

# Voltammetric Determination of Thymol in Oregano Using CeO<sub>2</sub>-Modified Electrode in Brij® 35 Micellar Medium

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## Abstract

© 2016, Springer Science+Business Media New York. Glassy carbon electrode (GCE) modified with CeO<sub>2</sub> nanoparticles dispersed in 0.01 M Brij® 35 (CeO<sub>2</sub>-Brij® 35/GCE) has been developed for the determination of thymol in micellar medium. Scanning electron microscopy (SEM) data confirm immobilization of the nanomaterial on the electrode surface. The electrooxidation of thymol on CeO<sub>2</sub>-Brij® 35/GCE is an irreversible diffusion-controlled process with participation of two electrons and two protons. Differential pulse voltammetry has been used for the quantification of thymol. The linear dynamic range of the thymol determination is 0.700–10.1 and 10.1–606 µM with the limits of detection and quantification 0.20 and 0.65 µM, respectively. The approach developed has been applied for the quantification of thymol in oregano spices using preliminary micellar extraction with Brij® 35. The results of voltammetric determination are in good agreement with the data of standard spectrophotometric method.

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## Keywords

Chemically modified electrodes, Differential pulse voltammetry, Food analysis, Micellar media, Nanoparticles, Thymol

## References

- [1] Abu-Lafi S, Odeh I, Dewik H, Qabajah M, Hanus LO, Dembitsky VM (2008) Thymol and carvacrol production from leaves of wild Palestinian Majorana syriaca. *Bioresour Technol* 99:3914–3918
- [2] Aeschbach R, Löliger J, Scott BC, Murcia A, Butler J, Halliwell B, Aruoma OT (1994) Anti-oxidant action of thymol, carvacrol, 6-gingerol, zingerone and hydroxytyrosol. *Food Chem Toxicol* 32:31–36
- [3] Al-Abachi MQ, Al-Ward HS (2012) Batch and flow-injection spectrophotometric determination of thymol using procaine hydrochloride as a new chromogenic reagent. *Baghdad Sci J* 9:302–310
- [4] Alekseeva LI (2009) Determining thymol and carvacrol by reversed-phase high-performance liquid chromatography. *Pharm Chem J* 43:665–667
- [5] Backheet EY (1998) Micro determination of eugenol, thymol and vanillin in volatile oils and plants. *Phytochem Anal* 9:134–140
- [6] Bard AJ, Faulkner LR (2001) *Electrochemical methods: fundamentals and applications*, 2nd edn. John Wiley & Sons, New York
- [7] Behpour M, Masoum S, Meshki M (2014) Determination of trace amounts of thymol and caffeic acid in real samples using a graphene oxide nanosheet modified electrode: application of experimental design in voltammetric studies. *RSC Adv* 4:14270–14280
- [8] Braga PC, Dal Sasso M, Culici M, Bianchi T, Bordoni L, Marabini L (2006) Anti-inflammatory activity of thymol: inhibitory effect on the release of human neutrophil elastase. *Pharmacology* 77:130–136

- [9] Cantalapiedra A, Gismera MJ, Sevilla MT, Procopio JR (2014) Sensitive and selective determination of phenolic compounds from aromatic plants using an electrochemical detection coupled with HPLC method. *Phytochem Anal* 25:247-254
- [10] Evans WC (2009) *Trease and Evans Pharmacognosy*, 16th edn. Saunders Elsevier, New York
- [11] Falcone P, Speranza B, Del Nobile MA, Corbo MR, Sinigaglia MJ (2005) A study on the antimicrobial activity of thymol intended as a natural preservative. *Food Pro* 68:1664-1670
- [12] Fiori GML, Bonato PS, Pereira MPM, Continia SHT, Pereira AMS (2013) Determination of thymol and carvacrol in plasma and milk of dairy cows using solid-phase microextraction. *J Braz Chem Soc* 24:837-846
- [13] Gan T, Lv Z, Deng Y, Sun J, Shi Z, Liu Y (2015) Facile synthesis of monodisperse Ag@C@Ag core-double shell spheres for application in the simultaneous sensing of thymol and phenol. *New J Chem* 39:6244-6252
- [14] Ghiasvand A, Dowlatshah S, Nouraei N, Heidari N, Yazdankhah F (2015) A solid-phase microextraction platinized stainless steel fiber coated with a multiwalled carbon nanotube-polyaniline nanocomposite film for the extraction of thymol and carvacrol in medicinal plants and honey. *J Chromatogr A* 1406:87-93
- [15] Haeseler G, Maue D, Grosskreutz J, Bufler J, Nentwig B, Piepenbrock S, Dengler R, Leuwer M (2002) Voltage-dependent block of neuronal and skeletal muscle sodium channels by thymol and menthol. *Eur J Anaesthesiol* 19:571-579
- [16] Hajimehdipoor H, Shekarchi M, Khanavi M, Adib N, Amri M (2010) A validated high performance liquid chromatography method for the analysis of thymol and carvacrol in *Thymus vulgaris* L. volatile oil. *Pharmacogn Mag* 6:154-158
- [17] Haque MDR, Ansari SH, Najmi AK, Naquvi KJ (2012) Validated HPLC analysis method for quantification of thymol content in *Trachyspermum ammi* and polyherbal unani formulation Arq zeera. *Int J Pharm Pharm Sci* 4:478-482
- [18] Jaiswal PV, Ijeri VS, Srivastava AK (2001) Voltammetric behavior of  $\alpha$ -tocopherol and its determination using surfactant + ethanol + water and surfactant + acetonitrile + water mixed solvent systems. *Anal Chim Acta* 441:201-206
- [19] Karami-Osboo R, Khodaverdi M, Ali-Akbari F (2010) Antibacterial effect of effective compounds of *Satureja hortensis* and *Thymus vulgaris* essential oils against *Erwinia amylovora*. *J Agric Sci Technol* 12:35-45
- [20] Kiyanpourea V, Fakharia AR, Alizadeh R, Asghari B, Jalali-Heravi M (2009) Multivariate optimization of hydrodistillation-headspace solvent microextraction of thymol and carvacrol from *Thymus transcaspicus*. *Talanta* 79:695-699
- [21] Lau O-W, Luk S-F, Wong W-C (1998) Simultaneous determination of methyl salicylate and thymol in various pharmaceutical formulations by differential-pulse voltammetry using a glassy carbon electrode. *Analyst* 113:865-868
- [22] López MMC, Vilariño JML, Rodríguez MVG, Losada LFB (2011) Development, validation and application of micellar electrokinetic capillary chromatography method for routine analysis of catechins, quercetin and thymol in natural samples. *Microchem J* 99:461-469
- [23] Michelitsch A, Rittmannsberger A, Hüfner A, Rückert U, Likussar W (2004) Determination of isopropylmethylphenols in black seed oil by differential pulse voltammetry. *Phytochem Anal* 15:320-324
- [24] Mika J, Berek J, Zima J, Dejmekova H (2015) New flow-through coulometric detector with renewable working electrode material for flow injection analysis and HPLC. *Electrochim Acta* 154:397-403
- [25] Nicholson RS, Shain I (1964) Theory of stationary electrode polarography. Single scan and cyclic methods applied to reversible, irreversible, and kinetic systems. *Anal Chem* 36:706-723
- [26] Piech R, Paczosa-Bator B (2015) Application of glassy carbon electrode modified with Nafion/MWCNTs for sensitive voltammetric determination of thymol. *Acta Pol Pharm* 72:1081-1088
- [27] Razzaq ZL, Mohammed HJ (2014) Spectrophotometric determination of thymol in lastarine antiseptic by diazotization of 4-aminoantipyrine in the presence of triton X-100. *Int J Eng Technol* 14:104-111
- [28] Roosta M, Ghaedi M, Daneshfar A, Sahraei R (2015) Ultrasound assisted microextraction-nano material solid phase dispersion for extraction and determination of thymol and carvacrol in pharmaceutical samples: experimental design methodology. *J Chromatogr B* 975:34-39
- [29] Scholz F (ed) (2002) *Electroanalytical methods. Guide to experiments and applications*. Springer-Verlag, Berlin Heidelberg
- [30] Simić A, Manojlović D, Šegan D, Todorović M (2007) Electrochemical behavior and antioxidant and prooxidant activity of natural phenolics. *Molecules* 12:2327-2340
- [31] Stanković DM (2015) Sensitive voltammetric determination of thymol in essential oil of *Carum copticum* seeds using boron-doped diamond electrode. *Anal Biochem* 486:1-4
- [32] Vinas P, Soler-Romera MJ, Hernandez-Cordoba M (2006) Liquid chromatographic determination of phenol, thymol and carvacrol in honey using fluorimetric detection. *Talanta* 69:1063-1067
- [33] Yanishlieva NV, Marinova EM, Gordon MH, Raneva VG (1999) Antioxidant activity and mechanism of action of thymol and carvacrol in two lipid systems. *Food Chem* 64:59-66

- [34] Zhao X, Du Y, Ye W, Lu D, Xia X, Wang C (2013) Sensitive determination of thymol based on CeO nanoparticle-decorated graphene hybrid film. *New J Chem* 37:4045–4051
- [35] Zima J, Cienciala M, Barek J, Moreira JC (2007) Determination of thymol using HPLC-ED with glassy carbon paste electrode. *Chem Anal* 52:1049–1057
- [36] Ziyatdinova G, Giniyatova E, Budnikov H (2010) Cyclic voltammetry of retinol in surfactant media and its application for the analysis of real samples. *Electroanal* 22:2708–2713
- [37] Ziyatdinova GK, Giniyatova ER, Budnikov GK (2012a) Voltammetric determination of  $\alpha$ -tocopherol in the presence of surfactants. *J Anal Chem* 67:467–473
- [38] Ziyatdinova G, Ziganshina E, Budnikov H (2012b) Voltammetric determination of  $\beta$ -carotene in raw vegetables and berries in Triton X100 media. *Talanta* 99:1024–1029
- [39] Ziyatdinova GK, Ziganshina ER, Budnikov HC (2012c) Application of surfactants in voltammetric analysis. *J Anal Chem* 67:869–879
- [40] Ziyatdinova G, Ziganshina E, Budnikov H (2013) Voltammetric sensing and quantification of eugenol using nonionic surfactant self-organized media. *Anal Methods* 5:4750–4756
- [41] Ziyatdinova GK, Ziganshina ER, Nguyen Cong P, Budnikov HC (2016) Determination of the antioxidant capacity of the micellar extracts of spices in Brij® 35 medium by differential pulse voltammetry. *J Anal Chem* 71:573–580