodes are connected using a salt bridge to avoid contamination of the analyte [32].

2.2.1. Type of Working Electrode

Electrodes can be classified as macroelectrodes and microelectrodes based on the size of electrode. Macroelectrodes are electrodes whose characteristic dimensions lie within the mm to cm range. Macroelectrodes can further be of liquid and solid type. Solid electrodes consist of platinum, glassy carbon, gold or silver amalgam. They must be polished or cleaned in order to maintain a smooth and active surface after a sample is run. Generally, alumina or diamond powder is used to produce a mirror like surface. Commercial polishing pastes are now available which contain organic additives. Electrode surface can also be renewed using laser activation, electrochemical cleaning, and plasma treatment. Due to the limitation of surface maintenance, solid electrodes have low reproducibility and are less used.

Paste electrodes consist of suitable material such as graphite powder mixed with a suitable liquid such as nujol to form a paste. The liquid to be used must be immiscible in the electrolyte solution. Contrary to solid electrodes, paste electrodes produce a consistent and smooth surface, which results in good reproducibility. Low background current is another advantage of paste electrodes, which results in good sensitivity in the form of high signal to noise ratio. Voltammograms of paste electrodes often reveal the chemical nature of the additives which might interfere with the actual voltammogram. One of the most common paste electrodes used are carbon paste electrodes. Advantages of carbon paste electrodes (CPE) include their non-toxic nature. CPEs produce low background current and can be used over a wide range of potential. CPEs offer rapid renewal and easy fabrication, which makes them an ideal choice as electrodes. CPEs are often coated with a film of mercury.

Mercury film deposited on glassy carbon electrode was used for electrochemical determination of metals in wine [33–41] in whiskey samples [42], in beer [43] and in various distilled beverages[44]. Thick film graphite electrode has been used for determination of metal content in wines[45], in rum[46], and in distilled alcoholic beverages[31]. Thick film modified graphite containing electrode (TFMGE) was used by Brainina et al. for the determination of heavy metals in wines [45]. TFMGE has high sensitivity and selectivity. Moreover, the amount of mercury transferred to the waste after analysis with TFMGE is several orders of magnitude lower than with ordinary mercury electrodes[45]. Other metals used for film coating include bismuth [27].

A liquid electrode produces a new and reproducible surface without any interference from previous measurement or from contaminant, and cleaning or refreshing procedures are not required. [47]. The most important material for a liquid electrode is mercury, with the advantage of a high hydrogen overvoltage. Two variants of mercury electrodes can be used as the “working” electrode: the Dropping Mercury Electrode (DME) and the hanging Mercury Drop Electrode (HMDE) (also known as Static Mercury Drop Electrode (SDME)), along with the other types of mercury coated electrodes mentioned above.

The hanging mercury drop electrode is a modification of the conventional dropping mercury electrode. It consists of a fine capillary tube and a mercury reservoir. Mercury from the reservoir is forced through the capillary by a piston arrangement driven by a micrometer screw which can be manually adjusted to produce mercury drops of different sizes. This results in high reproducibility and an error rate of 5% or less [24, 25]. It has been utilized for determination of zinc content in wine [30, 48–53] in various other distilled beverages [44]. Rapid metal deposition is observed in a short time interval because of higher surface to volume ratio. Limitation of HDME lies in the shielding effect produced at the neck of the drop formed at the capillary tip, which can be countered by using a tapered capillary [24].

The static mercury drop electrode is based on the same principle as the hanging drop mercury electrode, but the difference lies in the method to control the formation of mercury drop. The outflow of mercury from the capillary is controlled using a valve so that a perfectly uniform, round, and static mercury drop is generated, which is easily dislodged once the analysis has been done [25]. It has been utilized for copper speciation in white wines [29, 54], lead and copper in port wine [55], and in various distilled beverages [44]. Due to constant surface area during each measurement, SDME produces reduced capacitive currents, which leads to increased signal to noise ratio. SDME can be used to determine substances in the presence of more positively reducible species, which is almost impossible while using dropping mercury and hanging mercury electrodes [56].

Microelectrodes have the characteristic dimension in the order of the thickness of the diffusion layer [25]. Microelectrodes can be of different shapes ranging from discs to rings and cylinders. A series of microelectrodes can also be used as electrode array for the analysis. Due to their small size, microelectrodes can be used to measure concentrations of analytes in very small volumes. Also, because the scan time is very small the technique can be used for successive scans, increasing the reproducibility of the instrument; however, it is very difficult to reproduce the dimensions of microelectrodes with certainty. Since the current is in the order of nanoamperes, it appears to be challenging to eliminate noise from signals [24]. Modified electrodes have been used in determination of metals by Pena et al. [58].

2.2.2. Electrode Materials

Mercury is the most commonly used electrode material, because of its inert nature and the ability to evolve hydrogen at negative potentials. Moreover, mercury can easily form amalgam with a wide variety of metals; however, in recent years, the use of mercury has seen a decline because of its toxicity, its environmental impact and the availability of substitute electrodes.

Carbon electrodes are available in many shapes and sizes. Carbon electrodes allow working at more negative potentials than gold or platinum. Glassy carbon electrodes are the most common type of carbon electrodes and can be modified further to produce desirable results. Carbon electrodes have been used in determination of metals in alcoholic beverages in various forms [43, 59, 60].

The bismuth film electrode was used for determination of lead in beer samples [27] and for determination of cadmium, lead and copper in wine samples [57]. It has been reported that Bismuth coated microelectrodes produce reliable results for determination of cadmium and lead but due to the overlapping electrode potential of bismuth and copper, these cannot be used for determination of bismuth and copper [57].

The platinum rotating disc electrode (Pt-RDE) was used as a working electrode for determination of metals in various distilled beverages [44] by Barbeira and Stradiotto and for determination of copper in tequila by Carreon-Alvarez et al. [61]. The method was sensitive and reproducible. The gold electrode has been applied to metal determination in wines [62] and various distilled beverages [44]. It was observed that glassy carbon electrodes produced the best reproducible results for determination of copper in sugarcane spirits as compared to gold and platinum electrodes, which were least efficient in analyzing copper [44]. This may be attributed to the adsorption of organic matter onto glassy carbon electrodes.

The dental amalgam electrode has been used for determination of metal content in wine [63, 64]. Dental amalgam is a solid, and non-toxic material. These electrodes are made by binding mercury to a stable Ag_2Hg_3 alloy in an excess of silver. The excess of silver makes it non-toxic for analytical purposes. Properties of dental amalgam electrodes are similar to that of silver electrodes, but the disturbing formation of hydrogen is significantly lower than at silver electrodes but higher than at mercury electrodes [47].

2.3. Voltammograms

A voltammogram is the plot of the current vs. the electrochemical potential, which is scanned in a predefined range. In addition to varying the direction of the scan, the way the potential is scanned may also differ. The simplest method of potential scan is linear sweep voltammetry (LSV) where the potential is changed as a linear function of time. Other possibilities are the different kinds of pulse voltammetry such as normal pulse voltammetry (NPV), differential pulse voltammetry (DPV), and square wave voltammetry (SWV). In NPV, a series of potential pulses of increasing amplitude is applied. The measurement of the current is usually carried out near the end of each pulse [65]. DPV and SWV are explained in section 2.3.3 [66].

2.3.1. Linear Scan Voltammograms

Linear scan voltammograms at the DME or RDEs are sigmoidal in nature and are also known as ‘Voltammetric waves’. As the potential is increased, current increases steeply until it reaches limiting current. Limiting current is achieved because the rate at which the reactant can be brought to the surface of the electrode by mass transport processes limits the current i.e. surface concentration of the analyte becomes zero. This limiting current is directly proportional to the reactant concentration. A variant of linear voltammetry is hydrodynamic voltammetry in which the solution is stirred vigorously either by use of a magnetic stirrer or by passing the analyte solution through a tube fitted with a working electrode.

2.3.2. Cyclic Voltammograms

Cyclic voltammograms are generated when the direction of voltage scan after the forward run is reversed. To attain this, the resulting current is recorded when the applied potential at working electrode is both in forward and reverse direction [67]. Cyclic voltammetry has been used for detection of trace metals in distilled alcoholic drinks [31] as well as in determination of organic compounds such as polyphenols [67, 68].

2.3.3. Pulse Voltammograms

In pulse voltammetry, square-wave pulses of 50 mV, for example, are overlaid over the linearly increased potential. The improvement of sensitivity in pulse voltammetry techniques is based on the difference in the rate of the decay of the charging and faradaic currents following a potential step (or ‘pulse’). The charging current decays exponentially, whereas the faradaic current (for a diffusion-controlled current) decays as a function of 1/(time)¬1/2, that is, the rate of decay of the charging current is considerably faster than the decay of the faradaic current [25]. Two types of pulse voltammetry, differential pulse voltammetry (DPV) and square wave voltammetry (SWV), are often used for determination of metals in alcoholic beverages. Differential pulse voltammetry relies on measuring the current at a time of each pulse when the difference between the desired faradaic current and the interfering charging current is large. DPV has been successfully utilized for quantitative measurement of free copper ions in undigested samples of white wine [54]. Dostalek et al. and Companys et al.

used DPV for estimation of Zinc concentration in wines [48, 49]. DPV provides high resolution for substances with half wave potential, differing by as little as 0.04 to 0.05V; therefore, well defined peaks are obtained and the sensitivity of DPV is high.

Square wave voltammograms are obtained by superimposing the pulse train onto the staircase signal. In a reduction reaction, the difference between forward and reverse currents is always zero, except at the redox potential. This difference between the forward and reverse current is plotted to give the voltammograms. This difference is directly proportional to the concentration of analyte; the potential of the peak corresponds to the voltammetric half wave potential [69]. Square-wave voltammetry (SWV) is a variant of linear potential sweep voltammetry. It provides excellent analytical sensitivity and outstanding resolution [70]. It is successfully applied for the quantitative determination of metallic components in wines. It was observed to produce good linearity with low detection limit [33, 40]. The advantage of the technique lies in its speed, sensitivity and reproducibility. Since the technique is very fast, it is possible and practical to increase the precision of analysis by signal averaging data from signal scans [25].

2.3.4. Stripping Methods

Stripping voltammetry is an electroanalytical technique consisting of three steps: 1) Electrodeposition (The metal is deposited on the electrode at sufficiently negative potential), 2) Equilibration (Metal deposition reaches the peak and further deposition stops), and 3) Stripping (Deposited metal is stripped from the electrode when the potential is linearly changed in positive direction). The amount of current in the third step is directly proportional to the amount of metal in the solution. Depending on the type of electrode where the stripping takes place, stripping voltammetry can be of two types: anodic stripping and (more seldom) cathodic stripping [56].

Companys et al. used a variant of the conventional stripping method, Absence of Gradient and Nernstian Equilibrium Stripping (AGNES), [49] for determination of zinc in wine. In this technique, in the mercury electrode the amalgamation of the metal occurs during the deposition step until the Nernstian equilibrium is achieved [71].

To eliminate interference due to organic material in conventional stripping voltammetry, the technique of medium exchange may be employed. In this technique, the medium is changed after the enrichment step and a new medium is used for the stripping step [36]. While changing the medium, electrical contact between the three electrodes must be maintained which can be successfully performed in a flow system [41]. The medium exchange results in a significant improvement of the long term stability of mercury film electrodes. Generally, a chloride free medium during stripping step results in further increase of sensitivity due to minimization of adsorption of wine components on the surface of the film electrode. The only limitation of medium exchange stripping voltammetry lies in time delay caused by longer run time [36, 41, 60].

Another advancement of stripping methods is adsorptive stripping voltammetry (AdSV). In this technique, the working electrode is immersed in a solution for several minutes during which the analyte is deposited on the electrode surface through the process of adsorption instead of electrolytic deposition. After a fixed interval of time, when sufficient analyte has deposited the stirring is discontinued. The analyte concentration is determined by linear or pulse scan [25]. Wang and Mannino used AdSV for the determination of iron concentration in wines [72].

2.4. Advantages and Limitations of Voltammetric Methods

Voltammetric methods have been designed to record the potentiometric response generated by the targeted metals. These methods produce highly accurate and precise results producing high sensitivity even for low metal concentrations. Moreover, its ability regarding direct measurement of free metals and low maintenance costs make it a favorable technique of analysis of metals in alcoholic beverages [73, 74]. Various disposable and non-disposable electrodes are available for the analysis and have proved successful for determination of Cd, Cu, Co, Fe, Ni, Pb and Zn [75]. Because of the inert nature of the glassy carbon – mercury film electrode to the interferences of organic molecules present in the matrix differential pulse stripping, voltammetry requires minimal or zero sample pretreatment [35].

A limitation of voltammetric methods, in comparison to the presently preferred use of ICP-MS, is that some metals such as Na, K, Mg, Ca, Al, As, Sb, Se and others are either not measureable or only measureable under very specific conditions. In addition, isotope ratios cannot be determined by electrochemical methods. Furthermore, because of the complicated nature of the underlying redox process at the electrode surface, electrochemical methods are more sensitive to the composition of the matrix and need a higher qualified and experienced analyst.

3. Conclusion

The present review was conducted to evaluate the role and importance of voltammetric methods in analysis of metals in various alcoholic beverages. Ascertaining metal concentration in alcoholic beverages is very important. Therefore, techniques must be developed which allow easier, faster and cheaper analysis of alcoholic beverages. It has been found that voltammetric stripping methods offer a sensitive, accurate, precise and cheap alternative for qualitative and quantitative analysis of metals in alcoholic beverages. The type of voltammetry used for the analysis plays an important role in sensitivity. Also, with advancements in types of electrodes and the materials used in electrodes, the sensitivity has increased considerably.

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