ELECTROCHEMICAL DETERMINATION OF ETHYL MALTOL ON A GLASSY CARBON ELECTRODE MODIFIED WITH GRAPHENE

MEIFENG CHEN XINYING MA*

Department of Chemistry and Chemical Engineering, Heze University, Heze 274015, PR China.

Affiliation: Department of Chemistry and Chemical Engineering, Heze University, Heze 274015, PR China.

(Received: December 18, 2012 - Accepted: February 4, 2013)

ABSTRACT

Ethyl maltol can be used to enhance the scent of foods. Its monitoring in foods is very important due to the potential harmfulness to human beings if large amounts of this flavor enhancer are ingested. A novel electrochemical method for the determination of ethyl maltol in food samples based on the electrochemical catalytic activity of graphene modified glassy carbon electrode is reported in this paper. The sensor exhibited excellent oxidation activity towards ethyl maltol. Using 1 mol L⁻¹ NH₃·H₂O–NH₄Cl buffer solution (pH 8.0) as supporting electrolyte, ethyl maltol yielded a sensitive oxidation peak on the modified electrode. The influence of some experimental variables for EMA determination, such as supporting electrolyte, scanning rate, accumulation time and concentration of ethyl maltol, were studied. The oxidation peak current showed a linear relationship with the concentrations of ethyl maltol over the range between 6.0×10^{-7} and 1.0×10^{-4} mol L⁻¹, with the detection limit of 1.0×10^{-7} mol L⁻¹. The prepared electrode was used for EMA determination in beer samples with good results.

Keywords: Ethyl maltol; Graphene; Modified electrode; Electrochemical detection

1. INTRODUCTION

Ethyl maltol, chemically known as 2-Ethyl-3-hydroxy-4-pyranone (EMA) is often used as flavor enhancer in many foods such as coffee, soybeans, cereals, breads, beverages, and chocolate milk. The enhancing effect of ethyl maltol is approximately six times higher than that of maltol^{1,2}. Although it can be used to enhance the flavor of foods, concerns on this synthetic food additive regarding its biological safety have been reported. The maximum permitted usage levels of EMA for human beings are 2 mg kg⁻¹ body-weight per day³. If large amounts of this flavor enhancer are ingested, headaches, nausea and vomiting could be caused and the functions of liver and kidney could be affected. The maximum permitted level in food products is 200 mg kg⁻¹⁴. Therefore, it is of great importance to develop a fast and efficient method for its determination in food products. Various methods such as high performance liquid chromatography (HPLC)^{5,6}, photometric determination^{7,8}, gas chromatography–mass spectrometry methods (GC–MS)⁹ have been reported for the determination of EMA. However, the above noted techniques usually require expensive instruments and/or materials, large amount of high purity solvents, and are time-consuming. Chemically modified electrodes have been used widely in analytical chemistry^{10,11}. Electrochemical methods provide a simple, convenient, and fast means for detecting biological and environmental molecules. Graphene nanomaterials are an interesting area for researchers because of its exceptional mechanical properties and electrical conductivity¹². It has been used to modify electrodes for electrochemical studies^{13–18}. Electrochemical methods can be used to detect EMA because of the electro-active group (-OH) in its molecule. Electrochemical determination of EMA using an electrode such as a glassy carbon electrode¹⁹ has been reported. But electrochemical determination of EMA using graphene modified electrode (GME) has not been reported so far, to the best of our knowledge.

In this work, a GME was prepared using graphene sheets. A new method for the detection of EMA was developed. The electrochemical behaviours of EMA are studied. The results show that the oxidative peaks increased linearly with EMA concentration in the range of 6.0×10^{-7} and 1.0×10^{-4} mol L⁻¹, with a detection limit of 1.0×10^{-7} mol L⁻¹. The method was successfully applied to detect EMA in beers with good results.

2. EXPERIMENTAL

2.1 Chemicals and Apparatus

EMA was purchased from Anhui Haibei Import & Export Co., Ltd (China) and a 2×10^{-3} mol L⁻¹ EMA stock solution was prepared by dissolving it in double distilled water. All other reagents were of analytical grade and were used as received. All solutions were prepared in double distilled water.

All electrochemical measurements were performed on a Electrochemical Workstation (Model CHI660C, Chen-hua, Shanghai, China) with a three-electrode consists of a working electrode (a bare or graphene modified glassy carbon electrode), a counter electrode (a platinum wire electrode), and a

reference electrode (a Ag/AgCl electrode). The pH values was measured by pH Meter (Model pHs-3B, Shanghai, China), and Ultrasonic Cleaner was used (Model KQ-100Kunshan, China). All experiments were performed at room temperature.

2.2 Synthesis of Graphene and Characterization of the Electrode Surface

Graphene was prepared according to a slightly modified literature procedure^{20,22}. The morphology and chemical composition of the electrode surface was investigated by AFM and SEM. We have reported the synthesis procedure of graphene and characterization of the electrode surface in our previous work²³.

2.3 Preparation of the GME

A glassy carbon electrode (GCE, $\varnothing = 3$ mm) was polished before each experiment with gold sand paper and Al₂O₃ slurry, respectively, and was then rinsed with distilled water between each polishing step. Next, it was sonicated successively with 50% nitric acid, ethanol and doubly distilled water, and dried in air. The GME was prepared by casting 8 μ L of graphene suspension (0.3 mg mL⁻¹) on the electrode surface and drying under an infrared lamp.

2.4 Analytical Procedure

Electrochemical measurements were performed with a CHI 660C Workstation using 1 mol L⁻¹ NH₃·H₂O–NH₄Cl buffer solution (pH 8.0) as the supporting electrolyte. After stirring 40s, cyclic voltammograms (CVs) were obtained by scanning in the potential range from 0.2V to 1.0 V. The modified electrode was placed in a 1 mol L⁻¹ NH₃·H₂O–NH₄Cl buffer solution (pH 8.0) and scanned until no peak for reuse.

3. RESULTS AND DISCUSSION

3.1 Electrochemical response of EMA

The electrochemical response of EMA was studied on a bare GCE and a GME by CV method. The results are shown in Fig.1. No current response of EMA was observed on the bare GCE, while the current response of EMA remarkably increased at the GME. At the same time, CVs of the GME was examined in a blank 1 mol L⁻¹ NH₃·H₂O–NH₄Cl buffer solution (pH 8.0). It can be seen that no observable redox peaks appear. From the CVs of EMA at the modified electrode, it is now known that $E_{pa} = 0.614$ V and $i_{pa} = 2.59 \times 10^{-2}$ A, which indicates that the reaction process of EMA on the GME is an irreversible redox process in this potential window.

3.2 Effect of supporting electrolyte

The influence of supporting electrolyte on the responses of EMA was studied. A variety of supporting electrolyte, such as an NH₃·H₂O–NH₄Cl solution (pH8.0~10.0), phosphate buffer (pH2.2~8.0), and BR buffer (pH2.2~12.0), were investigated, respectively. The peak current reaches its maximum peak value in the NH₃·H₂O–NH₄Cl solution. Thus, 1 mol L⁻¹ NH₃·H₂O–NH₄Cl buffer solution was chosen as the supporting electrolyte. Fig.2 shows the influence of solution pH on oxidation peak current of EMA. Using a NH₃·H₂O–NH₄Cl

buffer solution of various pH (8.0 to 10.0), the oxidation peak current of EMA reached the maximum at pH 8.0. Furthermore, the potentials of the irreversible peaks shift negatively as the pH increases, indicating that this electrode process involves proton participation. The relationship between the peak potential (E_{pa}) and the solution pH can be described by the following equation: $E_{pa} = 1.07 - 0.050 \text{ pH}$, $R = 0.9976$, which indicates that the number of electrons and protons involves in the reaction is equal.

Fig.1: Curves 1 and 2 are CVs of EMA on the bare GCE and the GME when placed in $1 \text{ mol L}^{-1} \text{ NH}_3 \cdot \text{H}_2\text{O} - \text{NH}_4\text{Cl}$ buffer solution (pH 8.0) in the presence of $2.0 \times 10^{-5} \text{ mol L}^{-1}$ EMA. Curve 3 is CVs of the GME when placed in blank $1 \text{ mol L}^{-1} \text{ NH}_3 \cdot \text{H}_2\text{O} - \text{NH}_4\text{Cl}$ buffer solution (pH 8.0). Scan rate: 120 mV s^{-1} .

Fig.2: CVs of GME in $1 \text{ mol L}^{-1} \text{ NH}_3 \cdot \text{H}_2\text{O} - \text{NH}_4\text{Cl}$ buffer solution (pH 8.0) with $2.0 \times 10^{-5} \text{ mol L}^{-1}$ EMA at different pH: 1, 8.0, 2, 9.0, 3, 10.0; Scan rate 120 mV s^{-1} .

3.3 Effect of Scan Rate

The effect of the scan rate on irreversible oxidative of EMA was investigated at a concentration of $2.0 \times 10^{-5} \text{ mol L}^{-1}$ in $1 \text{ mol L}^{-1} \text{ NH}_3 \cdot \text{H}_2\text{O} - \text{NH}_4\text{Cl}$ buffer solution (pH 8.0) (Fig.3). The oxidation peak currents increased linearly with the scan rates changing from 40 to 600 mV s^{-1} . The linear regression equations expressed as $Z'_{pa}(\text{A}) = -5.49 \times 10^{-6} + 2.33 \times 10^{-8} v (\text{mV s}^{-1})$, $R = 0.9924$, indicating that the electrode reaction of EMA is an adsorption process. The potential becomes worse after 120 mV s^{-1} , therefore, 120 mV s^{-1} was chosen in this study.

Fig.3: (A) CVs of $2 \times 10^{-5} \text{ mol L}^{-1}$ EMA in $1 \text{ mol L}^{-1} \text{ NH}_3 \cdot \text{H}_2\text{O} - \text{NH}_4\text{Cl}$ buffer solution (pH 8.0) at the GME at different scan rates (from inner to outer): 40, 80, 120, 160, 200, 240, 280, 320, 360, 400, 440, 480, 520, 560, 600 mV s^{-1} , respectively. Inset is the plot of oxidation EMA peak currents versus scan rates.

3.4 Effect of Accumulation Time

For the effect of accumulation time on the oxidation peak current, the accumulation time was varied between 20 s and 100 s for $2.0 \times 10^{-5} \text{ mol L}^{-1}$ EMA. CVs of EMA were recorded every 20 min (Fig.4). The oxidation peak current increased greatly with time and reached a maximum at 40 s. Therefore, 40 s was used as the accumulation time.

Fig.4: CVs of EMA on the GME between 20 s and 100 s for $2.0 \times 10^{-5} \text{ mol L}^{-1}$ EMA in $1 \text{ mol L}^{-1} \text{ NH}_3 \cdot \text{H}_2\text{O} - \text{NH}_4\text{Cl}$ buffer solution (pH 8.0). Accumulation time: 1, 20s, 2, 40s, 3, 60s, 4, 80s, 5, 100s.

3.5 Calibration curve and Detection Limit

Fig. 5: DPVs of different concentrations of EMA at GME in 1mol L⁻¹ NH₃·H₂O-NH₄Cl buffer solution (pH 8.0). Each of the letters from 1 to 11 correspond to concentrations of 0.60, 0.80, 1.0, 2.0, 4.0, 6.0, 8.0, 25.0, 50.0, 80.0, 100, respectively (in μmol L⁻¹). Inset is the plot of the oxidation peak currents versus concentrations of EMA.

The linearity statistical test between the oxidation peak current and the concentration of EMA was carried out by differential pulse (DPV). Fig. 5 shows the Differential pulse voltammograms and linear relationship for different concentrations of EMA in the range of 6.0×10^{-7} - 1.0×10^{-4} mol L⁻¹. The linear regression equation is $i_{pa} \text{ (A)} = 0.032c + 3.51 \times 10^{-6}$, $R = 0.9958$. The limit of detection was estimated by decreasing the concentration levels of EMA^{10,24}. The limit of detection was evaluated to be 1.0×10^{-7} mol L⁻¹.

3.6 Interference Studies

For the practical analytical application of the proposed method, the influence of various species likely to be present in samples was evaluated in detail. EMA easily forms a complex compound with an iron ion²⁵. Ethylenediaminetetraacetic acid, typically shortened to EDTA, is a chemical compound with the ability to form multiple bonds with metal ions, making it an important chemical to analytical scientists and industry alike. Therefore, EDTA was added in the experiments to shield iron ions. Experiments were performed in a 5.0×10^{-5} mol L⁻¹ EMA solution spiked with various excess amounts of these species under the same experimental conditions. The tolerance limit for a foreign species was defined as the largest amount that caused a relative error of $\leq \pm 5\%$ for the determination of EMA. It was found that Na⁺ (500times), Mg²⁺ (500 times), CO₃²⁻ (500 times), SO₄²⁻ (500 times), citrate ion (100 times), ascorbic acid (10 times) and tartaric acid (10 times) caused negligible interference in the quantitative analysis of EMA under the selected experiment conditions. The results suggested that the proposed method had good selectivity for the determination of EMA.

3.7 Analysis of Beer Samples

For testing the accuracy of the proposed method, the method was applied for analysis of real samples. Three kinds of commercially available beers were employed, in which EDTA was added. The EMA content was tested by DPV on the GME under optimized conditions. After determination, some standard EMA solution was added into the sample. As shown in Table 1, the recovery evaluated was between 95.5% and 97.0%. This result confirmed that the electrochemical method for the detection of EMA was accurate and reliable.

Table 1 Recovery of determination of EMA in beer samples (n=6).

No.	Content in samples	EMA added (mvL)	Average found (L ⁻¹)	Recovery (%)	R.S.D (%)
1	1.45×10^{-4}	2.0×10^{-4}	3.36×10^{-4}	95.5	2.74
2	1.86×10^{-5}	2.0×10^{-5}	3.78×10^{-5}	96.0	3.18
3	No Detected	2.0×10^{-6}	1.94×10^{-6}	97.0	2.44

3.8 Reproducibility and Stability

Six parallel measurements for 2.0×10^{-5} mol L⁻¹ EMA were conducted. It was found that the modified electrode had good reproducibility when the related RSD was within the range of 1.51% to 3.18%. When the electrode was stored for 7 days at room temperature when not in use, 95.2% of its initial responses was kept after storage, indicating that GME had good stability.

4 CONCLUSIONS

In this paper, a new, rapid and simple method was developed for the detection of EMA, with high sensitivity and selectivity as well as a wide linear range. The electrochemical behavior of EMA was greatly promoted with an increased oxidation peak current, which provided a sensitive method for EMA. Due to the specific characteristics of graphene, the method was successfully applied to beer samples' detection with the recovery in the range from 95.5 % to 97.0 %. The modified electrode exhibited good stability and reproducibility.

ACKNOWLEDGEMENTS

This work was supported by A Project of Shandong Province Higher Educational Science and Technology Program (J12LD53).

REFERENCES

- 1.- H. H. Rennhard, *J. Agr. Food Chem.* **19**, 152, (1971)
- 2.- D. T. LeBlanc, H. A. Akers, *Food Technol.* **43**, 78, (1989)
- 3.- E. J. Gralla, R. B. Stebbins, G. L. Coleman, C. S. Delahunt, *Toxicol. Appl. Pharm.* **15**, 604, (1969)
- 4.- J. Zhou, K. Zhang, Y.M. Li, K.J. Li, B.X. Ye, *Anal. Methods* **4**, 3206, (2012)
- 5.- C. H. Risner, M. J. Kiser, *J. Sci. Food Agr.* **88**, 1423, (2008)
- 6.- H. Wang, Y. Q. Liu, H. M. Yang, Y. L. Tian, L. N. Kou, *Food Sci. Technol. Int.* **31**, 235, (2006)
- 7.- Y. N. Ni, G. W. Zhang, S. Kokot, *Food Chem.* **89**, 465, (2005)
- 8.- Y. N. Ni, Y. Wang, S. Kokot, *Food Chem.* **109**, 431, (2008)
- 9.- M. Adahchour, R. J. J. Vreuls, A. van der Heijden, U. A. Th. Brinkman, *J. Chromatogr. A*, **844**, 295, (1999)
- 10.- H.G. Lin, G. Li, K. B. Wu, *Food Chem.* **107**, 531, (2008)
- 11.- T. R. Zhan, L. L. Cao, W. Sun, W. G. Hou, *Anal. Methods*, **3**, 2651, (2011)
- 12.- W. Yang, K. R. Ratinac, S. P. Ring, P. Thordarson, J.J. Gooding, F. Braet, *Angew. Chem. Int. Ed. Engl.* **49**, 2114, (2010)
- 13.- M. Zhou, Y. Zhai, S. Dong, *Anal. Chem.* **81**, 5603, (2009)
- 14.- Y. Li, X. Li, C. K. Dong, J. Y. Qi, X. J. Han, *Carbon*, **48**, 3427, (2010)
- 15.- Y. R. Kim, S. Bong, Y. J. Kang, Y. Yang, R. K. Mahajan, J. S. Kim, H. Kim, *Biosens. Bioelectron.*, **25**, 2366, (2010)
- 16.- C. X. Guo, Y. Lei, C. M. Li, *Electroanal.* **23**, 885, (2011)
- 17.- X.H. Kang, J. Wang, H. Wu, J. Liu, I. A. Aksay, Y. H. Lin, *Talanta*, **81**, 754, (2010)
- 18.- M. Pumera, *Chem. Soc. Rev.* **39**, 4146, (2010)
- 19.- Y. Zhang, Y. N. Ni, *Journal of Nanchang University (Natural Science)*, **30**, 478, (2006)
- 20.- W. S. Hummers, Jr.; R.E. Offeman, *J. Am. Chem. Soc.* **80**, 1339 (1958)
- 21.- L. Fu, H. B. Liu, Y. H. Zou, B. Li, *Carbon*, **4**, 10, (2005)
- 22.- Y. C. Si, E. T. Samulski, *Nano Lett.*, **8**, 1679, (2008)
- 23.- M. F. Chen, X. Y. Ma, X. Li, *J. Solid State Chem.* **16**, 3261, (2012)
- 24.- T. Gan, K. Li, K. B. Wu, *Sensor. Actuat. B-Chem.* **132**, 134, (2008)
- 25.- A. Jafarian, L. Saghaei, S. Rajabzadeh, *Iran. J. Pharm. Sci.* **3**, 101, (2007)