



16th International Scientific Conference “Chemistry and Chemical Engineering in XXI century”
dedicated to Professor L.P. Kulyov, CCE 2015

Voltammetric determination of organic ecotoxicants on modified electrodes

G.B. Slepchenko^{a*}, T.M. Gindullina^a, V.I. Deryabina^a, Yu.A. Akeneev^a, V. I. Otmakhov^b

^a National Research Tomsk Polytechnic University, Tomsk, 634050, Russia

^b National Research Tomsk State University, Tomsk, 634050, Russia

Abstract

In this paper the contemporary state and the use of voltammetric methods for the determination of organic toxicants on the modified electrodes are shown. A review of works on the application of voltammetric methods for the analysis of environmental objects - water (natural, drinking, waste, etc.), published in the last 5 years, has been made. The main trends in electroanalytical control over the content of toxicants in the waters are noted. The experimental results on the expansion of determined organic toxicants are represented.

© 2015 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Peer-review under responsibility of Tomsk Polytechnic University

Keywords: Voltammetry, organic substances, water, modified electrode technique, environmental objects.

1. Introduction

Because of the imperfection of the technology as well as applications in industry and agriculture a wide variety of organic contaminants, such as phenols, phthalates, pesticides and others enters the environment. In addition to high toxicity most of these substances have a pronounced cumulative effect manifesting in the change of the immunological status of living organisms, mutagenic and teratogenic effects. Natural matrices are the most difficult objects of analytical chemistry, especially in those cases where it is necessary to determine contaminants present in trace amounts. To determine them, different physical and physico-chemical methods, primarily chromatography and

* Corresponding author, tel: +83822563860
E-mail: microlab@tpu.ru

mass-spectrometry, are widely used. Voltammetry has a special place in the analysis of complex multicomponent systems. The method is relatively simple, characterized by low detection limits and high selectivity determination. The required selectivity and high detection sensitivity are provided by the specific properties of the surface of chemically modified electrodes (CME). Interest in CME is associated not only with the use of a voltammetric analysis, but also by using them as a biochemical response of the transducers in biosensors, the number of which is continuously increasing.

2. Results and discussion

We have studied the literature on the applicability of modified electrodes when determining toxicants. More than 180 works devoted to the electrochemical methods for monitoring water content of toxicants on the modified electrodes have been allocated. Among these publications more than 150 works are dedicated to the use of the voltammetry method (and its variants). Conditions for the determination of a number of organic ecotoxicants are combined in the Table in which an analyte, a type of electrode and modifier and a method and object of analysis are presented.

In the table the following abbreviations are used: S – sensor; BS – biosensor; E - electrode; CE - carbon electrode; GCE - glassy carbon electrode; CPE - carbon-paste electrode; CNT - carbon nanotubes; NP - nanoparticles; SAM - self-assembled monolayers; VA - voltammetry; IVA - inversion voltammetry; CVA - cyclic voltammetry; SWVA – squarewave voltammetry; DPVA - differential pulse voltammetry.

Table. Conditions for the determination of a number of organic ecotoxicants

Analyte	Object analysis	Indicator electrode/ Modifier	Method	Determination range, detection limit	Reference
Benzenes, dihydroxybenzenes					
Nitrobenzene		GCE/chitosan, chloride-2-hydroxypropyltrimethyl-ammonium	DIVA	3.0-120 mg/l detection limit 0.7 mg/l	[1]
Hydroquinone	waste water	CNT; C/ ionic liquid, CNT, β -cyclodextrin;	VA; DIVA CVA	$1.0 \cdot 10^{-8}$ – $2.2 \cdot 10^{-3}$ M, detection limit $5.0 \cdot 10^{-9}$ – $9.0 \cdot 10^{-7}$ M	[2-7]
Pyrocatechol Resorcin		AuE/CNT, dimethyldiallylammonium; GCE/NP La(OH) ₃ ; BS: AuE/nanocomposite: hydroxyapatite-Chitosan, tyrosinase; CE/NP TiO ₂ , ZrO ₂			
Phenols					
Phenols	Water tests	GCE/CNT, tyrosinase; CE/NP TiO ₂ , ZrO ₂	CVA	0.4–10 μ M, detection limit 0.2 μ M	[7,8]
4-nitrophenol	Drinking water, river water	GCE/ nanopowder hydroxyapatite; CNT; Ag-amalgam paste; boron-doped diamond substrate E	CVA, DPVA; Ads. VA	$5.0 \cdot 10^{-8}$ – $30 \cdot 10^{-4}$ M, detection limit $1.1 \cdot 10^{-8}$ – $3.0 \cdot 10^{-7}$ M	[9-12]
2,4 -, 2,5-dinitrophenol	Drinking water, river water	GCE/ CNT ; boron-doped diamond substrate E	VA ; DPVA	$4.0 \cdot 10^{-6}$ – $5.0 \cdot 10^{-4}$ M, detection limit $1.1 \cdot 10^{-7}$ – $2.1 \cdot 10^{-7}$ M	[12,13]
nitrophenol isomers		E/CN	VA		[14]
4-chlorophenol	Water	AgE/ porous graphite, zeolite	CVA, DPVA		[15]
Biphenol A	Water	Sensor, GCE/ CNT, melamine	CVA	detection limit 5 nM	[16]
Dihydroxyphenols: dihydroxycinnamic-3,4, 3,4-dihydroxyphenylacetic, 4-hydroxyphenylacetic acid	Waste water, production of olive oil	Solid E, NP Au	VA	detection limit 80 nmole	[17]
Pesticides, fungicides, insecticides					
Parathion		nanocomposite film, ZrO ₂ /Au, CNT; AuE/COMC, NP ZrO ₂	CVA, SWVA	0.005–1.0 μ g/ml, detection limit 0.8–3 ng/ml	[18,19]

Analyte	Object analysis	Indicator electrode/ Modifier	Method	Determination range, detection limit	Reference
Methylparathion	Water	C: GCE / graphene, NP Au ; GCE/CNT, NP palladium. The nanocomposite: CNT, poly (acrylamide); BS based on acetylcholinesterase	SWVA, DPVA	0.001—14 µg/ml, detection limit 0.05–0.6 ng/ml	[20-23]
Thiodicarb		BS: AuE/ monolayers of L-cysteine, alfalfa peroxidase	SWVA	$2.27 \cdot 10^{-6}$ – $4.4 \cdot 10^{-5}$ M, detection limit $5.75 \cdot 10^{-7}$ M	[24]
Paraoxone		BS: CPE/C-CNT, acetylcholinesterase	CVA, mode FIA	detection limit $1.7 \cdot 10^{-7}$ mg/l ($6.2 \cdot 10^{-13}$ M)	[25]
Carbaryl	Natural water	Coal E/ CNT, cobalt phthalocyanine	SWVA,	0.33–6.61 µM, detection limit 1.09 µg/ml	[26]
atrazine	Natural water	Bi film	DPVA		[27]
Isoprene-Turonian, voltage, dicofol		CE/CNT, polyaniline	DIVA	0.01–100 mg/l, detection limit 0.01–0.1 µg/l	[28]
thiamethoxam	Natural water	CPE/ tricesylphosphate	DIVA,	3.72–41.5 µg/ml	[29]
benzophenone-3, triclosan	Water	GCE/ NP carbon, tosylates	VA	detection limit 5–10 µmol/l	[30]
Other					
4-aminobiphenyl	Sewage water	AuE/ COMC β-cyclodextrin	SWVA	10^{-3} – 10^{-4} M	[31]
Phenylhydrazine		CPE/ ferrocenemonocarboxylic acid, CNT	DIVA	0.8–700 µM, detection limit 0.42 µM	[32]
Sudan		CG/ ordered mesoporous carbon	DIVA	$4.03 \cdot 10^{-7}$ – $6.0 \cdot 10^{-5}$ M, detection limit $2.44 \cdot 10^{-9}$ M	[33]
Formaldehyde		C/ composite chitosan ionic liquid, NP Ag Pd	VA	0.06–20 mM, detection limit 0.022 mM	[34]
Surfactants (alkylbenzene sulfonate, ethoxylated fatty alcohols, etc.)	Sewage water	VA- electronic language with conductometric detector			[35]

The table shows that a variety of nanocomposite materials in combination with organic compounds and inorganic compounds is widely used. The sensitivity increases by 2-4 times, the detection limit is reduced. Much attention in the literature is paid to pesticides, fungicides, insecticides, phenol and benzene. Generally, cyclic and differential pulse voltammetry are used. Thus, differential pulse voltammetry was used for the simultaneous determination of dihydroxybenzene isomers on the carbon electrode modified with the ionic liquid, multi-walled carbon nanotubes and β-cyclodextrin. The measurements were performed on the background phosphate buffer with pH 7.0 (1.15 M) in the presence of a cationic surfactant of cetylpyridinium bromide. When using differential pulse voltammetry, the range of linear calibration curves were $1.2 \cdot 10^{-7}$ – $2.2 \cdot 10^{-3}$ (hydroquinone), $7.0 \cdot 10^{-7}$ – $2.2 \cdot 10^{-3}$ (pyrocatechol) and $2.6 \cdot 10^{-6}$ – $9.0 \cdot 10^{-4}$ M (resorcinol).

The electrode was used for the determination of analytes in artificial waste water [3]. The glassy-carbon electrode, modified with nanoparticles $\text{La}(\text{OH})_3$, was used to determine pyrocatechol and hydroquinone in wastewater catalytic electrooxidation current. Differential pulse voltammetry was not interfered with the various ions, ascorbic acid and phenol [5]. The use of the biosensor based on the hydroxyapatite-chitosan nanocomposites with immobilized tyrosinase, deposited on a gold electrode, allowed decreasing the limit of the detection of catechol to 5 nM [6].

A biosensor, based on the glassy carbon electrode, modified with tyrosinase, immobilized on multi-walled carbon nanotubes, detects an exceptional electrochemical catalytic activity at the reduction of benzoquinone produced in the enzymatic reaction. When determining phenol by cyclic voltammetry, cathode current is linear in the range of 0.4 and 10 µM; the detection limit of 0.2 µM. The method is used to determine phenol in water samples [8].

One of the most dangerous toxic substances is phosphorus and chlorinated pesticides, as evidenced by a fairly large number of publications on the development of methods for their control. So, for the voltammetric determination of organophosphorus pesticides a nanocomposite film electrode ZrO_2 -Au, obtained by combining sol-gel techniques and gilding without power imposing, has been proposed. The method of square wave voltammetry has indicated that zirconium nanooxide exhibits strong affinity for phosphate groups of parathion molecules; the detection limit of 3 ng/ml [18].

A method for producing new sensor sensitivity without using enzymes to determine organophosphate pesticides is described in [20]. A glassy carbon electrode is modified with graphene nanoflakes and decorated with gold nanoparticles. Methyl parathion is used to determine the option of stripping voltammetry. The effectiveness of the new composite in the inversion variation is confirmed by cyclic voltammetry and square wave voltammetry. Calibration curves are linear within the range of 0.001-0.1 and 0.2-1.0 $\mu\text{g/ml}$, the detection limit of 0.6 ng/ml. The sensor provides reproducible results.

The composite with deposited palladium nanoparticles has been obtained by simple reduction with ethylene glycol under heating at an oil bath. A glassy carbon electrode is used as a basis one to determine methyl parathion by differential pulse voltammetry. The calibration graph is linear in the range of 0.10 to 14 $\mu\text{g/ml}$ of the analyte; detection limit of 0.05 $\mu\text{g/ml}$ [21].

A biosensor based on the carbon-paste electrode modified with carbon nanotubes and acetylcholinesterase is used in the mode of flow-injection analysis for determining paraoxone by cyclic voltammetry; $1.7 \cdot 10^{-7}$ detection limit mg/l (6.2-10-13 M). The biosensor gives reproducible signals. This is a new effective tool for determining organophosphorus pesticides [25].

The study on the choice of operating conditions for the study of certain selected compounds under the following conditions: supporting electrolyte - 0.1M Na_2HPO_4 ; indicator electrode – modified, glassy carbon (for amino-, hydroxyl- compounds and compounds with fused benzene rings); Mercury film (for nitro- compounds) has been conducted by the research team of the trace contaminant laboratory of Tomsk Polytechnic University.

Research results of the potential peak dependence on the substitute nature indicate that electropositive groups, introduced into the molecule of aromatic hydroxy compounds, facilitate the oxidation of a substance, and electronegative ones lead to the potential shift to a more positive region, that is in good agreement with [36].

In the case of hydroquinone and pyrocatechol the effect of the substitute position on the nature of the signal was observed. Oxidation of hydroxy- groups in the p-position was easier than in the o-position. Benzyl alcohol was taken to compare the oxidation process of the hydroxide group linked directly to a benzene ring and the hydroxide group in the side chain. It indicated that the oxidation of the hydroxide groups in the side chain was easier than in the case of phenol derivatives. Good reproducible results in the determination of nitro- compounds were obtained on a mercury-film electrode in the negative potential range. The operating conditions of the determination of aromatic compounds with condensed benzene rings: naphthalene and acenaphthene on a supporting electrolyte (0.1 M Na_2HPO_4) and indicator electrode (MSUE) have been experimentally obtained.

3. Conclusion

Thus, the presented study shows that the voltammetric determination of organic toxicants on the modified electrodes allows increasing the sensitivity of their determination; reducing the detection limit (by 1-4 orders of magnitude); decreasing overvoltage potential of analytical signals; increasing determination selectivity and expanding the range of the determined compounds. The modified electrodes are widely used in electroanalysis; in chemical sensors and biosensors, as well as in flow detecting (HPLC, FIA).

Acknowledgments

This work was supported by the State program «Science» of the RF Ministry of science and education.

References

1. Hu Rong, Li Wei, Chi Wei-lin, Peng Hui-e, Qin Cai-qin. *J. Instrum. Anal.* 2008; **27**:11-1176.
2. Wang Zh., Li S., Lu Q. *Sens. and Actuators.* 2007; **127**:2-420.
3. Yu Q., Liu Y., Liu X., Zeng X., Luo Sh., Wei W. *Electroanalysis.* 2010; **22**:9-1012.
4. Yang Sh.-M., Wei Zh.-P., Hu G.-H., Jiang D., Huang A.-H., Zheng L.-Zh. *Chem. J. Chin. Univ.* 2010; **31**:2-264.
5. Sun J.-G., Wang G.-F., Jiao Sh.-F., Wei Y., Fang B. *Chin. J. Anal. Chem.* 2007; **35**:3-335.
6. Lu L., Zhang L., Zhang X., Huan Sh., Shen G., Yu R. *Anal. chim. acta.* 2010; **665**:2-146.
7. Lunsford S. Nanoscale modification of carbon electrodes for the detection of harmful organic chemicals . PITTCON Conference and Expo 2012, Orlando, Fla, March 11-15, 2012. Madison (Wisc.). 2012; 2320/7.
8. Ren J., Kang T.-F., Xue R., Ge Ch.-N., Cheng Sh.-Y. *Microchim. acta.* 2011; **174**:3-4- 303.
7. Lunsford S. Nanoscale modification of carbon electrodes for the detection of harmful organic chemicals . PITTCON Conference and Expo 2012, Orlando, Fla, March 11-15, 2012. Madison (Wisc.), 2012. 2320/7.
9. Yin H., Zhou Y., Ai Sh., Liu X., Zhu L., Lu L. *Microchim. acta.* 2010; **169**:1-2-87.
10. Zhu Sh., Niu W., Li H., Han Sh., Xu G. *Talanta.* 2009; **79**:5-1441.
11. Niaz A., Fischer J., Barek J., Yosypchuk B., Sirajuddin B. M. *Electroanalysis.* 2009; **21**:16-1786.
12. Musilová J., Barek J., Pecková K. *Electroanalysis.* 2011; **23**:5-1236.
13. Wang X.-G., Wu Q.-Sh., Fan Y.-J. *Chin. J. Appl. Chem.* 2008; **25**:6-642.
14. Luo L., Zou X.-I., Ding Y., Wu Q.-sh. *Sens. and Actuators.* 2008; **135**:1-61.
15. Pop A., Manea F., Proca C., Radovan C., Burtica G., Malchev P., Picken S., Schoonman J. *Bul. sti. Univ. "Politehn." Timisoara. Ser. Chim. si ing. med.* 2008; **53**:1-2-22.
16. Li Y., Gao Y., Cao Y., Li H. *Sens. and Actuators.* 2012; **171**:172-726.
17. Mena M. L., Carralero V., González-Cortés A., Yáñez-Sedeño P., Pingarrón J. M. *Int. J. Environ. and Anal. Chem.* 2007; **87**:1-57.
18. Wang M., Li Zh. *Sens. and Actuators.* 2008; **133**:2-607.
19. Zhou J.-H., Deng Ch.-Y., Si Sh.-H., Wang Sh. *Microchim. acta.* 2011; **172**:1-2- 207.
20. Gong J., Miao X., Zhou T., Zhang L. *Talanta.* 2011; **85**:3-1344.
21. Huang B., Zhang W.-D., Chen C.-H., Yu Y.-X. *Microchim. acta.* 2010; **171**:1-2-57.
22. Zeng Y., Yu D., Yu Y., Zhou T., Shi G. *J. Hazardous Mater.* 2012; **217**:218-315.
23. Raghu P., Madhusudana R. T., Kumara S. B. E., Chandrashekar B. N., Reddaiah K., Sreedhar M. *J. Electroanal. Chem.* 2012; **665**:1-76.
24. Mocellini S. K., Vieira I.C., de Lima F., Lucca B. G., Barbosa A. M.J., Ferreira V. S. *Talanta.* 2010; **82**:1-164.
25. Ebrahimi B., Shojaosadati S. A., Daneshgar P., Norouzi P., Mousavi S. M. *Anal.chim.acta.* 2011; **687**:2-168.
26. Moraes F.C., Mascaro L.H., Machado S. A. S., Brett C. M. A. *Talanta.* 2009; **79**:5-1406.
27. Figueiredo-Filho L., Azzi D., Janegitz B., Fatibello-Filho O. *Electroanalysis.* 2012; **24**:2-303.
28. Manisankar P., Sundari A. P., Sasikumar R., Palaniappan S. *Talanta.* 2008; **76**:5-1022.
29. Papp Z. J., Guzsvány V. J., Kubiak S., Bobrowski A., Bjelica L.J. *J. Serb.Chem.Soc.* 2010; **75**:11-681.
30. Vidal L., Chisvert A., Canals A., Psillakis E., Lapkin A., Acosta F., Edler K. J., Holdaway J. A., Marken F. *Anal.chim.acta.* 2008; **616**:1-28.
31. Carrillo I., Quintana C., Esteva A. M., Hernández L., Hernández P. *Electroanalysis.* 2011; **23**:12-2862.
32. Khalilzadeh M. A., Karimi-Maleh H. *Anal. Lett.* 2010; **43**:1-186.
33. Yang D., Zhu L., Jiang X., Guo L. *Sens. and Actuators.* 2009; **141**:1-124.
34. Wang Q., Zheng J., Zhang H. J. *Electroanal. Chem.* 2012; **674**-6.
35. Olsson J., Ivarsson P., Winquist F. *Talanta.* 2008; **76**:1-91.
36. Shikata Y, Tachi, Mem. Coll.Agr.Kyoto Imp.Univ. 1997; **4**:19-234.