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Review Article

Electrochemical Sensors for Histamine Detection: A Review

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Abstract

Electrochemical sensor development is increasing across various applications, including food, pharmaceutical, medical, and environmental assessment. The sensors offer advantages, including enhanced detection performance, rapid response, portability, high sensitivity, and selectivity, which are important for portable sensing applications, such as histamine detection. Histamine is usually found in protein-rich foods as a biogenic amine produced by histidine decarboxylation. The presence of histamine is a marker of food spoilage and a potential for scombroid poisoning. Therefore, a reliable, sensitive, and rapid detection is required. This review discusses the principle of electrochemical detection and the parameters governing sensor performance, including sensor material, surface modification, temperature, pH, and interferences. Some materials were studied include carbon nanotubes, graphene, metal nanoparticles, conductive polymers, and enzymes. Furthermore, this review provides recent trends, challenges, and future perspectives in histamine detection.

Keywords: Electrochemical sensor, Electrode material, Future perspective, Histamine, Surface modification

1 Introduction

Histamine, a biogenic amine, is essential in regulating normal physiological and pathological conditions [1]. In food safety, especially seafood, histamine is a marker for spoilage and a potential cause of scombroid poisoning [2]. Reliable, sensitive, and rapid detection of histamine is essential [3]. Histamine is available in food, which is produced through microbial-mediated decarboxylation of histidine present in foods with high protein content [2], such as wine, fish, meat, and dairy. It is also available in the body as a synthesis product of mast cells, basophils, and neurons, as part of allergic and inflammatory responses [1]. Based on the European Union (EU) and the Food & Drug Administration (FDA), the maximum limit of histamine for fish products should be ~ 50 mg kg^{-1} for daily intake limits and safety thresholds for sensitive populations [4], [5].

Extensive research on histamine detection has primarily been conducted using high-performance liquid chromatographic (HPLC) [6], [7], gas chromatographic (GC) [8], and mass spectrometry analysis (MS) [9]. Although these techniques are effective in detecting histamine in biometrics, they often require labor-intensive sample preparation [7], specialized expertise [10], and time-consuming procedures, which restrict their practical application in fishery enterprises and market supervision. Therefore, research was conducted to develop a simpler detection method, such as an electrochemical sensor.

Electrochemical sensors are increasingly favored for their simplicity, portability, sensitivity, and low cost [11], [12]. The types of electrochemical sensors include enzyme-based and non-enzyme-based sensors. The principle of enzyme-based histamine sensors is to convert histamine to H_2O_2, which is measured electrochemically via diamine oxidase (DAO) catalytic activity. On the other hand, non-enzyme-based sensors utilize the direct chemical interaction (redox) of histamine with the electrode surface, for example, with metals, NPs, or porous materials. Ahmed *et al*., reported that modifying the working electrode with a molecularly imprinted polymer (MIP) significantly influences the overall performance of the sensor [13]. Ngwekazi *et al*., [11] also successfully immobilized CB[7] onto a glassy carbon electrode for the detection of histamine in red wine with good recovery. Other research developed a Nafion/MWCNTs composite membrane that improved sensitivity, electron-transfer efficiency, and measurement reproducibility [14]. In addition, nanocomposites also show strong potential as promising sensing materials [15]. Recently, several researchers have developed screen-printed carbon electrodes (SPCEs) due to their suitability for on-site applications, ease of surface modification, and cost-effectiveness for mass production. Moreover, they are highly compatible with portable readers or smartphones. Munir *et al*., [16] successfully modified the electrode using polyurethane and lithium perchlorate. In addition, SPCEs have also been modified with Ag/Cu [17], chitosan-based enzyme [12], and nanomaterial WS_2 [18].

This review describes the electrochemical detection of histamine, including the application of the modified electrode incorporating organic, inorganic, and biomaterials. In addition, it discusses the challenges of application and the prospects of electrochemical-based sensors designed for histamine analysis. For initial consideration, Table 1 provides an electrochemical sensing comparison to other histamine analysis methods.

2 Principle of Electrochemical Detection

Electrochemical sensors detect histamine based on its redox activity or through enzymatic reactions leading to electroactive byproducts. In general, electrochemical reactions are carried out using a three-electrode setup, including a working electrode (WE) as the sensing electrode, the reference electrode (RE), and the counter electrode (CE) [32], [33] (Figure 1). Modification of the working electrode is crucial for enhancing the sensor's analytical performance by improving sensitivity and lowering the detection limit [34]–[36]. SPCEs serve as a platform for electrochemical sensors, created by coating carbon materials onto substrates such as plastic, ceramic, or flexible polymers.

Table 1: Methods, principles, and sensitivity of histamine analysis.

Method	Principle	Sensitivity	Ref.
Chromatographic:			
High-Performance Liquid Chromatography (HPLC)	Differential interactions between the stationary and mobile phase	High sensitivity and reproducibility	[19]
Gas Chromatography	Volatilities and affinity of the compound	Good resolution for volatile compounds	[19]
LC-MS/MS (Liquid Chromatography–Mass Spectrometry)	Differences in physicochemical properties and mass ratios	High selectivity, multi-analyte detection	[20]
Spectrophotometric:			
UV- Vis Spectrophotometry	Measure the absorbance of the histamine derivative	moderate	[21], [22]
Colorimetric Kits	Enzymatic reaction producing a color change	Easy to use, semi-quantitative	[23], [24]
Electrochemical sensors:			
Amperometric/ Voltammetric	Measures current from redox reactions or enzymatic product (e.g., H_2O_2)	Rapid, low-cost, portable	[18]
Impedimetric	Monitors changes in electrical impedance upon histamine binding	High sensitivity	[25], [26], [27]
Biosensors & Immunoassay			
Enzymatic Biosensor	DAO or HAO to catalyze histamine	High sensitivity but limited stability	[12][22]
Aptamer-based sensors	Nucleic acid aptamers bind histamine	High selectivity, reusable	[28], [29]
ELISA (Enzyme-Linked Immunosorbent Assay)	Antibody-antigen interaction	Accurate but labor-intensive	[30], [31]

The advantages of SPCEs include their ease of mass production and low cost, owing to the natural abundance of carbon. Their rough and porous electrode surfaces facilitate modification with various materials. Additionally, the carbon surface of the electrode is chemically inert, providing stability under various conditions, including different pH levels, aqueous media, and other environments. Meanwhile, the primary measurement techniques commonly employed are amperometry, voltammetry, and impedimetric sensors. This electrochemical-based sensor functions as a transducer, converting chemical sensing into a detectable signal for calculating the target analyte concentration [37].

Amperometric measurements are performed to monitor the current response generated by the working and reference electrodes at a fixed potential arising from the redox reaction of histamine or related enzyme products. This is used as a quantitative parameter to determine the histamine concentration in the sample [38]. The amperometric techniques provide low detection limits, fast measurement times, and ease of signal processing [39]. The study conducted by Puthongkham *et al.*, [40] showed that histamine oxidizes at +1.1 V, while no oxidation was observed below +0.9 V. In addition, impurities were observed on the electrode surface due to histamine oxidation, as indicated by a decrease in the histamine signal. Meanwhile, voltammetry measures current in response to potential changes by scanning the potential at the working electrode relative to the reference electrode. The current measured from the scan is then plotted as a function of potential [41]. Voltammetry (CV, DPV, SWV) provides detailed redox behavior and quantification. A polyurethane (PU)-modified screen-printed electrode (SPE) can be used as a substrate for adsorbing histamine prior to oxidation. The test was carried out using CV, with PU-SPE as the working electrode, an Ag/AgCl reference electrode, and a platinum wire (Pt) used as the counter electrode [42]. The determination of histamine using an impedimetric sensor depends on resistance changes at the Schiff base complex-modified electrode surface when the lone electron pair of histamine nitrogen binds to the metal center d-orbitals in the Schiff base complex. Monitor changes in impedance due to histamine binding or reaction. The study conducted by Sahudin *et al.*, [43] developed TiO_2 nanoparticles, which were then immobilized on a fluorine-modified tin oxide conductive electrode. This aimed to improve the conductivity properties of the FTO and enhance the density of chemical receptors on the surface.

In the literature, when the measurement aims to achieve rapid, quantitative detection, amperometry is generally the most effective technique. Meanwhile, the voltammetry technique is well-suited for studying reaction mechanisms or for distinguishing multiple analytes within a single sample. On the other hand, impedimetry is most commonly employed to study surface interactions and antifouling properties [44], [45], [46].

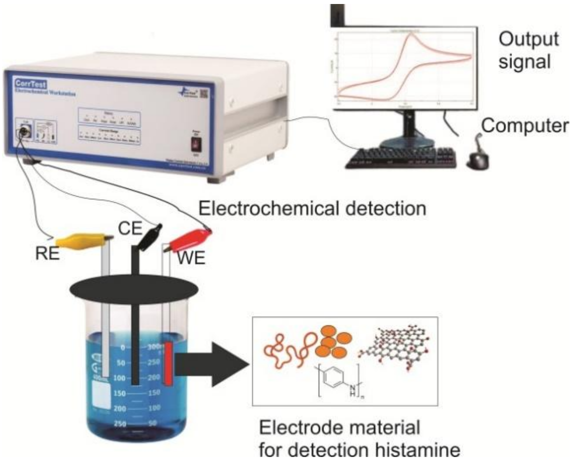

Figure 1: Conceptual schematic illustrating the electrochemical mechanism involved in histamine determination.

3 Types of Electrochemical Histamine Sensors

3.1 *Enzyme-based sensor*

The working mechanism of an enzyme-based sensor utilizes enzymes like histamine oxidase (HAO), diamine oxidase (DAO) to catalyse histamine into imidazole acetaldehyde, hydrogen peroxide, and ammonia [34], [35]. The electrochemical oxidation of histamine produces hydrogen peroxide (H_2O_2), which induces a measurable change in current. Related studies have shown that the use of enzymes provides high specificity and good sensitivity. However, enzyme instability disrupts the redox process.

A study conducted by Torre *et al.*, [47] successfully employed DAO immobilized on SPCE using glutaraldehyde (GA) in combination with bovine serum albumin (BSA). The technique used amperometric measurement, requiring only 40 µL of sample solution and yielding a response duration of approximately 60 s. The results showed that a cathodic current was clearly observed in the range of -0.6 and 0

V, depending on the histamine concentration, with recovery values from fish samples of around ~100% [48]. Furthermore, excellent reproducibility was observed for the sensor. The scheme of the proposed mechanisms for the enzyme and electrochemical reactions in histamine detection (Figure 2). It indicates that the current increases with increasing concentration. Meanwhile, Leonardo *et al*., [49] have developed a mono-enzymatic biosensor using DAO conjugated to magnetic beads (MBs) immobilized on Co(II)-phthalocyanine/carbon and Prussian Blue/carbon electrodes. This sensor detects biogenic amines (BAs) in a sea bass sample and is compared with a colorimetric enzyme assay, which shows no significant difference. A histamine biosensor was constructed using a screen-printed carbon electrode modified with Prussian Blue and an MWCNTs/chitosan/AuNPs composite. The sensor exhibited two linear response ranges, namely 2.50-125.0 µmol L^{-1} and 125.0-400.0 µmol L^{-1}. This method achieved a LOD of 1.81 µmol L^{-1} and demonstrated good reproducibility (RSD = 5.46%), high selectivity, excellent operational stability, and outstanding long-term stability [12].

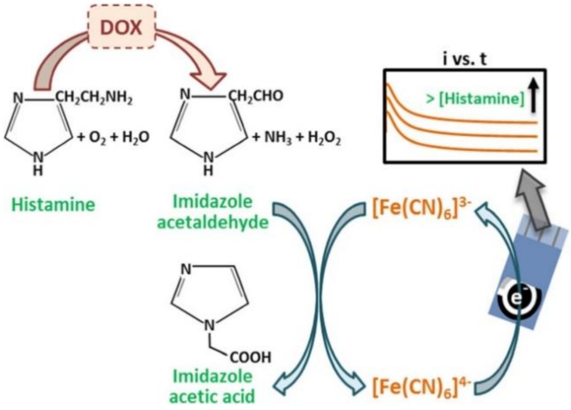

Figure 2: Scheme of proposed mechanisms for the enzyme and electrochemical reaction for histamine detection. Reproduced from the reference [50]; under CC-BY 4.0 license.

Although enzyme-based electrochemical methods have high sensitivity and selectivity for histamine detection, enzymes still have several disadvantages, including the typically slow reaction with enzymes and the fact that enzymes are proteins, making them susceptible to degradation and instability [42], [43], [47]. Therefore, special treatment is required to prevent enzyme inactivation [51], [52], [53]. Besides that, electrode modification, such as the incorporation of nanomaterials, is required to enhance electron transfer and support enzyme immobilization [12].

3.2 *Non-enzymatic sensor*

In addition to enzyme modification, an electrochemical sensor may be modified by adding graphene oxide, metal-organic frameworks (MOFs), or nanocomposites. Graphene is a single-layer, honeycomb-shaped material with a 2D structure. Meanwhile, graphene oxide (GO) is a derivative of graphene, formed by a functionalized two-dimensional carbon honeycomb lattice with groups containing an oxygen atom [49], [50]. This structure yields diverse characteristics, including extensive surface area, high electron mobility, and strong mechanical strength [54], [55]. Therefore, the graphene can increase the detection area of target molecules. For example, Saghatforoush *et al*., [56] fabricated a sensor using a glassy carbon electrode functionalized with polystyrene-graphene oxide. The GO modification produced a highly efficient nanosensor for the electro-oxidation of histamine, achieving a detection limit of 0.03 µmol L^{-1} and spike recovery values ranging from 98.2% to 103.1%. Moreover, a graphene oxide/multi-walled carbon nanotube (GO/MWCNTs) composite has been synthesized and immobilized onto the surface of a humanoid-shaped tapered optical fiber (HTOF) incorporating gold nanoparticles. This sensor demonstrated a detection limit of 59.45 µM, indicating its high suitability for histamine detection in marine products [57].

Molecularly Imprinted Polymers (MIPs) are synthetic polymers used to recognize target molecules such as histamine. The basis of MIPs is the formation of a 3D polymer matrix with nano- or micro-sized particles, specific to the target molecule [37]. In the synthesis process, binding occurs involving interactions between the template species and the functional monomer using a binding group. Polymerization then occurs due to the excess cross-linking agent. The selection of functional monomers depends on the medium in which the MIPs will be prepared, for example, organic or aqueous [58]. However, this method requires a reengineering of the fabrication process to avoid additional costs in large-scale production. These polymers are prepared by copolymerizing functional monomers using a template and a cross-linking agent to stabilize the resulting polymer network (Figure 3) [53], [59]. A flexible polymer-based sensor, such as polymers for histamine detection with a range of 100-500 ppm [60]. MIPs-based electrochemical sensors offer excellent sensitivity, selectivity, stability, and reproducibility [61], [62]. Munir *et al*., [63] synthesized PU-based MIPs coated onto SPE with the addition of lithium perchlorate, which were capable of detecting histamine in mackerel. These detections required only about 2 minutes, which is faster than chromatographic methods, and they demonstrated higher selectivity toward histamine compared to putrescine and cadaverine. Nevertheless, the use of MIPs as sensors also has disadvantages, including complex polymer preparation and imperfect template fabrication, which can hinder the detection of small molecules [30]. Meanwhile, other researchers have successfully detected histamine in red wine employing CB[7] functionalized electrodes. The addition of an interferent to the cell caused a potential shift to 1.06 V. Square-wave voltammetry demonstrated that the CB[7]-modified electrode enabled detection of histamine (HI) at levels below [11].

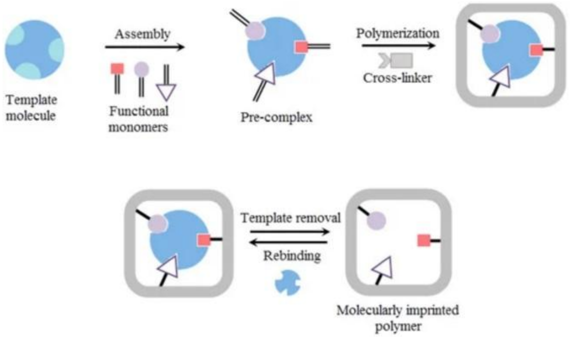

Figure 3: Schematic overview of the molecular imprinting polymer preparation procedure. Reproduced from the reference [64] under CC BY 4.0 license.

In addition to MIPs, aptamers are also used for selective molecular recognition, in which the single-stranded DNA or RNA oligonucleotides of aptamer capable to bind specific targets due to their selectivity and sensitivity [65]. However, it required an immobilization strategy to maintain aptamer binding stability to the sensor matrix [66]. The aptamer recognizes and interacts with target molecules such as histamine, and a transducer converts the molecular interaction into a signal [67]. Combining an aptamer to a sensor surface was successfully conducted by Eksin *et al*., [68] for histamine detection, who immobilized aptamers to the working electrode surface, followed by incubation with histamine to produce an aptamer-histamine complex. The electrode was assembled as an electrochemical Paper-based Analytical Devices (ePADs) and then tested by Differential Pulse Voltammetry (DPV) to understand its sensing performance.

MOFs are commonly used in electrochemical sensing platforms for selective recognition of biogenic amines. Hadi *et al*., [69] fabricated a sensor using Ni-BTC MOF crystals combined with a modified glassy carbon electrode. Excellent sensitivity and stability were achieved with the modified electrode. A linear calibration was obtained between 1.00 and 160.00 µM, with an LOD of 0.41 µM and a sensitivity of 0.19 µA µM^{-1}. The research conducted by Xu *et al*., [70] is the development of electrodes with MOF-derived Ni@C to determine histamine with an LOD of 3.2 × 10^{-4} µM. However, not all MOFs can be used for electrochemical-based sensors. Sensor performance is influenced by several important characteristics and conditions, such as MOFs that have high conductivity, large pores, and uniform distribution [71], [72], normal pH and temperatures less than 60 °C because sensitive to decomposition [73]. Furthermore, recent progress has been made in the application and design of MOFs (Figure 4).

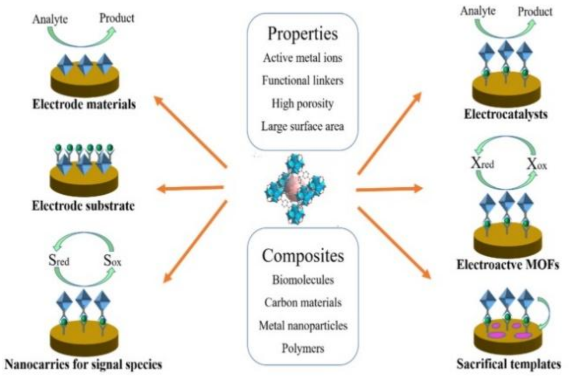

Figure 4: The schematic of the distinct properties of MOFs and their composites in an electrochemical sensor. Reproduced from the reference [74] under CC BY 4.0 license.

An electrochemical sensor can also be produced from a composite nano-material, which exhibits excellent mechanical, optical, thermal, and electrical properties [75]. Nanocomposite consists of two or more matrix phases (ex, polymers and metals) and a reinforcing phase (ex., Carbon, oxide, MOFs, metal nanoparticles) with one of them being nanometer-sized (1-100 nm) [76]. Azizi *et al*., [77] developed a CuO NPs/GO composite-SPCE for the determination of histamine and uric acid. The modified electrode exhibited good stability, simple preparation, and high sensitivity for detecting HIS and UA. The detection limits (LODs) of HIS and UA were 0.94 µM and 0.25 µM, respectively. Non-enzymatic sensors hold considerable promise owing to their enhanced durability, reusability, and reduced cost compared to enzymatic counterparts [78]. However, because they lack the biological structural specificity of enzymes, non-enzymatic sensors require electrode surface modification to improve sensitivity and selectivity.

4 Key Factors Affecting Electrochemical Sensor Performance

4.1 *Electrode material and surface*

Electrochemical sensor performance is influenced by multiple factors, including electrical conductivity, the surface area, and the functional material used for sensor production. Graphene, CNTs, and gold particles have been proven to enhance electron transfer in a sensor and subsequently accelerate histamine detection [12]. Nontipichet *et al*., [12] designed an enzyme-based biosensing system using SPCE modified with a chitosan-AuNPs composite cryogel on Prussian blue-coated MWCNTs. SEM image of MWCNTs/SPCE after Prussian Blue electrodeposition shows the presence of spherical particle aggregation at the surface of the MWCNTs/SPCE electrode. Meanwhile, a highly macroporous network in the DAO-CS-AuNPs cry/PB/MWCNTs/SPCE film enhances mass transfer rate and expands the active area for enzyme attachment. In 2025, Navarro et al. developed an electrochemical-based histamine sensor using a screen-printed gold electrode modified with an L-Cys/Cu(II) complex. The LOD was determined within the histamine concentration range of 0.1–1.0 µM, resulting in an LOD of 0.126 µM [79]. The complexation of Cu is formed through the –SH, -NH_2, and –COOH groups on L-Cys [79].

Another effort to enhance sensor performance is by incorporating functional materials into the sensor. Ye *et al*., [80] incorporated bio-functionalized magnetic nanoparticles (MNPs) into an electrochemical sensor (Figure 5). TEM images of the MNPs-modified sensor show the MNPs' diameter at around 10 nm. Furthermore, around the MNPs, there is a thin layer of modification with antibodies. Meanwhile, the cross-sectional image shows no blocking in the nanopore, indicating no target capture. When the antibody-MNPs capture a target molecule, the MNPs adhere to the nanopore walls, and the nanoparticles act as labels, even though their presence may block further ion flow.

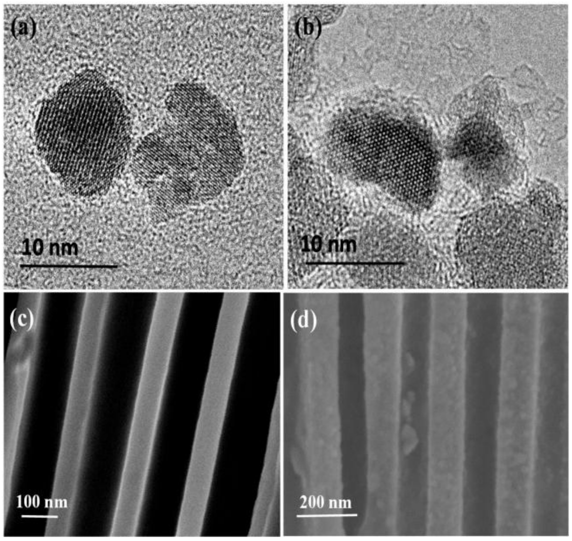

Figure 5: TEM images of MNPs before (a) and after conjugation (b); SEM images of cross-sections of the histamine-MNPs porous alumina membrane unmodified (c) and modified with antibodies (d). Reproduced from the reference [80] under CC-BY 4.0 license.

Another work found that modifying Au@Fe-BDC with the sensor. It was found that the modification enhanced bonding with polymers due to their unique structure [62]. These nanostructured particles provide more active sites, thus facilitating enzyme immobilization. A study by Rivera *et al*., [81] found that combining the sensor with Au particle size yielded high sensor performance, with a detection limit of 0.72 µM in the 1-10 ppm range. In addition, material functionalization is needed to increase selectivity and compatibility with biomolecules. Moreover, the performance of several sensor types is presented in Table 2.

Table 2 shows that the MOF-based sensor, i.e., Ni-BTS/CNT-modified, exhibits a lower LoD than the enzyme-based sensor. It indicates that MOF offered better electrochemical performance because of its chemical and thermal stability [82], which is more resistant to environmental conditions, pH, and solvents. So, they are not easily degraded during electrochemical processes.

Table 2: Performance of several types of sensors for histamine detection.

Transduser	Bioreceptor	Material modification	Real sample	Detection Range	LoD	Reproducibility (%)	Stability (day)	Recovery (%)	Ref.
Glassy carbon electrode	-	Ni/CoMOFs	wine	18–333 μM	0.55 μM	< 5	28	98.13	[84]
Diamond Electrodes	-	Boron	fish	0–150 ppm	20.9 ppm			88.2–99.9	[53]
Glassy carbon electrode	-	Ni-BTC/CNT	Spiked human urine	1–160 μM	0.41 μM = 0.046 ppm	1.13–3.11	-	96.44–98.24	[69]
Nano carbon electrode	Molecularly imprinted polymer (MIPs)	-	Human serum	$(1\times10^{-10} – 7\times10^{-9})$ M & $(7\times10^{-9} – 4\times10^{-7})$ M	7.4×10^{-11} M	2.02–3.58	-	95–105	[85]
Screen-printed carbon electrode	Diamine oxidase	TiO_2 nanoparticles, CNTs, rtthenium hexaamine	cheese	1–120 ppm	0.8 ppm	3.4	-	101.1–103.0	[86]
Flexible paper-based electrode	-	Conductive nano-silver ink	meat	10–1000 nM	10 nM	2.33–3.04	-	-	[87]
Glassy carbon electrodes	Thiolated aptamer, MIPs	AuNPs/CNTs	Tuna fish	0.46–35 $mmol.L^{-1}$	0.15 $nmol.L^{-1}$	2.59–3.96	14–21	95.3–104.4	[88]
Screen-printed carbon electrode	Diamine oxidase	Chitosan-AuNPs	fish	2.50–125.0 $\mu mol.L^{-1}$ & 125–400 $\mu mol.L^{-1}$	~1.81 $\mu mol.L^{-1}$	5.46	35	93–108	[12]

In addition, the presence of high sensitivity active site enables a greater number of histamine molecules to be adsorbed [83]. Beyond material characteristics, the production cost of enzyme-based sensors is relatively higher because enzymes require complex purification and specialized storage media.

4.2. *Immobilization of biorecognition elements*

In an immobilized bio-recognition sensor, the amount of enzyme and its bioactivity are key factors influencing the biosensor signal. An increase in enzyme concentration can enhance the signal; however, an excessive amount may lead to steric hindrance and reduced activity due to interactions among immobilized proteins [89], [90]. Steric hindrance can be prevented by inserting or attaching spacers (e.g., alkyl chains, amino acids, etc.) to the carrier molecule. The spacer increases the distance between the reactive groups and the carrier, making the reaction proceed more easily [91].

The most commonly used immobilization techniques are physical adsorption, covalent bonding, and entrapment in polymers (Figure 6). The immobilization aims to prevent the undesired release of enzymes from the matrix surface and to enhance thermal stability [92]. The immobilization process plays a crucial role in determining sensor stability and sensitivity. This is due to the electron transfer mechanism between the enzyme and the electrode surface, which enables electrical conduction. Effective interaction between the enzyme and the supporting matrix can enhance direct electron transfer (DET), thereby improving biosensor performance [93].

In the physical adsorption method, enzymes bind to the support material through hydrophobic interactions, hydrogen bonding, and van der Waals forces. In addition, ionic bonding is also possible through salt linkages. The physical adsorption method is reversible; once the enzyme activity has decreased, the support material can be regenerated [94].

The entrapment method confines the enzyme within the matrix, forming a solid or gel, thereby isolating it and making it more stable, easier to separate, and reusable. However, there is still an issue regarding the limitations of mass transfer and enzyme leaching [95].

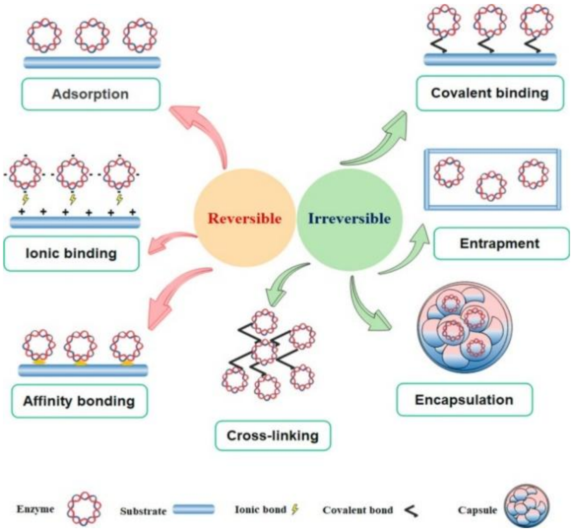

Figure 6: Techniques of enzyme immobilization. Reproduced from the reference [96]; under CC BY-NC-ND 4.0 license.

4.2 *Mathematical text and equations*

In enzyme-based sensors, the electrolyte pH is a key factor governing sensor performance and stability. Since enzymes are biological catalysts with specific active sites, their catalytic activity depends on the pH of the surrounding medium. Enzymatic activity reaches its maximum within a specific pH range, making pH optimization necessary to prevent structural change, activity decrease, or denaturation [97]. It also affects electron transfer between enzymes, mediators, and electrode interfaces [98]. Based on several studies, it is stated that the histamine oxidase enzyme has optimum activity at pH 6.5–7.5 [99]. Apetrei *et al.*, [100] reported the development of a biosensor whose performance was evaluated using amperometric techniques, with measurements taken in solution at pH 7.4 as the optimal operating condition. Several studies have also published that enzyme-based sensors show the most optimal performance under neutral pH conditions [48], [101]. Therefore, careful adjustment and control of the electrolyte are essential for designing enzyme-based sensors to achieve optimal performance, long-term stability, and reliable detection.

Although non-enzymatic electrochemical sensors do not depend on biological catalytic activity, the electrolyte pH still plays a crucial role in determining their analytical performance. Variations in pH can modify the configuration of the electrochemical double layer (EDL). Structure change in charge distribution at the electrode interface can influence the local electric field and electrode-electrolyte interactions. Furthermore, pH significantly impacts the surface adsorption energy of reactant or product molecules on the electrode, thereby affecting the overall reaction mechanism as well as the rate of electron and proton transfer [102].

The Nernst equation states that the redox potential of proton-coupled electron transfer (PCET) reactions shifts linearly with pH, typically by about 59 mV per pH unit at 25 °C [103], [104]. The study conducted by Biabangard *et al.*, [105] varied the pH from 0.6 to 1. Electrochemical studies demonstrated that pH strongly influences redox behavior, adsorption, and charge transfer at the gold surface of nanopolyaniline (nPANI). The peak potential decreases linearly with pH at a slope of about 60 mV per pH unit, indicating complete protonation, whereas at higher pH values only partial protonation occurs. Histamine and uric acid detection with a carbon paste electrode functionalized with CuO Nanoparticles/Graphene, resulting in the highest oxidation peak for uric acid and histamine at pH 7. The result was obtained after a performance test of 200 µM uric acid and 200 µM histamine in 0.1 M PBS over a pH range of 3 to 8 [77]. Additional measurements were conducted at pH 8.4, as this condition was compatible with the characteristics of BDD electrodes, which showed high stability. In addition, under these conditions, histamine remains relatively stable and can readily participate in electrochemical reactions [53].

4.3 *Temperature*

Temperature contributes to regulating enzyme activity. A moderate heat can enhance kinetic energy and active-site flexibility, leading to higher reaction rates and more efficient substrate binding. The temperature increase will also enhance charge-carrier mobility, improve conductivity, and accelerate electron-transfer kinetics, thereby speeding up the sensor's response time. However, excessive heat disrupts the enzyme's structural bonds, leading to denaturation, thermal inactivation, and loss of function. Therefore, an optimum temperature is important to provide an efficient enzyme utilization, and support environmental and industrial sustainability [106]. Several studies have mentioned that 25–37 °C is the optimum temperature for the catalytic activity of diamine oxidase [50], [107].

Therefore, many researchers use room-temperature conditions (25 °C) for histamine measurements with the DAO enzyme. On the other hand, non-enzymatic sensors exhibit greater temperature tolerance than enzyme-based sensors, typically operating between 25–60 °C. As the temperature rises, the molecular kinetic energy increases, leading to a higher resulting current response. For example, Wang *et al.*, [108] reported that temperature-switchable systems based on carbon nanotubes and polymers can influence dopamine sensors, where sensor sensitivity and response were directly controlled by temperature change. At lower temperatures, relatively little electron exchange occurs in dopamine because the polymer stretches, obscuring the electrically active site. Meanwhile, at higher temperatures, the polymer shrinks, exposing active sites and allowing normal dopamine redox reactions.

4.5 *Interfering substances*

Electrochemical sensor applications for real food samples still face challenges posed by interfering substances. Some of those interfering substances generate an electrochemical signal, allowing less selectivity [11]. Electrochemical detection of histamine also faces challenges from interfering substances with oxidation potentials close to histamine, which produce overlapping signals. Therefore, strategies are required to overcome this issue. A study on a sensor preparation combined the sensor with MOF and aptamer, resulting in IRMOF-3@PDMS as a flexible substrate and AuNR-DTNB@Ag-HA aptamer as a Raman probe, resulting in a highly sensitive detection of histamine with a detection range of 0.0001–400 mg/L and LOD of 3.6 × 10^{-5} mg.L^{-1} (R^2 = 0.990) [109]. The sensor was tested with a wine sample and produced an accurate and reliable result. In an additional study, a cucurbituril[7] (CB[7]) was used to functionalize the surface of a glassy carbon-based electrode. The result showed that the sensor successfully detected histamine in red wine using square-wave voltammetry. The sensor achieved nanomolar sensitivity with high recovery rates (98.15% ± 0.93) and showed that histamine concentrations remained stable in wine after 24–96 hours of contact with air [11].

4.6 *Analyte concentration and diffusion*

In electrochemical sensing, the migration of analyte species from the bulk phase to the electrode surface depends on mass transport mechanisms, including diffusion, convection, and migration (Figure 7) [43], [110]. Diffusion occurs when species move down a chemical potential gradient, typically from regions of higher concentration to regions of lower concentration. Convection involves the transport of species by fluid motion, which can result from natural processes such as density gradients or be induced by external forces such as stirring. Meanwhile, migration is defined as the transport of charged species driven by an electric field, which is driven by an electrical potential gradient [111].

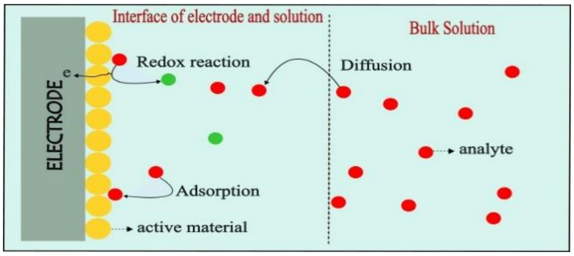

Figure 7: Schematic illustration of diffusion, adsorption, and electrochemical processes.

4.7 *Electrode fouling*

Electrode fouling is a phenomenon in which certain substances adsorb onto the electrode surface, reducing the sensor's sensitivity. The fouling effect was studied on the working electrode, a carbon fiber micro-electrode (CFME), on the Ag/AgCl reference electrode, and on both electrodes. Biofouling was simulated with Bovine Serum Albumin (BSA) solution (40 g.L^{-1}), and chemical fouling was studied with 25 μM serotonin solution [112]. The results showed that fouling reduces the electrode's active surface area, inhibits electron transfer, and leads to lower sensor sensitivity and reproducibility. In histamine detection, this problem is particularly significant because food and biological samples are rich with interfering compounds that compete with histamine for electrode surface sites [113].

Fouling can be prevented by applying antifouling coatings such as polyethylene glycol (PEG) [114] and zwitterionic polymers [115] so that large molecules such as proteins are not adsorbed.

Therefore, it is important to follow regular cleaning protocols and adhere to the electrode life instructions. Research by Lee *et al.*, [116] suggests that the regenerative strategy for gold electrodes in biosensors offers a cost-effective way to extend electrode lifespan, making them suitable for long-term use. Gold electrodes are widely used because thiol-modified molecules can be easily immobilized on their surfaces. However, repeated measurements often damage gold, making it difficult to reuse. There are two approaches to solving this problem. The first approach is a cyclic voltammetry sweep in dilute sulfuric acid, followed by a sweep in potassium ferricyanide.

5 Recent Trends, Challenges, and Future Perspectives of Histamine Sensors

Recently, some research has incorporated nanometer-sized material, such as metal nanomaterials, carbon-based materials, and quantum dots, into histamine sensors to enhance signal transduction. Metal nanomaterials exhibit distinctive physicochemical characteristics, including outstanding electrical, optical, and catalytic properties, together with a uniform particle size distribution and an enlarged active surface area [117]. Using these properties, electrochemical sensors based on metal nanomaterials demonstrate outstanding performance, particularly in sensitivity, linear working range, and high selectivity toward heavy metal ions.

Further research should not only focus on electrode materials but also on making it easier for users to apply the sensor. Some of these include lab-on-a-chip technology and microfluidics, which can also be integrated with smart devices, such as smartphones [118]. One new method for addressing challenges in scientific and medical fields is a microfluidic lab-on-a-chip system. This method is expected to address the control of transport phenomena and fluid flow, as well as the analysis and manipulation of minute fluid volumes at the microscale [119]. Microfluidics technology can also be integrated with smartphones to detect histamine in situ in canned tuna. The first step is to create a molecularly imprinted polymer via precipitation as a dispersive solid-phase extraction sorbent for extracting histamine from canned tuna. Then, this is followed by testing with fluorescence from dark red to bright blue following histamine addition [118]. Meanwhile, smart sensor-based packaging systems enable real-time assessment of food quality deterioration. Smart sensors typically combine chemical or biological receptors (e.g., enzymes, antibodies, aptamers with a signal transducer responsible for transforming recognition events into detectable outputs [120].

Histamine analysis is essential for assessing the freshness of histamine-containing foods, such as fish-based products, to ensure they remain safe for consumption. However, advances in histamine detection still face numerous challenges, including matrix complexity, sensor fouling, reagent instability, and others. Sample matrix characteristics depend on food types and the microbial activity present in the food. The microbial activity that affects histamine production, causing food degradation and releasing chemical constituents [121]. A complex matrix of food contains proteins, lipids, and other compounds. Those components may reduce the detection signal in histamine analysis. The components can also produce high-noise signals. Therefore, sample preparation is a crucial step in histamine analysis. Research conducted by Richard *et al.*, [122] showed that histamine extraction from mackerel with methanol yielded different results when performed with methanol plus 25% HCl (0.4 N). Because histamine in mackerel may be bound to protein, when the extraction is carried out with methanolic HCl, the acidic conditions promote protein denaturation, thereby releasing the bound histamine.

In addition, the structural similarity of histamine to other biogenic amine compounds, such as tyramine, putrescine, and cadaverine, can lead to cross-reactivity in testing. Most biogenic amines have primary or secondary amine groups and short-chain structures, resulting in similar redox properties in electrochemical processes. This can be seen from the overlapping oxidation peaks of some amines. This condition can interfere with the histamine sensor's selectivity. The complex matrix that interferes with histamine analysis arises not only from biogenic constituents naturally present in food products but also from chemical and biochemical changes occurring during storage and transportation. For instance, aromatic compounds may be generated through lipid degradation, where lipase enzymes hydrolyze fats into free fatty acids [14]. Meanwhile, electrode fouling in the sensing system occurs when undesired species deposit on the sensor electrode [123]. Oxidized histamine forms fouling on the electrode surface, which operates at potentials equal to or higher than 1.3 V relative to Ag/AgCl (vs Ag/AgCl), is needed to obtain a well-defined Faradaic peak in FSCV measurements. Meanwhile, the high applied potential will initiate electro-polymerization of the species in the sample, which can cause further fouling [40]. Fouling inhibits electron transfer at the electrode, thereby decreasing sensor sensitivity. Therefore, strategies are applied to minimize or prevent surface fouling on the electrode, including nanomaterials for electrode production, antifouling modifiers, for example, polyethylene glycol (PEG) [124], [125], and zwitterion materials [126], [127].

Another issue may arise from the instability of the reagents used. Humidity, temperature, pH, and ionic strength are some factors that cause enzymes and antibodies to degrade. Enzymes are commonly used as reagents in the detection of histamine. The enzyme catalyzes the conversion of amines into aldehydes, producing ammonia and hydrogen peroxide [128]. Therefore, specific enzymes, such as PAO and DAO, were used in combination with nanomaterials such as gold nanoparticles, carbon-based materials, and ZnO nanoparticles, to increase electrochemical performance and catalytic efficiency, also preventing degradation [103].

However, when developing sensors for large-scale applications such as in the food and fisheries industries, considerations related to cost and on-site usability become essential. A sensor may demonstrate excellent analytical performance, but it is unlikely to gain widespread adoption if the production costs are high and the operational procedures are complex. Therefore, in histamine analysis, it is crucial to address and mitigate existing challenges by developing high-quality electrode materials, selecting appropriate analytical methods, and implementing effective strategies to reduce production costs while ensuring the sensor remains practical and easy to use.

Even though remarkable developments have been reported in the advancement of materials and technologies for histamine detection methods, future research is expected to address challenges related to complex matrices, minimize reagents and hazardous solvents, design functional materials, and integrate the sensor with smart devices. Effective identification of histamine and other biogenic amines requires sensors with high sensitivity and selectivity, because food ingredients, processed products, and other food items inevitably contain multiple biogenic amines, which may lead to false detections. Therefore, a specific compound, such as MOF nanozyme, was used to increase selectivity in histamine detection, with the availability of the three other biogenic interferences [32], [104].

Furthermore, researchers should also minimize the use of hazardous reagents and solvents. The solvent most commonly employed to extract biogenic amines from fish-derived products is trichloroacetic acid (TCA), as it provides high recovery. However, TCA is a dangerous solvent due to its corrosivity, which can harm the environment. This formed the basis for research on the use of a 41% NaCl solution to extract histamine from fish. The extraction result was 98.65–99.45%, which was relatively similar to the extraction result obtained with a 10% TCA solvent, yielding 99.15–100.1% of histamine [33]. Regarding the environmental issues associated with TCA solvent, some studies have proposed alternative solvents for histamine extraction, including dilute HCl (0.1-0.4 M) [129], perchloric acid (PCA) [59], and water extraction [33].

Another future perspective for histamine analysis is integrating a smartphone sensor with the Internet of Things (IoT) into an on-site analytical system. The integration aims to make the sensor for histamine detection easier and more user-friendly. Smartphones offer powerful built-in features, including high-resolution cameras, processors, and wireless connectivity, that can be utilized for signal acquisition, data processing, and visualization. When combined with IoT technologies, including Bluetooth, Wi-Fi, NFC, and cloud computing, these systems enable reliable data transfer, remote monitoring, and real-time decision-making [118], [130].

Recently, many researchers have been developing electrochemical sensors based on screen-printed carbon electrodes (SPCEs). This method involves depositing a carbon material onto a non-conducting substrate comprising three electrodes. SPCEs offer advantages for precise and cost-effective electrochemical measurements. In addition, they provide ease of use and portability, enabling rapid on-site analysis. Additionally, this sensor, a portable, smartphone-controlled device, was fabricated and delivered reliable on-site results for both test solutions and real seafood (Figure 8). The roles of various materials in electrode modification for histamine detection are summarized in Table 3. Therefore, despite conventional techniques such as Liquid Chromatography–Mass Spectrometry, Gas Chromatography (GC), and High-Performance Liquid Chromatography (HPLC), electrochemical and biosensor-based techniques offer rapid, sensitive, and field-deployable methods. Ongoing innovation in materials science and microfabrication continues to drive the development of next-generation histamine sensors.

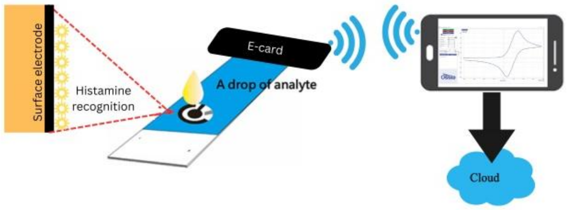

Figure 8: Schematic of a smartphone-integrated portable device for detecting histamine.

Table 3: The Role of various materials for electrode modification in histamine detection.

Material	Role	Reference
Carbon Nanotubes (CNTs)	Enhance conductivity and surface area	[12], [78]
Graphene/Graphene oxide	High surface area, improved electron transfer	[131]
Metal Nanoparticles (Au, Ag, Pt)	Good electrical conductivity, Catalytic enhancement	[132]
Conductive Polymers (e.g., polyaniline)	Support enzyme immobilization, increasing sensitivity	[133], [134]
MOFs & MIPs	Selective recognition and preconcentration of histamine	[79]
Enzymes	High specificity and sensitivity	[22], [50]
Aptamers	Good stability, high sensitivity, specificity, and affinity	[65], [135]

6 Conclusion

An electrochemical-based histamine sensor is a promising approach due to its rapid, sensitive operation and its portable device design. Based on the latest literature, electrode modification or sensor fabrication significantly improves sensitivity and selectivity for histamine detection. Enzyme-based sensors offer high specificity and selective detection of histamine, making them superior for food or biological sample analysis. However, due to the sensitivity of enzyme stability to pH, temperature, and solvents, as well as high production cost, they are less desirable for long-term commercial applications. In contrast, non-enzymatic sensors exhibit greater stability and reproducibility, though strategies are needed to improve sensor selectivity. Therefore, advances in nanomaterial-modified sensor prototypes will pave the way for commercialization. SPCEs have become widely popular because they are easy to modify. Additionally, cost optimization, portability, and resistance to real-world conditions (e.g., complex food samples) must be prioritized for practical electrochemical sensor applications.

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Author Contributions

V.N.: investigation, writing-original draft, M.A.M.: funding acquisition (University Malaysia Sarawak Side), writing-review & editing, Y.H: writing-review & editing, F.R.: conceptualization, funding acquisition (Sebelas Maret University side), writing review & editing, supervision.

Conflicts of Interest

The authors declare no conflict of interest.

Data Availability

This review does not involve the use of primary data. All information is from publicly available sources, as cited in the manuscript.

Declaration of generative AI and AI-assisted technologies in the writing process

The authors used ChatGPT and Grammarly Pro to enhance the language and readability of the manuscript.

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