Asian Journal of Chemistry; Vol. 24, No. 8 (2012), 3533-3536

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Study on Electrochemical Fingerprints of Traditional Chinese Medicine Cortex Moutan from Different Origins

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(*Received*: 28 July 2011; *Accepted*: 14 March 2012) AJC-11184

The electrochemical fingerprints of traditional Chinese medicine Cortex Moutan from different origins are studied by Belousov-Zhabotinskii (B-Z) oscillation system of H_2SO_4-$HOOCCH_2COOH$-$Ce_2(SO_4)_3$-$KBrO_3$. Effects of various variables for the chemical oscillation system were studied. Finally, 12 mL (3 mol/L) sulfuric acid, 6 mL (0.4 mol/L) malonate, 3 mL (0.005 mol/L) cerium ammonium sulfate and 3 mL (0.2 mol/L) sodium bromate, 300 K temperature and 0.300 g of Cortex Moutan powder were chosen as optimal experimental condition. The results indicated that the electrochemical fingerprints of Cortex Moutan from different origins (Tongling, Phenix Mountain, Bozhou, Qingyang) showed significantly different characteristics, such as the maximum potential, induction time and oscillation lifetime, *etc*. and the electrochemical fingerprints of Cortex Moutan from the same origins showed the same characteristic parameters, so the electrochemical fingerprints could be used to identify the origins of Cortex Moutan. The method is simple, fast and sensitive and does not need sample preparation. Futhermore the electrochemical fingerprint is objective and has good repeatability.

Key Words: Cotex moutan, Electrochemical fingerprint, B-Z oscillation, Different orings.

INTRODUCTION

Cortex Moutan is a traditional Chinese medicine from the root bark of *Paeonia suffruticos* Andr. It can be used for the treatment of antiinflammatory, sedative, lower blood pressure, antithrombosis, antiatherosclerosis and antiarrhythmia[1]. As a result, a fast and convenient determination method is required in pharmaceutical analysis. Currently identification of Cortex Moutan has been mainly performed by the high-performance liquid chromatography[2-5] approach. High-performance liquid chromatography has high sensitivity and good selectivity, but it requires the complex sample pre-treatment.

Compared to the HPLC method, using oscillation system for identification of traditional Chinese medicine has gained interests from several analysts work[6-9] because of its simplicity, high speed and good sensitivity[10-14].

This paper presents a study we have conducted to identify Cortex moutan using oscillation system. Present study shows that addition of some amount of Cortex Moutan powder in oscillation system causes a change in the E-t curve. Such response suggests that some components in Cortex Moutan are reacting to some components in this system. The E-t curve is then correlated with different origin areas to identify the origin areas of Cortex moutan, called electrochemical fingerprint. The study shows that this method is very fast and convenient in identifying traditional Chinese medicine. In addition, it has advantages of good reproducibility, sensitivity and precision.

EXPERIMENTAL

All chemicals used in the study are of analytical reagent grade and from Sinopharm Chemical Co., Ltd. (Shanghai, China). Solutions of 0.2 M $KBrO_3$, 0.4 M $HOOC-CH_2-COOH$, 3 M H_2SO_4, 0.005 M $Ce(NH_4)_4(SO_4)_4$ were made immediately before the experiment. Double distilled water was used in the entire experiment.

Cortex Moutan used in the study are from Phoenix Mountain, Bozhou, Tongling, Qingyang (Anhui China) and were identified prior to the experiment.

Oscillating experiments were performed in a glass container with a Model CJJ78-1 magnetic stirrer (Jiangsu, China) regulated by a Model HH-501 thermostat at 38 ± 0.05 ºC (Jiangsu, China), changes in potential were followed by a type 213 platinum electrode (Shanghai, China), a model 217 saturated calomel electrode (Shanghai, China) as reference electrode. Potentials (E) of the electrode as a function of time (t) were recorded by LK2005A electrochemical instrument (Tianjin, China) to record kinetic curves (E-t) of the oscillation reaction.

The following procedure was used in all experiments to get electrochemical fingerprint: A 12 mL of 3 M H_2SO_4, 6 mL of 0.4 M HOOC-CH_2-COOH and 3 mL of 0.005 M $Ce(NH_4)_4(SO_4)_4$, along with a certain amount of Cortex moutan powder through 100 mesh. Then the platinum electrode and reference electrode were immersed in the reaction mixture. The mixture was then homogenized by continuous magnetic stirring at 500 rpm and kept constant at 310 ± 0.05 K. Finally 3 mL of $KBrO_3$ was injected to the reaction and oscillations began immediately. At the same time, the E-t curve of the reaction was recorded, the E-t curve of traditional Chinese medicine is also called electrochemical fingerprint. The block diagram of experiment setup including reaction devices is shown in Fig. 1.

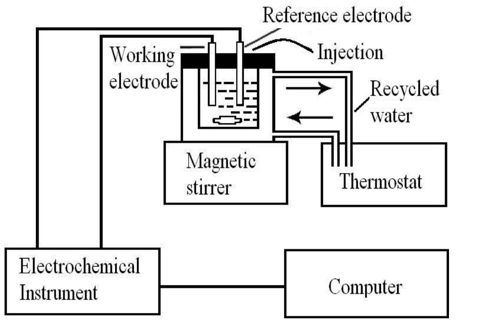
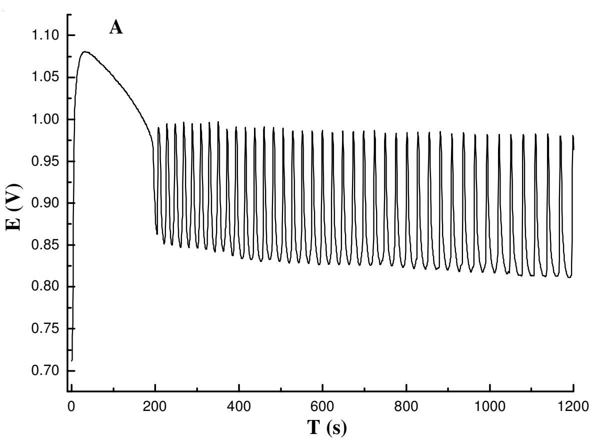


Fig.1. Scheme of Belousov-Zhabotinskii (B-Z) oscillation device

RESULTS AND DISCUSSION

E-t curve of Belousov-Zhabotinskii oscillation system and electrochemical fingerprint: The $KBrO_3$-H_2SO_4-HOOC-CH_2-COOH-$Ce(NH_4)_4(SO_4)_4$ system exhibits periodic changes of solution colour (colourless-yellow-colourless) during the oscillation[15]. Colour change is due to concentration changes of the oxidized and reduced forms of Ce^{3+} and Ce^{4+}, which demonstrates colourless and yellow, respectively.

Fig. 2A shows the first part of a typical E-t curve obtained in the $NaBrO_3$-H_2SO_4-HOOC-CH_2-COOH-$Ce(NH_4)_4(SO_4)_4$ system under the optimum conditions. Fig. 2B shows that the E-t curve changes when an amount of Cortex Moutan powder from Qingyan (Anhui, China) was added to the B-Z system. The response to one origin area Cortex moutan perturbation was different from the other. It suggests that electrochemical fingerprint can be used to identify the origins of traditional Chinese medicine.



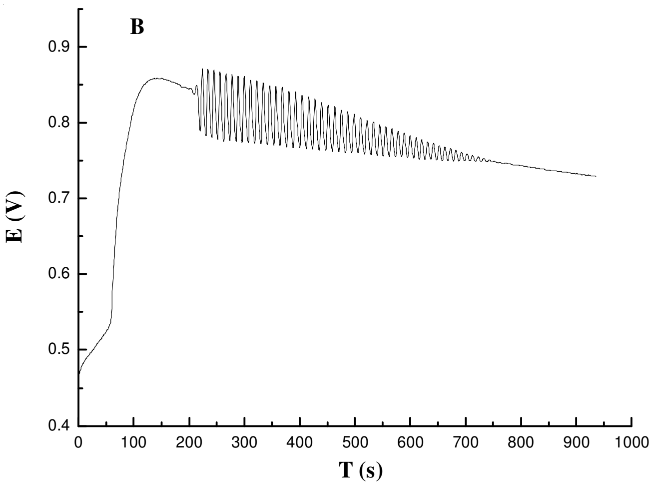
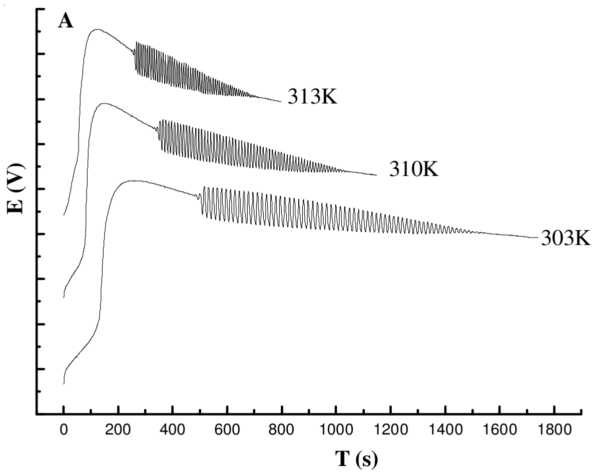


Fig. 2. Typical oscillation curves obtained in the absence (A) and presence (B) of 0.300 g Cortex moutan powder from Tongling

Influence of experimental variables: To obtain a stable electrochemical fingerprint for identifying Cortex Moutan from different origins with higher sensitivity and accuracy, the effects of various variables on the behaviour of the oscillation system were tested thoroughly in the study. The effect of H_2SO_4 concentration was studied within the range of 0.5-5.0 M. With increasing the H_2SO_4 concentration, the oscillation life and oscillation amplitude would be decreased very slowly and eventually disappeared. If the concentration of HOOC-CH_2-COOH were changed from 0.1 to 0.6 M, the oscillation life would be lengthened. The concentration of $NaBrO_3$ and $Ce(NH_4)_4(SO_4)_4$ have strong effects on the oscillation reaction, in which the oscillation life increased with increase of $KBrO_3$ concentration from 0.05 to 0.5 M. The influence of the $Ce(NH_4)_4(SO_4)_4$ concentration was also examined. It can be seen that an increase of $Ce(NH_4)_4(SO_4)_4$ in the range of 0.002-0.008 M would cause an increase in the oscillation life.

The effect of temperature and Cortex moutan powder amount on the oscillation is shown in Fig.3. The oscillation parameters including the amplitude, the period, the induction period, oscillation life decreased with increasing temperature and Cortex moutan powder amount from 303 K to 313 K, 0.100 g to 0.600 g, respectively. In order to control the oscillation life at about 1200 s, 310 K and 0.300 g were the optimum temperature and Cortex moutan powder amount.



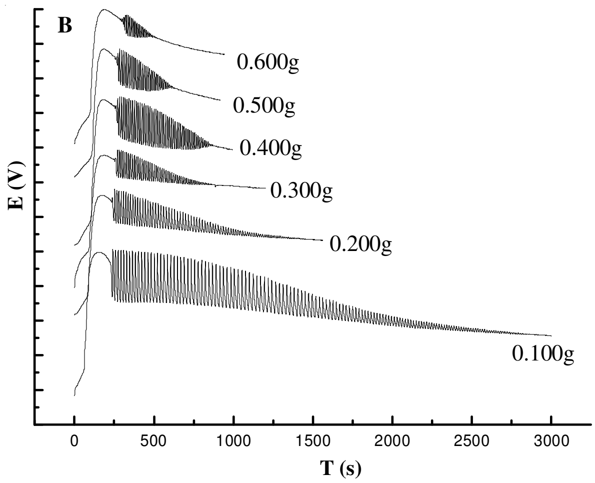


Fig. 3. Influence of the temperature (A) and Cortex Moutan (Tongling) powder amount (B)

In order to obtain the electrochemical fingerprint for identifying Cortex moutan from different origins, 3 M H_2SO_4, 0.4 M, HOOC-CH_2-COOH, 0.2 M $KBrO_3$ and 0.005 M $Ce(NH_4)_4(SO_4)_4$ were chosen. The temperature is 310 K. The amount of Cortex moutan powder is 0.300 g.

Stability of the electrochemical fingerprint of Cortex moutan: Under the optimum conditions, a stable regular oscillating profile (Fig. 4) was obtained from the same sample, which were 4 years old from Tongling (Anhui, China), the oscillation parameters are almost the same for five times, so the electrochemical fingerprints have good stability.

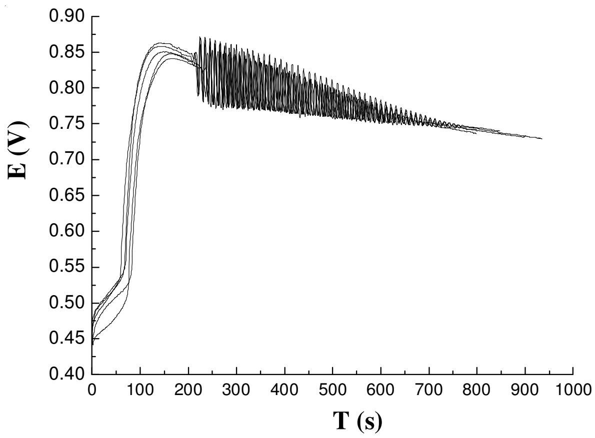


Fig. 4. Stability of the electrochemical fingerprint of Cortex moutan

Electrochemical fingerprint of Cortex moutan: We performed perturbation experiments under the optimal experimental conditions described above. Applying the E-t curve in oscillation system tested the response to perturbation of Cortex moutan powder from different origins. The electrochemical fingerprint obtained by the E-t curve matched the Cortex moutan from different origins, Fig. 5 shows the electrochemical fingerprints of four Cortex Moutan from Tongling, Phoenix Mountain, Bozhou, Qingyang (Anhui, China), respectively. It is shown that one Cortex moutan from an origin has its own electrochemical fingerprint. In particular, the oscillation parameters, including the life, the period, the induction period and the amplitude are significantly different from those from other origins.

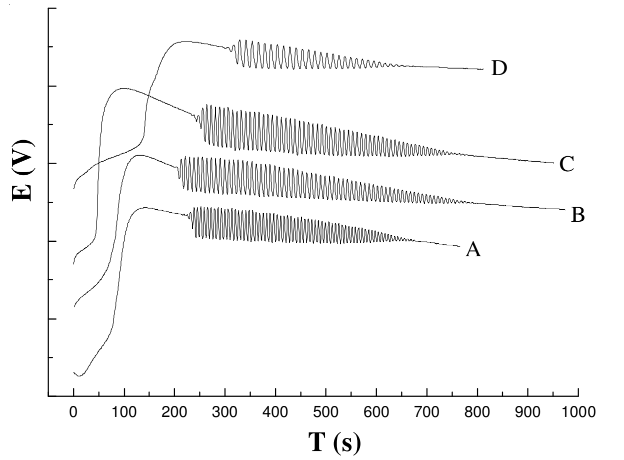


Fig. 5. Electrochemical fingerprint of Cortex moutan from different origins of A: Tongling, B: Phenix mountain, C: Bozhou, D: Qingyang

On the other hand, the Cortex moutan samples exhibit the same electrochemical fingerprint when their origins are same, Fig. 6 shows the electrochemical fingerprint of Cortex moutan. The samples were from Phoenix mountain (Anhui, China) and oscillation parameters are almost the same as each other, even if ages and gathering times of the Cortex moutan are different. This implies that electrochemical fingerprint can be used to identify the origin areas of Cortex moutan.

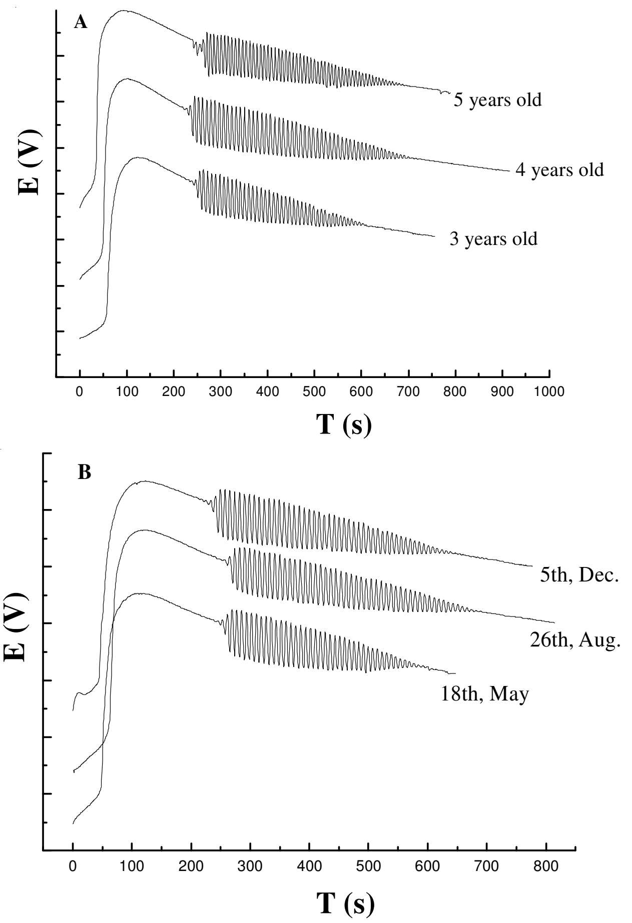


Fig. 6. Electrochemical fingerprint of Cortex moutan from Phenix mountain with (A) different years old at September, (B) different harvest time at 5 years old

Conclusion

Cortex moutan is an important traditional Chinese medicine in China. The HPLC method used to identity Cortex Moutan is time- and energy-consuming. Compared with the HPLC method, the electrochemical fingerprint approach proposed in the paper is simple, fast and sensitive. Electrochemical fingerprints show significantly different characteristics and provide a useful tool for identifying the origins of Cortes moutan. This approach can be used not only in traditional Chinese medicine, but also in such other fields as vegetables and fruits, thus expanding the scope of application in the B-Z oscillation system.

ACKNOWLEDGEMENTS

This work was supported by National Key Technology R & D program of China (grant no. 2011BAI04B05), the Nature Science Foundation of the Anhui Province Ministry of Education (grant no. KJ2011Z220), the Nature Science Foundation of Anhui College of Traditional Chinese Medicine (grant no. 2011zr016B) and the Xu's Foundation, USA.

REFERENCES

1. Chinese Pharmacopoeia Commission, Pharmacopoeia of the People's Republic of China, China Medical Science and Technology Press, Beijing. Volume I, pp. 1/60-1/61 (2010).
2. P. Li, X. Zhao, L. Zhang and A. Ding, *Chin. J. Chin. Mater. Med.*, **34**, 2463 (2009).
3. C. Yu, S. Liu, J. Fan, Z. Bai, Y. Yang and X. Zang, *Chin. Tradit. Pat. Med.*, **28**, 1098 (2006).
4. L. Zhou, S. Liang, S. Wang, M. Wu and C. Chen, *Lishizhen Med. Mater. Med. Res.*, **19**, 1337 (2008).
5. Q. Liang, H. Wen, Y. Wang and G. Luo, *Chin. J. Anal. Chem.*, **33**, 1555 (2005).
6. M. Zhang, *Chin. Tradit. Herbal Drugs*, **37**, 961 (2006).
7. T. Zhang, Y. Liang, B. Yuan, F. Ding, Y. Zhang, M. Wei and X. Chen, *Chin. Sci. Bull.*, **52**, 1012 (2007).
8. T. Zhang, Y. Liang, B. Yuan, F. Ding, Y. Zhang and W. Chen, *Chin. Sci. Bull.*, **52**, 1513 (2007).
9. X. Fang, T. Zhang, Z. Zhao, F. Xiang, Y. Liang, M. Wang, R. Zhu, S. Chen and J. Qiao, *Chin. Sci. Bull.*, **55**, 2937 (2010).
10. J. Gao, H. Dai, W. Yang, H. Chen, D. Lv, J. Ren and L. Wang, *Anal. Bioanal. Chem.*, **384**, 1438 (2006).
11. P. Chen, G. Hu, W. Wang, J. Song, L. Qiu, H. Wang, L. Chen and J. Zhang, *J. Appl. Electrochem.*, **38**, 1779 (2008).
12. I.R. Epstein and K. Showalter, *J. Phy. Chem.*, **100**, 13132 (1996).
13. P.E. Strizhak, O.Z. Didenko and T.S. Ivashchenko, *Anal. Chim. Acta*, **428**, 15 (2001).
14. M. Harati, S. Amiralaei, J. Green and J. Wang, *Chem. Phys. Lett.*, **439**, 337 (2007).
15. J.F. Richard and B. Maria, Oscillations and Traveling Waves in Chemical Systems, John Wiley & Sons, New York (1985).