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Electrochemical Detection of 2-Methylisoborneol (MIB) Using a Gold Electrode

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Odorant substances have been detected in the drinking water of several countries and regions. Although the specific harm of these substances to the human body is not yet clear, they can lead to the decline of drinking-water sensory indicators. In addition, odorants also affect the development of the water-dependent beverage industry and aquaculture industry. Dimethyl isoborneol (2-MIB) is the most common odorant substance that causes soil mildew in drinking water. In this work, for the first time, we first report the electrochemical determination of 2-MIB based on an Au electrode. The electrochemical oxidation of 2-MIB can be achieved due to the excellent conductivity and electrocatalytic property of the Au electrode. The proposed electrochemical sensing method is simple, quick and reliable for 2-MIB determination.

Keywords: 2-MIB; Fishy odor; Gold electrode; Electrochemical sensor; analytical determination

1. INTRODUCTION

With the increase of pollutants in water and the intensification of eutrophication caused by human activities, more and more people are paying attention to the fishy odor in drinking water sources. This odor in drinking water will directly affect the taste of water and reduce the sensory index, while some compounds that produce odor have potential hazards to human health. Dimethyl isoborneol (2-MIB) is the most common odorous substance causing a fishy odor in drinking water. The olfactory threshold of 2-MIB is approximately 5-10 ng/L. 2-MIB, a saturated cyclic tertiary alcohol, is mainly a secondary metabolite of cyanobacteria and actinomycetes and possesses a certain volatility. With the rapid development of the economy and improvementsto people's living standards, the public is increasingly paying attention to the problem of fishy odor in drinking water. The detection and control of 2-MIB in drinking water is an important precondition to ensure the safety of drinking water.

Odor generation in water bodies is very complex, and to date, there is no consensus on the mechanism. It is generally believed that 2-MIB is mainly produced by some phytoplankton and actinomycetes. In addition, other organisms, such as certain fungi, protozoa, a select few plants and polypods, can produce odorous substances. In 1891, Berthefot and Andre discovered that the odor produced by actinomycete fermentation was similar to that of soil. In 1964, Gerber studied the fermentation broth of actinomycetes and found a compound, which was identified as a substance that produced an odor in soil [1]. Soon afterwards, Gerber isolated another common earthy substance, 2-MIB [2]. Therefore, the main source of soil odor compounds was initially considered to be actinomycetes [3,4]. Subsequently, attention turned to algae, mainly cyanobacteria, such as *Oscillatoria* and *Anabaena*[5-7]. In addition, some diatoms are sources of odorants. 2-MIB secretion could also be produced by protozoan amoeba [3], limited fungi [8,9], a very small number of plants [10-12], and polypod arthropods [13].

The detection methods of 2-MIB include sensory analysis and instrumental analysis. Sensory analysis includes olfactory threshold detection (TON) and the olfactory analytic hierarchy process (FPA). TON was the first method to describe odor, and the lowest olfactory concentration of odor is known as the olfactory threshold [14]. The principle behind FPA is similar to that of TON.However, TON initiallyrequiresdilution of thewater sample, which may cause unnecessary errors, whereasFPA does not need sample dilution. It divides the characteristics and intensity of an odor into different levels and explains the levels in words [15-20]. Through sensory analysis,the physical characteristics of odor-producing substances in water can be understood at a low cost and with high efficiency. However, this method relies on subjective judgment and is affected by environmental factors. Consequently, the experimental deviation is large. The method cannot be qualitative, quantitative and reliable. Therefore, its effective implementation in water-quality management and experimental operation is difficult. Instrumental analysis is based on the physical and chemical properties of 2-MIB and mainly includes liquid-liquid microextraction with flame ion detection [21], solid phase extraction with gas chromatography and high-performance mass spectrometry [22], and the closed-loop stripping method [23]. However, these analytical techniques require expensive instruments and complicated operation processes, which cannot be used for field analytical purposes. Therefore, the development of a simple, quick and reliable analytical method for 2-MIB detection is necessary for field applications.

The electrochemical sensor is a special sensor in modern chemical analysis and detection [24-26]. It is a kind of instrument that uses an analyte to react electrochemically on the surface of an electrode and then converts the sensing information into recognizable information through a specific transducer. The electrical signal is proportional to the change in concentration of the target substance, consequently achieving a qualitative or quantitative determination[24,27-30]. Based on our knowledge, there is no report with regards to the electrochemical determination of 2-MIB so far. In this work, for the first time, we report the simple electrochemical determination of 2-MIB based on a gold electrode, and its analytical performance has been investigated. We believe this work will serve as guidance for future electrochemical sensor development in 2-MIB detection.

2. EXPERIMENTAL

2-Methylisobornel(MIB) was purchased from Dr. Ehrenstorfer GmbH (Germany). Inorganic ions and potassium ferricyanide were purchased from Aladdin Co., Ltd.and was used without further purification.

The electrochemical measurement was conducted using a CHI 760E electrochemical workstation coupled with a three-electrode system. A gold electrode or glassy carbon electrode (GCE) was applied as the working electrode. A Pt wire electrode and an Ag/AgCl (3 M) electrode were applied as the counter electrode and reference electrode, respectively. The GCE and Au electrode were polished with α-Al_2O_3 until the surface was mirror-like, then it was sequentially washed with distilled water and anhydrous alcohol for 5 min, and dried at room temperature. Cyclic voltammetry was used for analyzing the electrochemical reaction of 2-MIB at the glassy carbon electrode and gold electrode. The scan range for 2-MIB was between 0.2 and 1.6 V. The scan rate was set as 100 mV/s. After each test, the electrodes were placed in a 0.1 mol/L PBS (pH=6.0) solution and scanned several times. The purpose of this step was to remove 2-MIB on the surface of the electrodes and to effectively restore the activity of the measured electrodes. Electrochemical impedance spectroscopy (EIS) was performed using the same three-electrode system in a 10 mmol/L $K_3[Fe(CN)_6]$ + 0.1 M NaCl solution with addition of different concentrations of 2-MIB. All experiments were carried out at room temperature (25 °C).

3. RESULT AND DISCUSSION

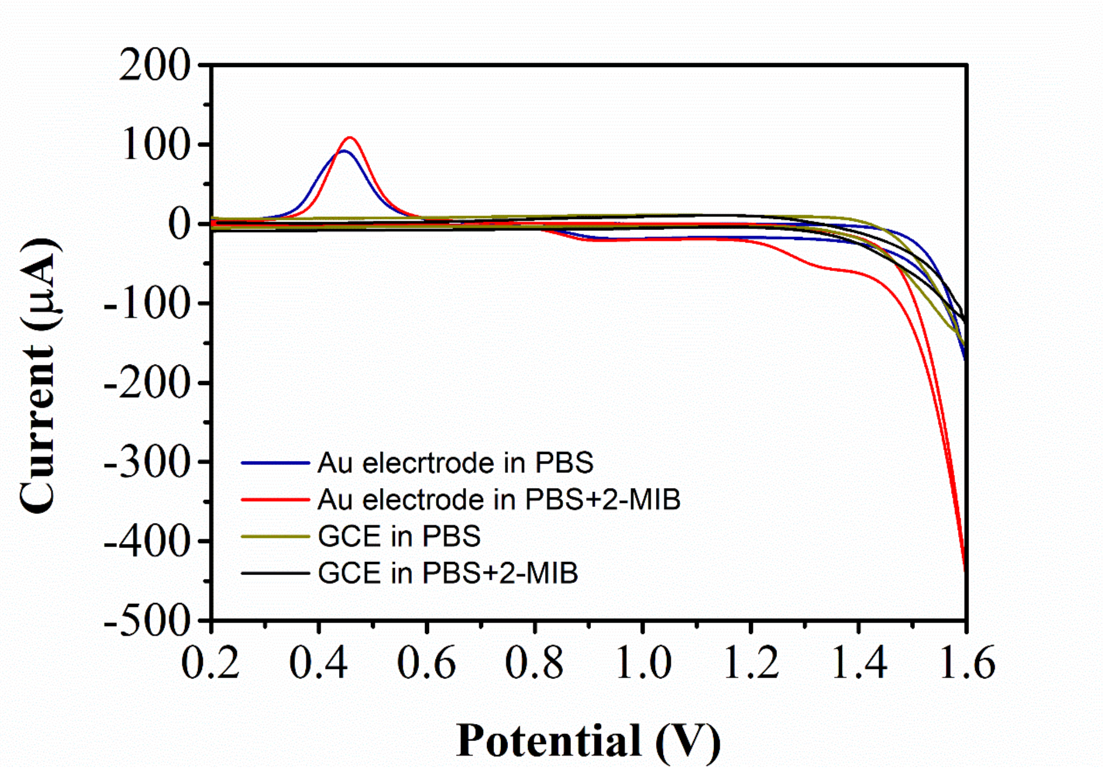

Figure 1. CV curves and of GCE and Au electrode in 0.1 mmol/L PBS in the absence and presence of 100 ng/mL 2-MIB (scan rate = 50 mV/s).

Cyclic voltammetry was used to characterize the electrochemical behavior of 2-MIB at the GCE and Au electrode. As shown in Figure 1, GCE shows no peak in 0.1 M pH 7.0 PBS. In contrast, the Au electrode shows the redox peaks of gold at 0.93 V and 0.46 V. When a certain amount of 2-MIB was added to the buffer solution, GCE shows no peak, suggesting 2-MIB cannot be oxidized or reduced at the electrode surface. In contrast, an oxidation peak appeared at a potential of 1.3 V for the Au electrode, suggesting 2-MIB can be oxidized at the Au electrode surface, probably due to the excellent conductivity and electrocatalytic activity of Au. The Au-based electrochemical sensor has widely been fabricated and applied for the detection of certain analytes [31-34].

Potassium ferricyanide is often used to evaluate the performance of electrodes because of its high electrochemical reversibility. It is generally believed that the potential difference of potassium ferricyanide in cyclic voltammetry is less than 100 mV, and the conductivity of the electrodes themselves will not greatly hinder the transmission of electrons [35-37]. Figure 2A shows the CV curves of the GCE and Au electrode in a 10 mmol/L $K_3[Fe(CN)_6]$ and 1 mol/L NaCl solution at a scanning speed of 50 mV/s. The potential differencesin the redox peaksare 91 mV and 82 mV for the GCE and Au electrode, respectively. This result suggests the Au electrode has a superior electrochemical property compared with that of the GCE. In the meantime, both electrodes exhibit good electrochemical responsiveness and stability. Electrochemical impedance spectroscopy (EIS) is an important method to determine the change in surface impedance of electrodes [31,38,39]. The spectrum mainly consists of two parts: a semicircle and straight line. The semicircle sectioncorresponds to the electron transfer process in the high-frequency region, and the diameter of the semicircle is equal to the value of the electron transfer resistance. In Figure 2B,the diameter of the semicircle in the Au electrode impedance diagram is clearly smaller than that of the bare GCE, indicating that the resistance of the Au electrode is lower than that of the GCE. The resultalso proves that the Au electrode possesses a good conductivity and can provide more electron transfer channels, therefore, the Au electrode exhibits a good electrochemical performance.

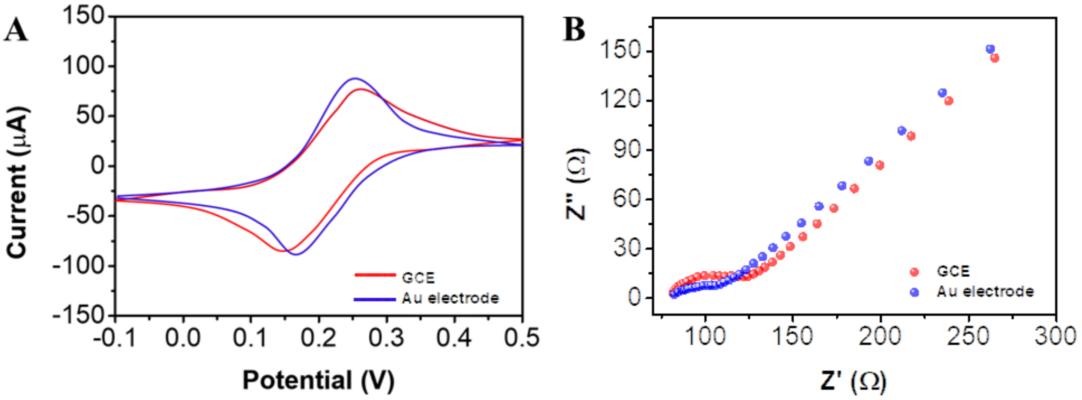

Figure 2. (A) CV curves and (B) EIS spectra of the GCE and Au electrode in a 10 mmol/L $K_3[Fe(CN)_6]$ and 0.1 mol/L NaCl solution (scan rate = 50 mV/s).

As shown in Figure 3A, the electrochemical response of the Au electrode to 2-MIB was further studied by cyclic voltammetry. The parameters of cyclic voltammetry include starting potential: 0.2 V andterminating potential: 1.6 V. A certain amount of 2-MIB solution was successively added to the electrolyte. After each sample addition, the analyte was detected by the CV method after 30s. The peak current increases with the amount of 2-MIB solution. As shown in Figure 3B, when the concentration of 2-MIB ranges from 5 ng/mL to 350 ng/mL, the peak current presents a good linear relationship with the concentration of 2-MIB. As shown in Table 1, the performance of the 2-MIB determination using the electrochemical method is compared with other reported methods.

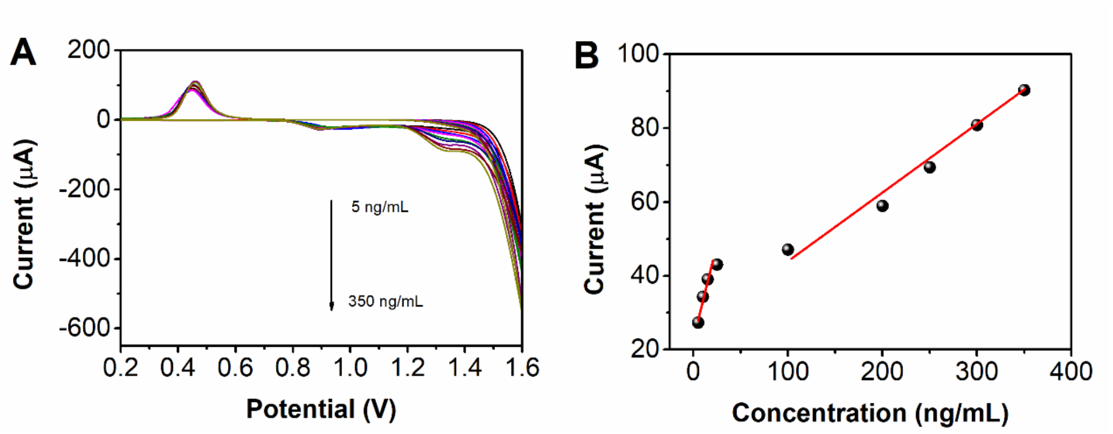

Figure 3. (A) Electrochemical responses of the Au electrode to different concentrations of 2-MIB,as measured by CV. (B) The linear relationship between peak current and 2-MIB concentration.

EIS is an electrochemical measurement method with a small-amplitude sinusoidal wave potential (or current) as the disturbance signal. Compared with other conventional electrochemical methods, EIS requires only small-amplitude electrical signals to disturb the system, avoiding damage to the structure of modified membranes. At the same time, EIS is used to study an electrode system based on impedance spectroscopy of a wide frequency range [40-44]. Therefore, EIS can obtain additional information about the kinetics and interface structure of electrodes andrepresents a new sensitive research method in electrochemical testing technology. To further explore the 2-MIB detection mechanism of the gold electrode, different concentrations of 2-MIB were added to the potassium ferricyanide solution, and the resistance and capacitance of the double layer of the electrode and solution were measured by EIS. Figure 4A shows the AC impedance Nyquist plots of the Au electrode in 10 mmol/L potassium ferricyanide containing different concentrations of 2-MIB. The electron transfer resistance of potassium ferricyanide on the surface of the electrode increases with the 2-MIB concentration. This result indicates that the adsorption of 2-MIB molecules on the surface of the electrode hinders the adsorption and redox reaction of iron cyanide ions on the electrode and increases the electron transfer resistance of iron cyanide ion on the electrode.

Table 1. Analytical performance of various methods for 2-MIB determination.

Methods	Determination performance	Reference
Solid phase micro extraction procedures	μg/L range	[45]
Headspace solid-phase microextraction + GC	LR: 0–500 pg/mL; LOD: 0.9 pg/mL	[46]

GC-MS	LOD: 0.33 ng/L	[47]
Headspace solid-phase microextraction + GC-MS	LR: 5–1000 ng/L	[48]
GC-MS	LR: 0.3–100 ng/L	[49]
Electrochemical sensor (Gold electrode)	LR: 5 ng/mL to 350 ng/mL	This work.

To verify the accuracy of the above detection mechanism, the variation in the Zeta potential of gold nanoparticles with 2-MIB concentration in phosphate buffer solution at pH=7 was investigated. The results are shown in Figure 4B. In the phosphate buffer system at pH=7, the Zeta potential is -7.4 mV. When 2-MIB was added to the solution, the Zeta potential of the gold nanoparticles moves further to the negative direction and the absolute value increases. This observation indicates that the surface negative charge of the gold nanoparticles increases, which proves that 2-MIB adsorbed on the gold nanoparticles. With increasing 2-MIB concentration, the absolute Zeta potential of the gold nanoparticles increments almost linearly, which is the same behavioras the current response of the Au electrode during the 2-MIB detection. This result shows that the detection mechanism of the Au electrode is mainly the adsorption of 2-MIB.

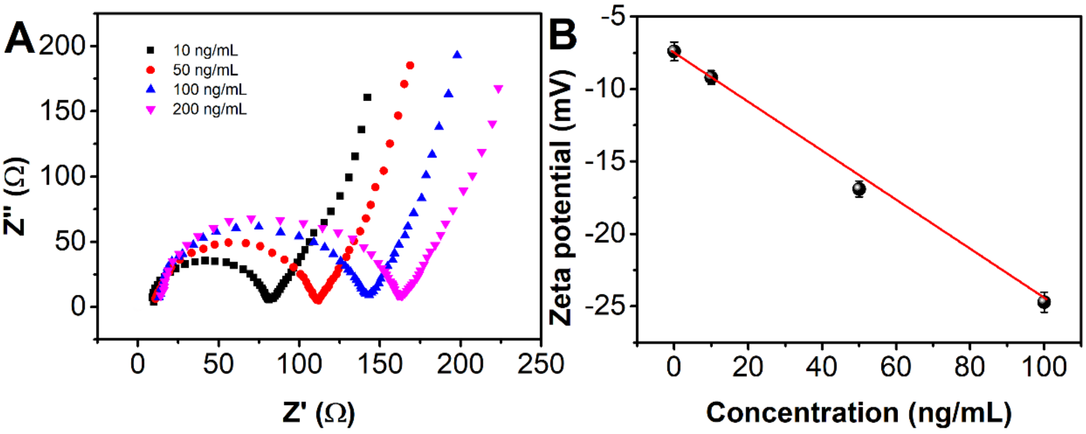

Figure 4. (A) EIS of different concentrations of 2-MIB in a 10 mmol/L potassium ferricyanide solution. (B) The change in the Zeta potential of gold nanoparticles with the 2-MIB concentration.

To test the reproducibility of the electrodes, the Au electrodes were placed in a PBS solution containing ethanol after each measurement. The oxidation peaks were scanned by the CV method until their disappearance. Then, the electrodes were washed with water and dried. The obtained RSD is 3.15% after six consecutive measurements with the same electrode. Under the same experimental conditions, three different electrodes were used for six consecutive measurements and yielded an RSD of 4.21%. Therefore, the Au electrode exhibits good reproducibility for 2-MIB detection.

The anti-interference test of this experimental method was carried out. Common metal ions such as Na^+, Cu^{2+}, Zn^{2+}, K^+, Fe^{3+}, $A1^{3+}$, Mg^{2+} and Ca^{2+}at 20-fold concentration do not interfere with the detection of 100 ng/mL 2-MIB. When the same amount of odorant, ascorbic acid and hydrogen peroxide were added, the experimental results reveal that these substances do not interfere with the determination as well. Therefore, the Au electrode can be effectively used for 2-MIB determination.

4. CONCLUSION

In conclusion, we report the first electrochemical determination of 2-MIB using a simple Au electrode. The electrocatalytic oxidation of 2-MIB can be observed at the Au electrode using a CV scan. The proposed analytical method can be used for the determination of 2-MIB between 5 to 350 ng/mL.

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