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Electrochemical sensors; Types and applications in the food industry

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ABSTRACT

Today, the use of new technologies in the food industry has become very important and widely used. Identifying these technologies and expanding them is very important for industrial societies. One of the new methods for analyzing and measuring materials in trace levels is elecptrochemical sensors. In the electrochemical sensors the reaction between food analytes and sensors are happen. These sensors have the ability to generate electrical signals appropriate to the concentration of the analytes. These sensors have been very effective in measuring and determining compounds and are being developed using new techniques. These sensors have many advantages over older and more expensive methods, while also being highly accurate. These sensors have a lot of potential and benefits, so in this study, it has been tried to define these new methods by using practical examples and described the use of these new methods in various industries, especially in the food industry.

1. Introduction

In general, a sensor is a device that responds to a physical or chemical stimulus (such as chemical gas, heat, light, sound, pressure, magnetic field, or motion). A chemical sensor is a device that changes its physical properties (such as electrical conductivity, capacity, or mass) when exposed to a compound or mixture of several compounds. The change in these physical properties is used as a physical signal to sense analyte. Electrochemical sensors act through the redox reaction of the species on the electrode surface and generate an electrical signal commensurate with the concentration of the analyte species. Electrochemical biosensors are an important subset of chemical sensors in which electrodes are used as converters that convert biological information into electronic signals. To date, extensive studies have been conducted on electrochemical sensors, and in some cases the sensors obtained from these studies have been commercialized and widely used in various clinical, industrial, environmental, and agricultural fields [1-4]. Electrochemical biosensors are a class of electrochemical sensors whose component detector (receptor) is the biological element. The electrochemical biosensor is able to combine the analytical capability of electrochemical techniques with the specific function of the biological element. The biological receptor is stabilized on the appropriate electrode and the interaction of the analyte (the measured substance) with the biological receptor leads to the production of an electrical signal (Amperometric response, potentiometric response, etc.) which the signal amount depends on the analyte concentration [5].

2. Classification of electrochemical biosensors

According to the structure of biomaterial and detection process, electrochemical biosensors are divided into two categories: 1. Catalytic (enzymatic) biochemical biosensors, whose biological component is an enzyme, cell, or tissue. 2. Optional biosensors, in which antibodies, membrane receptors, or nucleic acids are stabilized on the electrode.

Enzymes are an important class of proteins that catalyze chemical reactions in biological systems. These catalysts are highly efficient and selectable. To make enzymatic sensors, a layer of an enzyme is fixed on a suitable electrode by various methods such as surface

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adsorption, covalent bonding, electrostatic adsorption, polymer trapping, etc. Such a sensor is able to measure the specific substrate inhibitor or substrate with high specificity and efficiency. Oxidoreductase enzymes are most commonly used in the manufacture of enzymatic electrochemical biosensors for clinical applications. The glucose-based enzyme glucose oxidase sensor and the ethanol sensor based on the alcohol dehydrogenase enzyme are valuable examples of enzymatic biosensors. The limited stability of individual enzymes, the high cost of some enzymes, and sometimes their difficult purification have led to the use of cells and tissues as a source of enzymatic activity in the construction of some catalytic biosensors [5].

Optional electrochemical biosensors use selective bonding of some biological molecules, such as antibodies and polynucleotides, with the desired analytes to create the necessary electrical signals. The high selectivity of biochemical bonding reactions (such as the coupling of two strands of DNA or the formation of an antigen-antibody complex) leads to the production of highly sensitive and selective sensors. Immunosensors are an important category of optional electrochemical sensors that are fabricated based on immune responses and specific antigen-antibody interactions. These sensors are very useful for identifying and measuring proteins. The receptor (antigen or antibody) is marked with an enzyme and the enzyme acts on a substrate that produces a product that can be detected by amperometer or potentiometer. Phosphatase and peroxidase enzymes are the most common enzymes that are used in optional electrochemical biosensors.

3. Measurement methods in electrochemical biosensors

Electrochemical methods of analysis are based on measuring current changes, potential, conductivity properties between two electrodes, impedance, and field effect. These techniques are divided into static (with zero current) and dynamic (with the electrical current flow). Static techniques include direct potentiometry and potentiometric titration, and dynamic techniques include potentiostatic (potentially controlled) and galvanostatic (controlled-current) methods. Potential control methods include: Voltammetry, amperometer and polarography types [1]. Electrochemical biosensors are able to use the electrode as an amperometer, potentiometer, conductivity, and impedimetric converter to convert a chemical signal into a measurable electrical signal [5]. The control electrode is usually made of Ag/AgCl and the detector electrode acts as a converter in the biosensor [7-8]. In potentially controlled methods, the potential of the detector electrode is adjusted relative to the control electrode (reference electrode). Therefore, the potential of the control electrode needs to remain constant. In cases where the current passing through the reference electrode changes its potential, a third electrode called the auxiliary electrode is used to pass the current (Fig. 1). In these three electrode systems, a current is established between the auxiliary electrode and the identifier, and the reference electrode is used only to control the potential of the identifying electrode [6].

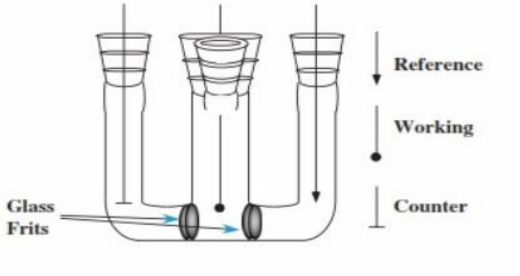

Fig.1. Electrochemical cell of three electrodes system

3.1. Potentiometry

Measuring the potential difference between two floating electrodes in a solution is called potentiometry when almost no current passes through the circuit [6]. In the potentiometric method, information about the composition of a sample is obtained through the potential that appears between two electrodes. This method usually provides information about the concentration (activity) of ions in the sample. The potentiometer is a classic analytical method that has been widely used since the 1970s with the rapid expansion of new selective electrodes and highly sensitive and stable electronic components. Selective potentiometric electrodes are used to evaluate many ions and electrolytes [5]. Potentiometry takes place in two forms: direct potentiometry and potentiometer titrations [7]. In direct potentiometry, by using measured potential and using the Nernst equation (1), the concentration of the desired chemical species can be measured.

$$E_{cell} = E_{0cell} - RT/nF \ln Q \quad (1)$$

Where, R is the gas constant, F is the Faraday constant, and T is the absolute temperature, and Q is the ratio of the ion concentration in the anode to the ion concentration ratio in the cathode. The lowest detection potential is supplied by ionizing electrodes [8]. The ion selection electrode is an identification electrode that can selectively measure the concentration of a particular ion species. Ion selective electrodes are mainly membrane-based instruments composed of an ionic conducting material with a selective permeability [8]. The pH meter is a widely used example of ion-selective electrodes in which the potential difference due to the difference in H+ concentration is used to determine the acidity of the sample [4]. In potentiometric titration, changes in the potential of the electrode during the chemical reaction during titration are measured at zero or constant electrical current. A sudden change in potential at the equilibrium point determines the end of the measurement (the equivalent point) [7].

3.1.1. Chronopotentiometry

In this method, by applying a constant current or square wave, the potential is measured as a function of time [8]. The most basic feature of chronopotentiometry is the change in the potential of the work electrode in proportion to time (Fig. 2). This change in potential results from a gradual decrease in the Ox concentration (oxidized form) and an increase in the R concentration (reduced form) at the electrode surface to the point where the Ox concentration reaches zero and the R concentration reaches its maximum value. At this point the potential suddenly changes. The most important relationship in chronopotentiometry is the Sand equation, which shows the dependence between the time of evolution, the concentration of the experimental species, and the used current step.

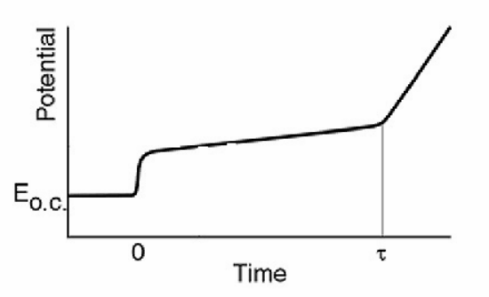

Fig. 2. Chronoproteiogram

3.2. Amperometry

In the amperometry method, the intensity of the current resulting from the interaction of oxidation or reduction of the electroactive species is measured at the applied potential during the electrochemical reaction. The amperometry is based on the relationship between the intensity of the emission current and the concentration of the electroactive compound (which is involved in the production or consumption of electrons). These biosensors are more sensitive than potentiometer biosensors. The working electrode (identifier) is covered with the biological component of the identifier and acts as a converter [8].

Because potential should be controlled in amperometry systems, a third electrode called helping electrode is sometimes used for passing current. In this way, by preventing the current from passing through the main system, the potential difference between the control electrode and the working electrode remains constant over time [7]. Because most analytes are not electroactive, electrochemical mediators are used to react the analyte to the working electrode [8]. These mediators change electrode surface electro activity. Ferrosin is one of the most widely used intermediaries in electrochemical processes.

3.2.1. Chronoamperometry

Chronoamperometry is an amperometry technique in which a potential step is applied to the working electrode and the current is measured as a function of time. Cottrell equation relates the resulting current to the analyte concentration (2):

$$I=nFAC_0D^{1/2}/\pi^{1/2}t^{1/2} \quad (2)$$

Where, I is the current, n is the number of electrons exchanged, F is the Faraday constant, A is the electrode surface, C0 is the analyte concentration, D is the penetration coefficient and t is the time [8].

3.3. Voltammetry

The study of the changes in current caused by a reaction between two electrodes during controlled potential changes is called Voltammetry. Voltammetry is a subset of the amperometry technique. The type of potential (AC, DC) and how it is applied (scanning, pulse and square wave) create different types of voltammeters. The voltage is applied between the control and working electrodes and the current is measured between the working and auxiliary electrodes. The diagram will show the changes in current versus potential changes. In voltammeters with potential, the scan rate should be optimized [8]. The differences between different voltammetric methods are related to how the potential is applied to them.

3.3.1. Normal Pulse Voltammetry (NPV)

In this method, the potential is applied in the form of pulses with increasing amplitude and fixed time intervals to the working electrode. The current is measured at the end of each pulse and the current diagram is plotted according to the potential (Fig. 3).

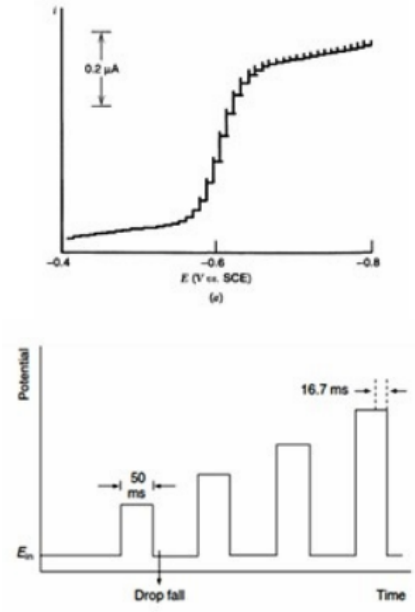

Fig. 3. Potential-time and current-potential diagrams in normal pulse voltammetry

3.3.2. Differential pulse voltammetry (DPV)

In differential pulse voltammetry, the potential is applied in the form of constant-amplitude pulses to an increasing potential. The current for each pulse is applied in two stages, before the potential is applied and at the end of the pulse life, and the difference diagram of

these two currents is plotted according to the potential (Fig. 4). The resulting graph is in the form of a peak. This method has a low detection and high sensitivity diagram due to the elimination of the background current.

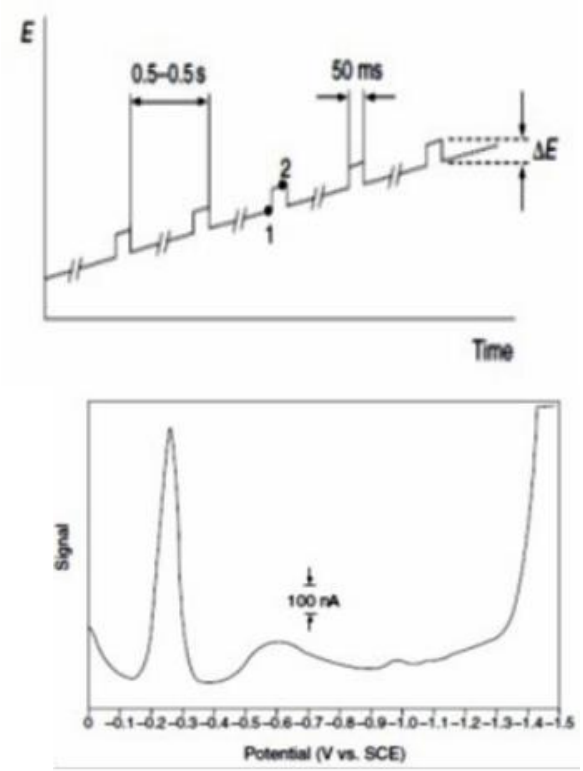

Fig. 4. Potential-time and current-potential diagrams in normal pulse voltammetry

3.3.3. Square wave voltmeter (SWV)

A square wave voltmeter is a large-amplitude differential voltammetry technique. Pulses with a large and constant amplitude are mounted on the increasing potential (Fig. 5). The current is measured at the end of the pulse and the end of the return pulse is measured and these two currents are reduced from each other. The resulting current difference is plotted according to the increasing potential. The most important advantage of the square wave method over the differential pulse method is the high speed of the method. If voltammetry is done on the droplet of dripping mercury instead of a solid electrode, it is called a polarography [8].

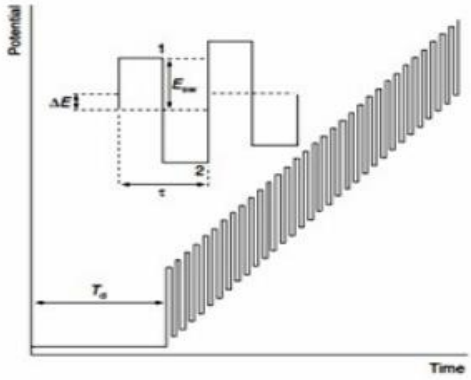

Fig. 5. Potential-Time diagram in square wave voltammetry

3.4. Impedimetric (impedance measurement)

Electrochemical impedance spectroscopy is an effective technique for studying the rate of electron transfer and diffusion in electrochemical reactions. The nature of impedance is the complex resistance that occurs when current flows through a circuit consisting of a resistor, capacitor, and inductor. Electrochemical events at the common location of the electrode and the solution are investigated as components of the electrochemical circuit (resistor, capacitor, and inductor). The impedance spectrum of such an orbit can be used to study electrode surface events. By applying a small sine voltage at W frequency, the current (resistance) changes are measured. The resulting spectrum is drawn as an imaginary resistance to the actual resistance under the name of the Nyquist plot (Fig. 6). The semicircular section at high frequencies is related to the electron transfer process and the linear section at low frequencies is related to the diffusion phenomenon. The specific interaction at the electrode surface can be traced by studying the impedance resistance of the electrode by studying the impedance spectrum. The conductivity technique is a subset of the spectroscopy impedance technique [9-20].

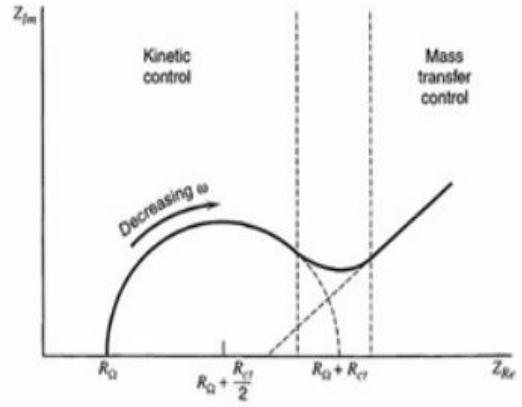

Fig. 6. Impedance diagram of electrochemical system

3. 5. Field-effect transistor (FET)

FET is a type of transistor that uses an electric field to control the conduction of a channel (empty area of electrical charge carriers) between two electrodes (source and drain) in a semiconductor material. The electrical conductivity is controlled by changing the electric field potential of the third electrode (gate) relative to the electrodes (Fig. 7). Depending on the structure and doping performed on the semiconductor material, the presence of sufficient positive and negative potential in the gate electrode will cause the electrical charge carriers to be absorbed or repelled in the channel. As a result, the conduction in the channel is controlled. FET-based systems are suitable for cases with low signal or high impedance and have increasing applications in electrochemical biosensors. FET is converted into sensory instruments by replacing the gate electrode with

a biochemical sensitive surface (such as an analytical-sensitive membrane or a conductive ion solution) that comes in contact with the analytical solution [8].

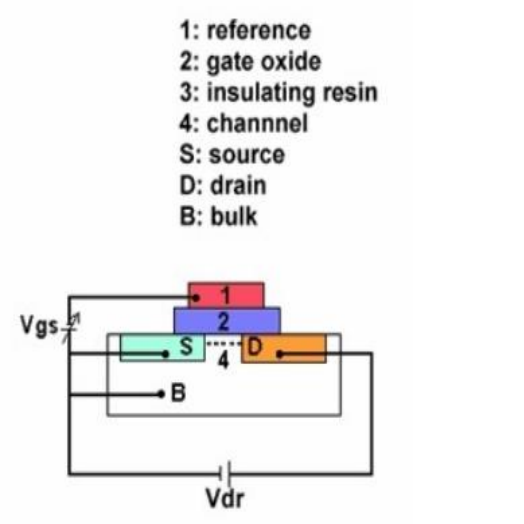

Fig.7. Field-effect transistor

4. Characteristics of suitable chemical biosensor

An optimal biosensor should meet the following requirements:

- The biological catalyst used in the sensor must be completely specific to the intended degradation target and have good stability under normal storage conditions.
- The reaction must be independent of changes in physical conditions such as stirring, pH and temperature.
- The sensor response must be accurate, correct, repeatable, within the desired concentration range, linear and noise-free as much as possible.
- Sensor should be cheap, small, and portable and can be used by non-specialists [5-8].

Biosensors based on electrochemical measurements have attracted a lot of attention due to their small size, portability, fast measurement and low sample size. Surface modification techniques, various electrochemical conversion mechanisms, and the selection of receptor molecules all affect the final sensitivity of the sensor. The signal conversion and the performance of the electrochemical sensors are strongly influenced by the electrode surface design, which connects the sensor element to the nano-scale biological sample. New nanotechnology-based achievements such as the use of ion channels designed in lipid bilayers, encapsulation of enzymes in vesicles, polymersomes, or polyelectrolyte capsules make it possible to amplify the signal as much as possible [6-8]. Nanostructures make it possible to shrink the sensor by building array systems to simultaneously analyze multiple analyzes, high sensitivity to a single molecule, reduce costs, and require a small amount of sample [6-8].

5. Application of electrochemical sensors in the food industry

As the food industry has improved dramatically in recent years and the world's population has grown to more than 7 billion, the day-to-day problems of the industry have become more complex. Due to food storage for a long time and to prevent microbial and chemical spoilage and to prevent food spoilage by insects and microbial agents, the production and storage of food has become very important. Controlling the quality of food is very important for both the consumer and the food industry. A qualitative study of a product in the food industry is examined through a number of different chemical and microbial methods [6-8].

5.1. Application of sensor in the yogurt

Since 2010, electrochemical sensors have been used to measure various analyzes in yogurt. The table below shows the research that has been done so far in the yogurt analysis (Table 1).

Safina et al. (2010) reported rapid and simple approach of lactose analysis based on 3rd generation amperometric biosensors employing cellobiose dehydrogenase (CDH) from *Trametes villosa* or *Phanerochaete sordida* immobilized on screen-printed carbon electrodes (SPCEs). Fabricated sensors were able to detect lactose in a concentration range between 0.5–200 μM and 0.5–100 μM employing T.

villosa and P. sordida CDH, respectively. The limit of detection was 250 nM (90 μg/L) for both. Biosensors based on SPCEs modified with multiwalled carbon nanotubes showed a higher sensitivity than unmodified SPCEs. Cross-linking with glutaraldehyde or poly (ethyleneglycol) diglycidyl ether improved not only the stability but also the analytical response. The developed sensor has been successfully applied for the determination of lactose in dairy (milk with different percentages of fat, lactose-free milk and yogurt) with a good reproducibility (RSD = 1.5–2.2%) [23].

Radoi et al (2010) developed an amperometric biosensor for the determination of L-lactic acid in probiotic yogurts using L-lactate dehydrogenase (EC 1.1.1.27, LDH) entrapped in 1% (v/v) neutralized Nafion® solution deposited on Variamine blue redox mediator modified screen-printed electrodes. The Variamine blue was previously covalently linked to oxidized single-walled carbon nanotubes and used for modifying screen-printed electrodes. The electrochemical cell, containing the L-lactate biosensor operating at an applied working potential of +200 mV vs. Ag|AgCl, was coupled with a microdialysis fiber and connected with a flow system, thus obtaining a microdialysis based sampling experimental set-up. The dynamic linear working range was comprised between $2 \cdot 10^{-4}$ and $1 \cdot 10^{-3}$ M. The proposed biosensor was challenged with real samples of yogurt, properly diluted in working buffer, and the performances of the L-lactate biosensor were compared with a commercially available kit for the determination of L-lactic acid in foodstuffs from R-Biopharm GmbH, Germany, showing a good agreement [24].

Table 1. Electrochemical sensors used for yogurt

Reference	Analyte	Nanoparticle	Electrode type	Year
[21]	NADH	Graphene and graphene oxide	Glassy carbon	2013
[22]	Cu	Azide	Au	2011
[23]	Lactose	Multi-wall carbon nanotube	Screen-printed carbon	2010
[24]	L-lactic acid	Single-wall carbon nanotube	Screen-printed	2010
[25]	Lactose	Mercaptopropionic acid	Au	2010

5.2. Application of electrochemical sensor in meat industry

One of the most important applications of sensors in the food industry is their use in quality control of meat products. The gaseous compounds in the upper space of the meat packages indicate the quality of the meat, the storage time and the storage conditions of the meat. By examining the compounds in the upper space of meat packages, it can be estimated even with the microbial content in the meat package.

Varidi et al. (2018) Designed and developed of application of electronic nose instrument to rapidly detect spoilage of air, vacuum and modified atmosphere packaged camel minced meat. They reported that electronic nose system was used as a rapid technique to classify the freshness of camel minced meat samples during 20 cold storage days in different modified atmosphere packaging. Headspace gas analysis and Microbiological measurements were performed simultaneously as spoilages indices. Sample delivery was based on the dynamic headspace method. The volatile compounds in the headspace of meat samples were introduced into a sensor chamber and the response signals of seven tin dioxide based Taguchi gas sensors (TGS) were recorded as a function of time and packaging type. They found that meat samples could be grouped into fresh and aged categories based on cold storage days and type of packages. Samples of all packages on the first day, those of the fifth day at oxygen, dioxide carbon and nitrogen and samples of days ten and fifteen only at dioxide carbon were fresh. Their results were align with head space gas and total viable count analyses. In conclusion dioxide carbon could be considered as the best package [26].

Due to the negative impact of nitrate and nitrite on human health, their presence exceeding acceptable levels is not desired in foodstuffs. Thus, nitrite determination at low concentrations is a major challenge in electroanalytical chemistry, which can be achieved by fast, cheap, and safe electrochemical sensors. Uzer et al., (2016) studied electrochemical determination of food preservative nitrite with gold nanoparticles/p-Aminothiophenol-modified gold Electrode. They reported that the working electrode (Au) was functionalized with p-aminothiophenol (p-ATP) and modified with gold nanoparticles (Au-NPs) to manufacture the final (Au/p-ATP-Aunano) electrode in a two-step procedure. In the first step, p-ATP was electropolymerized on the electrode surface to obtain a polyaminothiophenol (PATP) coating. In the second step, Au/p-ATP-Aunano working electrode was prepared by coating the surface with the use of $HAuCl_4$ solution and cyclic voltammetry. Determination of aqueous nitrite samples was performed with the proposed electrode (Au/p-ATP-Aunano) using square wave voltammetry (SWV) in pH=4 buffer medium.

Characteristic peak potential of nitrite samples was 0.76 V, and linear calibration curves of current intensity versus concentration was linear in the range of 0.5–50 $mg{\cdot}L^{-1}$ nitrite with a limit of detection (LOD) of 0.12 $mg{\cdot}L^{-1}$. The finally used the sensor for determination of nitrite in sausage samples. The proposed voltammetric sensing method was validated against the colorimetric nanosensing method in sausage samples [27].

5.3. Application of electrochemical sensor in juices

Juices are among the food products that are mostly cheated. These frauds include the addition of artificial essential oils, water and sugar. Mixing cheap juices with more expensive juices is another scam in the juice industry. Due to the fact that in each fruit, a chemical compound as an active and major compound has a standard and specific amount, so by tracking and measuring the effective compound in juices, fraud in the juice can be detected. For example, tartaric acid is the active ingredient in grapes and ascorbic acid is the active ingredient in oranges. By detecting these two acids by electrochemical sensors, possible frauds in these juices can be detected.

Nasirizadeh et al., (2016) Fabricated a novel electrochemical sensor for determination of hydrogen peroxide in different fruit juice samples. They designed hydrogen peroxide (H2O2) sensor based on a multiwalled carbon nanotube-modified glassy carbon electrode (MWCNT-GCE) and reactive blue 19 (RB).

The RB-MWCNT-GCE showed a dramatic increase in the peak current and a decrease in the overvoltage of H_2O_2 electroreduction in comparison with that seen at an RB modified GCE, MWCNT modified GCE, and activated GCE. The detection limit of 0.27 μM and three linear calibration ranges were obtained for H_2O_2 determination at the RB-MWCNT-GCE surface using an amperometry method. In addition, using the newly developed sensor, H_2O_2 was determined in real juice samples with satisfactory results [28].

5.4. Application of electrical sensors in other food samples

In 2016, Sheikh-Mohseni and Pirsa Developed an electrochemical sensor based on carbon paste electrode (CPE) modified with a nanocomposite. The structure and morphology of the nanocomposite were prepared by a combination of polypyrrole nanoparticles and copper oxide (PPy/CuO). This nanocomposite showed good electro catalytic activity. The nanocomposite-based electrochemical sensor (CPE-PPy/CuO) showed a very good electro analysis signal compared to dopamine (DA) and acetaminophen (AC) oxidation. This effect is achieved by high conductivity, low electron transfer resistance and PPy/ CuO catalytic effect. The designed sensor had lower voltage and higher electrical current than the non-modified CPE, for DA and AC. Also, this sensor can eliminate the interfering peaks of DA and AC and is therefore used in simultaneous determination of DA and AC. Interpretation and preparation of calibration with wide linear ranges showed that this sensor has the appropriate sensitivity for differential pulse voltage measurement for DA and AC. Suitable Detection limits were also observed, including 0.020 μM for DA and 0.025 μM for AC. Finally, an electrochemical sensor was used to determine DA and AC in the actual salt [29].

In another study, Bagheri et al. In 2016 developed a new electrochemical sensor based on copper metal nanoparticles/reduced graphene oxide nanotubes with multi-walled carbon nanotubes (copper/MWCNT/RGO) for individual and simultaneous determination of nitrate and nitrate ions. The nanocomposite morphology prepared on the surface of the glassy carbon electrode (GCE) was identified using various methods such as scanning electron microscopy (SEM), atomic force microscope (AFM) and electrochemical impedance spectroscopy. Under optimal laboratory conditions, the modified GCE showed excellent catalytic activity and electrolyte reduction of nitrate and nitrate ions in pH = 3.0 compared to the non-modified GCE. Using square wave voltammetry (SWV), the designed sensor showed a wide linear range of 0.1 to 75 M and detection limit of 30 nm and 20 nm for nitrate and nitrate ions respectively. In addition, the proposed modified electrode was used to measure nitrite and nitrate in food products such as sausages, cheese and drinking water [30].

In 2016, Sheikh-Mohseni and Pirsa Developed a modified carbon paste (CPE) electrode with a nanostructured material. The nanostructures were synthesized by electro catalytic activity with a combination of polypyrrole nanoparticles and copper oxide (PPy/CuO). The modified electrode (CPE-PPy/CuO) exhibited excellent electro catalytic activity over L-dopamine (L-DOPA) and uric acid oxidation (UA) due to its high conductivity, low electron transfer resistance, and catalytic effect. CPE-PPy/CuO had lower voltage and amplified electric current compare to unmodified CPE for both L-DOPA and UA. This electrode was used to simultaneously determine of L-DOPA and UA. The electrochemical sensor responded to L-DOPA and UA, respectively, in the 0.050-1200 and 0.040-1000 μM. The detection limit was obtained with a voltammetric pulse differential as 15 nM for L-DOPA and 20 nM for UA. Finally, the proposed electrode was used to determine L-DOPA and UA in real samples using the standard addition method [31].

In 2011, Araujo et al. Designed and evaluated a simple, low-cost carbon graphite electrode to directly determine citrate in food samples. The electrode could detect citrate with a detection limit of 3.0 mol L^{-1}. The electrode is easily made at a relatively low cost and has a fast response time (within 120 seconds). Finally, the performance of the graphite sensor was tested to determine citrate in beverage samples (fruit juice and an isotonic drink). The proposed sensor compare to the previous reported sensors was fast, cheap, selective, and sensitive [32].

In 2016, Galstyan et al. developed a special sensor to detect volatile organic compounds by producing a nanostructure composite based on graphene oxide and ZnO. Sensor responses were studied for different concentrations of ethanol and acetone. Modification of graphene structure using ZnO nanostructures showed significantly higher response to than ethanol and acetone unmodified sensor. The results show that the designed sensor is a suitable tool for monitoring environmental pollutants and for use in respiratory tests in assessing exposure to volatile organic compounds [33].

In a study, Ikhsan et al (2016) studied the effect of ascorbic acid on the formation of reduced graphene-silver oxide (rGO-Ag) nanocomposite and reported its effect on electrochemical oxidation of nitric oxide (NO). Crystalline and spherical silver nanoparticles (NPs) with an average particle size of 2 nm were combined in rGO-Ag nanocomposite. The electrochemical properties of the modified rGO-Ag (GC) nanocomposite glass carbon electrode for NO oxidation were investigated. Electro analytical application of the nanocomposite was performed using the amperometric technique, and the detection limit (LOD) for the detection of NO was 2.84 μM. The designed sensor to detect NO was stable, sensitive, and selective in the presence of conventional physiological drugs such as ascorbic acid, uric acid, dopamine, glucose, urea, and calcium [34].

Routine is a type of flavonoid. Flavonoids have antioxidant properties and are found in fruits and vegetables. For these reasons, routine diagnosis is important based on the sensitive procedure. In 2017, Yola et al. developed a new electrochemical sensor based on ionic liquid CoFe2O4 nanocomposite for routine analysis in orange water samples. Sensor detection limit for measuring routine was 3.0 × 10-11 M [35]. In 2019, Pirsa and Shamusi designed the electrical

conductive film based on cellulose-polypyrrole-ZnO film. They used the film to intelligently pack chicken thighs meat. The researchers examined the electrical conductivity changes of the cellulose-polypyrrole-ZnO film during the storage time of the chicken thigh meat and identified the physicochemical properties of the chicken thigh and the shelf life of the chicken thigh meat. They reported that the film, as a smart sensor, can detect the time of chicken thigh spoilage [36].

Pirsa and Mohammad Nejad (2017) used an electric array sensor based on polypyrrole–zinc oxide (PPy–ZnO) and PPy–vanadium (V; chemical formula: V2O5) fibers to measure volatile substances in food products such as milk. They reported that the sensors were able to simultaneously measure several volatile compounds in food products. They used a response surface regression analysis for correlating the responses of the sensors to diacetyl, lactic acid and acetic acid concentrations during the gas phase in food samples. The developed multivariate model was used for simultaneous determination of diacetyl, lactic acid and acetic acid concentrations. Some food samples with unknown concentrations of diacetyl, lactic acid and acetic acid were provided, and the responses of array sensors to each were recorded. The responses of each sensor were considered as target response in a response optimizer, and by an overall composite desirability, the concentration of each analyte was predicted. The present work suggests the applicability of the response surface regression analysis as a modeling technique for correlating the responses of sensor arrays to concentration profiles of diacetyl, lactic acid and acetic acid in food samples [37].

Pirsa et al. (2016) used a sensor based on polypyrrole/silver nanoparticles to detect milk spoilage. They reported that the changes in the electrical conductivity of the Polypyrrole-Ag sensor in the presence of spoiled milk are very different from those of healthy milk. The researchers reported that this sensor is very sensitive to pH changes, and because rotten milk has a different pH than healthy milk, the sensor can easily detect milk spoilage [38].

Ghasemi et al. (2020) used a bacterial cellulose/polypyrrole/TiO2-Ag (BC/PPy/TiO2-Ag) nanocomposite conducting film to detect and measure the growth of 5 pathogenic bacteria. Their results showed that by increasing the bacterial concentration, the electrical resistance of sensors was decreased and there was a relation between bacterial concentration and bacterial type with electrical resistance change of sensors. The obtained data showed that the sensitivity of the sensors was increased with increasing the concentration of polypyrrole and TiO_2-Ag. The BC/PPy/TiO_2-Ag biosensors was portable and the response time of these sensors was very short for target analysis. Therefore, these sensors have the potential to improve biological safety as diagnostic tools [39].

6. Conclusion

Introducing new methods for food analysis is one of the most important issues in food quality control. These methods, along with their accuracy and repeatability, should have advantages such as high accuracy of measurement, sensitivity, cheapness, etc. One of the new methods is the use of electrochemical sensors, which due to their structure, and the way they work is very good for the food ingredients analysis, so these are the reasons why researchers and active scientists in this industry are thinking about the efficient use of this technique. The important advantages of sensor application in food industry include response accuracy, short response time, widespread use for a variety of compounds, low measurement time, low cost, and more.

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