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Polyurethane modified screen – printed electrode for the electrochemical detection of histamine in fish M A Munir¹ L Y Heng² and K H Badri^{2, 3*} ¹Department of Pharmacy, Faculty of Health Science, Universitas Alma Ata, 55183 Bantul, D.I. Yogyakarta, Indonesia ²Department of Chemical Sciences, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia ³Polymer Research Center, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia *Corresponding E-mail: kaybadri@ukm.edu.my Abstract. Histamine needs to be determined because of its toxicity.

Histamine is commonly determined using chromatography, where not only that the instrument is expensive, the process is very tedious and require an expert. A sensor was developed using palm-based polyurethane as an electro-sensor substrate. Palm-based polyurethane (PU) was produced via condensation polymerization between palm kernel oil- b nosterplI P)and44 - diphenylmethane diisocyanate (MDI). PU offers high porosity and capability to attach onto screen – printed electrode (SPE) sturdily without being disintegrated. PU – SPE adsorbed histamine onto its pores, before being oxidized.

The oxidation process was detected using cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Histamine was oxidized electrochemically at +0.31 V (vs. Ag/AgCl, 1 mol·L⁻¹, pH 7.5). Differential pulse voltammetric approach were used in order to get a satisfactory response, thus the histamine concentration was made in the range from 1 × 10⁻⁴ to 1 mmol·L⁻¹. A good sensitivity of 0.1 mmol·L⁻¹ was attained with 3.07 % during intraday and 9.55 % during interday. The detection and quantification limits of histamine acquired at 0.17 mmol·L⁻¹ and 0.53 mmol·L⁻¹, respectively.

A wide variety of interfering compounds were also examined in order to establish their

effect, if any, on the determination of histamine at the PU modified electrode. The sensor showed an excellent anti – interference property towards the other amines. The developed chemical sensor using PU – SPE has a good potential to determine histamine level in mackerel (*Rastrelliger Brachysoma*) owing to its simplicity and reproducibility.

Keywords: Histamine, polyurethane, electrode, conducting, mackerel Track Name: Chemistry STACLIM 2021 IOP Conf. Series: Earth and Environmental Science 880 (2021) 012032 IOP Publishing doi:10.1088/1755-1315/880/1/012032 2 1.

Introduction The production of food protein increases significantly owing to the high demand. Protein has an important role in human growth. Nevertheless, it will give impact to food security due to foods protein have been thoroughly investigated due to the possibility of biogenic amines accumulation, particularly histamine. The common biogenic amines obtained in foods are cadaverine, tyramine, putrescine, spermine, spermidine and histamine.

However, histamine has been receiving great attention by several organization such as Food and Drug Administration (FDA) and European Food Safety Authority (EFSA) due to its toxicity [1]. Histamine is produced by the decarboxylation process of histidine, it is caused by many factors such as microbial or enzymatic process. In order to stop this microbial process, cooking or heating becomes an alternative to destroy the bacteria, nevertheless, histaminolytic bacteria found in foods, which acts as oxidizing agent, has the ability to survive inside the foods during the cooking or heating process [2,3]. Thus, the detection of histamine is imperative, in order to ensure the safety of human consumption.

Several approaches such as chromatography and electrochemical techniques have been applied and studied to detect histamine in foods. Liquid and gas chromatography are techniques that have been applied in decades. These methods are well developed, sensitive and very selective [4-9]. However, many conflicts occur during the application of these methods such as very expensive, require many chemical materials, time – consuming and only people who have background in analytical chemistry can use it.

Moreover, both HPLC and GC methods need derivatization step using specific derivatizing reagent in order to increase the sensitivity of HPLC and GC. Derivatization step is needed since biogenic amines have low volatility and lack of chromophores [10]. Thus, in order to tackle these issues, electrochemical sensors are applied. Electrochemical sensors are cost-effective and have the capability to detect histamine either using biological receptors such as enzyme – modified and antibodies or using chemical receptors such as conducting polymers.

They are still using chromatography methods [11,12]. Histamine biosensors coupled with a specific enzyme have attracted significant attention such as methylamine dehydrogenase, diamine oxidase and amine oxidase [13]. Nevertheless, the application of these enzymes to the sensor has some drawbacks such as life cycle and price of enzymes. Several studies have reported that immobilization enzymes causes instability. The instability of enzymes can be influenced by several factors such as pH and temperature. Some foods also containing metal that inhibit the enzyme activity [14,15].

Furthermore, biological receptors such as enzymes and antibodies are costly, complicated to produce and the selectivity is questionable. The receptors also cannot survive in high concentration of organic solvents, can be destroyed in high temperature and unstable in a specific pH. Furthermore, a synthetic receptor is strongly required so it can avoid the biological receptor issues. Chemical sensors become another alternative in order to avoid the application of antibodies, enzyme and DNA [16]. These methods use a specific receptor to capture biogenic amines physically or chemically where the electrodes must be modified chemically.

The electrodes also must be both chemically stable and conductive. Carbon nanotube, graphene, gold, lithium, platinum and silicon are materials that generally applied by researchers as electrode modifiers to analyze biogenic amines. They are also friendly because they do not use organic solvents. Other advantages of chemical sensors could also be robustness, selective to small samples, tiny and need no skill on analytical chemistry to operate this sensor [17, 18]. However, the use of conducting materials such as gold, platinum and carbon are costly and the modification procedures are not straightforward.

In order to solve these issues, polymers modified electrode can be applied to determine biogenic amines from samples using electrochemical technique. Conducting polymer application based composite materials as sensing elements in electrochemical sensor technology has proved to be reliable instrument based on analytical performances [19]. STACLIM 2021 IOP Conf. Series: Earth and Environmental Science 880 (2021) 012032 IOP Publishing doi:10.1088/1755-1315/880/1/012032 3 In this study, we have developed a bio – polymer that can be used to modify screen printed electrode (SPE) and has capability to adsorb histamine by physical adsorption. SPE modified can also operate at a lower potential.

Histamine was then determined using a cyclic voltammetry (CV) and differential pulse voltammetry (DPV) methods. The chemical sensor was used to evaluate histamine in fish mackerel in order to monitor the level of histamine. Furthermore, the detection of histamine using polyurethane modified electrode has not been studied and issued

elsewhere. 2. Materials and method 2.1 Instrument and chemicals Voltammetric methods such as cyclic voltammetry and differential pulse voltammetry were performed by using Metrohm Autolab Electrochemical Workstation (UKM, Bangi, Malaysia).

Three conventional electrodes used in this study such as polyurethane modified electrode as a working electrode, platinum wire as an auxiliary electrode and Ag/AgCl electrode as a reference electrode. All experiments were conducted at ambient temperature. Histamine dihydrochloride (HIS) was purchased (99% purity) from Merck Sdn. While polyurethane was produced in UKM laboratory (Malaysia) via reaction of palm-based polyol (PKO-p, OHV of about 370 mg KOH/g and moisture content less than 0.1%) with polymeric isocyanate of 4,4-diphenylmethane diisocyanate (MDI) manufactured by BASF Germany was acquired from Cosmopolyurethane (M) Sdn. Bhd., Klang, Malaysia (NCO content of 32%). Potassium chloride (KCl 0.1

M) and potassium hexacyanoferrate (III) ($K_3Fe(CN)_6$) were used as supporting electrolyte, HCl and NaOH were purchased from Sigma Aldrich Sdn. Bhd. and applied in order to adjust the pH solution. The sodium dihydrogen phosphate and disodium hydrogen phosphate were supplied by Sigma Aldrich Sdn. Bhd. The phosphate buffer (0.1 M) was prepared by mixing 0.1 M sodium dihydrogen phosphate and 0.1 M disodium hydrogen phosphate to the desired pH. All chemicals are of analytical grade and were used without further purification. Solutions were prepared using water purified through a Milli-Q system and kept at 4 °C until required. 2.2

Analytical procedure 10 mM of histamine stock solution was prepared using 0.1 M phosphate buffer solution (PBS) at pH 7.5. Histamine working solution was also prepared from stock solution by performing series of dilution to obtain the calibration curve. Polyurethane film was put on the electrode surface by casting method. Unmodified electrode and modified electrode were measured using cyclic voltammetry (CV) technique in the range of potential 0 to +1.6 V. After optimization of histamine standard solution using differential pulse voltammetry (DPV) method applied, calibration curve of $y = 30.917x + 1.3977$ was obtained using a series of standard histamine solution ($1 - 10^{-4}$ mmol·L⁻¹). 2.3

Preparation of polyurethane modified screen – printed electrodes The polyurethane modified screen-printed electrode (Figure 1) was prepared with minor modification. A screen printed electrode (SPE) was first rinsed with deionized water. The SPE was plunged in pH 7.5 PBS for 60 sec and immediately activated using electrochemical instrument by applying a scan potential started from -1.2 and +1.5 V (vs Ag/AgCl) for ten cycles and scan rate at 50 mV·s⁻¹. Afterward, 0.1 mg of polyurethane put onto the electrode surface and dried at ambient temperature for 24 h. The polyurethane

electrode was flushed with the deionized water to expunge the materials on the electrode surface.

Then, the polyurethane electrode stabilized in pH 7.5 PBS by performing a scan potential started at -0.5 and +1.5 V until a satisfactory response acquired. Finally, the polyurethane electrode was air-dried and ready for further experiments. STACLIM 2021 IOP Conf. Series: Earth and Environmental Science 880 (2021) 012032 IOP Publishing doi:10.1088/1755-1315/880/1/012032 4 2.4 Real sample preparation Fish and canned mackerel were purchased from a local market in Dengkil, Malaysia and were kept in a refrigerator prior to analysis. About 5 g of fish muscle was weighed and blended with 20 mL of 0.1 mol·L⁻¹ PBS at pH 7.5.

The mixture was centrifuged for 5 min and filtered through a Whatman filter paper. 100 µL of this solution was moved to a 10 mL volumetric flask and diluted to the mark with the PBS to make the final determination. Then, two concentrations of 0.1 and 0.01 mmol·L⁻¹ of histamine standard solutions were obtained from a series of standard histamine solution. This method applied in order to validation the method and can be applied for histamine determination in real samples. (a) (b) Figure 1. (a) The polyurethane modified screen – printed electrode and (b) The potentiostat instrument used to undergo the cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques. 3. Results and discussion 3.1

Potentiostatic deposition of polyurethane on the surface of SPE The electrochemical behavior of histamine was studied using cyclic voltammetry (CV) technique through both unmodified and modified electrodes. It was conducted at various pH values (6 – 8) in phosphate buffer solution (PBS) at 0.1 mol·L⁻¹. The studies showed that PBS was the best media in detecting the presence of histamine. Several studies reported that PBS gives the best analytical response whereas the use of hydrochloric acid (HCl) and sodium hydroxide (NaOH) were not suitable owing to the histamine can be detected by electrochemical technique [16,20].

The performance of PBS (pH 7.5) was also evaluated at concentration of 0.01, 0.05, 0.10 and 0.50 mol·L⁻¹. However, concentration of PBS did not affect the histamine analytical response when analysed using cyclic voltammetry technique. Nevertheless, 0.1 mol·L⁻¹ PBS at pH 7.5 have been applied in numerous studies and found to be precise owing to a satisfactory response of histamine detection acquired. Thus, it was applied for further studies. Following to the experimental part, polyurethane film was deposited on the electrode surface by casting method with a specific weight of polyurethane. Figure 2 shows the cyclic voltammograms of unmodified SPE (A) and polyurethane modified SPE (B) in 0.1

mM KCl containing 5 mM of $(K_3Fe(CN)_6)$. The conductivity of unmodified SPE and modified SPE was compared. Solutions containing 5 mM of $K_3Fe(CN)_6$ used and determined by CV technique by applying a scan potential started at 0.0 to +1.0 V and 0.05 V·s⁻¹ scan rate was performed. The voltammogram of the unmodified SPE and modified SPE exhibited similar redox couples. However, the conductivity of modified SPE was lower. The polyurethane used in this study made use of palm kernel oil – polyol as a natural polymer. It exhibited weak electrochemical signals due to its low electrochemical conductivity [21].

According to Figure 2, it shows that the anodic peaks that approximately at +0.5 V represent the oxidation process of unmodified SPE and modified SPE. The first oxidative scan of unmodified SPE and modified SPE starting from -0.2 to +1.0 V, showed a significant anodic peak at +0.5 V. Using the redox couple $(K_3Fe(CN)_6)$ as the probe, the unmodified SPE showed higher current owing to its high electrical properties and active surface area, compared to the modified SPE which showed lower current.

Since the conductivity of polyurethane was low, the current was also low. Smaller (a) The screen - printed electrode modified by polyurethane film and applied as a working electrode. Auxiliary electrode Reference electrode STACLIM 2021 IOP Conf. Series: Earth and Environmental Science 880 (2021) 012032 IOP Publishing doi:10.1088/1755-1315/880/1/012032 5 overpotential (η) of the $K_3Fe(CN)_6$ redox reaction on the polyurethane modified SPE compared to the SPE itself. Apparently, polyurethane can decrease the electron transfer owing to its low catalytic property. The formula of Randles – Sevcik employed in this study in order to measure the electrochemical area (A) of the polyurethane electrode [20]: $I_p = 2.65 \times 10^5 n^{3/2} A^{1/2} CD^{1/2}$ (Equation 1) Where, C is the concentration of analyte, D represents the diffusivity of solution (5 mM $K_3Fe(CN)_6$ diluted in 0.1 mM KCl) and n represents the total electrons transferred. The area of SPE approximately 0.2 cm² (0.44 cm × 0.44 cm) while 0.25 cm² for PU/SPE (0.5 × 0.5 cm). It shows the surface of modified electrode wider than the SPE.

Furthermore, the formula below employed in order to measure the (η) or the concentration of corresponding surface concentration: $I_p = (n^2 F^2 / 4RT) A \nu$ (Equation 2) I_p represents the peak current, ν is the scan rate, A is the region of electrode, F iFaradas ant and T represents the temperature [22]. 3.2 Electrochemical behaviour of histamine on PU – SPE and SPE The sensitivity of polyurethane modified electrode and screen – printed electrode was studied and compared. 1.0 mmol·L⁻¹ of histamine were investigated using these electrodes and cyclic voltammetry was applied in the potential range from 0.0 to +1.0 V with a scan rate of 0.05 V·s⁻¹.

The peak currents of histamine acquired and observed on polyurethane modified electrode and screen – printed electrode. The voltammogram of the polyurethane modified electrode exhibited distinct redox couples with unmodified electrode. Figure 3 presents a well – defined anodic peak of histamine appeared approximately at +0.31 V at the modified electrode and the reverse scan found that there was no cathodic peak scanned, it was indicated that the reaction is irreversible due to no charge occurs. Whereas the peak of unmodified SPE appeared approximately at +0.58 V and there is no possibility for screen – printed electrode to react or attach with histamine whether by chemical or physical adsorption. Figure 2. Cyclic voltammograms of unmodified SPE (A) and polyurethane modified SPE (B) in 0.1

mM KCl containing 5 mM of (K₃Fe (CN)₆). Figure 3. Comparison of the cyclic voltammograms between polyurethane modified SPE and unmodified SPE to detect 1 mmol·L⁻¹ histamine in phosphate buffer, pH 7.5. A B STACLIM 2021 IOP Conf. Series: Earth and Environmental Science 880 (2021) 012032 IOP Publishing doi:10.1088/1755-1315/880/1/012032 6 Several studies have shown that the modification of electrode biologically or chemically and the use of different methods will influence the capability of electrode in order to detect histamine and giving various potential.

The use of carbon electrode and the application of amperometry method causing histamine was oxidized below +1.1 V [23]. Meanwhile, the distinct results showed when the carbon paste electrode and differential pulse voltammetry were applied. The anodic peak of histamine appeared approximately at +1.30 V whereas for carbon paste electrode modified with SWCNT, the anodic peak of histamine appeared approximately at +1.20 V [16]. Similar result reported by using lignin modified glassy carbon electrode [24]. However, the use of screen – printed electrode in this study showed different potential with others. Keow et al.

(2007) [25] reported the use of SPE to determine histamine in tiger prawn, where SPE itself unable to determine histamine, thus this sensor used a photocuring method to immobilize an enzyme and entrapped in a membrane and deposited onto a SPE. A satisfactory anodic peak of histamine appeared approximately at +0.35V. The oxidation of histamine can occur at the modified or unmodified electrode. Several studies reported that amines (-NH₂) group can be oxidized to nitro compounds (-N=O) [23]. Nevertheless, there are also several reports that histamine structure can loss 4H⁺ and alters to CN. Histamine can also be deaminated by various oxidants and enzymes such as diamine oxidase and horseradish peroxide [26].

Silver oxide has a capability to oxidize the amino acids with the implication of CO₂ loss. Nevertheless, this reaction needs to be done in high temperature and time consuming. The oxidation possibilities of histamine are illustrated in Figure 4. The oxidation of histamine on polyurethane modified screen – printed electrode. Figure 4. A possibility of histamine oxidation [20], with several modifications. The polyurethane modified electrode showed a specific response of histamine compare to unmodified electrode. The properties of polyurethane film causing it can react with the analyte.

The weigh of polyurethane film on the electrode surface was studied in order to obtain a satisfactory current response during analysis histamine using voltammetric techniques, such as CV and DPV. Approximately, 0.1, 0.3, 0.5 and 1 mg of polyurethanes investigated. The results of this study showed that the 0.1 mg of polyurethane amount giving the best response. Meanwhile, 0.3, 0.5 and 1 mg of polyurethanes reduce the current response. Furthermore, in order to obtain a satisfactory modified electrode, the thin polyurethane film suggested and the electron transfer between histamine and the electrode surface can occur. STACLIM 2021 IOP Conf.

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doi:10.1088/1755-1315/880/1/012032 7 The modification of screen – printed electrode using polyurethane is possible owing to polyurethane can be considered as a suitable material for adsorption. Many studies have noticed the advantage of polyurethane such as easy control of the pore size, stable maintenance of the quantity of cells and large-scale application at low price.

A liquid material can be adsorbed to PU by a physical adsorption, by an entrapment or by a coupled chemical and physical binding [26]. In this study, histamine adsorbed into polyurethane by a physical adsorption where histamine entraps into the polyurethane. During the physical attachment of a histamine to polyurethane, the amino groups of histamine will not react with the isocyanate groups of polyurethane. This process is quite suitable for chemical sensor using CV and DPV methods owing to histamine can undergo oxidation process [23]. A voltammogram of 1 mmol·L⁻¹ histamine in PBS (pH 7.5) at 0.1 mg of polyurethane film is shown in Figure 3.

It can be concluded that there is no presence of histamine, no cathodic and anodic peaks appeared in unmodified screen – printed electrodes. Hence, a modified screen – printed electrode containing 0.1 mg of polyurethane was selected for the electro – oxidation of histamine in all further experiments. 3.3 Effect of pH The shapes and heights of peak current of histamine may strongly influenced by the pH value. The pH value of PBS as a supporting electrolyte is an imperative factor that must be concerned owing to it effects the redox behavior of the histamine. Various pH of 0.1 mol·L⁻¹ PBS

started from 6.0 – 8.0

were investigated in order to study the correlation between pH and peak current (I_p), 1 mmol·L⁻¹ of histamine was employed. The scan potential applied in range of 0.00 until +1.50 V with a scan rate 0.05 V·s⁻¹ (Figure 5). Based on this study, the pH was strongly influence the current response and peak potential of histamine. The relationship between peak potential and pH of the supporting electrolyte presented in Figure 5 and can be presented by the following equation 3: $E_p (V) = -0.1022 + 0.7316 \times \text{pH}$ (Equation 3) The slope of 0.7316 V/pH is indicating that the presence of electrons and protons influence the electrode reaction (Stojanovic et al. 2016). The histamine peak current escalated at pH 6 and reached the highest peak current at pH 7.5 yet decreased at pH 8 (Figure 6).

Figure 5. Cyclic voltammograms of polyurethane modified electrode in PBS at various pH (6 – 8) containing 1 mmol·L⁻¹ histamine. Figure 6. Effect of pH on peak potential and peak current response of 1 mmol·L⁻¹ histamine in 0.1 mol·L⁻¹ PBS with scan rate of 0.05 V s⁻¹. STACLIM 2021 IOP Conf. Series: Earth and Environmental Science 880 (2021) 012032 IOP Publishing doi:10.1088/1755-1315/880/1/012032 8 The current signal were satisfactory developed at pH ranged 6.5 – 7.5. Nevertheless, 7.5 considered be the best pH in this study owing to giving the maximum current. A study reported, pH at 7 or 7.5 of PBS can protonate the histamine ring (pka 6.0) owing to the attraction of electrostatic, nevertheless the current can decrease when the pH 8 applied [16]. The relation between pH values and potential applied (v) of histamine at the polyurethane electrode was also studied.

According to the Figure 5, it can be seen that the pH values influence the position of potential applied (v) of histamine, started to the pH 6 until 8, the potential applied moved to the positive direction indicating the participation of electrons transfer. The application of pH (6 – 8) in this study showed linear dependence on the pH with a linear regression equation and correlation coefficient (R^2) of $E (V) = -0.1022 + 0.7316 \text{ pH}$ and 0.9922, respectively. A slope of 0.7316 indicated that the electrons and protons movement influencing the histamine oxidation at the surface of polyurethane electrode.

3.4 Effect of scan rate

Several scan rates employed in the range from 0.01 to 0.10 V·s⁻¹ using CV method in order to investigate the relation between potential applied, current peak and scan rate. Figure 7 shows the cyclic voltammograms of 1 mmol·L⁻¹ histamine in pH 7.5 PBS at polyurethane modified electrode using various scan rates.

The anodic peaks revealed in Figure 8 that the equation and correlation coefficient were $i_{pa} (\mu\text{A}) = 0.0507 + 4.59 v$ (v in mV·s⁻¹) and $R^2 = 0.9925$, respectively (Figure 8) signifying the oxidation reaction between polyurethane electrode and histamine is

adsorption controlled [24]. The obtained results indicated that current peak of histamine and scan rates employed was directly proportional and the relation between them calculated using the equation below: $I_p (\mu A) = 0.0507v^{1/2} (V^{1/2}s^{-1/2}) + 4.59$ ($r = 0.9925$) (Equation 4) Figure 7. Cyclic voltammograms of $1 \text{ mmol}\cdot\text{L}^{-1}$ histamine in $0.1 \text{ mol}\cdot\text{L}^{-1}$ PBS at pH 7.5 on polyurethane modified electrode for series of scan rates from 0.01 to $0.10 \text{ V}\cdot\text{s}^{-1}$. Figure 8.

Calibration curve of anodic peak current of histamine versus the scan rate in the range 0.01 to $0.10 \text{ V}\cdot\text{s}^{-1}$. In this study, the scan rates applied influenced the potential applied of histamine where the potential applied of histamine move to positive direction. A satisfactory calibration curve as shown in Figure 8 and the relation between them calculated using the equation below: $E_p (V) = 50.673 - 10.612 \ln v (V\cdot\text{s}^{-1})$ ($r = 0.9925$) (Equation 5) $0.01 \text{ V}\cdot\text{s}^{-1}$ $0.10 \text{ V}\cdot\text{s}^{-1}$ STACLIM 2021 IOP Conf.

Series: Earth and Environmental Science 880 (2021) 012032 IOP Publishing doi:10.1088/1755-1315/880/1/012032 9 3.5 Analytical performance Differential pulse voltammetry (DPV) technique has been applied in this study owing to its selectivity, simplicity and sensitivity compared to cyclic voltammetry (CV). DPV employed to verify and analyze the anodic current of histamine at polyurethane electrode. After several steps above validated and developed and in order to obtain fast analysis, the scan rate at $50 \text{ mV}\cdot\text{s}^{-1}$ employed.

The parameters of DPV technique that considered the optimal parameters chosen for further experiment such as the pulse amplitude of 100 mV and a pulse time of 25 ms . 3.5.1 Linearity The DP voltammograms shown in Figure 9 that representing several histamine concentrations by applying the validated and developed method as mentioned before. Based on the obtained results, the signals were directly proportional to the concentration of histamine ranged from 10^{-4} to $1.0 \text{ mmol}\cdot\text{L}^{-1}$. The validation study and the analytical characteristics for the developed method are summarized in Table 1.

Figure 10 presents the calibration curve of various concentrations of histamine in $0.1 \text{ mol}\cdot\text{L}^{-1}$ PBS at pH 7.5 on polyurethane modified electrode. Six replicates of every histamine concentrations analyzed and the relative standard deviation (RSD) was below 9%. Figure 9. DPV of different concentration of histamine in $0.1 \text{ mol}\cdot\text{L}^{-1}$ PBS at pH 7.5 on SPE modified PU. Figure 10. The calibration curve of different concentrations of histamine: 10^{-4} to $1.0 \text{ mmol}\cdot\text{L}^{-1}$. 3.5.2 Detection and Quantitation The detection limit (DL) and quantitation limit (QL) were measured using the formula of $(3.3 \cdot SD/\text{slope})$ and $(10 \cdot SD/\text{slope})$, respectively.

The detection and quantitation limits were 0.17 and 0.53 mmol·L⁻¹ of histamine, respectively. 3.5.3 Stability and precision The application of polyurethane modified electrode is not recommended use after one week owing to the sensitivity decreases day after day yet the selectivity is stable. The evaluation of stability of polyurethane electrode was investigated by measuring the anodic peak of histamine standard (0.1

mmol·L⁻¹) started from day 1 until 28 with the similar electrode stored in dark and dry place in order to maintain the condition of SPE modified PU. The experimental data showed that the current response was reduced from 23.37 μA to 14.16 μA showing 39% discrepancy in current response on seventh day compared to the first day oxidation current values. STACLIM 2021 IOP Conf. Series: Earth and Environmental Science 880 (2021) 012032 IOP Publishing doi:10.1088/1755-1315/880/1/012032 10 Table 1. Analytical characteristics for the determination of histamine by DPV in 0.1 mol·L⁻¹ phosphate buffer at pH 7.5 on the polyurethane modified screen – printed electrode. Analytical validated Value Detection potential Anodic peak +0.31 Linear concentration range (mmol·L⁻¹) 10⁻⁴ - 1 Coefficient of determination (R²) 0.9901 Intraday precision (RSD, %) 3.05 Interday precision (RSD, %) 9.02 LOD (mmol·L⁻¹) 0.17 LOQ (mmol·L⁻¹) 0.53 Furthermore, on the 28 th day, 82% reduction in current response was observed in comparison to the first day.

However, the reduction of anodic peak noticed and encouraged that the polyurethane electrode do not use more than 7 days due to the sensitivity of electrode will decrease. The reliability or reproducibility of polyurethane electrode was also studied by investigating the electro – analytical response of histamine solution at 0.01 mmol·L⁻¹ by performing similar conditions using six various polyurethane electrodes with the similar surface region, which were set up by the similar technique.

The intra and inter-day measurements applied in order to study the precision of the polyurethane modified electrode. The intra – day measurements were implemented at two different concentrations of histamine such as 0.1 and 0.01 mmol·L⁻¹, by six replicates analysis. The relative standard deviation (RSD) obtained below 3.05% and confirmed the satisfactory precision. Whereas, inter – day measurements were implemented the similar histamine concentration and polyurethane electrode and the investigation was reiterated every day for 7 days. The RSDs obtained at 7.54 and 9.02%, for concentration at 0.1 and 0.01 mmol·L⁻¹ of histamine, respectively, showed the satisfactory reproducibility of histamine detection by the validated approach.

Furthermore, this indicated the polyurethane modified electrode preparation procedure was quite easy and reliable method, including PU production, casting method and polishing step. 3.5.4. Disturbances In order to study the selectivity of validated method,

several amines were employed such as cadaverine and putrescine represent the biogenic amines, whereas aniline, xanthine and hexamine were used based on the number of carbons bonded to nitrogen atom. They were primary, secondary and tertiary amines, respectively. They were studied on similar method of histamine detection. Various amines detection at 1 mmol·L⁻¹ were implemented by applying similar method of histamine detection.

The obtained voltammograms showed various signal, nevertheless none of them had similar potential applied to histamine. The distinction peaks of each amines compared to histamine were negligible. Aniline as a primary amine as histamine appeared at +0.43 V, whereas putrescine and cadaverine that easily acquired in fish accompanied histamine also did not influence the histamine potential, a satisfactory potential applied of them were obtained at +0.18 and +0.19, respectively. The DPV signal height of other amines did not provoke the histamine signal. While the other amines such as xanthine and hexamine did not influence owing to appear in different potential applied compared to histamine potential. STACLIM 2021 IOP Conf.

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doi:10.1088/1755-1315/880/1/012032 11 3.6 The application of validated method The validated and developed method of histamine standard detection employed to analyze histamine in fish mackerel and its product. The fish samples investigated in six replicates. The concentration of histamine in samples calculated using the calibration curve of histamine standard. Based on the detection using validated method, histamine detected in fish mackerel samples and canned mackerel.

The content of histamine in both of them were 17 μmol·L⁻¹ (1.89 ppm) and 5.3 μmol·L⁻¹ (0.59 ppm), respectively. The study of recovery was performed at concentration 0.1 and 0.01 mmol·L⁻¹ of histamine, respectively. The recovery values obtained at 94 and 103%, respectively for those concentrations. This study indicated the validated and developed method has a satisfactory accuracy. Based on the FDA regulation, the safe level of histamine concentration is below 50 mg·kg⁻¹. Furthermore, the analyzed samples have no potential harm to human consumption.

To evaluate the potential of the validated and developed method, the performance of PU modified electrode for histamine detection was compared to several reported methods as shown in Table 2 in accordance with the linear concentrations range and detection limit. Table 2. Summary of the electrochemical performances of the validated technique compared to other studies for the determination of histamine. Electrode Method LOD (μM) Linear range (μM) Ref. Diamine oxidase/ carbon paste Amperometry 3.5 0.1 325.9 [25] Amine oxidase/ screen printed carbon FIA / amperometry 3.0 10 300

[27] Amine oxidase/horsedish peroxidase/ carbon Chronoamperometry 0.18 0.4 2.4 [28] MWCNT/ glassy carbon electrode DPV 0.076 0.1

100 [29] Pyrroloquinoline Quinone modified GCE Amperometry 341 360 1530 [30] Lignin modified GCE SWV 0.28 5 200 [24] Polyurethane + SPE CV and DPV 0.17 0.1 1000 This study 4. Conclusions This work presents an innovative **electrochemical sensor for histamine detection using** a polyurethane modified electrode. The polyurethane film **used in this study** has porous surface that offers high adsorption capacity for the histamine. The reaction between PU electrode and histamine was an irreversible oxidative. A satisfactory detection limit was obtained in the linear concentration range of 10^{-4} to $1 \text{ mmol}\cdot\text{L}^{-1}$.

Moreover, the simplicity of polyurethane film deposition and availability of the electrode modifier polymer, satisfactory accuracy, precision and errors that can be denied exhibited a great potential of validated and developed method for histamine detection in real samples. Although the modification of polyurethane reduced the electrochemical response of screen – printed electrode, nevertheless the capability of polyurethane film to adsorb histamine by physical reaction causing histamine can be oxidized compared to unmodified SPE. Several amines that have possibility to disturb histamine detection such as aniline, xanthine, hexamine, cadaverine and putrescine did not affect the electro – analytical response of histamine.

The obtained results show that the validated and developed DPV method propose a satisfactory electro – analytical approach for qualitative and quantitative of histamine level in fish samples.

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