Arabian Journal of Chemistry (2021) **14**, 103319

King Saud University

Arabian Journal of Chemistry

www.ksu.edu.sa
www.sciencedirect.com

ORIGINAL ARTICLE

Cys-AgNPs modified gold electrode as an ultrasensitive electrochemical sensor for the detection of 3-chloropropane-1,2-diol

Aka Alla Martin [a,b,c], Essy Kouadio Fodjo [c,*], Zran Vanh Eric-Simon [c], Zhen Gu [b,*], Guangxin Yang [a], Trokourey Albert [c], Cong Kong [a,*], Hui-Feng Wang [b]

[a] *Key Laboratory of East China Sea Fishery Resources Exploitation, Ministry of Agriculture and Rural Affairs, East China Sea Fisheries Research Institute, Chinese Academy of Fishery Sciences, Shanghai 200090, China*
[b] *Key Laboratory of Advanced Control and Optimization for Chemical Processes Ministry of Education, East China University of Science and Technology, Shanghai 200237, China*
[c] *Laboratory of Constitution and Reaction of Matter, UFR SSMT, Université Felix Houphouet Boigny, 22 BP 582 Abidjan 22, Cote d'Ivoire*

Received 7 May 2021; accepted 4 July 2021
Available online 14 July 2021

KEYWORDS

Cysteine–nanosilver modified gold electrode;
Food contaminant analysis;
3-chloropropane-1,2-diol;
Electrochemical sensor

Abstract A highly sensitive modified gold (Au) electrode using cysteine-coated silver nanoparticles (Cys-AgNPs) is designed. The electrochemical activity of this designed sensor has exhibited an excellent response for the detection of 3-chloropropane-1,2-diol (3-MCPD). Indeed, the investigation of electrochemical behavior of 3-MCPD at the Cys-AgNPs/Au electrode has shown that the electrocatalytic activity for the 3-MCPD oxidation in NaOH solution is enhanced by three-fold with the presence of Cys-AgNPs film. This Cys-AgNPs film is found to be stable on the Au electrode and the developed electrode can be reused several times while obtaining excellent results. Furthermore, using differential pulse voltammetry technique, the oxidation current peak shows a linear relationship with 3-MCPD concentration between 2.5 ng/mL and 200 ng/mL. The calculated limit of detection (LOD) and limit of quantification (LOQ) are found to be 2.4 ng/mL and 8.6 ng/mL, respectively. A recovery rate ranging from 96% to 105% in the presence of interfering compounds with similar structure to 3-MCPD or not are observed for the determination of 3-MCPD. Moreover, the developed sensor is successfully applied to the determination of 3-MCPD in smoked mackerel and palm oil samples with results which show 3-MCPD concentration ranging from 174 to 439 μg/kg and 895 to 1280 μg/kg in smoked mackerel and palm oil samples, respectively.

* Corresponding authors.
E-mail addresses: kouadio.essy@univ-fhb.edu.ci (E.K. Fodjo), guzhen@ecust.edu.cn (Z. Gu), kongc@ecsf.ac.cn, kongcong@gmail.com (C. Kong).

Peer review under responsibility of King Saud University.

Production and hosting by Elsevier

https://doi.org/10.1016/j.arabjc.2021.103319

In addition to the reusability and stability of the electrode, these results suggest that this Cys-AgNPs/Au electrode can be used as an effective sensor to monitor and determine trace level of 3-MCPD in foodstuffs.

1. Introduction

3-chloro-1,2-propanediol (3-MCPD) is known as one of the neo-formed contaminants of foodstuffs that belongs to chloropropanol groups, and the most stable in food among its isomers (Jiang et al., 2018). Indeed, 3-MCPD is produced via acidic hydrolysis of lipids in the presence of chlorine which is intensified by high deodorization temperature in the process of refining edible oils or during high-temperature processing of foods containing lipids. It has been detected and quantified in a large variety of processed foods, including infant formulas (Cheng et al., 2017; Gao et al., 2019). 3-MPCD and its isomers, especially 2-MCPD and glycidol can also be formed from their ester derivatives and are widely reported in edible oils. However, they have turned out to be highly toxic chemicals, and harmful to human health and the environment (Xing and Cao, 2007). Their toxicity has been demonstrated for rodents, and 3-MCPD absorption in human is well reported (Araujo et al., 2020). In fact, 3-MCPD is considered to be a potent human carcinogen, to have adverse effects on the kidney, striated muscle, immune and central nervous system functions, and testicular organogenesis (Buhrke et al., 2015; Schultrich et al., 2017). In addition, it has been found in human breast milk (originated from diets) suggesting that infants are also exposed (Zelinková et al., 2008). For this purpose, regulatory bodies such as the Commission Regulation of European Commission recommends 50 μg/kg for dry matter and 20 μg/kg for a liquid product containing 40% of dry matter as an acceptable concentration limit in edible products (European Commission, 2010; Stadler and Lineback, 2008) while the Food and Agriculture Organization of the United Nations (FAO) recommends a limitation of the quantity of the compounds involved in the appearance of these neo-formed contaminants in the manufactured food (FAO/WHO, 2017). Without further ado, the scientific community has developed several methods for extracting, detecting, and quantifying these toxic compounds, it is particularly the case of 3-MCPD. The used methods of detection and quantification are essentially divided into indirect and direct methods, and rely on the use of complex methods like gas chromatography or liquid chromatography coupled with mass spectrometry (Zhou et al., 2014b). The use of these high-resolution devices whether or not using deuterated standards, guarantees the specificity of the methods (Gao et al., 2019). In that respect, two main reference methods are accepted: one is recommended by the German Society for Fat Science (DGF (C-VI 17 (10)) and the other one by the American Oil Chemists' Society (AOCS (Cd 29c-13)) (Karl et al., 2016). Later, another approach that is based on a specifically mild alkaline ester cleavage so called SGS (Société générale de surveillance) 3-in-1 which is a methodology developed by Kuhlmann for heterogenous foods was introduced (Kuhlmann, 2011). These methods are upgraded regularly and correspond to ISO method 18363–1 (Lucas et al., 2017). The principle is quite the same as the MCPD esters are mostly converted into free analytes, namely into 2-MCPD, 3-MCPD and glycidol, and derivatized using phenylboronic acid (PBA) before gas chromatography-mass spectrometry (GC–MS) analysis. By multiple reaction monitoring approach, the limit of detection can reach 0.01 mg/kg with 0.05 mg/kg as limit of quantification (Goh et al., 2019). Recently, non-MS-based methods have been published. The detection and quantification of 3-MCPD is possible through attenuated total reflection-Fourier transform ion cyclotron resonance (Goh et al., 2019). All these methods have some drawbacks in terms of their cost, time-consuming and their experimental complexity.

In our recent work (Martin et al., 2021), cysteine–silver nanoparticles (Cys-AgNPs) based colorimetric method has been used for the determination of 3-MCPD. This technique has displayed rapid response, low cost, and good selectivity for 3-MCPD detection due to the rearrangement of the cysteine on the silver nanoparticles. In this rearrangement, the bond between the cysteine molecule and the silver nanoparticle is provided by the sulfur atom leaving the amine and carboxylic groups available which are sensitive to chemical reactions. Despite these advantages, the limit of detection (0.084 μg/mL) is not sufficient to guarantee food safety and quality as this value is higher than the recommended limit in foodstuffs. Moreover, the electrochemical technique has emerged as a promising analytical technique. In this technique, surface modification is the proper way to obtain good results for the determination of toxic compounds especially for the detection of 3-MCPD (Yaman et al., 2021; Yuan et al., 2019). In this trend, modified gold electrode has shown its effectiveness as analytical tool for the detection of wide range of compounds in different media especially for pharmaceuticals and human fluids (Bukkitgar et al., 2017; Shetti et al., 2015), and in food or environment (Shetti et al., 2017). However, study has demonstrated that the oxidation of 3-MCPD on gold electrode is better in basic media, especially in sodium hydroxide (NaOH) solution than in either of other electrolytes (Chbihi et al., 2008).

It should be noted that studies have demonstrated that the stability of Cys-AgNPs is higher when pH $>$ 7 in which the cysteine molecules are bound to silver nanoparticles through their sulfur atom, leaving free amine and carboxylic groups (Csapó et al., 2012; Martin et al., 2021). On the one hand, it is well known that the toxicological property of 3-MCPD esters is constituted by the release of 3-MCPD during digestion, and on the other hand, 3-MCPD is known to be preponderant with a ratio up to 10 when there is coexistence with its isomers, namely glycidol and 2-MCPD (Andres et al., 2013; Fu et al., 2007; Kuhlmann, 2011; Rahn and Yaylayan, 2011). For this reason, the determination of 3-MCPD instead of its esters or isomers is of utmost importance for food control. Therefore, a simple and rapid method for the detection of 3-MCPD would always be of prime importance.

In this current work, an electrochemical sensor is designed by depositing cysteine-modified silver nanoparticles on a gold electrode (Cys-AgNPs/Au). Indeed, a simple immersion of the gold electrode in a solution of Cys-AgNPs has allowed designing an ultra-sensitive electrode for the detection of 3-MCPD at trace level with a concentration as low as 2.4 ng/mL in NaOH electrolyte. This electrochemical sensor has the advantages of being low cost, high sensitive, and selective toward 3-MCPD detection. Furthermore, this technique has shown good reproducibility, reusability, stability, and recovery, thus providing a promising sensor for 3-MCPD detection in foodstuffs.

2. Material and methods

2.1. Reagents

All chemicals used were of analytical grade and were used as received without any further purification. The following chemicals were used throughout this work. Silver nitrate ($AgNO_3$, 99%), 3-monochloropropane-1,2-diol (3-MCPD, 98%), glycerol ($C_3H_8O_3$, 99%), sodium hydroxide (NaOH, 98%), iron sulfate ($FeSO_4$, $7H_2O$, 99%) and 3-Bromo-1,2-propanediol (3-MBPD, 97%) were purchased from Sigma-Aldrich (St. Louis, MO, USA), and L-cysteine ($C_3H_7NO_2S$, 98%) and zinc nitrate ($Zn(NO_3)_2$, $4H_2O$; 98%) were from Merck (Darmstadt, Germany). Glycidol ($C_3H_6O_2$, 98%) was supplied by Titan Scientific Ltd (Shanghai, China). Sodium chloride (NaCl, 99%) and copper sulfate ($CuSO_4$, $5H_2O$; 99–100%) were obtained from Pancreac (Germany). 2-monochloroproane-1,3-diol (2-MCPD, 100 µg/mL) was provided by Alta scientific Ltd. (Tianjin, China), and propylene glycol ($C_3H_8O_2$, 99.5%) was acquired from Aladdin Biochemical Technology Co. Ltd. (Shanghai, China) while ethylene glycol ($C_2H_6O_2$, 99.5%) was supplied by Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Ultra-pure water obtained from deionized (DI) water system (Sichuan Zhuoyue Water Treatment Equipment Co., Ltd, Chengdu, China) with a resistivity of 18.25 MΩ•cm was used throughout all the experiments. The smoked fish (mackerel) samples and palm oil were obtained from various wholesale markets, namely Abobo (Grand marche, Siaka Kone market and Abobote market), Adjame (Forum, Gouro market and Roxy market) and Yopougon (Niangon market, Gouro market and Abobodoume market). Fifty-four samples were collected for all.

2.2. Apparatus and instrumentations

All Electrochemical measurements were performed with a MiniONE Electrochemical workstation (plug and play style), a homemade equipment provided by East China University of Science and Technology (MiniONE Instruments, Shanghai, China). A conventional three-electrode system consisting of modified gold electrode (Cys-AgNPs/Au) as working electrode ((Φ = 1 mm), carbon leg wire as a counter electrode and a saturated calomel electrode (SCE) as reference electrode were employed. All experiments were performed at ambient temperature. Scanning electron microscopy (SEM) images were obtained using SEM FEG Supra 40VP Zeiss (Oberkochen, Germany). The electrode cleaning process was carried out in an ultrasonic cleaner (Bandelin electronic super AK 255, Germany).

2.3. Fabrication of Cys-AgNPs/Au electrode

Cys-AgNPs synthesis: The Cys-AgNPs nanostructures were synthesized according to the previous published method (Martin et al., 2021). Briefly, 0.005 g of L-cysteine was dissolved in 100 mL of DI water. Then 0.02 g of $AgNO_3$ was added and left under magnetic stirring for five minutes followed by the addition of 0.1 g of sodium hydroxide while heating at 60 °C under gently magnetic stirring for five hours.

Pretreatment of the Au electrode: Before the use of the Au electrode, the surface of the disc was polished with alumina (0.05 mm slurry diameter), followed by ultrasonic cleaning in DI water and ethanol for two minutes for each step. This electrode was electrochemically cleaned in sulfuric acid solution (H_2SO_4, 1 M) by polarizing the electrode for 60 s at −2 V and +2.5 V to form H_2 and O_2 bubbles, respectively, at the electrode surface. Then, cyclic voltammograms (CV) were recorded between −2 V and +2.5 V at 100 mV/s until reproducible cycles were obtained.

Cys-AgNPs/Au electrode fabrication process: After cleaning, the electrode was immersed in a colloidal solution of Cys-AgNPs for a certain time (the time was optimized) and dried at room temperature (28 °C) for approximately 30 min. This process was repeated several times (the number of layer deposits has been optimized). The obtained Cys-AgNPs/Au electrode was finally used in an aqueous NaOH solution as electrolyte for the detection of 3-MCPD in the potential range from −1.5 V to +1.5 V at 100 mV/s as scan rate through cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques.

2.4. Electrochemical detection of 3-MCPD

The response at bare and modified gold electrode towards 3-MCPD was studied using CV and DPV techniques. In a typical procedure for the detection of 3-MCPD, 50 mL of appropriate concentration of NaOH solution was transferred into an electrochemical cell. An appropriate amount of 3-MCPD was added from the stock solution into the cell. Then, after homogenizing, the CV was recorded from −1.5 to +1.4 V (only the useful part is displayed) in the cathodic direction using 100 mV/s as scan rate. For the calibration, different concentrations varying from 2.5 ng/mL to 530 ng/mL of 3-MCPD were prepared and used in the DPV technique. All DPV experiments were done between −0.5 V and +1.4 V at a scan rate of 100 mV/s, pulse time of 0.05 s, sample time of 0.1 s, stand time of 2 s, staircase potential of 7 mV and pulse amplitude of 100 mV.

2.5. Application in real sample

The quantification of 3-MCPD in a food sample was carried out using DPV technique by mixing 0.5 mL of sample extract in 50 mL aqueous solution of 4 M NaOH in the electrochemical cell. The extraction method is described in our previous study (Martin et al., 2021): Typically, to 5 g of the sample placed in a 50 mL centrifuge tube, 30 mL of a hexane/acetone mixture (1:1, v/v) was added. The mixture was homogenized for 10 min with a vortex and then filtered with Buchner. The solid residue was washed twice with 10 mL of the same hexane/acetone mixture and the filtrate was transferred to a sepa-

rating funnel containing 10 mL of water. The lower aqueous layer was separated from the organic layer, which was re-extracted with another 10 mL portion of water. The two combined extracts were evaporated in a 100 mL distilling flask under vacuum at 55 °C to evaporate the remaining acetone. The level of 3-MCPD was calculated from the calibration curve.

All experiments done throughout this work were carried out in triplicate (n = 3), unless otherwise specified.

3. Results and discussion

3.1. Electrochemical characterization of Cys-AgNPs modified Au electrode

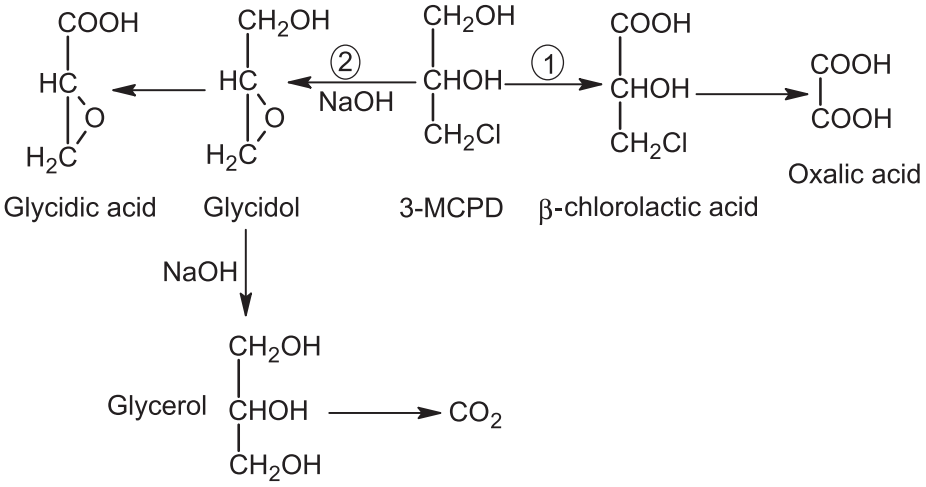
The electrochemical behavior of the electrode in the absence or presence of 3-MCPD was studied using CV technique in 6 M NaOH at a scanning rate of 100 mV/s (Figure 1A). As displayed, a classic form of CV in NaOH medium at bare Au electrode is obtained with two reduction peaks at −0.341 and +0.067 V/*vs*. SCE, and an oxidation peak at +1.011 V/*vs*. SCE (Figure 1A, a). However, coating Au electrode with Cys-AgNPs, except the reduction peak at −0.341 V/*vs*. SCE, the CV response of the Au electrode is significantly affected with an enhancement of the oxidation and reduction peaks (Figure 1A, b). In addition, all the potentials associated to these peaks are shift from their initial position. The change in redox current peak and potential shifts in these voltammetric graphs validate the electron transfer at the fabricated electrode and certify the formation of adsorbed thin film of Cys-AgNPs on the electrode surface (Pushpanjali et al., 2019) and may suggest an enhancement of the electrochemical properties. Moreover, the enhancement of the peak around +1.011 V/*vs*. SCE is more important than those of the reduction peaks indicating that the Cys-AgNPs film improves the process of 2.5 electron transfer (Tian et al., 2003). Based on the literature and these results, two pathways can therefore be suggested for the oxidation of 3-MCPD on the Cys-AgNPs/Au electrode as shown in Scheme 1: 1) a natural pathway which leads to the formation of beta-chlorolactic acid (involved in the inhibition of the glycolysis) followed by the formation of oxalic acid and 2) another one which leads to the formation of glycidic acid or carbon dioxide via glycidol (Andres et al., 2013; Jones and Fakhouri, 1979; Lynch et al., 1998; Wandel et al., 2001).

Besides, in the presence of 2 μg/mL of the contaminant 3-MCPD, using the Au electrode (Figure 1B, a), a pronounced oxidation peak around +0.078 V/*vs*. SCE is observed, suggesting that 3-MCPD has an activity on the Au electrode in the chosen potential range and can be used for the detection of 3-MCPD. However, by modifying the Au electrode with the Cys-AgNPs (Figure 1B, b), a significant increase in the activity of 3-MCPD is observed with a slight shift of the potentials (+0.081 V/*vs*. SCE) towards high potentials compared to that obtained with the bare Au electrode. This increase in the peak intensity and shift in the peak potential of the 3-MCPD show not only that the presence of the Cys-AgNPs film increases the specific surface and the conductivity of the Au electrode but also that there is indeed an adsorption of the 3-MCPD molecules on the Cys-AgNPS/Au electrode (Bibi et al., 2019; Pushpanjali et al., 2019; Sun et al., 2011). These observations support the electrocatalytic nature of the Cys-AgNPs/Au electrode for the oxidation of 3-MCPD (Sun et al., 2011). Indeed, cysteine has several sites (amine and carboxylic functions) which can interact with the 3-MCPD to attract this latter closer as possible to the active catalytic centers, which are not only on the surface of the Au electrode but also on Ag nanoparticles of the modified Cys-AgNPs/Au electrode.

To further confirm the electrocatalytic nature of the Cys-AgNPs/Au electrode, the electroactive surface area of the unmodified and fabricated electrodes was assessed. The Randles-Sevcik equation (Equation (1)) for a reversible process was used to evaluate the electrode surface area:

$$I_p = 2.69' 10^5 n^{3/2} A D^{1/2} n^{1/2} C \quad (1)$$

where Ip represents the oxidation current peak around +1.011 V/*vs*. SCE, n the number of transferred electrons (which is found to be 2.5), A stands for the area of the electroactive surface, D denotes the diffusion coefficient (D is 226 × 10^{-6} s/cm^2 in the case of 6 M NaOH (Zhang et al., 2009)) while ν and C represent the scan rate and the concentration of 3-MCPD, respectively.



Scheme 1 Probable pathways of 3-MCPD oxidation.

Using Equation (1) and the results from Fig. 1B, the values of A at Au electrode and Cys-AgNPs/Au electrode are 0.253 cm^2 and 0.739 cm^2, respectively. As indicated, the electroactive surface area of the Cys-AgNPs/Au electrode is three times higher than that of Au electrode confirming the enhancement of the electrocatalytic properties with the presence of Cys-AgNPs film on the Au electrode.

3.2. Effect of NaOH concentration

The effect of the concentration of NaOH used on the electrochemical response of Cys-AgNPs/Au electrode in the presence of 3-MCPD was evaluated in the concentration range from 0.5 M to 8 M (Fig. 1C&D). The results show that the intensity of the oxidation peak of 3-MCPD around +0.081 mV/*vs*. SCE increases with an increase in NaOH concentration until reaching a maximum at around 4 M and decreases beyond this concentration (Fig. 1D). This increase is due to the enhanced activation effect of the hydroxide ions for the oxidation reaction of 3-MCPD (Rudisirisak and Ngowattana, 2017). More precisely, these hydroxide ions promote the carboxylate and amide ions which can facilitate the 3-MCPD adsorption by substitution of the chloride ion as shown in Scheme 2 (Hamlet et al., 2002). This assertion assumes that the second route of oxidation in Scheme 1 is less likely. This is also confirmed by the fact that glycidol is stable in alkaline medium. On the other hand, the decrease observed beyond 4 M could be due to the effect of competition between the contaminant 3-MCPD and the excess of OH^- ions at the active sites on the Cys-AgNPs/Au electrode surface. These OH^- ions can lead to the formation of a metal oxide film and can play a role of inhibitor (Parpot et al., 2006). As the maximum is obtained at 4 M NaOH, the following experiments are done with this concentration.

3.3. Effect of immersion time of the Au electrode in the Cys–AgNPs solution

The effect of the immersion duration of the Au electrode in the Cys-AgNPs solution was studied at different immersion times from 30 min to 180 min in order to find the best immersion time for the fabrication of the modified electrode (Fig. 2A& B). Except the slight shifts of the oxidation and reduction peaks, the obtained results do not show any change in the profile of the different graphs, the same characteristic peaks of the Au electrode and 3-MCPD are observed. These shifts indicate that the thickness of the Cys-AgNPs film change with the increase of the immersion time. Furthermore, an increase in the intensity of the 3-MCPD oxidation peak is also displayed for an increase in the immersion duration up to 90 min (Fig. 2B) and a decrease is obtained beyond 90 min. This maximum suggests that the best immersion time is 90 min. The immersion time of the Au electrode in the Cys-AgNPs solution is therefore set at 90 min for the next experiments.

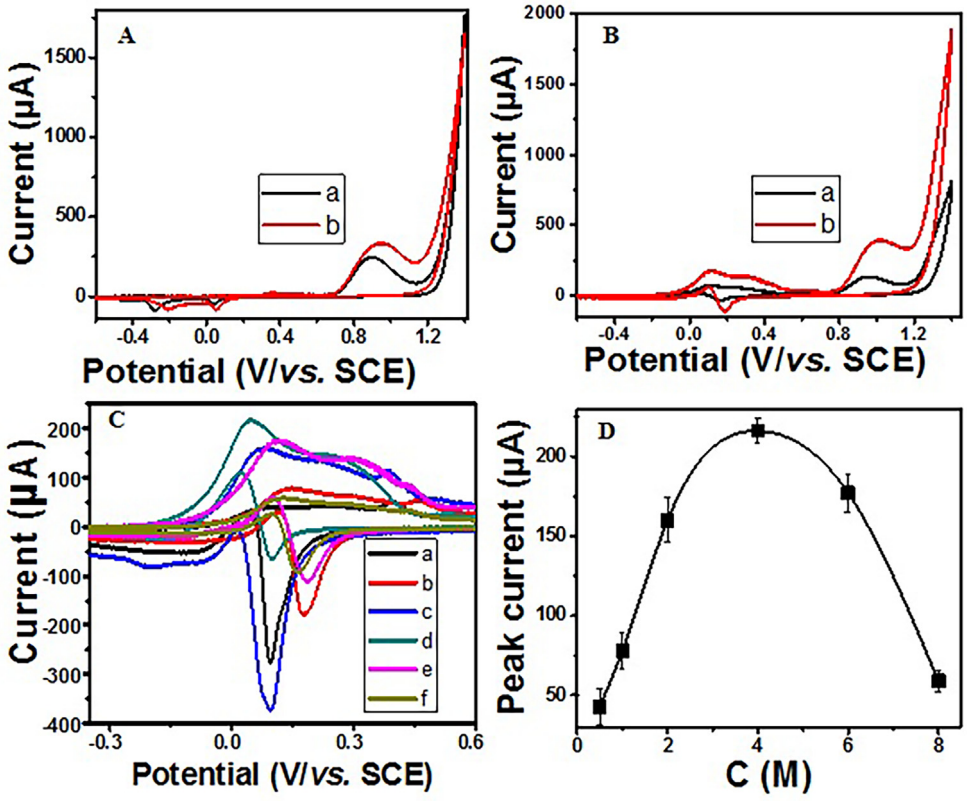
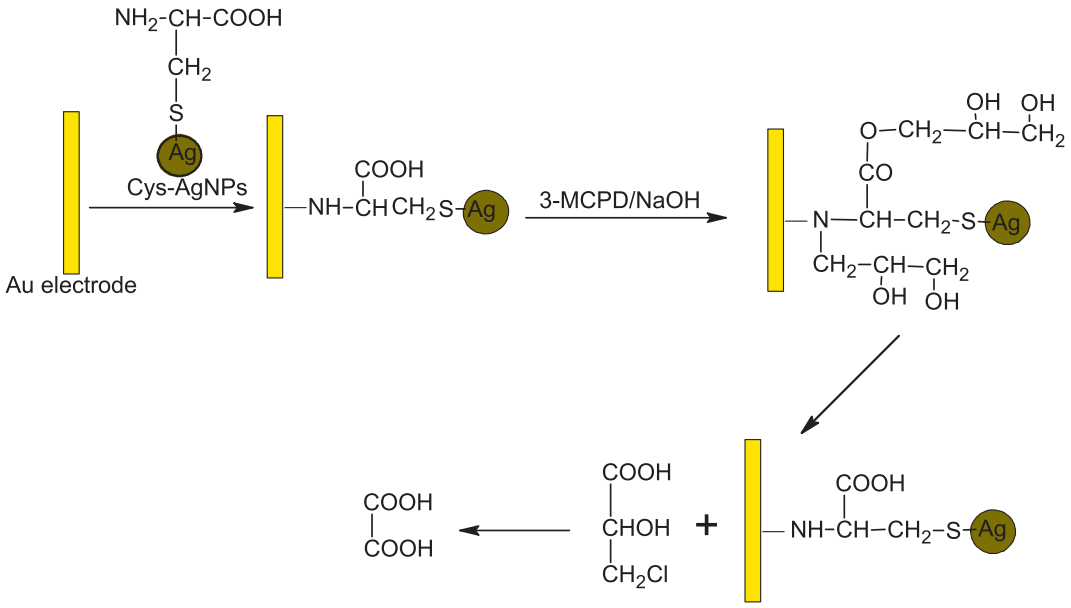


Fig. 1 Cyclic voltammograms A) in the absence and B) in the presence of 2 μg/mL of 3-MCPD at (a) bare Au, and (b) Cys–AgNPs/Au electrode in 6 M NaOH at 100 mV/s. C) Cyclic voltammograms of Cys-AgNPs/Au in the presence of 2 μg/mL of 3-MCPD at different concentrations of electrolyte: (a) 0.5 M; (b) 1 M; (c) 2 M; (d) 4 M; (e) 6 M and (f) 8 M of NaOH at 100 mV/s and D) corresponding intensity of the oxidation current peak of 3-MCPD at +0.078 V/*vs*. SCE for different concentrations of NaOH.



Scheme 2 Probable route of 3-MCPD oxidation on the Cys-AgNPs/Au electrode.

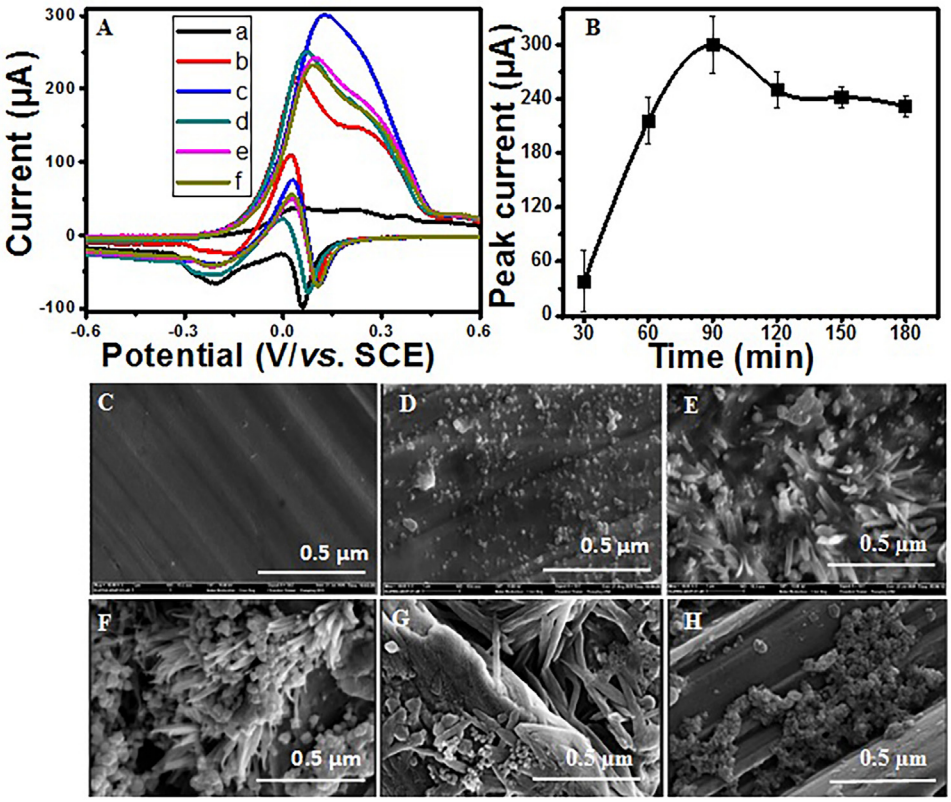


Fig. 2 A) Cyclic voltammograms recorded in 4 M NaOH solution at 100 mV/s in the presence of 2 μg/mL of 3-MCPD at different immersion times of the Au electrode in the colloidal solution of Cys-AgNPs. B) Peak of their intensity as a function of immersion time (a) 30, (b) 60, (c) 90, (d) 120, (e) 150 and (f) 180 min. SEM image obtained at: C) 0 min; D) 30 min; E) 60 min; F) 90 min; G) 120 min and H) 180 min of immersion of the Au electrode in Cys-AgNPs solution.

In order to understand this electrochemical response at 90 min, the SEM images for different immersion times, namely 0, 30, 60, 90, 120, and 180 min, were performed (Fig. 2C-H). The SEM images show that the size and dispersion of Cys–AgNPs particles on the Au electrode vary with the duration of immersion. Wire-like growth is observed over time, and

their arrangement is a function of time. For a duration of less than 90 min (Fig. 2D-F), perpendicular nanowire growth on the effective surface area of the disc Au electrode is observed. More particularly, the nanowires obtained at 90 min are well developed and distributed compared with the distribution for the other cases. Indeed, these Cys–AgNPs nanowires are uniformly and densely oriented vertically with respect to the Au electrode surface, forming a highly porous surface morphology with an average diameter of 30 nm on the surface of the Au electrode. Beyond 90 min, the nanowires are parallelly developed to the effective surface of the Au electrode (Fig. 2G&H), leading to low conductivity. This is clear evidence that the perpendicular arrangement of the wires on the effective surface of the electrode promotes a higher electrocatalytic activity, indicating that this orientation is appropriate for good conductivity and confirming 90 min as appropriate immersion time (Ning et al., 2014).

3.4. Effect of the deposition cycles of Cys–AgNPs

The optimum cycles of Cys-AgNPs layer on the Au electrode for better detection of 3-MCPD were examined by CV technique in the presence of 2 µg/mL of 3-MCPD (Fig. 3A&B). As shown in these figures, the 3-MCPD oxidation peak shows the strongest intensity for three layers, suggesting that the three-layer deposition is ideal for better fabrication of the Cys-AgNPs/Au electrode for the detection of 3-MCPD. Therefore, the number of Cys-AgNPs layers deposited on the Au electrode is set at three for the following experiments.

3.5. Effect of scan rate

The effect of the scan rate on the oxidation peaks of 3-MCPD was evaluated from 10 mV/s to 200 mV/s in a solution of 4 M NaOH in the presence of 2 µg/mL of 3-MCPD (Fig. 3C&D). As displayed, the oxidation peak of 3-MCPD increases linearly with the square root of scan rate (Equation (2)). This linear increase indicates that the oxidation process of 3-MCPD on Cys-AgNPs/Au electrode is controlled by a diffusion process on the surface of this electrode while the potential shift suggests the phenomenon of adsorption of the 3-MCPD molecules before their process of oxidation (Bibi et al., 2019). This is mainly attributed to the active sites and the porous nature of Cys-AgNPs film on the Au electrode. However, to avoid frequent overload during the experiment, the scan rate is set at 100 mV/s for the remaining experiments.

$$I_{3-MCPD} = 28123.6n^{1/2} - 29.1 \quad (2)$$

3.6. Determination of 3-MCPD and Cys-AgNPs/Au sensitivity

The sensitivity of Cys-AgNPs/Au electrode was evaluated by studying the DPV response of 3-MCPD oxidation on the Cys-AgNPs/Au electrode (Fig. 4A). As displayed in Fig. 2B & C, a good linearity ranging from 2.5 ng/mL to 200 ng/mL between the intensity of the oxidation peak and the concentration of 3-MCPD is obtained with associated linear equation I (µA) = 68.59 × C (µg/mL) + 2.66 (R^2 = 0.9997). The calculated limit of detection and quantification from the relation-

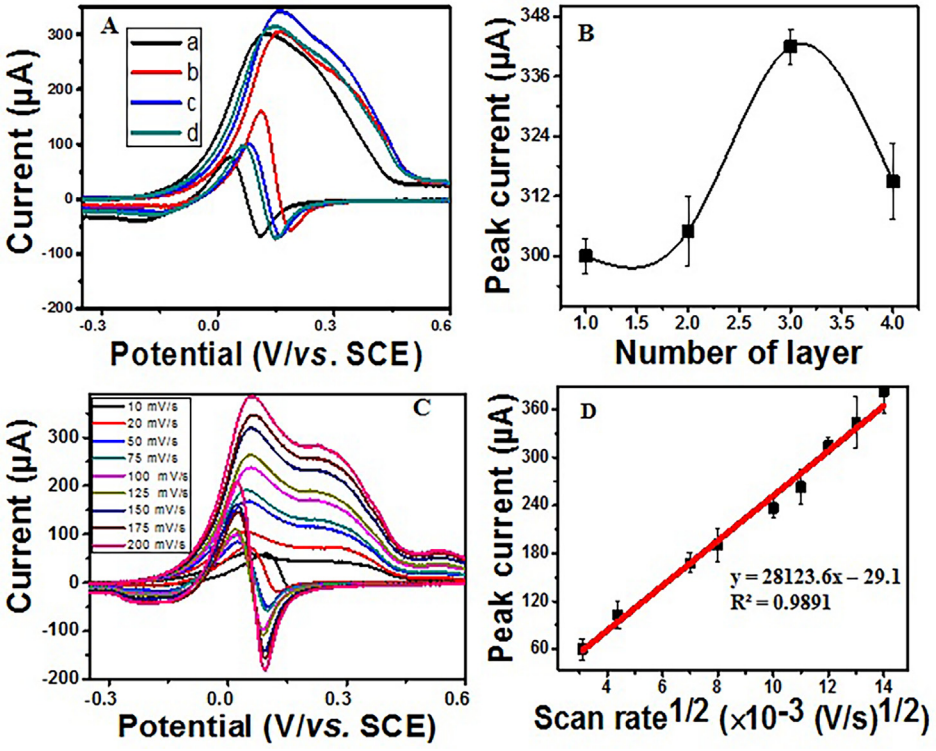


Fig. 3 A) Cyclic voltammograms of the Cys-AgNPs/Au electrode obtained from the deposition of a) one layer, d) two layers c) three layers and b) four layers of Cys-AgNPs on the Au electrode in 4 M NaOH solution at 100 mV/s containing 2 µg/mL of 3-MCPD. B) Number of layers versus the intensity of the 3-MCPD oxidation peak. C) Effect of the scan rate on the oxidation peak of 2 µg/mL of 3-MCPD on the Cys-AgNPs/Au electrode. D) Oxidation peak intensity as a function of the square root of the scan rate.

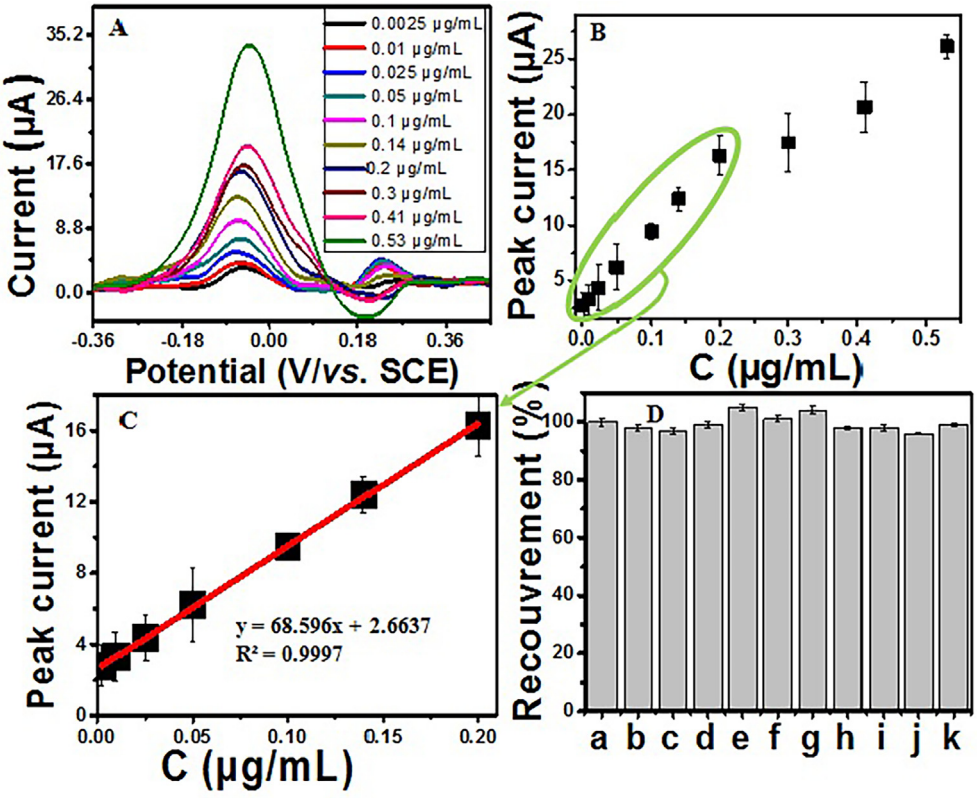


Fig. 4 A) DPV for different concentrations of 3-MCPD in 4 M NaOH. B and C) Relationship between the peak intensity of the oxidation current peak and the concentration of 3-MCPD. D) Selectivity diagram of (a) 0.01 µg/mL of 3-MCPD containing 0.1 µg/mL of (b) propylene glycol, (c) ethylene glycol, (d) glycerol, (e) glycidol, (f) 2-MCPD, (g) 3-MBPD, (h) Cu^{2+}, (i) Fe^{2+} and (j) Zn^{2+} and (k) Cl^{-}.

ships 3α/S and 10α/S (where α is the standard deviation and S, the slope of the calibration curve (n = 10) give 2.4 ng/mL and 8.2 ng/mL, respectively. This low concentration as a limit of detection indicates the high sensitivity of the modified electrode for the detection of 3-MCPD and suggests that this electrode can be used where tracking of 3-MCPD is necessary as these values are lower than the recommended limit in foodstuffs (European Commission, 2010).

3.7. Average recovery using the fabricated electrochemical sensor

The reliability of the proposed method has been assessed from recovery studies using six different concentrations of 3-MCPD. The recovery rate between 95% and 98% (Table 1) is obtained, showing good accuracy of this technique.

Table 1 Recovery using the fabricated sensor (n = 3).

Added (µg/mL)	Found (µg/mL)[a]	Recoverey (%)
0.20	0.193	96.5 ± 1.4
0.10	0.096	96.0 ± 3.0
0.05	0.049	98.0 ± 1.3
0.04	0.039	97.5 ± 1.0
0.03	0.029	96.7 ± 1.0
0.02	0.019	95.0 ± 1.1

[a] Average value of recovered 3-MCPD concentration.

3.8. Selectivity of Cys-AgNPs/Au electrode

The selectivity of Cys-AgNPs/Au electrode towards 3-MCPD detection was evaluated by determining the recovery rate in the presence of its analogues which can coexist, in particular 2-MCPD, 3-bromo-1,2-propanediol (3-MBPD), glycidol, glycerol, 1,2-propanediol and ethylene glycol with a concentration which is 10 times higher than that of 3-MCPD (Fig. 4D). The results from Fig. 4D reported in Table 2 show a recovery rate varying between 98% and 105%. As reported, the compounds,

Table 2 Recovery rate of 0.01 µg/mL 3-MCPD in the presence of 0.1 µg/mL of interfering compounds.

Compounds	C (µg/mL)[a]	C (µg/mL)[b]	Recoverey (%)
3-MCPD	0.01	0.010	100
Propanediol	0.01	0.098	98
Ethylène glycool	0.01	0.0101	101
Glycerol	0.01	0.0099	99
Glycidol	0.01	0.0105	105
2-MCPD	0.01	0.0101	101
3-MBPD	0.01	0.0104	104
$CuSO_4$	0.01	0.0098	98
$FeSO_4$	0.01	0.0098	98
$Zn(NO_3)_2$	0.01	0.0096	96
NaCl	0.01	0.0099	99

C[a]: Concentration added. C[b]: Concentration found.

even with slight structure difference show no visible response at all. Without the C-Cl bond on this structure (comparing 3-MCPD with propylene glycol), or even if the C-Cl bond is substituted with C-OH bond (comparing 3-MCPD with glycerol), carbon of C-Cl bond is removed (comparing 3-MCPD with ethylene glycol), these compounds do not undergo an oxidation reaction on the Cys-AgNPs/Au electrode. The same trend is observed when the Cl is in position 2 (2-MCPD). The above reactivity test strongly demonstrates the necessity of the presence of C-Cl bond at the end of the propanediol chain. Moreover, a slight interference (around 4–5%) is observed in the presence of glycidol and 3-MBPD. In the case of glycidol, the lower interference may be due to its stability in a solution with pH > 7 or the possibility to be transformed to glycerol or its oligomers in alkaline media (Hamlet et al., 2002). These results indicate that the second pathway of 3-MCPD oxidation as shown in Scheme 1 which produces glycidic acid or carbon dioxide via glycidol is less favorable. However, the weak interference of 3-MBPD does not seem to be clearly understood as it is expected to undergo the same oxidation process as that of 3-MCPD (Jones and Fakhouri, 1979). This weak interference from 3-MBPD may be explained by the type of heteroatoms in which the mobility of the molecule with the bromine atom (heavier) may be less than that with chlorine. It can be assumed that the Cys-AgNPs/Au electrode has high selectivity to 3-MCPD compared with its structural analogues and can be used for the detection of 3-MCPD in a matrix containing these compounds without further separation (Sun et al., 2014). This result therefore, confirms the oxidation pathway in which the byproducts are β-chlorolatic acid and oxalic acid as shown in Scheme 2.

Furthermore, it is also important to evaluate the effect of inorganic compounds which are frequently met in food products as they may interfere on the Cys-AgNPs/Au electrode while detecting 3-MCPD. Typically, the presence of certain metals such as Fe, Cu and Zn, and ion (Cl^-) are among the main factors contributing to the appearance of free 3-MCPD in foodstuffs (Sadowska-Rociek et al., 2018). Thus, the effect of the inorganic compounds containing the ions of these metals and the Cl^- ion in the presence of the contaminant at a concentration which is 10 times greater than that of the 3-MCPD was studied (Fig. 4D). As shown in Table 2, a slight decrease in the recovery rate of less than 4% is observed, suggesting that their interference effect in the detection of 3-MCPD may be negligible. These results indicate that the Cys-AgNPs/Au electrode is selective towards 3-MCPD.

3.9. Precision

The precision of the method was studied as intra-day and inter-day precision daily for three days by analyzing the same concentration of solutions (Table 3). All found values of RSD are less than 10%. This high precision suggests that this electrochemical sensor can be used for the monitoring of 3-MCPD.

3.10. Reusability and stability of the fabricated electrochemical sensor

The reusability and stability of the electrode were tested daily over 10 days and with 10 successive cycles, respectively. As shown in Fig. 5A, except the reduction peak of the first cycle, no obvious change in peak intensity nor change in the CV profile is observed for the oxidation current peak of 3-MCPD on the Cys-AgNPs/Au electrode, indicating that the Cys-AgNPs/Au electrode is stable. Furthermore, for the reusability procedure, the same Cys-AgNPs/Au electrode was used during ten days in solutions prepared daily with the same concentration of 3-MCPD (three parallel experiments were done). The electrode was washed successively with water and ethanol after its use and left to dry in ambient air. The results are reported in Fig. 5B and Table 4. As displayed, no effective decrease in the recovery is observed over the ten days for the same electrode (4–10% of relative standard deviation is obtained). These weak effects on the determination of 3-MCPD indicate that the developed Cys-AgNPs/Au electrode can be reused several times and days without drastic precautions.

3.11. Application of the fabricated electrochemical nanosensor in real samples

The developed electrochemical sensor was evaluated in real samples in which palm oil and smoked mackerel samples from three local markets, namely Abobo (Grand marche, Siaka Kone market and Abobote market), Adjame (Forum, Gouro market and Roxy market), and Yopougon (Niangon market, Gouro market and Abobodoume market) were used. Table 5 shows the levels of 3-MCPD in these food matrices. The obtained 3-MCPD concentrations vary from 307 to 337 μg/kg for the smoked mackerel and 854 to –1089 μg/kg for the palm oil. These values are well above the acceptable concentration in foodstuffs which is 50 $\mu g \dot{s} kg^{-1}$ for dry matter and 20 $\mu g \dot{s} kg^{-1}$ for a liquid product containing 40% of dry matter (European Commission, 2010; Ostermeyer et al., 2021). As reported in the literature, vegetable oils are one type of food products which contain a higher amount of 3-MCPD due to its manufacturing procedure in which high temperature is used (Becalski et al., 2015; MacMahon et al., 2013; Seefelder et al., 2008; Zhou et al., 2014a). On the other hand, smoking fish can generate a high level of 3-MCPD as the smoke is another source of 3-MCPD contamination and this contamination increases with the time of exposure (Chai et al., 2016; Martin et al., 2021). These results are in good agreement with those obtained in the literature (Karl et al., 2016). The use of these products (palm oil and smoked products) in cereal-based products, bread, refined oil, soups, and snacks, for example, may be considered as a potential source of exposure to free 3-MCPD. This work may therefore be important for those countries where palm oil and smoked products are mainly supplied in foodstuffs without any controls and where there is a lack of traditional analytic tools to make adequate monitoring to access secure foodstuffs.

3.12. Comparison with other used electrochemical methods for the detection of 3-MCPD

A Comparison of the LOD of other electrochemical sensors used for the detection of 3-MCPD with respect to the proposed sensor is done (Table 6). The result shows relatively low LOD in most cases except that proposed by Yama *et al.* (Yaman et al., 2021) who had proposed an electrochemical sensor providing almost the same level of LOD comparing with ours.

Table 3 Intra-day and Inter-day studies.

Concentration added (μg/mL)	Concentration found (μg/mL)		RSD (%) (n = 3)	
	Intra-day	Inter-day	Intra-day	Inter-day
0.20	0.199	0.190	7.050	4.521
0.10	0.098	0.102	0.900	9.904
0.05	0.050	0.048	3.958	3.958
0.04	0.038	0.039	3.368	4.111
0.03	0.028	0.029	2.105	7.358
0.02	0.021	0.020	6.763	7.843

RSD: Relative Standard Deviation.

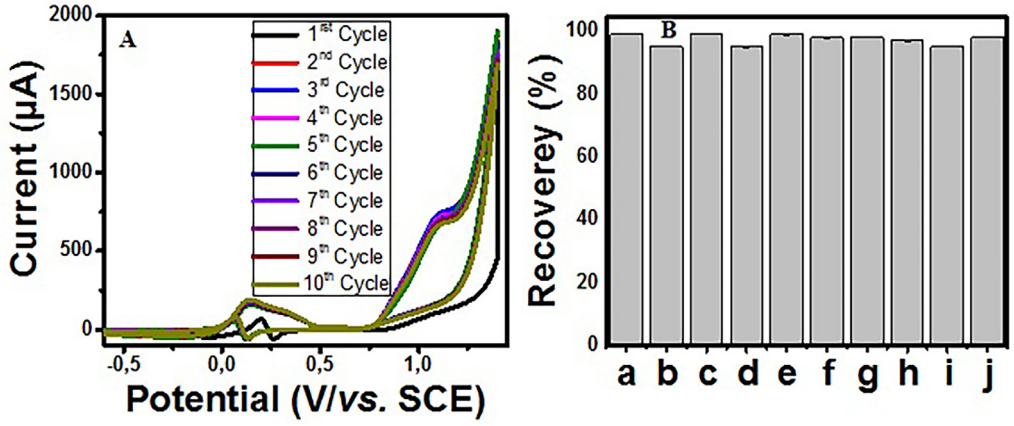


Fig. 5 A) Stability studies of the Cys-AgNPs/Au electrode, and B) Reusability tests of Cys-AgNPs/Au electrode at different days: a) first, b) 2nd, c) 3rd, d) 4th, e) 5th, f) 6th, g) 7th, h) 8th, i) 9th and j) 10th day.

Table 4 Stability of the Cys-AgNPs/Au electrode.

Day	Added (μg/mL)	Found (μg/mL)	Recovery (%)	RSD (%) (n = 3)
01	0.01	0.0099	99.0 ± 0.0	4
02	0.01	0.0095	95.0 ± 0.1	9
03	0.01	0.0099	99.0 ± 0,0	5
04	0.01	0.0098	98.0 ± 0.0	2
05	0.01	0.0095	95.0 ± 0.1	6
06	0.01	0.0098	98.0 ± 0.1	9
07	0.01	0.0098	98.0 ± 0.1	10
08	0.01	0.0099	99.0 ± 0.1	10
09	0.01	0.0097	97.0 ± 0.1	10
10	0.01	0.0095	95.0 ± 0.1	10

Table 5 Contents of free 3-MCPD in fishery products (Mackerel) and palm oil in three different zones.

Food Products	Municipality					
	Abobo		Adjame		Yopougon	
	Average	min–max[a]	Average	min–max[a]	Average	min–max[a]
Smoked mackerel (μg/kg)	337	223–393	348	172–469	307	174–439
Palm oil (μg/kg)	854	329–1239	892	842–941	1089	895–1280

min–max: minimum–maximum.

Table 6 Comparison with reported electrochemical sensors for the detection of 3-MCPD.

Type of electrochemical sensor	LOD	Linear range	Reference
Capillary electrophoresis/electrochemical (copper-disk electrode)	1.3×10^{-7}g/mL	2×10^{-4}–6.6×10^{-4} g/mL	(Xing and Cao, 2007)
Hemoglobin immobilized with magnetic molecularly imprinted nanoparticles and modified on a magnetic electrode (Hb/MMIPs NPs/GCE Hb/MMIPs NPs/GCE)	0.25 mg/L	1–160 mg/L	(Yuan et al., 2019)
Cyt c incorporated in Au@AgNSs/FeMOF nanocomposite (Cyt-c/Au@AgNSs/FeMOF/AuE)	0.41 mg/L	2–100 mg/L	(He et al., 2020)
Molecularly imprinted label-free sensor platform (MIP(oPPy)-GO/PGE)	1.82 nM	2–500 nM	(Yaman et al., 2021)
Cys-AgNPs/Au	2.4 ng/mL	2.5–200 ng/mL	This work

Regarding its simplicity, selectivity and low LOD far under the recommended value of 3-MCPD in foodstuffs, the proposed sensor from this work may be one of the best sensors for the monitoring and quantification of 3-MCPD. In addition, our electrochemical system is an on-site measurement system, making it the best among those proposed analytical tool for better control of food safety and quality.

4. Conclusion

The Cys-AgNPs/Au electrode is used for the first time for the detection of free 3-MCPD. The results show that the Cys-AgNPs/Au electrode possesses a good activity for 3-MCPD oxidation in alkaline media in which β-chlorolactic acid (involved in the inhibition of the glycolysis) and oxalic acid are produced. This electrocatalytic activity suggests a synergistic effect of cysteine, AgNPs and Au for the oxidation of 3-MCPD on the Cys-AgNPs/Au electrode. Moreover, this Cys-AgNPs/Au electrode is found to be stable and can be reused several times with satisfactory results, suggesting the limited use of a large number of electrodes. The limit of detection can be as low as 2.4 ng/mL, which is comparable with the LOD of traditional techniques. This LOD is lower than the recommended limit values in foodstuffs, indicating that this technique can be used for the monitoring of 3-MCPD. In addition, the method has been proved to be reliable with good recoveries and accuracy. All these results indicate that the Cys-AgNPs/Au electrode is ideal for the electrochemical detection of 3-MCPD with several advantages: low-cost, on-site measurement, simple procedures and facilities, etc. Importantly, this Cys-AgNPs/Au electrode with strong conductivity, high sensitivity, excellent reproducibility, and stability can be a good alternative and economical tool in 3-MPCD monitoring or quantification.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors would like to thank the financial support from the National Natural Science Foundation of China (31701698), Shanghai Agriculture Applied Technology Development Program (T2016010401), Shanghai Key Laboratory of Forensic Medicine (Academy of Forensic Science, KF1910) and the Standard Project of Ministry of Agriculture and Rural Affairs, China (SCB-20021, SCB-20025).

Author Contributions

Mr. Aka Alla Martin has carried out the experiments and written the first draft of the manuscript.

Dr. Essy Kouadio Fodjo and Dr. Cong Kong have suggested the project about this work, applied for funding, followed the execution of this work, and deeply checked the manuscript writing process.

Dr. Zhen Gu and Prof. Hui-Feng Wang are the designers of the homemade electrochemical working station used in this work.

Dr. Zran Vanh Eric-Simon and Dr. Guangxin Yang have prepared the method of extraction.

Prof. Trokourey Albert has supervised the electrochemical experiments.

References

Andres, S., Appel, K.E., Lampen, A., 2013. Toxicology, occurrence and risk characterisation of the chloropropanols in food: 2-Monochloro-1,3-propanediol, 1,3-dichloro-2-propanol and 2,3-dichloro-1-propanol. Food Chem. Toxicol. 58, 467–478. http://www.sciencedirect.com/science/article/pii/S0278691513003281.

Araujo, M., Beekman, J.K., Mapa, M.S.T., MacMahon, S., Zhao, Y., Flynn, T.J., Flannery, B., Mossoba, M.E., Sprando, R.L., 2020. Assessment of intestinal absorption/metabolism of 3-chloro-1,2-propanediol (3-MCPD) and three 3-MCPD monoesters by Caco-2 cells. Toxicol. In Vitro 67,. http://www.sciencedirect.com/science/article/pii/S0887233320303015 104887.

Becalski, A., Feng, S., Lau, B.P.Y., Zhao, T., 2015. A pilot survey of 2- and 3-monochloropropanediol and glycidol fatty acid esters in foods on the Canadian market 2011–2013. J. Food Compos. Anal. 37, 58–66. http://www.sciencedirect.com/science/article/pii/S0889157514001562.

Bibi, S., Zaman, M.I., Niaz, A., Rahim, A., Nawaz, M., Bilal Arian, M., 2019. Voltammetric determination of nitrite by using a multiwalled carbon nanotube paste electrode modified with chitosan-functionalized silver nanoparticles. Microchim. Acta 186 (9), 595. https://doi.org/10.1007/s00604-019-3699-8.

Buhrke, T., Frenzel, F., Kuhlmann, J., Lampen, A., 2015. 2-Chloro-1,3-propanediol (2-MCPD) and its fatty acid esters: cytotoxicity,

metabolism, and transport by human intestinal Caco-2 cells. Arch. Toxicol. 89 (12), 2243–2251. https://doi.org/10.1007/s00204-014-1395-3.

Bukkitgar, S.D., Shetti, N.P., Kulkarni, R.M., 2017. Electro-oxidation and determination of 2-thiouracil at TiO2 nanoparticles-modified gold electrode. Surf. Interfaces 6, 127–133. https://www.sciencedirect.com/science/article/pii/S2468023017300044.

Chai, Q., Zhang, X., Karangwa, E., Dai, Q., Xia, S., Yu, J., Gao, Y., 2016. Direct determination of 3-chloro-1,2-propanediol esters in beef flavoring products by ultra-performance liquid chromatography tandem quadrupole mass spectrometry. RSC Adv. 6 (114), 113576–113582. https://doi.org/10.1039/C6RA23417H.

Chbihi, M.E.M., Takky, D., Leger, J.-M., Lamy, C., 2008. Etude de l'electrooxydation et de l'adsorption du 1,3-propanediol sur des electrodes de platine et d'or en milieux aqueux. Annales De Chimie-science Des Materiaux 33 (5), 397–421.

Cheng, W.-W., Liu, G.-Q., Wang, L.-Q., Liu, Z.-S., 2017. Glycidyl fatty acid esters in refined edible oils: a review on formation, occurrence, analysis, and elimination methods. Compr. Rev. Food Sci. Food Saf. 16 (2), 263–281. https://onlinelibrary.wiley.com/doi/abs/10.1111/1541-4337.12251.

Csapó, E., Patakfalvi, R., Hornok, V., Tóth, L.T., Sipos, Á., Szalai, A., Csete, M., Dékány, I., 2012. Effect of pH on stability and plasmonic properties of cysteine-functionalized silver nanoparticle dispersion. Colloids Surf., B 98, 43–49. http://www.sciencedirect.-com/science/article/pii/S0927776512002494.

Commission, E., 2010. Commission Regulation (EC) No 165/2010 of 26 February 2010 amending Regulation (EC) No 1881/2006 setting maximum levels for certain contaminants in foodstuffs as regards aflatoxins. Off. J. Eur. Union 50, 8–12.

FAO/WHO, 2017. Expert Committee on Food Additives. Evaluation of certain contaminants in food: eighty-third report of the Joint FA. WHO Technical Report Series; 1002.

Fu, W.S., Zhao, Y., Zhang, G., Zhang, L., Li, J.G., Tang, C.D., Miao, H., Ma, J.B., Zhang, Q.i., Wu, Y.N., 2007. Occurrence of chloropropanols in soy sauce and other foods in China between 2002 and 2004. Food Addit. Contam. 24 (8), 812–819. https://doi.org/10.1080/02652030701246039.

Gao, B., Li, Y., Huang, G., Yu, L., 2019. Fatty acid esters of 3-monochloropropanediol: a review. Ann. Rev. Food Sci. Technol. 10 (1), 259–284. https://www.annualreviews.org/doi/abs/10.1146/annurev-food-032818-121245.

Goh, K.M., Wong, Y.H., Ang, M.Y., Yeo, S.C.M., Abas, F., Lai, O. M., Tan, C.P., 2019. Comparison assessment between SIM and MRM mode in the analysis of 3-MCPD ester, 2-MCPD ester and glycidyl ester. Food Res. Int. 121, 553–560. http://www.sciencedirect.com/science/article/pii/S0963996918309608.

Hamlet, C.G., Sadd, P.A., Crews, C., Velíšek, J., Baxter, D.E., 2002. Occurrence of 3-chloro-propane-1,2-diol (3-MCPD) and related compounds in foods: a review. Food Addit. Contam. 19 (7), 619–631. https://doi.org/10.1080/02652030210132391.

He, B., Wang, L., Li, M., 2020. A biosensor for direct bioelectrocatalysis detection of 3-MCPD in soy sauce using Cyt-c incorporated in Au@ AgNSs/FeMOF nanocomposite. J. Iran. Chem. Soc., 1–8

Jiang, X., Zhu, C., Li, X., Sun, J., Tian, L., Bai, W., 2018. Cyanidin-3-O-glucoside at low doses protected against 3-chloro-1,2-propanediol induced testis injury and improved spermatogenesis in male rats. J. Agric. Food. Chem. 66 (48), 12675–12684. https://doi.org/10.1021/acs.jafc.8b0422910.1021/acs.jafc.8b04229.s001.

Jones, A.R., Fakhouri, G., 1979. Epoxides as obligatory intermediates in the metabolism of α-halohydrins. Xenobiotica 9 (10), 595–599. https://doi.org/10.3109/00498257909042326.

Karl, H., Merkle, S., Kuhlmann, J., Fritsche, J., 2016. Development of analytical methods for the determination of free and ester bound 2-, 3-MCPD, and esterified glycidol in fishery products. Eur. J. Lipid Sci. Technol. 118 (3), 406–417. https://onlinelibrary.wiley.com/doi/abs/10.1002/ejlt.201400573.

Kuhlmann, J., 2011. Determination of bound 2,3-epoxy-1-propanol (glycidol) and bound monochloropropanediol (MCPD) in refined oils. Eur. J. Lipid Sci. Technol. 113 (3), 335–344. https://onlinelibrary.wiley.com/doi/abs/10.1002/ejlt.201000313.

Lucas, D., Hoffmann, A., Gil, C., 2017. Fully automated determination of 3-MCPD and glycidol in edible oils by GC/MS based on the commonly used methods ISO 18363–1, AOCS Cd 29c–13, and DGF C-VI 18 (10). Gerstel Application Note 191, 1.

Lynch, B.S., Bryant, D.W., Hook, G.J., Nestmann, E.R., Munro, I.C., 1998. Carcinogenicity of monochloro-1,2-propanediol (α-chlorohydrin, 3-MCPD). Int. J. Toxicol. 17 (1), 47–76. https://doi.org/10.1080/109158198226756.

MacMahon, S., Begley, T.H., Diachenko, G.W., 2013. Occurrence of 3-MCPD and glycidyl esters in edible oils in the United States. Food Addit. Contam.: Part A 30 (12), 2081–2092. https://doi.org/10.1080/19440049.2013.840805.

Martin, A.A., Fodjo, E.K., Marc, G.B.I., Albert, T., Kong, C., 2021. Simple and rapid detection of free 3-monochloropropane-1,2-diol based on cysteine modified silver nanoparticles. Food Chem. 338,. http://www.sciencedirect.com/science/article/pii/S0308814620316496 127787.

Ning, F., Shao, M., Zhang, C., Xu, S., Wei, M., Duan, X., 2014. Co3O4@layered double hydroxide core/shell hierarchical nanowire arrays for enhanced supercapacitance performance. Nano Energy 7, 134–142. http://www.sciencedirect.com/science/article/pii/S2211285514000780.

Ostermeyer, U., Merkle, S., Karl, H., Fritsche, J., 2021. Free and bound MCPD and glycidyl esters in smoked and thermally treated fishery products of the German market. Eur. Food Res. Technol. 247 (7), 1757–1769. https://doi.org/10.1007/s00217-021-03746-6.

Parpot, P., Nunes, N., Bettencourt, A.P., 2006. Electrocatalytic oxidation of monosaccharides on gold electrode in alkaline medium: Structure–reactivity relationship. J. Electroanal. Chem. 596 (1), 65–73. http://www.sciencedirect.com/science/article/pii/S0022072806003822.

Pushpanjali, P.A., Manjunatha, J.G., Shreenivas, M.T., 2019. The electrochemical resolution of ciprofloxacin, riboflavin and estriol using anionic surfactant and polymer-modified carbon paste electrode. ChemistrySelect 4 (46), 13427–13433. https://chemistry-europe.onlinelibrary.wiley.com/doi/abs/10.1002/slct.201903897.

Rahn, A.K.K., Yaylayan, V.A., 2011. What do we know about the molecular mechanism of 3-MCPD ester formation? Eur. J. Lipid Sci. Technol. 113 (3), 323–329. https://onlinelibrary.wiley.com/doi/abs/10.1002/ejlt.201000310.

Rudisirisak, K., Ngowattana, N., 2017. Electrochemical technique for 1, 3-dichloro-2-propanol analysis. Int. J. 13 (37), 40–43.

Sadowska-Rociek, A., Cieślik, E., Florkiewicz, A., 2018. Formation of free and bound 3-monochloropropane-1,2-diol in fat-rich cereal model systems: the impact of flour composition. Chem. Pap. 72 (2), 497–507. https://doi.org/10.1007/s11696-017-0302-9.

Schultrich, K., Frenzel, F., Oberemm, A., Buhrke, T., Braeuning, A., Lampen, A., 2017. Comparative proteomic analysis of 2-MCPD- and 3-MCPD-induced heart toxicity in the rat. Arch. Toxicol. 91 (9), 3145–3155. https://doi.org/10.1007/s00204-016-1927-0.

Seefelder, W., Varga, N., Studer, A., Williamson, G., Scanlan, F.P., Stadler, R.H., 2008. Esters of 3-chloro-1,2-propanediol (3-MCPD) in vegetable oils: significance in the formation of 3-MCPD. Food Addit. Contam.: Part A 25 (4), 391–400. https://doi.org/10.1080/02652030701385241.

Shetti, N.P., Malode, S.J., Nandibewoor, S.T., 2015. Electro-oxidation of captopril at a gold electrode and its determination in pharmaceuticals and human fluids. Anal. Methods 7 (20), 8673–8682. https://doi.org/10.1039/C5AY01619C.

Shetti, N.P., Nayak, D.S., Kuchinad, G.T., 2017. Electrochemical oxidation of erythrosine at TiO2 nanoparticles modified gold electrode — An environmental application. J. Environ. Chem. Eng. 5 (3), 2083–2089. https://www.sciencedirect.com/science/article/pii/S2213343717301331.

Stadler, R.H., Lineback, D.R., 2008. Process-Induced Food Toxicants: Occurrence, Formation, Mitigation, and Health Risks. John Wiley & Sons.

Sun, L., Zhang, L., Xu, W., Zhang, J., 2011. Electrochemical detection of low concentration chloropropanol using silver nanowire array electrodes in aqueous media. J. Nanosci. Nanotechnol. 11 (3), 2283–2286. https://www.ncbi.nlm.nih.gov/pubmed/21449381.

Sun, X., Zhang, L., Zhang, H., Qian, H., Zhang, Y., Tang, L., Li, Z., 2014. Development and application of 3-chloro-1,2-propandiol electrochemical sensor based on a polyaminothiophenol modified molecularly imprinted film. J. Agric. Food. Chem. 62 (20), 4552–4557. https://doi.org/10.1021/jf4055159.

Tian, M., Pell, W.G., Conway, B.E., 2003. Nanogravimetry study of the initial stages of anodic surface oxide film growth at Au in aqueous HClO4 and H2SO4 by means of EQCN. Electrochim. Acta 48 (18), 2675–2689. https://www.sciencedirect.com/science/article/pii/S0013468603003153.

Wandel, U., Machado, S.S., Jongejan, J.A., Duine, J.A., 2001. Enzymes involved in the glycidaldehyde (2,3-epoxy-propanal) oxidation step in the kinetic resolution of racemic glycidol (2,3-epoxy-1-propanol) by Acetobacter pasteurianus. Enzyme Microb. Technol. 28 (2), 233–239. https://www.sciencedirect.com/science/article/pii/S0141022900003215.

Xing, X., Cao, Y., 2007. Determination of 3-chloro-1,2-propanediol in soy sauces by capillary electrophoresis with electrochemical detection. Food Control 18 (2), 167–172. http://www.sciencedirect.com/science/article/pii/S0956713505002185.

Yaman, Y.T., Bolat, G., Saygin, T.B., Abaci, S., 2021. Molecularly imprinted label-free sensor platform for impedimetric detection of 3-monochloropropane-1,2-diol. Sens. Actuators B: Chem. 328, 128986. https://www.sciencedirect.com/science/article/pii/S0925400520313332.

Yuan, Y., Wang, J., Ni, X., Cao, Y., 2019. A biosensor based on hemoglobin immobilized with magnetic molecularly imprinted nanoparticles and modified on a magnetic electrode for direct electrochemical determination of 3-chloro-1, 2-propandiol. J. Electroanal. Chem. 834, 233–240. http://www.sciencedirect.com/science/article/pii/S1572665718308440.

Zelinková, Z., Novotný, O., Schůrek, J., Velíšek, J., Hajšlová, J., Doležal, M., 2008. Occurrence of 3-MCPD fatty acid esters in human breast milk. Food Addit. Contam. Part A Chem. Anal. Control Expo Risk Assess 25 (6), 669–676.

Zhang, C., Fan, F.-R.-F., Bard, A.J., 2009. Electrochemistry of oxygen in concentrated NaOH solutions: solubility, diffusion coefficients, and superoxide formation. J. Am. Chem. Soc. 131 (1), 177–181. https://doi.org/10.1021/ja8064254.

Zhou, H., Jin, Q., Wang, X., Xu, X., 2014a. Direct measurement of 3-chloropropane-1,2-diol fatty acid esters in oils and fats by HPLC method. Food Control 36 (1), 111–118. http://www.sciencedirect.com/science/article/pii/S0956713513003897.

Zhou, H., Jin, Q., Wang, X., Xu, X., 2014b. Effects of temperature and water content on the formation of 3-chloropropane-1,2-diol fatty acid esters in palm oil under conditions simulating deep fat frying. Eur. Food Res. Technol. 238 (3), 495–501. https://doi.org/10.1007/s00217-013-2126-3.