Sensor for Beverages Analyses a Review

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***Abstract*: The use of sensors is an innovative technique, cheaper and faster than others analytical ones. Furthermore, the advantages of this technique are short analysis time and low instrumentation cost. The sensors application in beverages analyses is widely used. Sensors are commonly used to characterize beverages, identify compounds of interest and monitoring quality and shelf life of beverages (wine, coffee, beer, water, milk, tea and juice). The aim of this review is to highlight the current application of sensor systems for the beverages analyses. Various examples of sensor applications are found in literature, such as the use of a single parameter sensor to alcohol determination in alcoholic beverages, the Electronic Nose application to characterize the flavour beverage or the Electronic Tongue use to detect polyphenols in wine and other beverages.**

***Index Terms*: Electronic Tongue; Electronic Nose; Beverages; Sensor; Compounds determination**

I. INTRODUCTION

Over the last years the beverages' industries have paid attention to new technologies which could fast identify some representative parameters. These new analytical techniques are attractive because they do not require highly trained operators [1]. Nowadays, industries prefer an analysis approach that reduces time, analysis cost and sample loss. New technologies such as sensors can also be sustainable [2]-[3]. Sensor are used in many applications. These devices are widely used in industrial and agro-food sector to simplify the operator practices in many fields, such as control of production processes, products quality certification and verification and food safety control. Sensors are a large class of analysis devices. These tools can be classified in different ways. They can be classified according to their working principle or to the type of output signal. The usual classification is based on the physical-chemical parameters that they measure. This last classification lead to divide the sensors into three great categories: physical sensors, chemical and biological ones.

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The first one allows to measure physical quantities such as temperature, pression, movement, radiation and others. The second one detects chemical analytes, such as phenolic compounds or pesticides in food matrix [4]. Instead, the last one reveals biological analytes as number or type of cells (i.e. *Salmolnella*) [1]. These tools are based on different working principles (e.g. mechanical, electrical, optical). The most used sensors are based on electrical working principles. In the case of electric type sensors, the output quantities (analogic or digital) are always convertible into electrical voltages, simpler to process [5]-[6]-[7]. Another classification divided sensor in multisensory systems and "traditional" ones. The first ones are multisensory systems, these devices can identify more analytes at the same time, e.g. electronic tongue or electronic nose. Despite of the second ones can identify just one analyte, e.g. biosensors [6]-[7].

Beverages require periodically chemical and microbiological analyses. Generally, these procedures are made using traditional techniques as chromatographic separation ones, mass spectrometry, titration, spectrophotometry, and other ones. An alternative to these procedures is sensors technology development. Therefore, the interest in these innovative techniques has increased in the last years. These new analysis tools are cheaper and faster than traditional techniques. Moreover, sensors method does not destroy the sample, as other analytical technique. The beverages' industries prefer this non-destructive approached [6]. In addition to traditional sensors, some multisensory systems have been developed to analyse beverages, as Electronic Tongue and Electronic Nose. The Electronic Tongue is an electrochemical liquid sensor [6], while the Electronic Nose is a gas sensor [7]. They are based on different working principles such as: potentiometry, conductimetry and voltammetry [6]-[7]. The electronic tongue consists on an array of liquid sensors, that has different selectivity. The principle of electronic nose is similar to E-tongue, except for sensors array that is specific for gas analytes [8]-[9].

The aim of this review is to highlight the different applications of sensors in beverages analyses, the most analysed compounds and future applications of sensors in beverages industry.

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II. BEVERAGES COMPOUNDS DETERMINATION BY SENSORS

In the beverage's analyses, the sensors practice is not widely diffused. Indeed, these new technologies are not yet fully applied for routine analyses of beverages. Different type of sensors has been involved in beverages analyses. These devices have different operating characteristics. Many studies report the application of biosensors, devices characterized by the presence of enzymes as interface, specific for a given compound. Recently, it has been reported the possibility of applying multisensory systems, such as electronic-tongue and electronic-nose, in the beverages analyses. These devices can recognize analyte, respectively, in liquid and gas samples. These tools have a similar configuration. It is possible to summarize the structure of a sensor in a block system, which is composed of the actual sensor (the material that interacts with the analyte), the transducer (that convert the measured quantity into an analogue signal) and the personal computer (which allows data analysis). Beverages are wired to fraud, the ones that have high rate of adulteration are alcoholic beverages, wine at first, coffee, tea and fruit juices. Usually the compounds investigated are alcohol (Table 1), antioxidants (Table 2), xanthine (Table 3), sugar (Table 4) and contaminates (Table 5). These compounds are usually determinate to characterize and to evaluate the quality and healthiness of each beverage [10].

A. *ALCOHOL*

Table 1 Determination of alcohol by sensors

Beverages Samples	Analytes	Sensor type	Trasducer	LOD*	Ref.
Wine	Ethanol	Biosensor	Potenziometric	0,05 mM	[9]
		E-tongue	Potenziometric	0.7 M	[10]
		Optical Sensor	PCF	-	[12]
		Optical Sensor	Infrared	-	[13]
	Ethanol	Pressure sensor	Hydrogel-based piezoresistive	-	[14]
		E-nose	MOX	-	[15]
		E-nose	-	0.1%	[16]
Beer	Ethanol	Biosensor	Photenziometric	0,05 mM	[9]
		E-tongue	Potenziometric	0.7 M	[10]
		Optical Sensor	Infrared	-	[9]
		Pressure sensor	Hydrogel-based piezoresistive	-	[14]
		E-tongue	Potenziometric	10%	[54]
Spirits-Distillates	Ethanol	Biosensor	Photenziometric	0,05 mM	[9]
		Optical Sensor	Infrared	-	[13]
Fruit juice	Ethanol	E-Nose	-	0.1%	[16]

*LOD= Limit of detection

Alcohol determination in beverages has great importance for industries, related to the alcohol taxes imposed by some Countries. Moreover, the alcoholic beverages have negative consequences on consumers health. The intake of large alcohol amounts causes several effects on the organism such as psychological ones. Alcohol can promote the appearance of cardiac and vascular disorders, damage to liver, intoxicate pancreas and brain and other effects that are caused to chronic intake of this substance [11].

Alcohol concentration in beverages is caused by alcoholic fermentation, a distinctive step of wine, beer and distillates production process. Instead, in other beverages, as fruit juice, the alcohol incidence shows a microorganism contamination. Alcohol monitoring are carried out by identification of ethanol and its concentration in alcoholic beverages. Quality control of alcoholic beverages, such as beer, wine, liquor and spirits, imply measurement of the alcoholic compounds and ethanol concentration. Furthermore, ethanol represents a quality indicator for beverages [13].

Nowadays alcohol determination in beverages is carried out by traditional techniques. There are many traditional techniques that can allow the identification of alcohol in beverage samples. The most common and used techniques to detect alcohol in beverages are gas and liquid chromatography [14]. Gas chromatography is the most common and preferred method used for the determination of alcohol in beverages. These techniques are relatively expansive, needs trained operators and requires pre-treatment of the sample [15]. In addition, other methods are also found such as ebullioscopy, gravity method, dichromate oxidation, picometric procedure and biodestruction by enzyme. Spectrometric and chromatographic methods are expensive and sometimes require sample pre-treatment. Drink industry, in the quality control step, requires rapid determination methods for routine analyses [13]. Over the last years, new techniques have been developed to detect alcohol. These techniques, chemical sensor or bio-sensor, can monitoring one or more parameters at the same time. Sensors, recent developed tools, can simplifies the traditional analyses. Generally, alcohol biosensor is based on enzymatic hydrolysis of alcohol. Enzymatic methods to ethanol determination usually use two enzymes, alcohol oxidase (AOD) or alcohol dehydrogenase (ADH) [13]. A redox reaction is generated, and the electronic transfer is reordered by the sensor [14]. Enzymatic methods and biosensors present some advantage as high selectivity, high specificity, relative low cost of construction and easy storage. Bacteria and yeasts are recognised as organisms metabolise in all kinds of substrates. Another biosensor, that has been developed, is based on the use of microorganism cells that selectively recognize ethanol. The main advantages of this biosensor are the construction simplicity and low cost [13]. Other tools developed to detect alcohol are photonic sensor and infrared sensor [16]-[17]. These sensors are part of physical-chemical sensors. In this case, sensors used a surface that interacts with the analyte and this interaction generates output proportional to the analyte concentration. The infrared sensor is used to monitoring the fermentation and the alcohol concentration in alcoholic beverages as beer, wine and spirit. This new technique uses an infrared spectrometer sensor, that is a device smaller than the laboratory ones. For these characteristics the device can be directly applied in the industrial process control or on-site inspections [17].

Another sensor that has been developed is photonic sensor. This device uses a photonic crystal fiber with a specific frequency band for alcohol detection. The advantages of this device are the simplicity of manufacture and the small size, faciliting the possibility of industrial application [16]. Another type of sensor, used

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to detect ethanol in beverages, is hydrogel-based piezoresistive sensor. This sensor uses hydrogel combined with piezoresistive sensors. In this case the sensor measures the reversible swelling of the gel after the interact with ethanol. This type of sensor has a good sensibility and a short response time [18]. Nowadays, the attention has been focused on devices that can monitoring more parameters at the same time. These devices, defined multisensory systems, have the capability to identify analytes in short time, without the sample pre-treatment. For this reason, these tools are used and studied to quickly identify chemical compounds. In beverages industries the possibility of use a fast and cheap device is an advantage. Furthermore, in beverages analyses has been studies the possibility to apply multisensory system, like electronic tongue and electronic nose. The possibility of applying these devices in beverages industry has high applicability. These multisensory systems have been widely applied to alcoholic beverages analysis, among these there are quality control, ageing control and fraudulence detection [19]. Two multisensory systems are frequently used in alcoholic beverages analysis. The electronic tongue that identify analytes in liquid samples and the electronic nose that identify gas compounds in complex mixtures. These devices are used to identify alcohol concentration or to monitoring alcoholic fermentation [14]-[19]-[20]. Electronic nose has been used to monitor and detect ethanol in fruit juice. In this case, the alcohol analysis is done to assess the presence of ethanol in fruit juices, developed by microbial activity [20]. Table 1 shows the sensors used in alcoholic beverages analyses.

B. ANTIOXIDANT

Table 2 Sensors for analysis of antioxidant

Beverages Samples	Analytes	Sensor type	Trasducer	LOD*	Ref.
Wine	Polyphenols	E-tongue	Voltammetric	5 mg mL^{-1}	[6]
	Polyphenols	E-nose	MOX	-	[18]
	Caffeic Acid	Electrochemical Sensor	Voltammetric	0,1 mg mL^{-1}	[23]
	Catechins	Taste sensor array	Voltammetric	-	[28]
	Catechins	Electrochimical sensor	Voltammetric	4.6 nM	[56]
Tea	Antioxidants	E-tongue	Optoelectronic	0.1 µM	[27]
	Ascorbic Acid	Electrochemical Sensor	Voltammetric	7 µM	[33]
	Theobromine	Nanobiocomposit sensor	Voltammetric	0.21 µM	[54]
Milk	Catechins	Electrochimical sensor	Voltammetric	4.6 nM	[54]
Juice	Antioxidants	E-tongue	Optoelectronic	0.1 µM	[24]
	5-CQA	Microelectrodes	Voltammetric	3.2×10^{-9} M	[27]
	Ascorbic Acid	Biosensor	ISFET	0.25 mM	[31]

*LOD= Limit of detection

Antioxidants are compounds that, if in low concentration, can prevent or significantly delays substrate oxidation [18]. Antioxidants action mechanism are different and can act in various ways in the biological systems. They can interact with the inhibition of oxidant-producing enzyme or can chelate the metal ions, catalysing oxidation reaction. Nevertheless, the most significant activity of antioxidants is to prevent the substrates oxidation. Antioxidants are commonly subjected to oxidation by oxygen and reactive oxygen species (ROS) and this reaction can stop or protect the oxidation of other substrates. This reaction forms oxygen reduced compounds: superoxide radical anion (O^{2-}) or hydrogen peroxide (H_2O_2). H_2O_2 is the major compound that is accumulated after the substrate's oxidation or antioxidant oxidase reduction [20].

Antioxidants, naturally present in beverages, have also biological properties. These compounds can have beneficial effects on human health. The main property is the radical scavenging activity. The other effects are protective action on the cardiovascular system, anti-inflammatory, anti-hypertensive, anti-viral, anti-fungal, immunoprotective, anti-cancer and neuroprotective activities [21]. Moreover, this compounds class can be classified in other two groups: enzymatic and non-enzymatic antioxidants. Commonly, the non-enzymatic antioxidants are obtained from dietary source (like fruit and vegetables) and these compounds are synthetized to secondary plants metabolism. Furthermore, the enzymatic antioxidants are endogenously produced by the human organism [22]. Natural antioxidants, secondary products of plants metabolism, are composed to a large variety of molecules. The largest class is characterized to polyphenols, that are composed to different chemical molecules structure. The other natural antioxidants are: tocopherols, ascorbic acid, carotenoids, stilbenes, and other.

The antioxidants type and concentration in beverages reflect fruit or vegetables from which they are produced. Beverages antioxidants prevent the oxidation and improve the products shelf-life [22]-[23]. The antioxidants are beneficial compounds for both human health and food preservation. For these reasons, different analyses methods are developed. Traditional methods are Folin-Ciocalteu [5], spectrophotometric and chromatographic methods, as GC [18] and HPLC [20]. The chromatographic methods are complex and usually requires samples pre-treatment. Valid alternatives to traditional technique are biosensors. Biosensors are developed to identify beverages polyphenols. In this case they use enzymes, like laccase, tyrosinase or peroxidase [7]. Currently, multisensory systems are studied to identify and to analyze polyphenols and others antioxidant analytes. Electronic tongue and Electronic nose are studied to analyze polyphenol and catechins concentration in wine matrix. Cycle voltammetry have been used to evaluate total antioxidant profiles in the beverage samples. This working principle is the most used to characterized antioxidant beverage profiles. These techniques permitted to identify in the same time more analytes [5]-[19].

Another method, that is used to identify polyphenols in wines, is thick-film electrochemical sensor with an iridium-carbon working electrode [20]. This electrochemical method is used for determining polyphenols and their antioxidant capacity in white wine. In this study, was considered the possibility to identify one or more polyphenols at the same time [21]. Optoelectronic tongue, based on an array of gold and silver nanoparticles, has been developed to discriminate twenty type of polyphenols in tea beverages. In this case, nanoparticles sensor array has been used to interact whit the polyphenols content in beverages, to extend affinity between sensor and polyphenols. After interaction, sensor array produces a colors combination for each antioxidant. This method has excellent potentiality for the antioxidant analysis in beverages [22].

A similar work has been carried out to Yig˘it et al. 2018. In this study, it has been used a Graphene-based Electrochemical Sensor for the simultaneal antioxidants identification in beverages matrix [23]. In other cases, electronic tongue has been applied coupled to a multivariate data analysis that can recognize some polyphenols, including catechins, in tea samples [24]. Other studies have focused their research on other beverages like fruit juices. In this case the most studied antioxidant is the ascorbic acid, because this is a quality index and because this compound reflects the state of beverages conservation. At first, Ascorbic Acid has been identified with a biosensor. The interface of biosensor device is composed to glucose oxidase and urease co-immobilized, this enzyme reacts whit ascorbic acid. This device has been proposed as detector for routine analysis of drinks [25]. In further studies, new analysis technique has been applied, like e-nose and e-tongue. This technique allowed to analyze this compound in short time and to describe a characteristic beverages profile [26]. Sensor analyses for antioxidants detection are usually applied to milk. In this case there are not many studies that used this device to detect ascorbic acid. Selective electrochemical sensor for ascorbic and uric acid analysis was developed. In this case, the tool can identify simultaneously both the analytes. This sensor was successfully applied for the determination of ascorbic and uric acid in milk samples [25]. In the table (Table 2) are shown the most used sensors in beverages antioxidant analysis.

C. *CONTAMINANTS*

Table 3 Determination of contaminants by sensor.

Beverages Samples	Analytes	Sensor type	Trasducer	LOD*	Ref.
Milk	Cd (2+)	Electrochimical sensor	SWASV	0.2 μg L^{-1}	[35]
	Pb (2+)			0.4 μg L^{-1}	
	Phthalate	Electochimical Sensor	EIS	-	[39]
	Cd (2+)	Nanocomposit sensor	Voltammometric	1.8 μg L^{-1}	[41]
	Pb (2+)			2.1 μg L^{-1}	
Water	Nitrate	Sensor chip	Colorimetric	0.0782 ppm	[36]
	Bisphenol A	Electrochimical sensor	Voltammometric	-	[37]
	Nitrite	Gold nanoparticles electrode	Voltammetric	0.314 μM	[38]
Wine and Beer	Histamine	Electrochemical sensor	Voltammetric	1.26 μmol L^{-1}	[44]

*LOD= Limit of detection

Each industrial product must preserve its characteristics by the entire supply chain. However, it can interact with exogenous substances that alter its characteristics, throughout its product life cycle. For this reason, the industries and consumers give attention to products' quality. To monitor these aspects, the industry carries out periodic checks on their products to identify the contaminants presence [28].

The contaminants are defined as any substance not intentionally added to foodstuffs, but present as residue of production, processing, manufacture, preparation, treatment, conditioning, packaging, transport and storage processes or as result of environmental contamination.

The chemical contaminants can be divided in: Natural toxins, which are synthesized by mushrooms, algae, plants and microorganisms; Environmental contaminants, industrial chemical agents present in water, soil and air; Process contaminants, that are formed during food preparation (e.g. cooking); Metals and inorganic substances; Others (e.g. unauthorized veterinary medicinal products) [29].

The chemical contaminants, present in low concentrations in food, are quite dangerous for human health. However, the chronic intake of these compounds can be harmful to consumers. For this reason, several limits have been defined and if a product exceed these limits cannot be sold [30].

The contaminant analyses, also, are often characterized by the use of traditional methods, e.g. chromatography, spectrophotometry, electrophoresis, titration and other ones. These conventionally methods are expansive, requires extraction steps or samples pre-treatment and well-trained operators. For these reasons, food and beverages industries require a non-destructive approach. Indeed, industries research new methods that are cheaper and faster than traditional techniques and that no requires trained operators [28]. Nowadays, new analyses methods have been developed. In beverage studies several kinds of chemical contaminants have been considered. Many chemical contaminants are present in water, wine, milk and fruit juice. The chemical contaminants usually found in beverages are phthalate, bisphenol A, sulphite, histamine, cadmium and plomb, nitrate and nitrite. These compounds are analyzed whit different approaches. In same studies are used MEMS sensors [31]-[35], voltammometric sensors [32]-[37]-[38], magnetic imprinted sensor [33], electronic tongue [34] and electrochemical sensors [36]-[39]-[40].

In each method the devices have the capability to identify in a short time the contaminants. These tools could be used to identify these contaminants along the entire supply chain.

The table (Table 3) shows the sensors commonly used in contaminant analysis in different beverages.

D. *XANTHINE*

Table 4 Xanthine Analysis in beverages samples.

Beverages Samples	Analytes	Sensor type	Trasducer	LOD*	Ref.
Coffee	Vanillin	Microelectrodes	Voltammetric	3.2×10^{-9} M	[27]
	Xanthine	Fluorescent Biosensor	-	0.09 μmol L^{-1}	[48]
	Xanthine	Nanobiocomposit sensor	Voltammetric	0.21 μM	[49]
Tea	Catechins	Taste sensor array	Voltammetric	-	[28]
	Catechins	Electrochemical sensor	Voltammetric	4.6 nM	[55]
	Xanthine	Fluorescent Biosensor	-	0.09 μmol L^{-1}	[48]

*LOD= Limit of detection

Xanthine are a compounds class that belongs to alkaloids family. This class of compounds includes both endogenous compounds synthesized by human body (e.g. guanin, adenine, hypoxanthine, uric acid, etc.) and exogenous compounds synthesized by secondary metabolism of plants.

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These last types of xanthine exist in beverages likes coffee, tea, guarana, mate and others plant's beverages [41]. The most common xanthine investigated are theobromine, theophylline and caffeine. These are three alkaloids with similar chemical structure. These xanthines are classified as methylxanthines, because have a methyl-group bound to structural ring. Many studies have been established methylxanthines health effects, showing neuroprotective, hypoglycaemic, anti-inflammatory or cardioprotective effects [42]-[43]. Limited studies on beverages xanthine were found, they involved just two types of drinks: tea and coffee. In these studies, different analysis approaches have been used. Graphene-based Electrochemical Sensor has been used to analysed caffeine in coffee samples. This device managed to identify in short time caffeine in a complex solution. This sensor can be used for the analysis of this compound [21].
Instead another study used fluorescent biosensor for the determination of xanthine in tea and coffee beverages. This device is characterized to functionalization with gold nanoparticles. The operating principle is based on enzymatically generation of uric acid. The uric acid induced gold nanoparticles degradation which caused in quenching fluorescence. This is a selective method to detect xanthine in real samples without the samples pre-treatment [44]. Another study has investigated the possibility to detect Theobromine with nano-biocomposit sensor based on voltammetry. In this study, three nervine drink, tea, coffee and chocolate, have been considered. In this study, it has been demonstrated that this sensor can detect and identify these compounds [45]. The table (Table 4) shows the sensors used to investigate xanthine in beverages.

E. SUGAR INDEX

Table 5 Sugar index in beverages samples.

Beverages Samples	Analytes	Sensor type	Transducer	LOD*	Ref.
Fruit juice	Sweetener	E-tounge	-	-	[50]
	Glucose	Biosensor	Impedenciometric	0.02 mM	[51]
	Glucose, Fructose and Sucrose	E-tongue	Potentiometric	-	[52]
	Glucose	Biosensor	Amperometric	-	[56]

*LOD= Limit of detection

Recently, the consumption of sugary drinks has increased significantly. This also lead to an increase in health problems. Furthermore, it has been demonstrated that a high consumption of sweet drinks (e.g. nectars and fruit juices) lead to increase the incidence of obesity, diabetes, dyslipidemia and insulin resistance. Overall, fructose is the most involved to intensification in metabolic pathologies [46]. Also, consumers attributed to these beverages, particularly to nectars and juices, healthy characteristics, as source of essential nutrients (e.g., vitamins) and antioxidants. Nevertheless, their overconsumption may upsurge risk of health problems [48]. For this reason, beverages sugar content is increasingly monitored to protect consumers health. Sensor devices are developed to detect sugar and sweeter content in beverages. Studies reported a greater application of sensors in fruit juices sugar analyses [25]. Different sensor techniques have been developed to identify and screen these beverages compounds. In these studies, three sugars are investigated to evaluate sugary index: glucose, fructose and sucrose. These sugars are naturally synthetized by plants and fruits [46]-[47]. In one case biosensor has been used to analyze glucose in some fruit juice samples. In this study the "bio-interface" is characterized to glucose oxidase enzyme [47]. In recent studies electronic tongue have been applied to identify sugar in fruit juice samples. In one study this device, based on potentiometric working principle, is used to characterize beverages based on glycemic load [48]. Instead in the other one electronic tongue has been used to discriminate different beverages, based on their sweetener [47]. Other studies have been applied biosensor, based on amperometry working principle, to identified glucose in different fruit juice samples (e. g. mango juice, pineapple juice and other). The following table (Table 5) summarizes sensors used for beverages sugary index analysis.

III. CONCLUSION

Nowadays, the beverage industries have paid attention to monitoring the quality and freshness of their products. For these reasons, they have encouraged development of new techniques that gain rapid analytes detection. Furthermore, beverages industries, usually involve traditional analytical methods to monitored drinks. However, these techniques are expensive, require highly trained operators and have long analysis times. Hence, the interest of new analytical technique, as sensors, was born to simplify operators work. Moreover, the industries prefer an analysis approach that reduce time, cost of analysis and loss of sample. Sensors are a valid alternative to analytical methods. Moreover, sensors are cheaper and practical tools to use. On the other hand, sensors have disadvantages such as the need to multivariate data analysis. Another disadvantage is the possibility that matrix samples can interfere in the analysis. The use of sensors in beverages analyses facilitates operations and reduces times. These techniques could be used to quality analyses ad to identify fraud in beverages. For these reasons, these devices are expected to be applied in the industrial field for any routine analysis.

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