Electropolymerized Dyes as Sensing Layer for Natural Phenolic Antioxidants of Essential Oils

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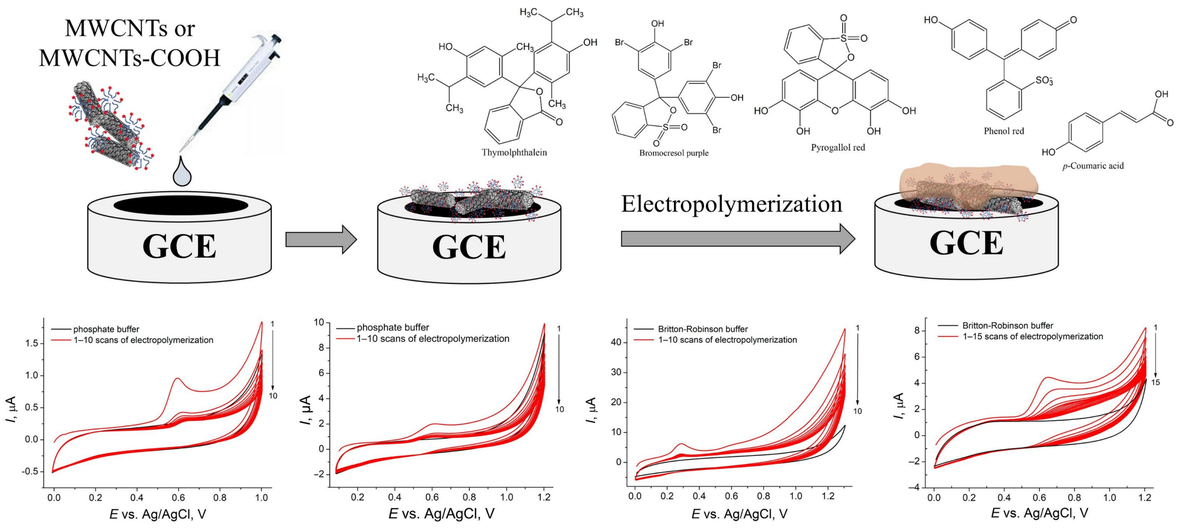
Essential oils have a wide application in aromatherapy as part of alternative medicine, in the food, pharmaceutical, and cosmetic industry as fragrance and flavor additives. The antibacterial, antimicrobial, antiviral, and antioxidant properties of essential oils are caused by the presence of bioactive compounds including natural phenolic antioxidants such as eugenol, *trans*-anethole, thymol, carvacrol, vanillin, etc. Thus, quantification of these marker compounds in essential oils is of practical necessity. The presence of electroactive fragments in the phenolic antioxidants structure makes it possible to use voltammetry for their determination. However, the number of voltammetric sensors for the determination of individual antioxidants in essential oils is quite limited. Almost all of them are based on the application of electrode surface modifiers, among which the polymeric coverages are out of consideration. Electropolymerized triphenylmethane dyes have been shown as effective sensing layer for antioxidants including phenolic compounds. Thus, the current work deals with the development of novel voltammetric sensors for the quantification of natural phenolic antioxidants of essential oils using electropolymerized dyes as a sensing layer.

Electrode surface modification



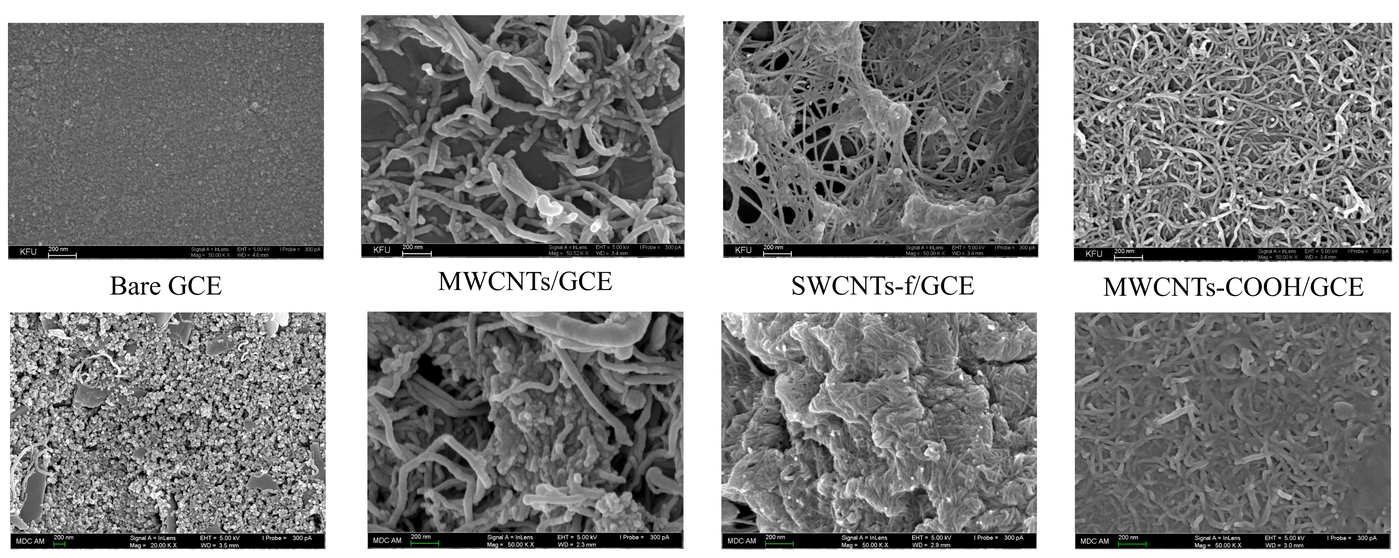
Optimal conditions for electropolymerization

Sensing layer	*c*, μM	Number of scans	Potential range, V	υ, mV s^{-1}	Supporting electrolyte
Poly(thymolphthalein)/MWCNTs	10	10	0.0–1.0	100	0.1 M Phosphate buffer pH 7.0
Poly(bromocresol purple)/SWCNTs-f	25	10	0.0–1.2	100	
Poly(pyrogallol red)/MWCNTs-COOH	100	10	0.0–1.3	75	Britton-Robinson buffer pH 7.0
Poly(phenol red–co–p-coumaric acid)/MWCNTs	100	15	0.0–1.2	50	

Electrochemical characteristics of the sensors

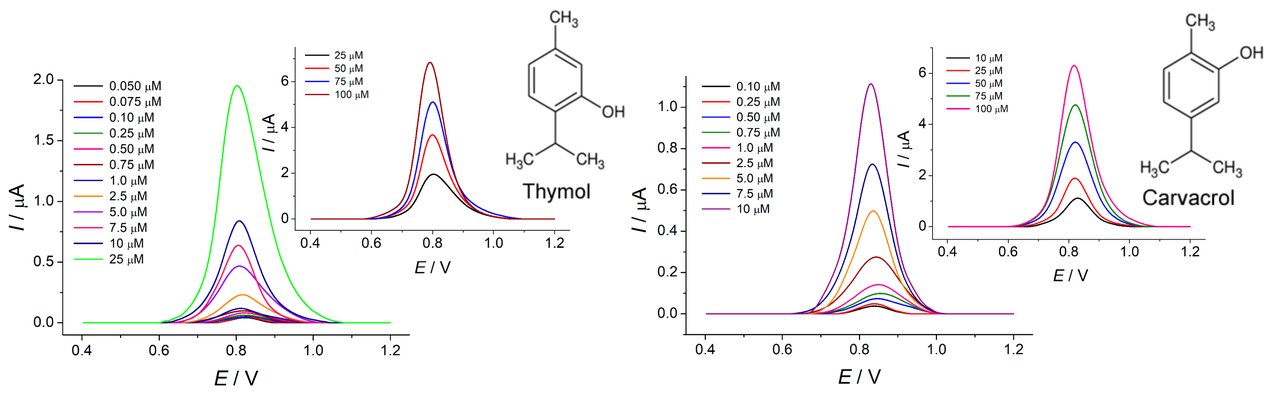
Electrode	*A*, mm^2	R_{ct}, kΩ	*Q*, $\mu\Omega^{-1}$	k_{et}, cm s^{-1}
Bare GCE	8.9±0.3	72±3	3.7±0.2	4.12×10^{-5}
Poly(thymolphthalein)/MWCNTs/GCE	88±5	7.3±0.1	0.704±0.09	4.14×10^{-5}
Poly(bromocresol purple)/SWCNTs-f/GCE	42±1	10.1±0.2	5.4±0.1	6.64×10^{-5}
Poly(pyrogallol red)/MWCNTs-COOH/GCE	96±2	3.04±0.09	5.71±0.05	9.12×10^{-5}
Poly(phenol red–co–p-coumaric acid)/MWCNTs/GCE	11.4±0.6	4.0±0.1	6.0±0.1	5.84×10^{-5}

SEM image of electrode surface

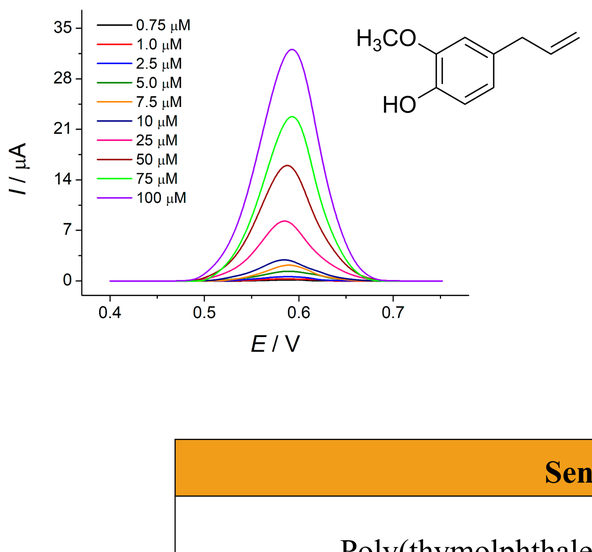


Voltammetric sensors for natural phenolic antioxidants of essential oils

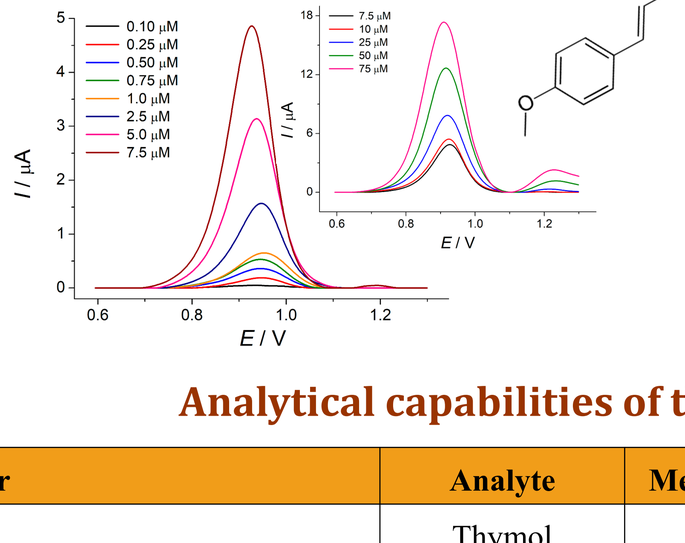
Isopropylmethylphenols at poly(thymolphthalein)/MWCNTs/GCE



Eugenol at poly(pyrogallol red)/ MWCNTs-COOH/GCE



trans-Anethole at poly(phenol red–co–*p*-coumaric acid)/MWCNTs/GCE



Interference	Tolerance Limit, M			
	1.0 μM thymol or carvacrol	1.0 μM vanillin	5.0 μM eugenol	1.0 μM *trans*-anethole
K^+, Mg^{2+}, Ca^{2+}, NO_3^-, Cl^-, SO_4^{2-}	1000	1000	5000	1000
Glucose, rhamnose, sucrose	100	100	500	100
Thymol	—	0	25	0.25
Cavacrol	—	0	50	0.25
Vanillin	0	—	500	0
trans-Anethole	0.10	0	500	—
Eugenol	1.0	100	—	15
α-Pinene	100	50	500	0.25
Limonene	100	50	500	0.50

Analytical capabilities of the developed sensors

Sensor	Analyte	Method	E_{ox}, V	Linear dynamic range, μM	Detection limit, μM
Poly(thymolphthalein)/MWCNTs/GCE	Thymol	DPV[1]	0.81	0.050 – 25 and 25 – 100	0.037
	Carvacrol		0.83	0.10 – 10 and 10 – 100	0.063
Poly(bromocresol purple)/SWCNTs-f/GCE	Vanillin	DPV	0.86	0.10 – 5.0 and 5.0 – 25	0.064
Poly(pyrogallol red)/MWCNTs-COOH/GCE	Eugenol	DPV	0.57	0.75 – 100	0.73
Poly(phenol red–co–*p*-coumaric acid)/MWCNTs/GCE	*trans*-Anethole	AdDPV[2]	0.95	0.10 – 7.5 and 7.5 – 75	0.095

[1] Differential pulse voltammetry, [2] Adsorptive differential pulse voltammetry.

Conclusions

Electropolymerized thriphenylmethane dyes have been shown to be an effective sensing layer for the potential application in electroanalysis of major phenolic antioxidants-markers of essential oils. The sensing system is easy to fabricate, highly reproducible, and provides a sensitive, selective, and reliable response to target analytes. Future development of the topic under study to be focused on the application of the sensors in real samples analysis for their standardization and quality control. Furthermore, the fabrication of screen-printed electrodes as a basis for sensing layer immobilization can significantly simplify the measurements, reduce it cost, and make more attractive for the use in practice.