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Voltammetric sensor based on the electropolymerized phenol red for the simultaneous quantification of syringaldehyde and vanillin

Guzel Ziyatdinova

Analytical Chemistry Department, Kazan Federal University, Kazan, 420008, Russia

INTRODUCTION & AIM

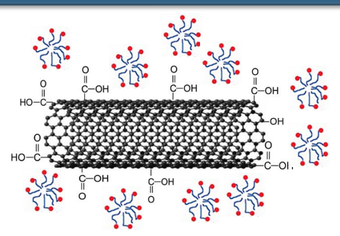
Syringaldehyde and vanillin are used as flavorings and odorants in food, pharmaceutical, and cosmetic industries. Moreover, their concentration ratio is considered as a significant parameter for brandy and cognac quality characterization allowing identification of adulteration. Thus, simultaneous quantification of syringaldehyde and vanillin is the topic on demand. Voltammetric sensors are a promising tool to solve this problem due to high sensitivity and sufficient selectivity, fast response and possibility of miniaturization. Glassy carbon electrode modified with carboxylated multi-walled carbon nanotubes and electropolymerized indicator phenol red has been developed as a voltammetric sensor for the simultaneous determination of syringaldehyde and vanillin.

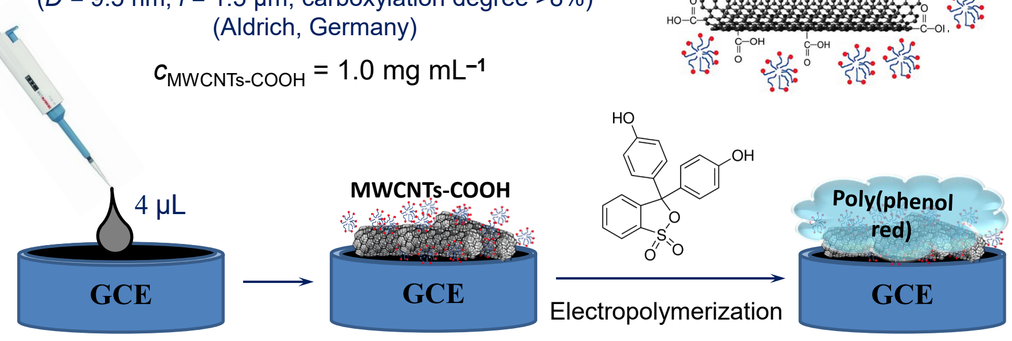
ELECTRODE MODIFICATION AND CHARCATERIZATION

Carboxylated multi-walled carbon nanotubes (MWCNTs-COOH) in 1% SDS

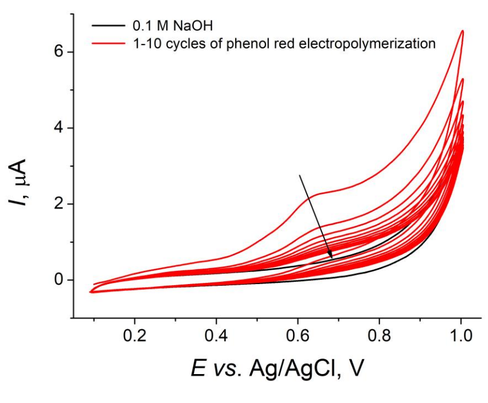
(*D* = 9.5 nm, *l* = 1.5 μm, carboxylation degree >8%) (Aldrich, Germany)

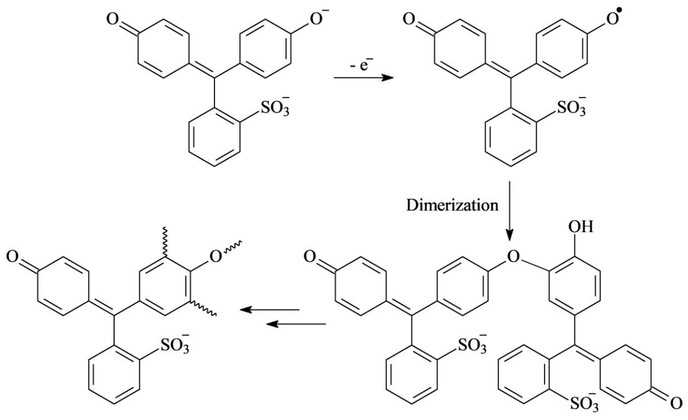
$c_{MWCNTs\text{-}COOH}$ = 1.0 mg mL^{-1}

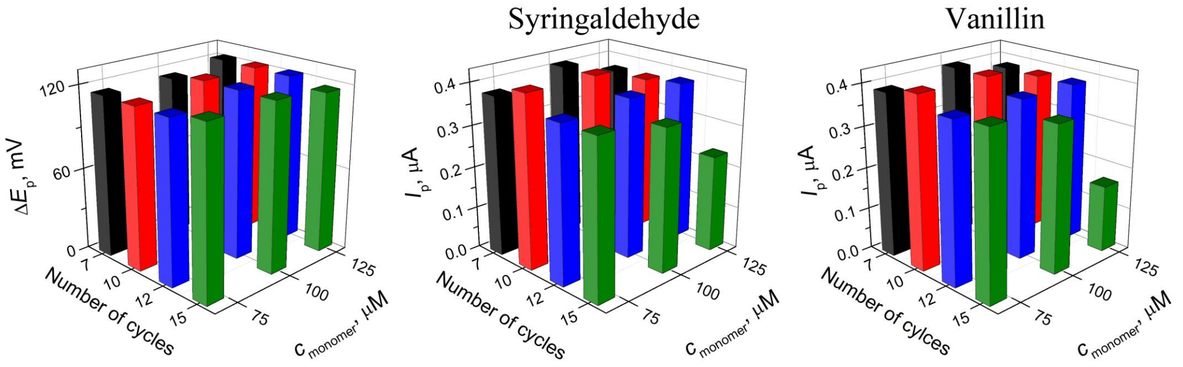


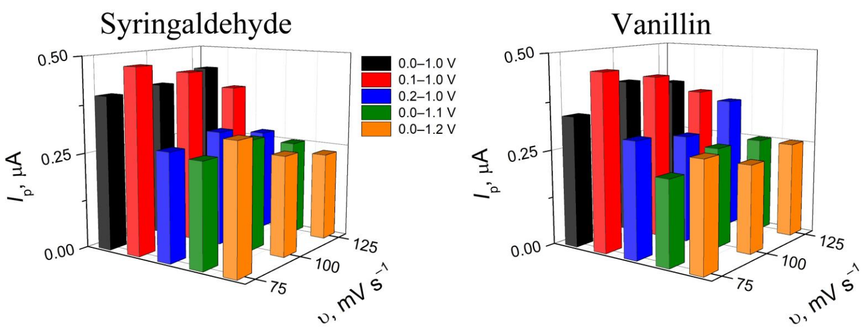


Optimization of phenol red electropolymerization









$c_{monomer}$ = 100 μM
Number of cycles = 10
υ = 75 mV s^{-1}
Potential range
0.1 – 1.0 V

Electrochemical characteristics of the electrodes (*n* = 5; *P* = 0.95)

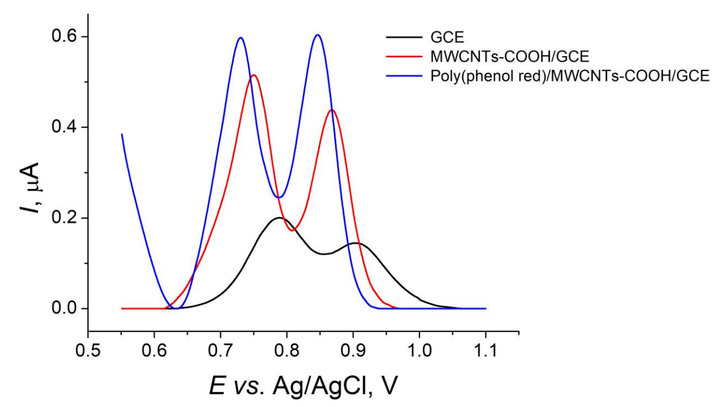
Electrode	*A* , mm^2	R_{ct} , kΩ	k_{et}, cm s^{-1}
GCE	9.05 ± 0.07	72 ± 3	4.08×10^{-5}
MWCNTs-COOH/GCE	20.1 ± 0.1	10.4 ± 0.3	1.27×10^{-4}
Poly(phenol red)/MWCNTs-COOH/GCE	14.0 ± 0.1	14.7 ± 0.7	1.29×10^{-4}

RESULTS & DISCUSSION

Voltammetric characteristics of aromatic aldehydes

10 μM mixture of aldehydes

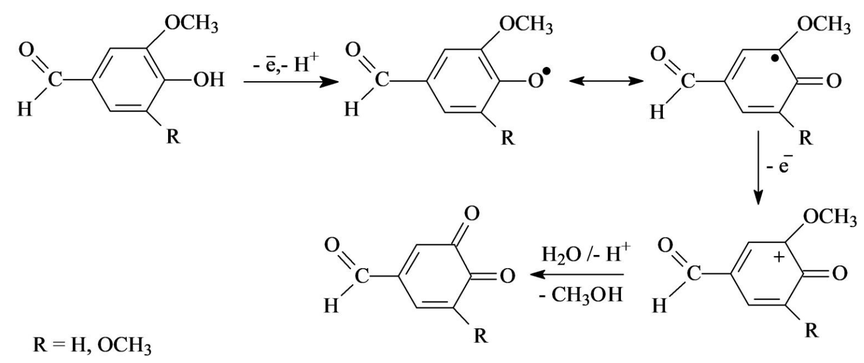
Britton-Robinson buffer pH 2.0
ΔE_{pulse} = 50 mV
t_{pulse} = 50 ms
υ = 10 mV s^{-1}



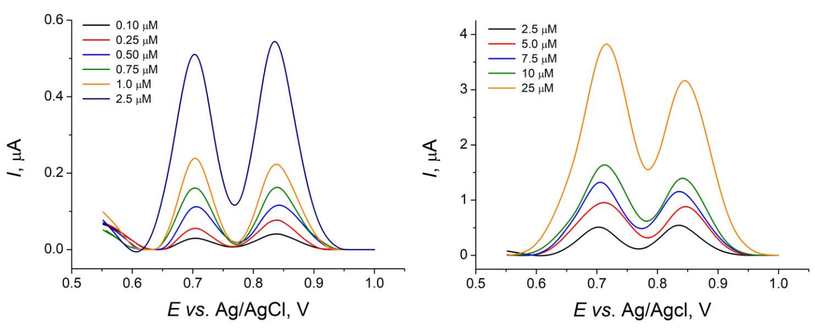
Electrode	Syringaldehyde		Vanillin	
	E_p, V	I_p, μA	E_p, V	I_p, μA
GCE	0.78	0.126±0.005	0.91	0.063±0.002
MWCNTs-COOH/GCE	0.75	0.40±0.02	0.87	0.34±0.01
Poly(pheno red)/ MWCNTs-COOH/GCE	0.73	0.52±0.02	0.85	0.50±0.02

Syringaldehyde and vanillin electrooxidation parameters

Analyte	Electrolyte	Limiting step nature	Electrooxidation parameters
Syringaldehyde	Britton-Robinson buffer pH 2.0	Diffusion	H$^+$ transfer involved α_a = 0.51 *n* = 2
Vanillin			H$^+$ transfer involved α_a = 0.53 *n* = 2



Simultaneous quantification of aromatic aldehydes



Linear dynamic ranges:
0.10-2.5 and 2.5-25 μM for both analytes
Detection limits:
44 nM of syringaldehyde
33 nM of vanillin

Britton-Robinson buffer pH 2.0. ΔE_{pulse} = 100 mV, t_{pulse} = 25 ms, υ = 20 mV s^{-1}

Added, μM	Found syringaldehyde, μM	RSD	*R*, %	Found vanillin, μM	RSD	*R*, %
0.10	0.102±0.009	0.04	102	0.100±0.007	0.05	100
0.75	0.75±0.02	0.02	100	0.752±0.006	0.007	100.3
2.5	2.49±0.07	0.02	99.6	2.50±0.03	0.01	100
7.5	7.53±0.06	0.006	100.4	7.50±0.08	0.009	100
25	25.0±0.6	0.02	100	25.0±0.3	0.009	100

CONCLUSIONS

Simple, reproducible, robust and reliable voltammetric sensor based on layer-by-layer combination of carbon nanotubes and electropolymerized phenol red has been developed for simultaneous determination of syringaldehyde and vanillin. It can be applied in the food industry for the control of both flavor additives and aged distilled beverages quality.