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Development of gold nanoparticles modified screen-printed carbon electrode for the analysis of thiram, disulfiram and their derivative in food using ultra-high performance liquid chromatography

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ABSTRACT

For the first time, gold nanoparticles (AuNPs) modified screen-printed carbon electrode (SPCE) was developed as working electrode in ultra-high performance liquid chromatography (UHPLC) coupled with electrochemical detection (UHPLC-ED) for simultaneous determination of thiram, disulfiram, and *N,N*-diethyl-*N,N*-dimethylthiuram disulfide, their derivative compound. The separation was performed in reversed-phase mode using C18 column, mobile phase consisting of 55:45 (v/v) ratio of 0.05 M phosphate buffer solution (pH 5) and acetonitrile at a flow rate of 1.5 mL min⁻¹. For the detection part, the amperometric detection was chosen with a detection potential of 1.2 V vs. Ag/AgCl. Under the optimal conditions, the good linear relationship was obtained in the range of 0.07–15, 0.07–12, and 0.5–15 µg mL⁻¹ (correlation coefficient more than 0.9900) for thiram, *N,N*-diethyl-*N,N*-dimethylthiuram disulfide, and disulfiram, respectively. The limits of detection (LODs) of thiram, *N,N*-diethyl-*N,N*-dimethylthiuram disulfide, and disulfiram were 0.022, 0.023, and 0.165 µg mL⁻¹, respectively. Moreover, this method was successfully applied for the detection of these compounds in real samples (apple, grape and lettuce) with the recoveries ranging from 94.3% to 108.8%. To validate this developed method, a highly quantitative agreement was clearly observed compared to standard UHPLC–UV system. Therefore, the proposed electrode can be effectively used as an alternative electrode in UHPLC-ED for rapid, selective, highly sensitive, and simultaneous determination of thiram, disulfiram, and *N,N*-diethyl-*N,N*-dimethylthiuram disulfide.

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1. Introduction

Nowadays, the designing of electrochemical sensor has been developed in the field of electrochemistry to improve the analytical efficiency in the terms of sensitivity, selectivity, reliability, ease of fabrication and use, and low cost. Screen printing is the technology used for fabrication of biosensors and chemical sensors instead of using large-scale electrode. Their various advantages such as miniaturization, versatility, and low cost of production are really attractive [1]. In addition, many laboratories use the screen-printing for in-house production of sensors. Screen-printed carbon electrode (SPCE) is an alternative material used instead of using the traditional electrodes based on economic substrate. Recently, SPCE have been successfully used as the electrochemical sensor for various researches due to the

simplicity to produce and still give the rapid responses [2]. Moreover, the main advantage of SPCE is able to use only once and then is discarded. This advantage can be used to solve the problems of surface fouling compared with those of conventional electrodes. However, the limitation of SPCE is small surface area of working electrode leading to the lack of sensitivity [3]. Therefore, electrode modification is necessary to solve this problem.

For electrode modification, metal-nanoparticles modified SPCE is focused to improve the electrochemical efficiency. Metal-nanoparticles are attractive catalyst in the electrochemical applications. Transition metals, especially precious metals, show very high catalytic abilities for catalyzing the redox process of some interested molecules, making the use of electroanalytical techniques for applications are extended [4]. Particularly, gold nanoparticles (AuNPs) have received significant attention in recent years. AuNPs are widely used in many fields due to their unique optical and physical properties, such as surface plasmon oscillations for labeling, imaging, and sensing [5]. For the electrochemical fields, AuNPs have been widely used for modification of electrode because of their benefits including catalysis, mass

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transport, and high effective surface area [1]. AuNPs have the ability to improve the detection signal, electron transfer, which make the limit of detection in electrochemical sensor is reduced. Moreover, the most importance is AuNPs showed strong specific interaction with the sulfur-containing compounds [6]. Therefore, AuNPs became an interesting nanomaterial used as modifier onto working electrode for electrochemical detection of sulfur-containing compounds.

Thiram (tetramethyl thiuram) and disulfiram (tetraethyl thiuram) are organosulfur compounds in the group of dithiocarbamates (DTCs) fungicides. DTCs have been used in agriculture as fungicides in foliage vegetable and fruit [7]. Besides these agricultural applications, DTCs are also used in industry such as vulcanization accelerator and antioxidant in rubber. The use of DTCs results in their release into the environment causing the contamination in food and water which leads to hazardous effect in the living organisms through diverse pathways [8]. Environmental problem resulting from uncontrollable use of fungicides in agriculture is one of the most important evidence. Therefore, it is necessary to continuously develop simple, selective, and sensitive methods for analysis of fungicides [9].

Various methods have been developed for analysis of DTCs. Spectrometry [10–12] and head space gas chromatography [13] have been used as the methods for the determination of DTCs after their decomposition to carbon disulfide (CS_2). From these methods, most of DTCs can degrade to CS_2 . Therefore, they are unable to distinguish among different DTCs. Moreover, gas chromatography [14,15], capillary electrophoresis [16–20], and high performance liquid chromatography (HPLC) were used for simultaneous determination of DTCs coupled with UV detection. Especially, HPLC is the simple technique used for easy separation of the disulfide substance. However, the drawback of the UV detection is low sensitivity. Therefore, HPLC coupled with electrochemical detection became an important choice for the determination of disulfides [21]. The main advantage of electrochemical detection compared to those of spectrometry is that the derivatization step is not needed, which makes the analysis time and cost reduced. In addition, the use of electrochemical detection after the separation by HPLC can provide more sensitive detection than UV [22].

Recently, ultra-high performance liquid chromatography coupled with electrochemical detection (UHPLC-ED) is a high potential alternative method for various analysis. UHPLC concerns to the development of short column packed with small particles for working at high pressures (> 400 bar). The use of UHPLC can enhance chromatographic performances in terms of efficiency, resolution, and analysis time [23]. In the detection part, AuNPs modified electrode was used as amperometric detection. Amperometry is an attractive potential technique because of its fast response, high sensitivity, relatively low cost of equipment, no need for complicated operation, and simplicity for direct sulfur assay [24].

With such benefits from the mentioned background, the objective of this work is to develop AuNPs modified SPCE in UHPLC-ED system for simultaneous determination of DTCs with high sensitivity, specificity, and rapid analysis. Thiram (tetramethyl thiuram) and disulfiram (tetraethyl thiuram) are chosen as representative compounds of DTCs because they are importantly applied to control a variety of pest [25]. Typically, when thiram and disulfiram are mixed together, the intermediate of *N,N*-diethyl-*N',N'*-dimethylthiuram disulfide (DEDMTDS) appears as the derivative of thiram and disulfiram. This compound is one of DTCs that affects human health and has the same effect of thiram and disulfiram. The presence of *N,N*-diethyl-*N',N'*-dimethylthiuram disulfide can also use to monitor thiram and disulfiram in samples. Therefore, the detection of *N,N*-diethyl-*N',N'*-dimethylthiuram disulfide is important. This derivative compound is also determined along with the measurement of thiram and disulfiram.

To the best of our knowledge, there is no publication report about the use of AuNPs modified SPCE as working electrode for ED

after the UHPLC separation to simultaneously determine thiram, DEDMTDS, and disulfiram. Moreover, this developed UHPLC-ED using AuNPs modified SPCE was applied for the first time to analyze thiram, DEDMTDS, and disulfiram in fruits and vegetables collected from local markets.

2. Materials and methods

2.1. Chemicals and reagents

All chemicals used in this work were of analytical grade, and all solutions were prepared using Milli-Q water from Millipore ($R \geq 18.2 \text{ M } \Omega \text{ cm}^{-1}$). Acetonitrile (HPLC-grade), chloroform, and sulfuric acid were obtained from Merck (Darmstadt, Germany). Potassium dihydrogen phosphate (KH_2PO_4) was acquired from BDH laboratory supplies (VWR International Ltd., England). Disodium hydrogen phosphate (Na_2HPO_4) and sodium hydroxide (NaOH) were purchased from Merck (Darmstadt, Germany). Standard thiram (tetramethyl thiuram) was obtained from Chem Service (West Chester, PA, USA). Standard disulfiram (tetraethyl thiuram) and gold (III) chloride solution were obtained from Sigma-Aldrich (St. Louis, MO, USA).

All of stock standard solutions ($1000 \mu\text{g mL}^{-1}$) were prepared by dissolving 10 mg of each analyte in acetonitrile. The solutions were then placed in an amber bottle and stored at 4°C . To prepare working standard solution, the standard solution was mixed and diluted in suitable proportions of acetonitrile:Milli-Q water (50:50; v/v), and kept for 5 min before measurement. All solutions and solvents were filtered by $0.22 \mu\text{m}$ nylon membranes prior to use in UHPLC separation.

2.2. Fabrication and modification of screen-printed carbon electrode

The working electrode was fabricated using screen printing and modified by electrodeposition techniques. The Ag/AgCl electrode and Pt wire was used as reference and auxiliary electrodes, respectively. To fabricate the in-house screen-printed carbon electrode (Fig. S1), the Ag/AgCl ink was first printed on the PVC substrate for using as a conductive pad. Then, the carbon ink was printed to create a working electrode. The each step of printing electrode was allowed to dry in an oven at 55°C for 1 h. The screen-printed carbon electrode was ready to modify in the next step.

For the electrodes modification, the 10 mM of gold (III) solution was used to modify onto electrode surface by electrodeposition technique. The three-electrode system was placed into cell containing 2 mL of solution of 10 mM of gold (III) solution in 0.5 M H_2SO_4 followed by deposition of gold onto the SPCE at a deposition potential of -0.6 V (vs. Ag/AgCl) for 50 s while the solution was stirred (by means of a mechanical stirrer bar). The gold nanoparticles (AuNPs) were obtained onto the electrode surface. After the modification, the AuNPs modified SPCE was carefully rinsed with distilled water and dried under N_2 gas prior to use.

2.3. Cyclic voltammetry

The electrochemical reaction and optimal parameters for electrodeposition step were studied by cyclic voltammetry (CV) using a CH instrument potentiostat 1232 A (CH Instrument, Inc., USA). The working electrodes used in this work were bare SPCE and AuNPs modified SPCE. The reference and auxiliary electrode were silver/silver chloride electrode and Pt wire, respectively. All experiments were done at room temperature.

2.4. UHPLC experiment and apparatus

The UHPLC system was performed in reversed-phase mode using an LC-20ADXR solvent deliver unit (Shimadzu Corporation,

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