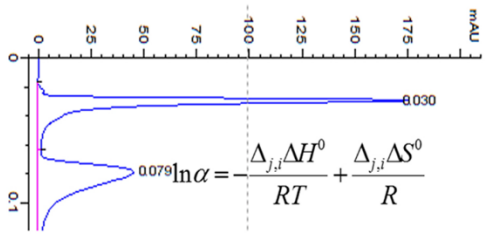
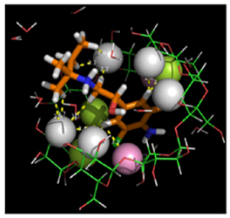


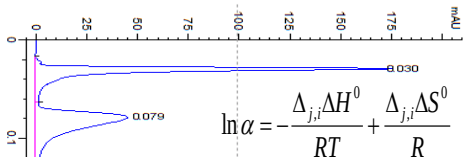


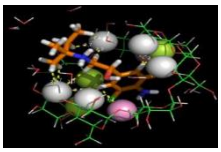
BOOK OF ABSTRACTS

10th Annual Symposium on Physical and Analytical Chemistry

Tbilisi State University
January 3-4, 2020
Tbilisi, Georgia

10th Annual Symposium on Physical and Analytical Chemistry
Tbilisi State University
January 03-04, 2020, Tbilisi, Georgia





10th Annual Symposium on Physical and Analytical Chemistry

Tbilisi State University

January 3-4, 2020

Tbilisi, Georgia

TSU Building 1, Auditorium №115

Scientific Committee

Bezhan Chankvetadze, Chairman	Tbilisi, Georgia
George Bezarashvili	Tbilisi, Georgia
Ramaz Botchorishvili	Tbilisi, Georgia
Jacques Crommen	Liege, Belgium
Salvatore Fanali	Verona, Italy
Tivadar Farkas	Torrance, CA, USA
Jun Haginaka	Nishinomiya, Japan
Alessandra Gentili	Rome, Italy
Vladimir Ioffe	PetachTikwa, Israel
Emmanuelle Lipka	Lille, France
Emirhan Nemutlu	Ankara, Turkey
Sibel A. Ozkan	Ankara, Turkey
Gerhard K.E. Scriba	Jena, Germany
Zuhre Senturk	Van, Turkey
William Tong	San Diego, CA, USA
Bengi Uslu	Ankara, Turkey
Alessandro Volonterio	Milan, Italy

Organizing Committee

Bezhan Chankvetadze, Chairman	Tbilisi, Georgia
Lali Chankvetadze	Tbilisi, Georgia
Izabela Giuashvili	Tbilisi, Georgia
Mehmet Gumustas	Ankara, Turkey
Giorgi Jibuti	Tbilisi, Georgia
Rusudan Kakava	Tbilisi, Georgia
Nunu Labartkava	Tbilisi, Georgia
Iza Matarashvili	Tbilisi, Georgia

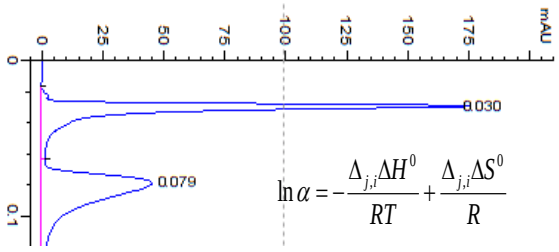
10th Annual Symposium on Physical and Analytical Chemistry
Tbilisi State University
January 03-04, 2020, Tbilisi, Georgia

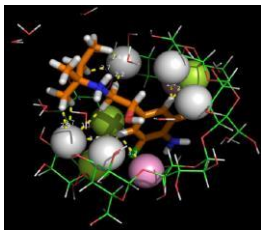
January 3rd, 2020	
10.00-10.10	**Symposium Opening**
10.10-10.30	Our studies on chiral recognition and enantioseparations in 2019 **Bezhan Chankvetadze,** Tbilisi State University, Tbilisi, Georgia
10.30-11.00	Chiral separation by nano-liquid chromatography using silica-based particulate and monolithic columns, **Salvatore Fanali,** University of Verona, Verona, Italy
11.00-11.30	**Symposium photo and coffee break**
11.30-12.00	Recent advances in carbon-based electrochemical nanosensors and biosensors in pharmaceutical and biomedical area **Sibel A. Ozkan**, Ankara University, Ankara, Turkey
12.00-12.30	How do surfactants work in electroanalysis? **Zühre Şentürk**, Van Yüzüncü Yıl University, Van, Turkey
12.30-13.00	Nanomaterial-based electrochemical sensors in drug analysis **Bengi Uslu,** Ankara University, Ankara, Turkey
13.00-14.00	**Lunch**
14.00-14.30	The trifluoroethylamine function as hydrolytically stable peptide bond surrogate **Alessandro Volonterio,** Politecnico di Milano, Milan, Italy
14.30-15.00	Chromatography in metabolomics analysis **Emirhan Nemutlu,** Hacettepe University, Ankara, Turkey
15.00-15.20	Synthetic approach to poly[3-93,4-dihydroxyphenyl)glyceric acid]-biopolymer from boraginaceae family **Maia Merlani,** Department of Plant Biopolymers, Kutateladze Institute of Pharmacochemistry, TSMU, Tbilisi, Georgia
15.20-15.40	Nanocomposite based electrochemical sensor for the quantification of antibiotic drug nadifloxacin in aqueous media **Nurgul K. Bakirhan,** University of Health Science, Ankara, Turkey
15.40-16.00	Thermal inhibition of flame propagation **George Bezarashvili**, Tbilisi State University, Tbilisi, Georgia
16.00-16.30	**Coffee break**
16.30-17.00	Laquinimod sodium capsules, 0.6mg: analysis of a foreign „small capsule“ in a container of a batch for clinical supply **Vladimir Ioffe,** Teva Pharmaceuticals, Petach Tikwa, Israel

17.00-17.20	Content of copper and some other microelements in soils and wines of Kakheti viticulture zone **Nunu Labartkava,** Tbilisi State University, Tbilisi, Georgia
17.20-17.40	Electrochemical sensors and biosensors prepared by molecular imprinting **Burcin Bozal-Palabiyik,** Ankara University, Ankara, Turkey
17.40-18.00	Structure determination of some heterocyclic compounds with advanced NMR techniques **Cigdem Karaaslan,** Ankara University, Ankara, Turkey
18.30-20.30	**Symposium Dinner**
	January 4th, 2020
09.00-09.30	Deep learning and numerical partial differential equations for smart measurements of air pollution with low-cost sensors **Ramaz Botchorishvili,** Kutaisi International University, Kutaisi, Georgia
9.30-10.00	Air sampling and pollution sensing research at SMART|AtmoSim_LAB **Giorgi Jibuti,** Tbilisi State University, Tbilisi, Georgia
10.00-10.25	New strategies in electrochemical approach of DNA-drug interactions **Burcu Dogan Topal,** Ankara University, Ankara, Turkey
10.25-10.50	Synthesis of some chiral cyclic sulfoxides **Rusudan Kakava,** Tbilisi State University, Tbilisi, Georgia
10.50-11.20	Recent studies on the development of analytical methods for achiral and chiral separations, **Mehmet Gumustas,** Ankara University, Ankara, Turkey
11.20-11.50	**Coffee break**
11.50-12.10	A novel electrochemical nanosensor based on NH2 –functionalized MWCNTS with gold nanoparticles for the sensitive determination of antipsychotic amisulpride **Goksu Ozcelikay,** PhD student, Ankara University, Ankara, Turkey
12.10-12.30	Comparative study of cellulose tris(3-chloro-5-methylphenylcarbamate) coated or covalently immobilized on silica for separation of enantiomers in high-performance liquid chromatography **Tamar Khatiashvili,** PhD student, Tbilisi State University, Tbilisi, Georgia
12.30-12.50	Enantioselective analysis of citalopram enantiomers with multiwalled carbon nanotube-C4-modified carbon paste electrode using adsorbtive stripping square wave voltammetry **Leyla Karadurmus,** PhD student, Adıyaman University, Adıyaman, Turkey and Ankara University, Ankara, Turkey

13.00-14.00	**Lunch**
14.00-14.20	Separation of enantiomers of newly synthesized chiral sulfoxide derivatives with supercritical fluid chromatography **Kenan Can Tok,** PhD student, Ankara University, Ankara, Turkey
14.20-14.40	Benchmarking source isotopic ratios of levoglucosan to better constrain the contribution of different wood-containing fuels to the air pollution **Nana Khundadze,** PhD student, Tbilisi State University, Tbilisi, Georgia
14.40-15.00	The effect of a chiral selector content and column internal diameter on separation of enantiomers with polysaccharide-based superficially porous and fully porous chiral stationary phases **Salome Pantsulaia,** PhD student, Tbilisi State University, Tbilisi, Georgia
15.00 – 15.15	Comparative evaluation of atmospheric pollution sensors with laboratory equipments **Ana Chelidze,** BS student, Tbilisi State University, Tbilisi, Georgia
15.15-15.30	Thermodynamic study of separation of fenoprofen enantiomers using amylose tris(3,5-dimethylphenycarbamate) coated on silica in high-performance liquid chromatography **Aluda Chelidze,** MS student, Tbilisi State University, Tbilisi, Georgia
15.30 -15.45	Thermodynamic study of separation of ibuprofen enantiomers using amylose tris(3,5-dimethylphenycarbamate) coated on silica in high-performance liquid chromatography **Gizo Dolidze,** MS student, Tbilisi State University, Tbilisi, Georgia
15.45 -16.00	Enantioseparation of some phenothiazine derivatives in high-performance liquid chromatography using acetonitrile as a mobile phase **Sandro Gogia,** BS student, San Diego State University-Georgia, Chemistry/Biochemistry Program
16.00-16.15	Enantioseparation of some phenothiazine derivatives in high-performance liquid chromatography using methanol as a mobile phase **Ani Rukhadze,** BS student, San Diego State University-Georgia, Chemistry/Biochemistry Program
16.15-16.30	Thermodynamic study of separation ketoprofen enantiomers using amylose tris(3,5-dimethylphenycarbamate) coated on silica in high-performance liquid chromatography **Giorgi Kobidze,** MS student, Tbilisi State University, Tbilisi, Georgia
16.30 -17.00	**Coffee break**
17.00-17.10	**Closing of the Symposium**

PLENARY LECTURES





10th Annual Symposium on Physical and Analytical Chemistry
Tbilisi State University
January 3-4, 2020
Tbilisi, Georgia

10th Annual Symposium on Physical and Analytical Chemistry
Tbilisi State University
January 03-04, 2020, Tbilisi, Georgia

OUR STUDIES ON CHIRAL RECOGNITION AND ENANTIOSEPARATIONS IN 2019

Bezhan Chankvetadze

[2]*Institute of Physical and Analytical Chemistry, Molecular Recognition and Separation Science Laboratory, School of Exact and Natural Sciences, Tbilisi State University, Tbilisi, Georgia*

In this presentation our research results on chiral recognition and enantioseparations published in 2019 are shortly summarized. References 1, 5 and 8 are book chapters and review papers summarizing various aspects of chiral recognition and enantioseparations in high-performance liquid chromatography (HPLC) and capillary electrophoresis (CE). Reference 2 deals with enantioseparations of native amino acids with polysaccharide-based chiral columns in supercritical fluid chromatography (SFC). Reference 3 describes separation of brombuterol enantiomers in CE and explains structural mechanisms of chiral recognition based on nuclear magnetic resonance (NMR) spectroscopy. References 4 and 6 deal with thermodynamic description of enantioseparation process in HPLC with polysaccharide-based chiral columns and explanation of some unusual observations in this field. Reference 7 describes application of novel polysaccharide-based chiral stationary phase in nano liquid chromatography and capillary electrochromatography (CEC) while reference 9 describes separation of enantiomers of novel chiral sulfoxides in HPLC.

References:

[1] B. Chankvetadze, Enantioseparations by High Performance Liquid Chromatography Using Polysaccharide-Based Chiral Stationary Phases – An Overview, (Chapter 6) in G. Scriba (Ed-r) Chiral separations, 3rd Edn, Springer, 2019, 93-126.

[2] E. Lipka, A-E. Dascalu, Y. Messara, E. Tsutsqiridze, T. Farkas, B. Chankvetadze, Separation of enantiomers of native amino acids with polysaccharide-based chiral columns in supercritical fluid chromatography, J. Chromatogr. A, 1585 (2019) 207–212.

[3] A. Gogolashvili, E. Tatunashvili, L. Chankvetadze, T. Sohajda, M. Gumustas, S. Ozkan, A. Salgado, B. Chankvetadze, Separation of brombuterol enantiomers in capillary electrophoresis with cyclodextrin-type chiral selectors and investigation of structure of selector-selectand complexes by using nuclear-magnetic resonance spectroscopy, Electrophoresis 40 (2019) 1904-1912.

[4] I. Matarashvili, G. Kobidze, A. Chelidze, G. Dolidze, N. Beridze, T. Farkas, B. Chankvetadze, The effect of temperature on separation of enantiomers with coated and covalently immobilized polysaccharide-based chiral stationary phases, J. Chromatogr. A, 1599 (2019) 172-179.

[5] S. Fanali, B. Chankvetadze, Some thoughts about enantioseparations in capillary electrophoresis, Electrophoresis, 40, 2019, 2420-2437.

[6] M. Maisuradze, G, Sheklashvili, A. Chokheli, I. Matarashvili, T. Gogatishvili, T. Farkas, B. Chankvetadze, Chromatographic and thermodynamic comparison of amylose tris(3-chloro-5-methylphenylcarbamate) coated or covalently immobilized on silica in high-performance liquid chromatographic separation of the enantiomers of select chiral weak acids, J. Chromatogr. A 1602 (2019) 228-236.

[7] G. D' Orazio, C. Fanali, A. Gentili, S. Fanali, B. Chankvetadze, Comparative study on enantiomer resolving ability of amylose tris(3-chloro-5-methylphenylcarbamate) covalently immobilized onto silica in nano-liquid chromatography and capillary electrochromatography, J. Chromatogr. A 1606 (2019) 460425 (8pp).

[8] B. Chankvetadze, Recent trends in preparation, investigation and application of polysaccharide-based chiral stationary phases for separation of enantiomers in high-performance liquid chromatography, Trends in Analytical Chemistry, 122 (2020) 115709 (13pp).

[9] Z. Shedania, R. Kakava, A. Volonterio, T. Farkas, B. Chankvetadze, Separation of enantiomers of chiral sulfoxides in high-performance liquid chromatography with polysaccharide-based chiral selectors and aqueous-acetonitrile as mobile phase, J. Chromatogr. A, in press.

10th Annual Symposium on Physical and Analytical Chemistry
Tbilisi State University
January 03-04, 2020, Tbilisi, Georgia

CHIRAL SEPARATION BY NANO-LIQUID CHROMATOGRAPHY USING SILICA-BASED PARTICULATE AND MONOLITHIC COLUMNS.

Salvatore Fanali[1], B. Chankvetadze[2], Z. Jiang[3], G. D'Orazio[4], C. Fanali[5], A. Gentili[6]

[1]*Teaching Committee Ph.D. School in Natural Science and Engineering, Univeristy of Verona, Verona, Italy*
[2]*Institute of Physical and Analytical Chemistry, Tbilisi State University, Tbilisi, Georgia*
[3]*Institute of Pharmaceutical Analysis, College of Pharmacy, Jinan University, Guangzhou, China*
[4]*Istituto per i Sistemi Biologici (ISB),CNR-Consiglio Nazionale delle Ricerche, Monterotondo, Italy*
[5]*University CampusBio-Medico of Rome, Rome, Italy*
[6]*Department of Chemistry, Università La Sapienza, Rome, Italy*

Nano-liquid chromatography (nano-LC) is an analytical technique used for the separation and determination of a large number of compounds including proteins, peptides, drugs, nutraceuticals, herbicides, phytochemicals, enantiomers, etc. Compounds are separated, after injection, into capillary columns containing a selected stationary phase (SP). According to the column type, three different modes can be employed: particulate, monolithic and open-tubular nano-LC. Mobile phase (MP) flow-rates in the range nL-μL/ min are usually involved depending by the capillary dimension and the type of the SP and mode. On-column UV detectors or mass spectrometry (MS) are frequently employed and appropriate pumping, injection, tube connections, and detection cell must be used in order to minimize the band-broadening effect [1].

Enantiomers are important compounds exhibiting quite similar physical-chemical properties due to the similar chemical structure. Therefore, they cannot be separated in an achiral environment. However, the use of a chiral SP (CSP) could be effective to achieve their resolution.

A significant number of chiral selectors (CSs) have been used in high-performance liquid chromatography (HPLC) and also in nano-LC. Among them, proteins, modified crown-ethers, cyclodextrins, polysaccharides, glycopeptides antibiotics are the most employed.

In this presentation the main features of nano-LC, the instrumentation currently employed will be presented. In addition, method optimization, considering the type of column (particulate or monolithic), mobile phase composition etc., will also be discussed. Some examples, employing amylose [2] or vancomycin [3] bonded to silica particles or monolithic material, will be presented.

References

[1] G. D'Orazio, C. Fanali, M. Asensio-Ramos, S. Fanali. Chiral separations in food analysis. TrAC-Trends Anal. Chem. 96 (2017) 151-171.

[2] G. D'Orazio, C. Fanali, S. Fanali, A. Gentili, B. Chankvetadze. Comparative study on enantiomer resolving ability of amylose tris(3-chloro-5-methylphenylcarbamate) covalently immobilized onto silica in nano-liquid chromatography and capillary electrochromatography. J. Chromatogr. A 1606 (2019) 460425.

[3] D. Xu, H. Shao, R. Luo, Q. Wang, E. Sanchez-Lopez, S. Fanali, Z. Jiang, M. L. Marina. A facile and efficient Single-step approach for the fabrication of vancomycin functionalized polymer-based monolith as chiral stationary phase for nano-liquid chromatography. J. Chromatogr. A 1557 (2018) 43-50.

10th Annual Symposium on Physical and Analytical Chemistry
Tbilisi State University
January 03-04, 2020, Tbilisi, Georgia

RECENT ADVANCES IN ELECTROCHEMICAL CARBON BASED NANOSENSORS AND BIOSENSORS IN PHARMACEUTICAL AND BIOMEDICAL AREA

Sibel A. Ozkan

Ankara University, Faculty of Pharmacy, Department of Analytical Chemistry, 06100 Ankara, Turkey

A sensor is a device that detects and responds to some type of input from the physical environment. The specific input could be voltage, light, or any one of a great number of other environmental phenomena. The sensor can be convert the measurement into a readable signal.

For electroanalytical sensor technologies, nanomaterials are mostly used for creating a biosensor, biomarker or nanosensor. In recent years, sensor technology with its wide applications has become very popular in the biomedical and pharmaceutical area. Sensor technology covers the synthesizing and using nanomaterials at the level of atoms, molecules, biomolecules and supramolecular structures. Nano-sized materials can give sensor beneficial properties from analytical perspectives.

Electrochemical approaches are useful for sensor technology since one atom level electrochemical change can be followed using electrochemical methods, such as cyclic voltammetry, differential pulse, square wave, adsorptive stripping voltammetry etc. Sensor studies provide an overview of some of the important and recent developments brought about by the application of carbon-based nanostructures to nanotechnology for both chemical and biological sensor development and their application in pharmaceutical and biomedical area.

Nanoscience is simply science and engineering carried out on the nanometer scale, that is, 10^{-9} meters. In the past two decades, researchers began developing the ability to manipulate matter at the level of single atoms and small groups of atoms and to characterize the properties of materials and systems at that scale. Electrochemical nanosensors have recently found extensive applications in pharmaceutical and biomedical industries with some advantages such as lower detection limits, wider linear response range, sensitivity, good stability and reproducibility when compared with other sensors and techniques. As the demand for smaller, , cheaper, and ultrasensitive qualification and quantification of samples rapidly increases, these methods provide a viable path toward the next generation of electrochemical sensors.

Nowadays, different analytical methods are used in environmental, pharmaceutical, or clinical laboratories and a number of the commercial point-of-care devices work using nanosensors. Electroanalytical biosensors and/or biomarkers are analytical devices that convert a biological response into an electrical signal. Biosensors have been applied in many fields namely food industry, Pharmaceutical industry, medical field, marine sector etc. Various types of biosensors being used are enzyme-based, immunosensors, DNA biosensors, and thermal and piezoelectric biosensors. They provide better stability and sensitivity as compared with the traditional methods. In the early stages of some diseases, trace levels of biomarkers exist in the cells and in the body fluids. Hence, it is very important to develop credible and sensitive detection tests. Commonly, new detection technologies need to be clearly sensitive than the current technologies to be seriously investigated for adoption. Therefore, electroanalytical biomarker studies and strategies for using different nanomaterials are continuously being verified, developed and utilized to increase the sensitivity of biomarkers determination in the body fluids and tissues.

Electrochemical biosensors and nanosensors have recently found extensive applications in pharmaceutical and biomedical industries with some advantages such as sensitivity, good stability and reproducibility when compared with other sensors. As the demand for smaller, faster, cheaper, and ultrasensitive quantification of samples rapidly increases, these methods provide a viable path toward the next generation of electrochemical sensors. Nowadays, many different analytical methods are used in environmental, pharmaceutical, or clinical laboratories and a number of the commercial point-of-care devices work using sensors.

10th Annual Symposium on Physical and Analytical Chemistry
Tbilisi State University
January 03-04, 2020, Tbilisi, Georgia

HOW DO SURFACTANTS WORK IN ELECTROANALYSIS?

Zühre Şentürk

Department of Analytical Chemistry, Faculty of Science, Van Yüzüncü Yıl University, Van, Turkey

Surfactants also known as surface active agents are amphiphilic compounds that contain two parts. One of them is hydrophobic tail group that consists of hydrocarbon chain or poly-ether, and another is hydrophilic head group which may be positive, negative, neutral or zwitterionic.

These structures form the ″heart″ of several electrochemical applications, such as electroplating, corrosion, fuel cells, electrocatalysis, and electroanalysis, and perform many different roles in these processes.

The molecular structure of surfactants means that they have unusual characteristic features. The properties of these compounds can be categorized into two types.

One of them is their adsorption at the interface between air and liquid, liquid (e.g. oil) and liquid (e.g. water) or solid and liquid. The adsorption of surfactants at solid-liquid interfaces is a transfer process from bulk solution phase to the surface/interface, which is considerably more complex than at two other interfaces. This phenomenon of surfactants can modify and control the hydrophobicity, surface charge, and other key properties of the solid. For each surfactant–solid surface, adsorption mechanism depends on the nature of solid, surfactant type, surfactant concentration, electrolyte, pH, etc.

Self-assembly of surfactant is the other property that surfactant molecules have of being able to self-associate in polar solvents such as water, thus forming different types of aggregates and structures of colloidal dimensions.

A better understanding the nature of surfactant adsorption and self-assembly is required for their extraordinary applications not only in electrochemistry (e.g. the modification of electrochemical sensors) but also in many technological and industrial processes, such as cosmetics, drug delivery, detergency, corrosion inhibition, dispersion/flocculation, oil recovery, nanolithography and so on. However, it is interesting to note that little work has been carried out for this purpose [1].

In view of the above knowledge, this presentation will be focused on the beneficial use of surfactants in voltammetric analysis, and some analytical applications performed by our research group [2-4].

References

[1] G.K. Ziyatdinova, E.R. Ziganshina, H.C. Budnikov. Application of surfactants in voltammetric analysis. J. Anal. Chem. 67 (2012) 869-879.

[2] N. Alpar, Y. Yardım, Z. Şentürk. Voltammetric sensing of triclosan based on the enhancement effect of the cationic surfactant at cathodically pretreated boron-doped diamond electrode. Int. J. Environ. Anal. Chem. 98 (2018) 1226-1241.

[3] P. Talay Pınar, Y. Yardım, Z. Şentürk. Electrochemical oxidation of ranitidine at poly(dopamine) modified carbon paste electrode: Its voltammetric determination in pharmaceutical and biological samples based on the enhancement effect of anionic surfactant. Sens. Actuat. B: Chem. 273 (2018) 1463-1473.

[4] Y. Yardım, A. Levent, E. Keskin, Z. Şentürk. Voltammetric behavior of benzo[*a*]pyrene at boron-doped diamond electrode: A study of its determination by adsorptive transfer stripping voltammetry based on the enhancement effect of anionic surfactant, sodium dodecylsulfate. Talanta 85 (2011) 441-448.

NANOMATERIAL BASED ELECTROCHEMICAL SENSORS

Bengi Uslu, Burcin Bozal-Palabiyik

Ankara University, Faculty of Pharmacy, Department of Analytical Chemistry

Electrochemical methods have easy application procedures. Analytes can be directly analysed from their matrix sample without any pretreatment steps such as purification, evaporation or extraction. Voltammetric detection provides a highly sensitive way to the electroanalysis of a wide area of analytes. On the other hand, because of the interference from the other redox active molecules, which may pass on electrolysis at similar potentials to the target species in the medium, this approach can sometimes be bounded by limitations of selectivity.

Nanomaterials are new class of materials, which provide a great potential for improving the performance of electrochemical sensing systems and extend their applications in various field of material sciences and biomedical sciences between others. Nanomaterials display physical properties such as adsorption, surface modification and catalytic features, which are different from bulk properties of the same materials.

Carbon nanotubes (CNTs) are commonly used nanomaterials at nanosensor development for quantification of analytes. CNTs based nanosensors have many advantages such as fast response time, high sensitivity, catalytic effect, reusability, resistance to surface fouling and etc.

For the production of nanocomposites, metal nanoparticles have been widely used for decades. Large surface-to-volume ratio, good electrical properties, strong adsorption ability, high surface reaction activity, small particle size and good surface properties have been mentioned for these materials in the literature. Recent developments in the improvements of electrochemical biosensors based on a wide variety of nanostructures, such as non-porous metals, nanotubes, and oxide nanomaterials.

In this study sensitive and selective electroanalytical methods were developed for the determination of vardenafil [1], oxymetazoline [2], desloratadine [3] and levocetirizine [4] at different modified electrodes. All results showed that the modified electrodes significantly enhanced the oxidation peak current of pharmaceutical compounds. Experimental conditions such as pH, scan rate, amount of nanoparticles, accumulation time and potential were optimized for assay. All methods were validated.

All modified electrodes showed good stability and reproducibility and they were successfully applied to the sensitive and selective determination of related pharmaceutical compounds in their dosage forms.

References

[1] E. Demir, B. Bozal-Palabiyik, B. Uslu et al. Voltammetric determination of vardenafil on modified electrodes constructed by graphite, metal oxides and functionalized multi-walled carbon nanotubes. Rev. Roum. Chim. 64(1) (2019) 45-54.

[2] A. Munir, B. Bozal-Palabiyik, A. Khan, et al. A novel electrochemical method for the detection of oxymetazoline drug based on MWCNTs and TiO_2 nanoparticles. J. Electroanal. Chem. 844 (2019) 58-65.

[3] K. Ozturk, N.K. Bakirhan, S.A. Ozkan, S.A. et al. Effect of catalytically active zinc oxide-carbon nanotube composite on sensitive assay of desloratadine metabolite. Electroanalysis (in press).

[4] K. Ozturk, N.K. Bakirhan, S.A. Ozkan, S.A. et al. Sensitive detection of levocetirizine as a new generation antihistamine by stripping square wave voltammetry. Curr. Pharm. Anal. (in press).

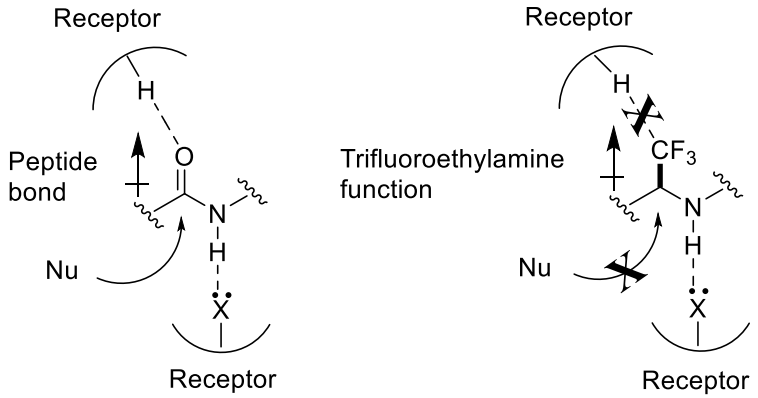
10th Annual Symposium on Physical and Analytical Chemistry
Tbilisi State University
January 03-04, 2020, Tbilisi, Georgia

THE TRIFLUOROETHYLAMINE FUNCTION AS HYDROLYTICALLY STABLE PEPTIDE BOND SURROGATE.

Alessandro Volonterio

Department of Chemistry, Material, and Chemical Engineering, Politecnico di Milano, via Mancinelli 7, 20131 Milano, Italy.

In the last decades, there was a growing interest for the use of peptides in the pharmaceutical industry. However, peptide-based drug development has often been hindered by peptides short plasma half-lives and poor oral bioavailability. Consequently, there is rising concern in the design and synthesis of peptidomimetics which mimic the structure and biological features of native peptides while possessing better drug-like properties. In this contest, the stereogenic trifluoroethylamine function[1] is a conceptually new peptide bond surrogate that has found the first validation in drug discovery thanks to the highly potent and metabolitically stable Cathepsin K inhibitor Odanacatib, which reached Phase III clinical trials for the therapy of postmenopausal osteoporosis.[2]



This function was first proposed by our research group, and was used to replace both a glycine amide bond and a malonamide of a partially modified retro (PMR) peptides in the synthesis of PMR Ψ[NHCH(CF_3)]Gly-peptides.[3] A few years later, we have described a significant advancement of our project, consisting in the stereocontrolled synthesis and the conformation analysis of a new class of peptidomimetics, much closer to natural peptides, having the trifluoroethylamine unit as a natural peptide bond surrogate, i.e. the Ψ[CH(CF_3)NH]Gly-peptides.[4] In this communication, the story of trifluoroethylamine bond surrogate, as well as new recent applications, will be presented.

[1] Sani, M.; Volonterio, A.; Zanda, M. *ChemMedChem*. **2007**, *2*, 1693-1700.
[2] Black, W. C., et al. *Bioorg. Med. Chem. Lett.* **2008**, *18*, 923-928.
[3] Volonterio, A.; Bellosta, S.; Bravin, F.; Bellucci, M. C.; Bruché, L.; Colombo, G.; Malpezzi, L.; Mazzini, S.; Meille, S. V.; Meli, M.; Ramirez de Arellano, C.; Zanda, M. *Chem. Eur. J.* **2003**, *9*, 4510-4522.
[4] Molteni, M.; Bellucci, M. C.; Bigotti, S.; Mazzini, S.; Volonterio, A.; Zanda, M. *Org. Biomol. Chem.* **2009**, *7*, 2286-2296.

10th Annual Symposium on Physical and Analytical Chemistry
Tbilisi State University
January 03-04, 2020, Tbilisi, Georgia

CHROMATOGRAPHY IN METABOLOMIC ANALYSIS

Cemil Can Eylem, Tuba Reçber, Ayşegül Doğan, Sedef Kır, Emirhan Nemutlu

Hacettepe University Faculty of Pharmacy Department of Analytical Chemistry Sıhhiye Ankara, 06100 enemutlu@hacettepe.edu.tr

Metabolomics is the identification and quantification of small molecules (metabolites) (<1000 Da) in a tissue or body fluid. Simultaneous and extensive fingerprint analysis of a large number of metabolites is required to exclude metabolic profiling of the disease. Changes in metabolite amounts are due to genetic or environmental factors as well as cellular and systemic variations from diseases, medicines, toxins and lifestyle. Analytical platforms developed to monitor these variations can be provided by the use of comprehensive analysis of hundreds of metabolites from complex biological samples (serum, urine, saliva, etc.). Thus, metabolomics has become increasingly used in the diagnosis of diseases, in response to treatment, and in the discovery of new biomarkers. For a comprehensive characterization of metabolic networks and functions, the concentrations of metabolites must be determined. Analyzes of metabolites that exhibit large physical and chemical differences (polar / apolar, acid / base, etc.) can not be performed with a single analytical method. The most widely used methods for the analysis of metabolomics are mass spectroscopy combined with liquid or gas chromatography. All two methods have different advantages over each other in terms of sensitivity, coverage and efficiency. While the number of metabolites that can be identified by GC-MS is around 100, this figure can be reached 300 by LC-MS. Although the dynamic ranges and separation mechanisms of the devices are different, it is generally possible to analyze about thirty metabolites in both systems. Generally, GC-MS is used to detect polar metabolites, especially sugar derivatives, while LC-MS is better for the analysis of apolar metabolites such as lipid. In this study, starting from sample preparation of samples to analysis and data handling and evaluation are compared for different chromatographic method used in metabolomics studies.

Keywords: Metabolomics, Chromatography, gas chromatography, liquid chromatography

10th Annual Symposium on Physical and Analytical Chemistry
Tbilisi State University
January 03-04, 2020, Tbilisi, Georgia

THERMAL INHIBITION OF FLAME PROPAGATION

George Bezarashvili

Institute of Physical and Analytical Chemistry, Molecular Recognition and Separation Science Laboratory, School of Exact and Natural Sciences, Tbilisi State University, Tbilisi, Georgia

The presented work is devoted to the important problem for modern fire-fighting: modeling of the inhibition of flame by the particles of inorganic salts. The main goal of the work was to answer the question if the effect of flame cooling (thermal inhibition) by mentioned particles contribute significantly in the process of flame propagation suppression. The inhibition of the combustion of simplest hydrocarbon - methane by the particles of sodium chloride of various size was selected as the model process. The velocities of heat release in the flame zone and of heat transfer to the cooling particles from the flame zone were calculated theoretically. The ratio of these velocities was taken as the quantitative measure of the efficiency of cooling action of solid particles. Numerical integration of appropriate functions was carried out by Simpson method. The results obtained show that the sufficiently large part of heat energy, released in combustion zone, is transferred to the solid particles and is not consumed for the flame further propagation, hindering the combustion process. Consequently, besides the chemical inhibition, thermal effects must be taken into account in the course of the study of complex process of the extinguishing of combustion reaction.

10th Annual Symposium on Physical and Analytical Chemistry
Tbilisi State University
January 03-04, 2020, Tbilisi, Georgia

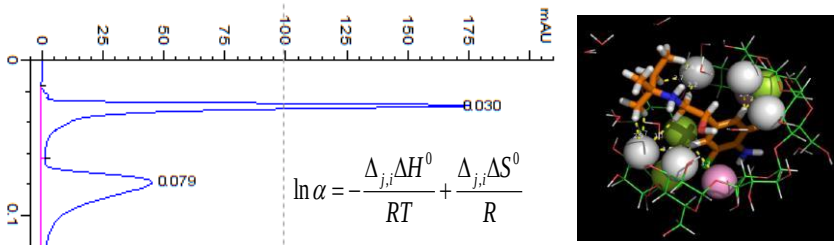
LAQUINIMOD SODIUM CAPSULES, 0.6 MG: ANALYSIS OF A FOREIGN "SMALL CAPSULE" FOUND IN A CONTAINER OF THE BATCH FOR CLINICAL SUPPLY

Shiri Zigman, Liron Sulimani, Vladimir Ioffe

Analytical Development, Global R&D, Teva Pharmaceutical Industries, Ltd., Kfar Saba, Israel

One "small capsule", different by its size and weight, was found among "bigger", regular capsules of Laquinimod, 0.6 mg, in one of the bulk containers at a Laquinimod clinical trials site in Europe. A real "detective story" occurred, to understand what it may be and how it came to the Teva's bulk container. All we had – just 61 mg of "white powder" removed from this suspicious object. Comparative analysis of the content of a foreign "small capsule" and the regular capsule was performed, based on in-house HPLC methods using tandem UV and MS detection. It was found, that this capsule contained an unknown API, very similar by its structure and properties to Fingolimod (Gilenya® of Novartis). Chemical structure of this API has been established. Its possible manufacturer has also been uncovered.
Important results of this investigation:
A concern about batch mixing at Jerusalem facility of Teva (as the major GMP violation) has been removed
A new, earlier unknown to Teva, competitor in the field of oral MS treatment has been revealed

KEYNOTE LECTURES



10th Annual Symposium on Physical and Analytical Chemistry
Tbilisi State University
January 3-4, 2020
Tbilisi, Georgia

10th Annual Symposium on Physical and Analytical Chemistry
Tbilisi State University
January 03-04, 2020, Tbilisi, Georgia

SYNTHETIC APPROACH TO POLY[3-(3,4-DIHYDROXYPHENYL)GLYCERIC ACID] –BIOPOLYMER FROM BORAGINACEAE FAMILY

Maia Merlani[1], *Vakhtang Barbakadze*[1], *Tamaki Nakano*[2], *Bezhan Chankvetadze*[3]

[1]*Department of Plant Biopolymers, Kutateladze Institute of Pharmacochemistry, TSMU, Tbilisi, Georgia*
[2]*Institute for Catalysis (ICAT) and Graduate School of Chemical Sciences and Engineering, Hokkaido University, Japan*
[3]*Institute of Physical and Analytical Chemistry, School of Exact and Natural Sciences, Tbilisi State University, Tbilisi, Georgia*

Poly[3-(3,4-dihydroxyphenyl)glyceric acid] (PDPGA) (Fig. 1), isolated from different species of Boraginaceae family: *Symphytum asperum (SA), S.caucasicum (SC), S.officinale (SO), S.grandiflorum (SG)* and *Anchusa italica (AI)* exhibits high wound healing and anticancer activity [1,2]. The repeating unit of PDPGA is 3-(3',4'-dihydroxyphenyl)glyceric acid (DHPGA) residue (Fig. 2). Moreover, it was found, that most of the carboxylic groups of PDPGA from *AI* and *SG* are methylated.

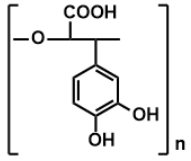


Fig.1. PDPGA

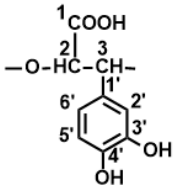


Fig.2. DHPGA

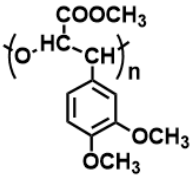
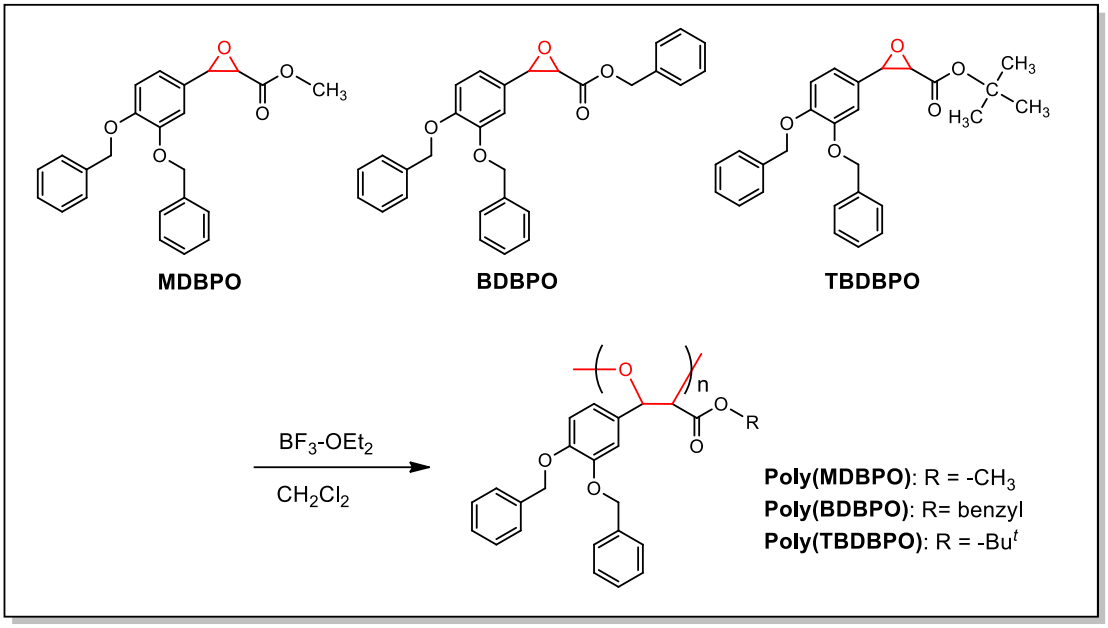


Fig. 3. Poly(MCDMPO)

We have recently reported the synthesis and cationic polymerization of 2-methoxycarbonyl-3-(3,4-dimethoxyphenyl)oxirane (MDMPO) as an unsymmetrically 2,3-disubstituted oxirane monomer [3]. In spite of the bulky structure, MDMPO was found to yield a polyether- poly(MCDMPO) (Fig. 3) and the resulting polymer had a rather stiff conformation leading to intramolecular charge-transfer (ICT) interactions. Methylated analogue of PDPGA- poly(MCDMPO) does not show anticancer activity [4].

The goal of present work was to obtain synthetic analogues of PDPGA by ring open polymerization of oxiranes**:** 2-methoxycarbonyl-3-(3,4-dibenzyloxyphenyl)oxirane (MDBPO), 2-benzyloxycarbonyl-3-(3,4-dibenzyloxyphenyl)oxirane (BDBPO), and 2-*t*-butyloxycarbonyl-3-(3,4-dibenzyloxyphenyl)oxirane (TBDBPO) using BF_3-OEt_2 in CH_2Cl_2 (scheme 1). The monomers smoothly led to the corresponding polyethers under the cationic conditions in spite of their rather bulky structures. The obtained polymers exhibited characteristic UV spectra with ICT bands, and the relative intensity of the ICT bands was highest for poly(TBDBPO) having bulky *t*-butyl ester group. These spectral features are considered to have connection (to be caused?) with rigidity of polymer chain. Poly(TBDBPO) having the bulkiest side-chain group may possess the most rigid chain conformation which can account for its strongest ICT interactions which may occur between the carbonyl group and the phenyl group directly attached to the main chain forming hetero p-stacked structure. The proposed rigid chain conformation of poly(TBDBPO) was supported by the fact that the polymer did not show clear T_g while the other two polymers did.



Scheme 1. Structures of the bulky 2,3-disubstituted oxirane monomers (MDBPO, BDBPO, TBDBPO), and corresponding polymers.

Acknowledgements

This work was supported in part by MEXT/JSPS KAKENHI Grant Number JP 19H02759 and in part by the MEXT program of the Integrated Research Consortium on Chemical Sciences (IRCCS).

References

[1] S.Shrotriya, G.Deep et al. Poly[3-(3, 4-dihydroxyphenyl) glyceric acid] from Comfrey exerts anti-cancer efficacyagainst human prostate cancer via targeting androgen receptor, cell cycle arrest and apoptosis. Carcinogenesis. 33 (2012) 1572-1580.

[2] V.Barbakadze, K.Mulkijanyan et al. Allantoin- and pyrrolizidine alkaloids-free wound healing compositions from *Symphytum asperum*. Bull. Georg. Natl. Acad. Sci. 3 (2009), N 1, 159-164.

[3] M. Merlani, Y. Koyama et al. Ring-opening polymerization of a 2,3-disubstituted oxirane leading to a polyether having a carbonyl–aromatic π-stacked structure. Polym. Chem. 6 (2015) 1932-1936.

[4] M.Merlani, V.Barbakadze, et al. Synthesis of new dihydroxylated derivatives of ferulic and isoferulic acids. Bull. Georg. Natl. Acad. Sci. 12 (2018) N 4, 119-123

10th Annual Symposium on Physical and Analytical Chemistry
Tbilisi State University
January 03-04, 2020, Tbilisi, Georgia

NANOCOMPOSITE BASED ELECTROCHEMICAL SENSOR FOR THE ELECTROCHEMICAL QUANTIFICATION OF ANTIBIOTIC DRUG NADIFLOXACIN IN AQUEOUS MEDIA

Saima Aftab[1, 2], Nurgul K. Bakirhan[3], Afzal Shah[4], Sibel A. Ozkan[1]*

1Ankara University, Faculty of Pharmacy, Department of Analytical Chemistry, Tandogan, Ankara, Turkey
2Department of Chemistry, Quaid-i-Azam University, Islamabad, 45320, Pakistan
3University of Health Science, Gulhane Faculty of Pharmacy, Department of Analytical Chemistry, Etlik, Ankara
4Department of Chemistry, College of Science, University of Bahrain, Sakhir 32038, Bahrain

An electrochemical sensor is described for the determination of nadifloxacin (NF). A glassy carbon electrode (GCE) was modified with amino-functionalized multiwalled carbon nanotubes and titanium dioxide nanoparticles. The modified GCE was characterized by electrochemical impedance spectroscopy, cyclic voltammetry and scanning electron microscopy. The electro-oxidation of NF follows a pH-dependent irreversible behavior. The effects of pH value, scan rate, supporting electrolyte, accumulation potential and accumulation time were optimized. Under optimum conditions and at a typical working potential of 600 mV (vs. Ag/AgCl), the adsorptive stripping voltammetric response is linear in the 5 nM to 5.0 µM NF concentration range. The limit of detection is 1.69 ×10−10 M in acidic solution of pH 1. The selectivity was investigated in the presence of 1 - 1000-fold concentrations of potentially interfering agents. Recoveries from cream formulations spiked with NF were performed to study precision and accuracy.

10th Annual Symposium on Physical and Analytical Chemistry
Tbilisi State University
January 03-04, 2020, Tbilisi, Georgia

CONTENT OF COPPER AND SOME OTHER MICROELEMENTS IN SOILS AND WINES OF KAKHETI VITICULTURE ZONE

Nunu Labartkava, Nino Takaishvili

Department of Physical and Analytical Chemistry, Faculty of Exact and Natural Sciences, Tbilisi State University, Tbilisi, Georgia

The alcoholic drinks have a special place in the humans' food ration and, therefore, in the national economy. Their quality, along with other factors, depends on the content of microelements. Most of microelements play a crucial role in the biochemical processes taking place in the alcoholic drinks. Their content in beverages is limited due to their toxic nature. Copper holds a specific position among microelements contained in the alcoholic drinks.

The main source of copper in the viticulture regions of Georgia is Bordeaux mixture, which is used for chemical spraying of vine.

Our purpose was to define the total copper content and its water-soluble forms in the soils of Kakheti viticulture regions in order to determine their distribution regularity and to make ecochemical assessment of the environment.

Kakheti viticulture zone soils are of neutral-weak alkaline reaction (pH 7.5-7.9). In such area copper ions generate stable immobile hydroxy-complexes and are fixed in the soil. Total copper content in the surveyed samples varies within a range of 35-193 mg/kg and equals 104 mg/kg in average that several times exceeds its Clark (20 mg/kg) and background content in Kakheti soils. It is established that water-soluble copper content in the surveyed samples is small, and varies within 0.8-1.4 mg/kg that is less than maximum permissible concentration (3 mg/kg). As for total iron content in soils it changes within the limits of 2.7-3.4%.

According to results obtained by us copper content in Kakheti viticulture zone wines doesn't exceed 0.5 mg/l (MPC is 1 mg/l). Iron and zinc were determined among the microelements in wines, as well. Their content doesn't exceed maximum permissible concentrations, too. Iron content varies from 0.44 mg/l to 4.38 mg/l (MPC 10 mg/l), and zinc content alters from 1.0 mg/l to 2.9 mg/l (MPC 5 mg/l).

10th Annual Symposium on Physical and Analytical Chemistry
Tbilisi State University
January 03-04, 2020, Tbilisi, Georgia

ELECTROCHEMICAL SENSORS AND BIOSENSORS PREPARED BY MOLECULAR IMPRINTING

Burcin Bozal-Palabiyik, Bengi Uslu
Department of Analytical Chemistry, Faculty of Pharmacy, Ankara University, Ankara, Turkey

One of the greatest challenges of sensing is designing receptors that could recognize the analyte (template/target molecule) in a way to mimic the biological systems. Molecular imprinting can be considered as a relatively novel but promising method to overcome this challenge, since it is used to prepare synthetic polymers with selective recognition sites for the molecule of interest. In doing that it creates artificial recognition sites, which fit with the template molecule in size, shape and spatial arrangement of the functional groups. In this technique, molecularly imprinted polymers (MIPs) are used [1-3]. The MIPs are tailor-made biomimetic structures, having significant advantages such as high affinity and selectivity similar to those of natural receptors, easier preparation; lower cost, and reusability as well as higher stability than the exhibited natural biomolecules [4].

Molecular imprinting has two phases. The first phase, namely polymerization, requires positioning the monomer around the template/target molecule either covalently or non-covalently. The next phase is the removal of the template/target molecule, which resulted in the emergence of a cavity on the polymer surface that matches with the molecule [1].

Since MIPs contribute to increase selectivity during sensing, they have been extensively preferred as recognition element in electrochemical sensors and biosensors, which are used in numerous fields such as biology, biomedicine, biotechnology, medical diagnosis, environmental and health analysis as well as food industry. Another significant advantage of employing MIPs in sensor design is the possibility of analyzing different analytes ranging from small and perilous molecules to biomacromolecules. MIP-based electrochemical sensors and biosensors are easy-to-prepare, low-cost, miniaturizable sensors which have quick response time and allow the researchers to make multiple analyte detection [1].

In preparing MIP-based electrochemical sensors, electropolymerization is preferred for simple, faster and inexpensive polymerization process; moreover, it allows the researcher to exert better control over film thickness and morphology and to provide better adhesion of the polymer layer to the substrate surface [1-2].

In this study, MIP-based electrochemical sensors and biosensors prepared via electropolymerization for different type of analytes such as drugs, pesticides, enzymes and biomarkers will be reviewed. In doing that, after briefly presenting the preparation and uses of MIPs and MIP-based sensors with specific reference to their advantageous, this study will focus on sample studies from the literature in explaining the higher selectivity provided by these sensors.

References

[1] B. Bozal-Palabiyik, C. Erkmen, B. Uslu. Molecularly Imprinted Electrochemical Sensors: Analytical and Pharmaceutical Applications Based on Ortho-Phenylenediamine Polymerization, Curr. Pharm. Anal. DOI: 10.2174/1573412915666190304150159.

[2] Sadriu I., Bouden S., Nicolle J., et al. Molecularly imprinted polymer modified glassy carbon electrodes for the electrochemical analysis of isoproturon in water. Talanta. 207 (2020) 120222.

[3] Bozal-Palabiyik B., Lettieri M., Uslu B. et al. Electrochemical Detection of Vascular Endothelial Growth Factor by Molecularly Imprinted Polymer. Electroanalysis. 31 (2019) 1458–1464.

[4] Ahmad O.S., Bedwell T.S., Esen C., et. al., Molecularly Imprinted Polymers in Electrochemical and Optical Sensors. Trends Biotechnol. 37 (2019) 294-309.

10th Annual Symposium on Physical and Analytical Chemistry
Tbilisi State University
January 03-04, 2020, Tbilisi, Georgia

STRUCTURE DETERMINATION OF SOME HETEROCYCLIC COMPOUNDS WITH ADVANCED NMR TECHNIQUES

Cigdem Karaaslan

Department of Pharmaceutical Chemistry, Faculty of Pharmacy, Ankara University, 06100 Ankara, Turkey

Heterocyclic compounds are widely used in drug discovery, such as benzimidazoles, purines, pyrimidines and many other nitrogen containing heterocycles, due to their important biological activities. Since they are designed as drugs, it is very important to determine their structure and purity as the first step. ^{1}H and ^{13}C NMR spectra maintain the first tool used to elucidate the structure of newly synthesized heterocyclic compounds on a routine basis. Primarily it is common to provide NMR data on both proton and carbon spectra based on one-dimensional experiments, however the increasing complexicity of heterocyclic compounds and their isomeric forms refers the use of some more 1D and 2D NMR techniques. NMR spectra of these complex heterocyclic compounds contain several resonance lines which cannot be resolved in a conventional 1D NMR experiment. Multidimensional NMR spectra maintain both increased resolution and correlations to make it easy to analyze. In this study some advanced NMR techniques like, COSY, NOESY, HSQC and HMBC are used to determine the complex structures of some newly synthesized regioisomeric heterocyclic compounds.

Acknowledgements
The Central Laboratory of Ankara University Faculty of Pharmacy provided support for acquisition of the advanced NMR techniques and mass spectrometer used in this work.

References

[1] Diana C. G. A. Pinto, Clementina M. M. Santos and Artur M. S. Silva. Advanced NMR techniques for structural characterization of heterocyclic structures. Recent Research Developments in Heterocyclic Chemistry, 2007: 397-475.
[2] Goker H., Ozden S. Regioselective N–alkylation of 2– (3,4–dimethoxyphenyl)imidazo[4,5–b] and [4,5–c]pyridine oxide derivatives : Synthesis and structure elucidation by NMR. Journal of Molecular Structure (2019), 1197, 183-195.

10th Annual Symposium on Physical and Analytical Chemistry
Tbilisi State University
January 03-04, 2020, Tbilisi, Georgia

DEEP LEARNING AND NUMERICAL PARTIAL DIFFERENTIAL EQUATIONS FOR SMART MEASUREMENTS OF AIR POLLUTION WITH LOW-COST SENSORS

Ramaz Botchorishvili[1], Asrid Kiendler-Scharr[2], Hanno Scharr[3], Andreas Wahner[2]

[1]*Kutaisi International University, 4600 Kutaisi, Georgia*
[2]*Insitute of Energy and Climate Research 8, Forschumgszentrum Jülich, 52428 Jülich, Germany*
[3]*Insitute of Bio- and Geosciences 2, Forschumgszentrum Jülich, 52428 Jülich, Germany*

Low-cost air pollution sensors are attractive because of their price, size, and weight. In theory, they can make feasible monitoring of air pollution in many locations. An unmanned aerial vehicle (UAV) equipped with low-cost sensors can make possible monitoring of air pollution in poorly accessible areas. Though at the current stage of development, using low-cost air pollution sensors is associated with some difficulties. Some approaches for handling these difficulties are proposed in this study.

Low-cost air pollution sensors give often lower data quality than results from state of the art laboratory instruments or official monitoring stations. Therefore, the challenge is improving the quality of measurements from low-cost sensors. For improving the quality of measurements from low-cost air pollution sensors using deep learning and numerical partial differential equations is proposed in this study. In particular, for solving the above problem four approaches are formed in this study. These approaches use a fully connected artificial neural network, convolutional neural networks, numerical parabolic partial differential equations coupled with convolutional neural networks, and deep residual networks motivated by numerical linear advection solvers.

Another challenge is creating high-quality pollution maps if measurements come from UAV with low-cost air pollution sensors.

For solving the problem an approach is proposed that combines variational data assimilation technique with artificial neural networks. One of the interesting subproblems is selecting measurement trajectories for UAV with air pollution sensors. Two approaches are proposed for solving the subproblem of trajectory selection. One approach uses a gradient-based chemotaxis model of biological organisms. Another proposed approach is stochastic gradient descent like technique.

10th Annual Symposium on Physical and Analytical Chemistry
Tbilisi State University
January 03-04, 2020, Tbilisi, Georgia

AIR SAMPLING AND POLUTION SENSING RESEARCH AT SMART|AtmoSim_LAB

Giorgi Jibuti[1], *Bezhan Chankvetadze*[1], *Ramaz Botchorishvili*[2], *Ketevan Kharaishvili*[1]
Email: giorgi.jibuti@tsu.ge

1. Institute of Physical and Analytical chemistry, School of Exact and Natural Sciences Tbilisi State University, 3, I. Chavchavadze Ave., 0179 Tbilisi, Georgia
2. Kutaisi International University

SMART|AtmoSim_Lab continues studies of air pollution and pollution monitoring methods. Main challenge of atmospheric research is that pollutants are present at very low concentration, requiring very sensitive equipment with low detection limit. In addition, concentration varies greatly over time often requiring fast detection.

To get better insights of atmospheric air pollution, it is desirable to have high spatial and temporal resolution of analysis. Research grade equipment have low detection limit, high sensitivity, and usually fast response time, but their spatial resolution is limited. usually they are fixed at location, They can be mounted or ground (cars), sea (boats) or aerial vehicles (zeppelins planes, space satellites) which increase spatial resolution, but still, it is not well suited for example for use in urban environment to evaluate pollution gradient from source (streets). To achieve high mobility, instrument sizes should be much smaller, which will allow their placement on more flexible platforms (such as drones).

Modern miniaturized gas sensors are based on several technologies, which are being developed and advanced rapidly, namely semiconductor, electrochemical catalytic or miniaturized optical-spectroscopic based sensors. They have much lower price than lab equipment, but currently they are lacking sensitivity and selectivity in some cases. Despite these drawbacks, our comparisons show promising results. Also, powerful modelling and machine learning approaches can be used to increase quality of data gathered from sensors.[1]

Another disadvantage of research grade instrument is their high price and maintenance costs, which limits their deployment. This limitation could be however somewhat alleviated by using air sampling canisters at desired locations, then bringing them back in the lab to analyze, granted highly active species such as ozone, or other radicals can not be measured this way, because they will degrade very quickly.

To get representative sample, air should be collected in a certain duration (few minutes to few hours depending on the requirement). Also it is important, to have relatively constant flowrate inside the canister. Since ordinary needle valves can not limit flowrate in wide range of values, special flow restrictor frits are used, designed to give fixed filling time for the given volume of sampling canister. Flow restrictor is also often equipped with filters (frit is very sensitive to the dust) and optional pressure gauge. This restrictor works well, but they are quite expensive (on top of expensive canisters itself) also it is not very convenient to vary sampling time. Our approach towards this issue is to use pieces of gas chromatography or capillary electrophoresis capillary columns, which are cheap and convenient in use.

References

[1] Application of smart gas sensors for monitoring of atmospheric air quality in urban areas – G. Jibuti, B. Chankvetadze1, R. Botchorishvili, D. Mchedlishvili, A. Wahner, A. Kiendler-Scharr, F. Rohrer- Euroanalysis 2019, Istanbul, Turkey, September 1-5, 2019.

10th Annual Symposium on Physical and Analytical Chemistry
Tbilisi State University
January 03-04, 2020, Tbilisi, Georgia

NEW STRATEGIES IN ELECTROCHEMICAL APPROACH OF DNA-DRUG INTERACTIONS

Burcu Dogan Topal

Ankara University, Faculty of Pharmacy, Department of Analytical Chemistry, Ankara, TURKEY

The drug-DNA interaction studies offer the opportunity to know about the effects of drugs in DNA structure and it may be useful to design new drugs. Electrochemical investigation presents the opportunity to discern the effects of drugs in DNA structure and elucidate the mechanism of interaction based on their unique electrochemistry. In this regard, designing electrochemical DNA biosensors contributed to the development of more selective and sensitive electrochemical methods for the detection of specific DNA binding. Generally, DNA-acting drugs can be classified as: covalently bound molecules, noncovalent interacting agents though groove binding or by intercalative mode or DNA backbone cleaving reagents.
In biomedical study, measuring small amounts of drugs, hormones or biological compounds, etc is highly desired. Moreover, cheap, fast, reliable technologies are also essential in clinical treatments. In recent years, nano-scale materials such as nanotubes, nanoparticles and nanowires
are used extensively for offering marvelous prospects in designing new strategies for DNA detection. These nanoparticles provide the researchers with more efficient techniques for interfacing DNA recognition with electrochemical signal transduction. CNTs have attracted attention for the students of electrochemistry thanks to their remarkable advantages such as promoting electron transfer reactions, high surface area, high electrical conductivity, mechanical
robustness, excellent chemical stability, and the possibility of immobilization of biomolecules. The resulting MWCNT modified electrodes can lead to the precise detection of bioanalytes such as DNA [1-5]. The amino functionalized MWCNTs is used to manufacture the nanosensor because of the great reactivity of the amino group.
An electrochemical dsDNA nanobiosensor is fabricated using amino-functionalized multi walled carbon nanotubes modified glassy carbon electrode (NH_2*f*MWCNTs/GCE) for the sensitive detection of DNA bases and electrochemical monitoring of drug-DNA interaction.

References

[1] H. El-Desoky, M. Ghoneim, M. Abdel-Galeil, A. Khalifa, *J. Electrochem. Soc.***2017**, *164*, H1133–H1147.
[2] K. Saeedfar, L. Y. Heng, C. P. Chiang, *Bioelectrochemistry***2017**, *118*, 106–113.
[3] A. Mirzapoor, B. Ranjbar, *Phys. E Low-Dimensional Syst. Nanostructures***2017**, *93*, 208–215.
[4] M. A. Tahir, S. Hameed, A. Munawar, I. Amin, S. Mansoor, W. S. Khan, S. Z. Bajwa, *J. Virol. Methods***2017**, *249*, 130–136.
[5] S. Gupta, C. N. Murthy, C. R. Prabha, *Int. J. Biol. Macromol.***2018**, *108*, 687–703.

10th Annual Symposium on Physical and Analytical Chemistry
Tbilisi State University
January 03-04, 2020, Tbilisi, Georgia

SYNTHESIS OF SOME CHIRAL CYCLIC SULFOXIDES

Rusudan Kakava[1], Iza Matarashvili[1], Alessandro Volonterio[2], Bezhan Chankvetadze[1]

[1]Institute of Physical and Analytical Chemistry, School of Exact and Natural Sciences, Tbilisi State University, Chavchavadze Ave 3, 179 Tbilisi, Georgia
[2]Dipartimento di Chimica, Materiali ed Ingegneria Chimica "Giulio Natta", Politecnico di Milano, via Mancinelli 720131 Milano, Italy

Phenothiazine derivatives are valuable drug compounds with wide range of pharmaceutical activities, including antipsychotic, antiadrenergic, anticholinergic, insecticidal, antifungal, antibacterial and antihistaminic activity [1]. Phenothiazine derivatives own three ring structure with two benzene rings linked by a nitrogen and a sulfur atom. When a sulfur atom in thioether group is oxidized to sulfynyl group it causes chirality of a molecule, in case of substituents asymmetrically attached to benzyne rings. Chiral phenothiazine sulfoxide derivatives shown on Fig. 1 were synthesized using three step synthetic path [2].

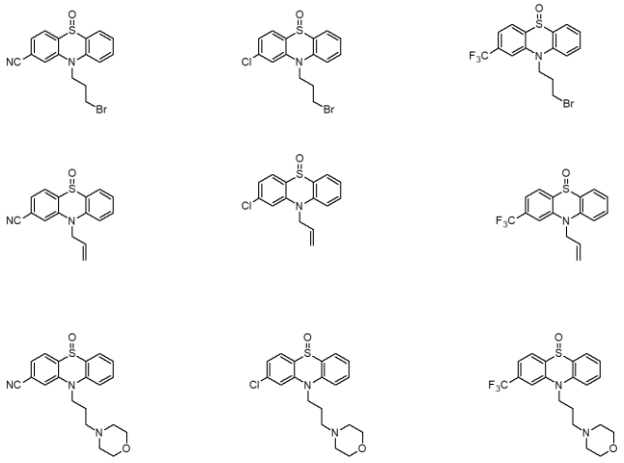


Fig.1. Structures of synthesized phenothiazine sulfoxide derivatives.

Synthesized compounds were isolated, purified and their structures were confirmed with IR, NMR spectroscopy and mass spectrometry techniques.

Acknowledgements

This study was supported by Shota Rustaveli National Science Foundation (SRNSF) of Georgia and CNR Italy joint grants (Grant no. 04/53, 2017-2019).

References

[1] Osorio C., Rivero J.J., Torre-Cisneros A. (2008). Epidemiology of invasive fungal infection. International of Antimicrobial Agents, 32 (2), S103-S109;

[2] Sasano Y., Kogure N., Nagasawa S., Kasabata K., Iwabuchi Y. (2018). 2-Azaadamantane N-oxyl Journal (AZADO)/Cu Catalysis Enables Chemoselective Aerobic Oxidation of Alcohols Containing Electron-Rich Divalent Sulfur Functionalities. Organic Letters 20 (19), 6104-6107.

10th Annual Symposium on Physical and Analytical Chemistry
Tbilisi State University
January 03-04, 2020, Tbilisi, Georgia

RECENT STUDIES ON THE DEVELOPMENT OF ANALYTICAL METHODS BOTH ACHIRAL AND CHIRAL SEPARATIONS

Mehmet Gumustas, Ozge Gun Esim, Canan Hascicek, Sibel A. Ozkan, Eric Leselier, Caroline West, Bezhan Chankvetadze

[1]*Ankara University, Institute of Forensic Sciences, Department of Forensic Toxicology, Ankara, Turkey*
[2]*Ankara University, Faculty of Pharmacy, Department of Pharmaceutical Chemistry, Ankara, Turkey*
[3]*Ankara University, Faculty of Pharmacy, Department of Analytical Chemistry, Ankara, Turkey*
[4]*Institut de Chimie Organique et Analytique (ICOA), Université d'Orléans et CNRS, UMR7311, Orléans, France*
[5]*Institute of Physical and Analytical Chemistry, School of Exact and Natural Sciences, Tbilisi State University, Tbilisi, Georgia*

The current presentation included two of our recent studies for the development of analytical methods both chiral and achiral separations based on high performance liquid chromatography and supercritical fluid chromatography.

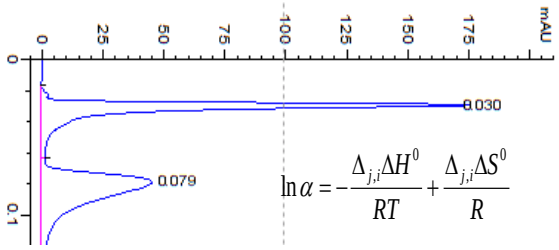
In the first part, the primary purpose is to develop and validate a novel simple, selective and also stability-indicating HPLC method for simultaneous determination of the combination of a conventional chemotherapeutic, carboplatin (CRB) and an epigenetic drug, decitabine (DEC) from their bulk and pharmaceutical preparations as well as developed nano-formulation. Therefore, various experimental parameters such as; stationary phase, organic solvents, organic solvent:buffer solution ratios, pH and concentration of the buffer solution, temperature of the column oven and flow rate of the mobile phase were optimized. Also, the developed method was successfully applied for the simultaneous determination and quantification of CRB and DEC co-encapsulated in albumin nanoparticles and released to in vitro dissolution medium.

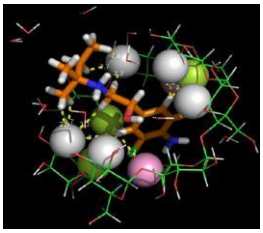
In the second part of the presentation, the supercritical liquid chromatography (SFC) method has been developed for the separation of some chiral sulfoxides. While enantioselective HPLC has been preferred method for this task, SFC is now taking the lead. This is due to benefits associated with the use of pressurized carbon dioxide as the major component of the mobile phase. First, CO_2 has a much lower cost than the organic solvents used in the normal-phase HPLC mobile phases (hexane or heptane). Aside solvent costs, solvent disposal costs have also impact on the overall economy. In the frame of this presentation we compared fully porous (FP) and superficially porous (SP) silica particles containing polysaccharide-type chiral selectors in SFC from the viewpoint of retention and separation behaviors. While chlorinated polysaccharide CSP have proven to be promising for the separation of chiral sulfoxide species in the past, we were interested in examining the SFC retention and separation in more detail by using some chiral sulfoxides. A practical conclusion made from these experiments is that carbon dioxide offers the possibility to enhance retention for those analytes that would be too weakly retained in the polar organic mode.

Acknowledgements

This project was partially supported by the Project Based Mevlana Exchange Program with the project number MEV-2018-1295 and by the Scientific and Technological Research Council of Turkey (TUBITAK), grant no. 116S395.

ORAL PRESENTATIONS





10th Annual Symposium on Physical and Analytical Chemistry
Tbilisi State University
January 3-4, 2020
Tbilisi, Georgia

10th Annual Symposium on Physical and Analytical Chemistry
Tbilisi State University
January 03-04, 2020, Tbilisi, Georgia

A NOVEL ELECTROCHEMICAL NANOSENSOR BASED ON NH_2 -FUNCTIONALIZED MWCNTS WİTH GOLD NANOPARTİCLES FOR THE SENSITIVE DETERMINATION OF ANTIPSYCHOTIC AMISULPRIDE

Goksu Ozcelikay[1], Yemna Abbade[1], Leyla Karadurmus[2]Nurgul K. Bakirhan[3], Sibel A.Ozkan[1]

[1]*Department of Analytical Chemistry, Faculty of Pharmacy, Ankara University, Ankara, Turkey*
[2]*Department of Analytical Chemistry, Faculty of Pharmacy, Adiyaman University, Adiyaman, Turkey*
[3]*Department of Analytical Chemistry, Faculty of Gulhane Pharmacy, University of Health Sciences, Ankara, Turkey*

Amisulpride (AMS), a substituted benzamide derivative, belongs to the relatively new class of second-generation (atypical) antipsycotics. The drug is effective mainly in the management of psychoses such as schizophrenia, with fewer adverse effects than conventional high-potency anti-psychotic drugs[1]. Electrochemical methods are most promising as compared to other detection techniques such as mass spectrometry, spectrophotometry, fluorimetry, capillary electrophoresis, high performance liquid chromatography etc. Electrochemical techniques are currently the leading probes for sensing and monitoring of pharmaceuticals [2]. Carbon nanotubes have attracted attention thanks to their remarkable advantages such as promoting electron transfer reactions, high surface area, high electrical conductivity, mechanical robustness, and excellent chemical stability[3].

In this study, an antipsychotic drug Amisulpride (AMI) is electrochemically investigated under optimized conditions using on amine-functionalized multiwalled carbon nanotubes (NH_2-*f*MWCNT) with Gold nanoparticles decorated over glassy carbon electrode (GCE). The AMI showed irreversible oxidation peak at 1.29 V, at all the investigated pH values. For experimental conditions optimization the influence of supporting electrolyte and pH was examined and pH 3 BRT was selected as the best electrolyte for getting intense current signals of the target analyte. Scan rate results showed that the oxidation of AMI at the nanosensor surface occurs under adsorption controlled manner. Therefore, Square wave adsorptive stripping voltammetric technique was employed for the determination of AMI. Optimum accumulation potential and time were found as 0 V and 120 s, respectively. Under these optimum conditions, response of AMI demonstrated a linear behavior in the concentration range from 1.00×10^{-6} to 1.00×10^{-4} M, with a limit of detection value and limit of quantification of 2.80×10^{-7} M and 8.51×10^{-7} M, respectively. The designed method was successfully applied for the determination of AMI in synthetic human serum.

References

[1] D. Wisher, Martindale: The Complete Drug Reference. 37th ed, J. Med. Libr. Assoc. 100 (2012) 75–76.
[2] B. Dogan, S.A. Ozkan, Electrochemical behavior of carvedilol and its adsorptive stripping determination in dosage forms and biological fluids, Electroanalysis. 17 (2005) 2074–2083.
[3] G. Ozcelikay, B. Dogan-Topal, S.A. Ozkan, An Electrochemical Sensor Based on Silver Nanoparticles-Benzalkonium Chloride for the Voltammetric Determination of Antiviral Drug Tenofovir, Electroanalysis. (2018) 1–13.

10th Annual Symposium on Physical and Analytical Chemistry
Tbilisi State University
January 03-04, 2020, Tbilisi, Georgia

COMPARATIVE STUDY OF CELLULOSE TRIS(3-CHLORO-5-METHYLPHENYLCARBAMATE) COATED OR COVALENTLY IMMOBILIZED ON SILICA FOR SEPARATION OF ENANTIOMERS IN HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

T. Khatiashvili[1], I. Matarashvili[1], T. Farkas[2], B. Chankvetadze[1]

[1]Institute of Physical and Analytical Chemistry, School of Exact and Natural Sciences, Tbilisi State University, Chavchavadze Ave 3, 0179 Tbilisi, Georgia.

[2]Phenomenex Inc., 411 Madrid Ave., Torrance, 90501 CA, USA

The first generation of polysaccharide-based chiral stationary phases (CSPs) for liquid-phase separation of enantiomers were prepared by physical coating of polysaccharide derivative onto the surface of silica. On the one hand, this is a quick method that does not require pre-activation of silica. However, the CSPs prepared by this way may suffer from stability problems in some solvents used as mobile phase components in high-performance liquid chromatography (HPLC). This problem can be solved by covalent immobilization of polysaccharide-based chiral selector (CS) on silica. The advantage of this method is that immobilized CSPs are stable, compatible with different type of mobile phase components and capable for reversal of enantiomer elution order at elevated temperatures.
The major research goal of the project is comparison of cellulose tris(3-chloro-5-methylphenylcarbamate) [1, 2] coated or covalently immobilized on silica for separation of enantiomers in acetonitrile, methanol and mixture of n-hexane and isopropanol (v/v) as mobile phases. In the frames of the present project we also describe the thermodynamics of chiral separation.

References

[1] B. Chankvetadze, L. Chankvetadze, S. Sidamonidze, E. Kasashima, E. Yashima, Y. Okamoto, 3-Fluoro-, 3-chloro- and 3-bromo-5-methylphenylcarbamates of cellulose and amylose as chiral stationary phases for high- performance liquid chromatographic enantioseparation, Journal of Chromatography A, 787 (1997) 67-77.
[2] B. Chankvetadze, Recent developments on polysaccharide-based chiral stationary phases for liquid-phase separation of enantiomers, Journal of Chromatography A, 1269 (2012) 26–51.

10th Annual Symposium on Physical and Analytical Chemistry
Tbilisi State University
January 03-04, 2020, Tbilisi, Georgia

ENANTIOSELECTIVE ANALYSIS OF CITALOPRAM ENANTIOMERS WITH MULTIWALLED CARBON NANOTUBE- C4- MODIFIED CARBON PASTE ELECTRODE USING ADSORPTIVE STRIPPING SQUARE WAVE VOLTAMMETRY

Leyla Karadurmus[1, 2], *Bezhan Chankvetadze*[3], *Sibel A. Ozkan* [1]

[1] *Ankara University, Faculty of Pharmacy, Department of Analytical Chemistry, Ankara, Turkey*
[2] *Adıyaman University, Faculty of Pharmacy, Department of Analytical Chemistry, Adıyaman, Turkey*
[3] *Institute of Physical and Analytical Chemistry, School of Exact and Natural Sciences, Tbilisi State University, Tbilisi, Georgia*

Electroanalytical methods are re-gaining their popularity in pharmaceutical analysis [1], especially for continuous process monitoring. Enantiomers are non-super imposable mirror images. Enantioselective analysis of Citalopram (CIT) enantiomers was investigated on carbon paste electrode (CPE) modified with chiral selector Cellulose tris(4-chloro-3-methylphenylcarbamate) (C4) [2] and multiwalled carbon nanotube (MWCNT) employing adsorptive stripping square wave voltammetric (AdSSWV) technique. Electrochemical chiral discrimination was obtained due to C4. Polysaccharide derivatives are the most commonly used for direct liquid chromatographic (LC) enantioseparation of chiral compounds. Their enantioresolution ability often depends on the structure of the chiral polymers but also on the substituents of the phenyl group in the case of phenylcarbamate derivatives.

Enantioselectivity of present electrode system of MWCNT and C4 modified carbon paste electrode (MWCNT-C4-CPE) gives difference in anodic oxidation peak potential of enantiomers S-CIT and R-CIT in phosphate buffer solution in pH 8 confirming successful enantiomer detection respectively. The electrocatalytic response of CIT at MWCNT-C4-CPE was measured using cyclic voltammetry (CV) and square wave voltammetry (SWV). The proposed enantioselective electrochemical sensor was highly efficient and capable of sensing enantiomers of CIT stereoselectively. In the present work, polysaccharide phenylcarbamate derivative was used for the first time for enantioselective sensing of chiral drug enantiomers.

References

[1] Ozkan S.A., Electroanalytical Methods in Pharmaceutical Analysis and Their Validation. HNB Publishing, New York, 2012.

[2] Chankvetadze, B., Yashima, E., & Okamoto, Y. (1994). Chloromethylphenylcarbamate derivatives of cellulose as chiral stationary phases for high-performance liquid chromatography. Journal of Chromatography A, 670 (1-2), 39-49.

10th Annual Symposium on Physical and Analytical Chemistry
Tbilisi State University
January 03-04, 2020, Tbilisi, Georgia

SEPARATION OF ENANTIOMERS OF NEWLY SYNTHESIZED CHIRAL SULFOXIDE DERIVATIVES WITH SUPERCRITICAL FLUID CHROMATOGRAPHY

Kenan Can Tok[1], Mehmet Gumustas[1], Rusudan Kakava[2], Bezhan Chankvetadze[2]

[1]Department of Forensic Toxicology, Institute of Forensic Sciences, Ankara University, Ankara, Turkey
[2]Institute of Physical and Analytical Chemistry, School of Exact and Natural Sciences, Tbilisi State University, Tbilisi, Georgia

Supercritical fluid chromatography (SFC) is a form of liquid chromatography that uses a supercritical carbon dioxide as the mobile phase. HPLC and SFC are often seen as complementary techniques. While enantioselective HPLC has been used for enantioseparation of the chiral compounds, SFC is now becoming popular, too. This is because of the major advantages like fast analysis, lower viscosity of the mobile phases, which allows high flow rates without high backpressures and higher plate numbers. In addition, reduction of the amount of used solvents is possible compared with liquid chromatography; SFC also has less environmental impact and is ease in processing collected sample fractions. In the present study, we aimed to separate the enantiomers of chiral sulfoxides by using chiral columns made based on fully porous (FP) and superficially porous (SP) silica particles in SFC. Obtained results evaluated from the viewpoint of retention and separation behaviors.

HPLC grade methanol was acquired from Merck (Darmstadt, Germany). Chiral columns packed with FP silica particles of 3 µm nominal particle size and 1000 A° nominal pore size and containing 0.1 % (50x4,6mm) and 0.5 % (30x4,6mm) chiral selector, namely cellulose tris(4-chloro-3-methylpenyl)carbamate. In parallel, we used the columns packed with chiral stationary phases made of SP silica particles of 2.6 µm particle size and 449 A° average pore size and containing 0.5% (30x4,6mm) same chiral selector. Aurora SFC Fusion combined with Agilent HPLC 1200 Series was used for the separations. It was equipped with a binary solvent delivery pump compatible with mobile phase flow rates up to 5 mL/min and pressures up to 400 bar, an autosampler that included a partial loop volume injection system, a back-pressure regulator, a column oven and a diode-array (DAD) detector. OpenLAB ChemStation (Agilent) was used to process the chromatograms. The other conditions used in this study is following, 25° C column oven temperature, 150 bar back pressure regulator (BPR) pressure, and 220 nm detection wavelength.

As a result of the study, separation behaviors of the chiral sulfoxide derivatives were examined by the means of efficiency of the both SP and FP silica particles, analysis time and enantioselectivity.

Acknowledgements

This project was partially supported by the Project Based Mevlana Exchange Program with the project number MEV-2018-1295

10th Annual Symposium on Physical and Analytical Chemistry
Tbilisi State University
January 03-04, 2020, Tbilisi, Georgia

BENCHMARKING SOURCE ISOTOPIC RATIOS OF LEVOGLUCOSAN TO BETTER CONSTRAIN THE CONTRIBUTION OF DIFFERENT WOOD CONTAINING FUELS TO THE AIR POLLUTION

Nana Khundadze

Department of Analytical and Physical Chemistry, Tbilisi State University, School of Exact and Natural Sciences, Tbilisi State University, Tbilisi, Georgia

Biomass burning is an important source of atmospheric pollutants in gas and particulate phase. Domestic heating as a form of biomass burning is a major source of pollution, comparable with that from traffic. Since it occurs where people live and at times when they are at homes, it has a negative impact on human health. For the necessary mitigation, it is clear that there is a strong interest for detailed description of the sources. Isotopic analyses are an innovative tool for source apportionment. The concept behind is that stable isotopes can give additional information on the source and sinks aerosol, based on two s properties of isotopes: fingerprinting of sources and footprinting of the chemical processing.

In this work the stable isotope ratios of levoglucosan in aerosol particles emitted from the combustion of 18 different biomass fuel (soft and hard woods, corn cobs and coal materials) were determined. Compound specific isotopic measurements were carried out by Thermal Desorption- two-dimensional Gas Chromatography- Isotope Ratio Mass Spectrometer (TD-2DGC-IRMS).

δ^{13}C values of levoglucosan in C3 plant samples were found in the range from -23.6 to -21.7‰, being a bit higher in case of softwoods. The lignite samples showed higher isotopic composition than soft and hard wood, i.e.-19‰, denoting a heavier plant rest in the coal. Furthermore, the isotopic ratio of levoglucosan from the combustion of corn cob was found to be -12.9‰, as expected for a C4 sample. Isotopic measurements of total carbon in aerosol showed different signatures for the C3 and lignite samples, from -27.2 to-23.7‰, and for the C4 corn cob sample, i.e. -13.8‰, in good agreement with the parent plant material.Additionally, the isotopic composition of hollocellulose, as a parent material, was determined with δ^{13}C values between - 27.5‰ (for C3 plants) and -10.9‰ (for C4 plants). Moreover, the isotopic fractionation between the cellulose and levoglucosan, showed a mean value of 1.94‰.

This work contributes to the database enlargement of source specific isotopic ratios of levoglucosan, which is compulsory to get more insight in the biomass burning aerosol origin.

References

1. Gensch, I., Kiendler-Scharr, A., & Rudolph, J. (2014). *Isotope ratio studies of atmospheric organic compounds: Principles, methods, applications and potential*. International Journal of Mass Spectrometry, *365*, 206-221. doi: DOI 10.1016/j.ijms.2014.02.004
2. Bernd R.T. Simoneit.*Biomass burning — a review of organic tracers for smoke from incomplete combustion*. 2000Environmental and Petroleum Geochemistry Group, College of Oceanic and Atmospheric Sciences, Oregon State University, Corvallis, *OR 97331-5503, USA*
3. Christian Dye and Karl Espen Yttri *Determination of Monosaccharide Anhydrides in Atmospheric Aerosols by Use of High-Performance Liquid Chromatography Combined with High-Resolution Mass Spectrometry*. 2005. Norwegian Institute for Air Research, Instituttveien 18, P.O. Box 100, N-2027 Kjeller, Norw*ay*

10th Annual Symposium on Physical and Analytical Chemistry
Tbilisi State University
January 03-04, 2020, Tbilisi, Georgia

THE EFFECT OF CHIRAL SELECTOR CONTENT AND COLUMN INTERNAL DIAMETER ON SEPARATION OF ENANTIOMERS WITH POLYSACCHARIDE-BASED SUPERFICIALLY POROUS AND FULLY POROUS CHIRAL STATIONARY PHASES

Salome Pantsulaia, Khatia Targamadze, Rusudan Kakava, Bezhan Chankvetadze

Department of Physical and Analytical Chemistry, School of Exact and Natural Sciences, Tbilisi State University, Tbilisi, Georgia

Nowdays chiral sulfoxides attract a great attention due to the importance of chiral sulfoxides in biology, pharmaceutical chemistry and organic synthesis. Chiral sulfoxides are characterized by various biological activities, including anticancer, antiviral, antischizophrenic, and others. For this reason several of them are active ingredients in commercially available drug formulations. In addition, they are used as synthetic intermediates, ligands or catalysts. In our previous studies we separated the enantiomers of chiral sulfoxides on various polysaccharide-based chiral columns with very high enantioselectivity [1, 2] while in the recent study the emphasis was made on the separation speed and baseline separation of enantiomers were achieved within less than 1 minute [3].

In this study, the effect of column internal diameter, pore size of silica and the content of a chiral selector in chiral stationary phase on separation of enantiomers of chiral sulfoxides was studied. It was found that at least in our experimental setup the column performance is jeopardized by reduction of column internal diameter from 4.6 down to 2.1 mm. In addition, wide-pore material offers certain advantages from the viewpoint of column performance for both, fully porous (FP) and superficially porous (SP) silica. As for comparison between FP and SP silica, the latter offers significant advantages when the content of a chiral selector in chiral stationary phase is less than 2% w/w while at higher content of a chiral selector FP silica is advantageous.

References

[1] B. Chankvetadze, C. Yamamoto, Y. Okamoto, Extremely high enantiomer recognition in HPLC separation of racemic 2-(benzylsulfinyl)benzamide using cellulose tris (3,5-dichlorophenylcarbamate) as a chiral stationary phase, Chem. Lett., 29 (2000), 1176-1177.
[2] T. Khatiashvili, R. Kakava, I. Matarashvili, H. Tabani, C. Fanali, A. Volonterio, T. Farkas, B. Chankvetadze, Separation of enantiomers of selected chiral sulfoxides with cellulose tris(4-chloro-3-methylphenylcarbamate)-based chiral columns in high-performance liquid chromatography with very high separation factor, J. Chromatogr. A, 1545 (2018) 59-66.
[3] N. Khundadze, S. Pantsulaia, C. Fanali, T. Farkas, B. Chankvetadze, On our way to sub-second separations of enantiomers in high-performance liquid chromatography, J. Chromatogr. A, 1572 (2018) 37-43.

10th Annual Symposium on Physical and Analytical Chemistry
Tbilisi State University
January 03-04, 2020, Tbilisi, Georgia

COMPARATIVE EVALUATION OF ATMOSPHERIC POLLUTION SENSORS WITH LABORATORY EQUIPMENT

Ana Chelidze, Ketevan Kharaishvili, Monika Kartvelishvili, Ledi davitinidze, Ana Tavartkiladze, Giorgi Meshvildishvili, Bezhan Chankvetadze, Giorgi Jibuti

Institute of Physical and Analytical chemistry, School of Exact and Natural Sciences, Tbilisi State University, 3, I. Chavchavadze Ave., 0179 Tbilisi, Georgia
Email: Cheloochelo1@gmail.com

Atmospheric studies are an important subject in many scientific fields. The study of anthropogenic pollutants, such as traffic emissions, microparticles and other aerosols are one of the most important subjects as those pollutants have a direct effect on human health and life quality.

SMART | AtmoSim_LAB at Ivane Javakhishvili Tbilisi State University, Chair of Physical and Analytical Chemistry is equipped with the following equipment:

- ECO PHYSICS CLD 780 TR for NO and NO_2 measurements based on ozone chemiluminescence,
- Ansyco O_3 41 M-O_3 measurement via UV spectroscopy,
- PICARRO CRDS Analyzer - CO, CO_2, CH_4, H_2O measurement via cavity ringdown spectroscopy,
- GRIMM Aerosol Monitor 11.09 via optical scattering.

Disadvantage of research grade equipment is their high price and large size. In addition, they are not easy to be used in field measurements. Recent development in miniaturized gas sensors, previously used in safety equipment (e.g. leak sensors) allows scientists to test their feasibility as pollution sensors.

In the present project we used Alphasense ™ sensors to measure CO, NO, NO_2, O_3. For this purpose, sensors are placed in special manifold and connected to lab equipment sampling line directly and synchronous data is recorded from sensors. In parallel, air samples were collected from the same place with special air sampling canisters and later analyzed in the laboratory. In other case, sensor manifold is attached to separate air pump to investigate the effect of flow rate on the measurement sensitivity and accuracy?

10th Annual Symposium on Physical and Analytical Chemistry
Tbilisi State University
January 03-04, 2020, Tbilisi, Georgia

THERMODYNAMIC STUDY OF SEPARATION OF FENOPROFEN ENANTIOMERS USING AMYLOSE TRIS(3,5-DIMETHYLPHENYCARBAMATE) COATED ON SILICA IN HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

Aluda Chelidze, Iza Matarashvili, Bezhan Chankvetadze

Institute of Physical and Analytical Chemistry, School of Exact and Natural Sciences, Tbilisi State University, Tbilisi, Georgia

The goal of our research was the calculation of thermodynamic parameters of enantioseparation in high-performance liquid chromatography. This can help to predict the suitable analytical conditions for the given compound on given column for achieving the desired selectivity and enantiomer elution order.

Also we compared thermodynamic parameters using amylose tris(3,5-dimethylphenyl carbamate) coated or covalently immobilized on silica gel as stationary phase. Separation of enantiomers was performed at different temperatures and in different mobile phases. For analyzed compounds, the difference in adsorption enthalpy and adsorption entropy between enantiomers were calculated using the plot of natural logarithm of the separation factor versus the reciprocal of the absolute temperature. We studied if the enantioseparation mechanism was controlled by enthalpic or entropic terms and what was the influence of temperature on retention and separation.

Firstly, we analyzed 28 chiral substances, particularly arylpropionic acid derivatives, which are nonsteroidal anti-inflammatory drugs (NSIDs). They are used as painkillers and antipyretics. It is important to separate their stereoisomers, as frequently only one enantiomer has pharmacological activity and the other one is inactive or even toxic. From these compounds we selected fenoprofen for detailed thermodynamic studies.

References :

[1] I. Matarashvili, G. Kobidze, A. Chelidze, G. Dolidze, N. Beridze, G. Jibuti, T. Farkas, B. Chankvetadze, J. Chromatogr. A, 1599, 2019, 172-179

10th Annual Symposium on Physical and Analytical Chemistry
Tbilisi State University
January 03-04, 2020, Tbilisi, Georgia

THERMODYNAMIC STUDY OF SEPARATION OF IBUPROFEN ENANTIOMERS USING AMYLOSE TRIS(3,5-DIMETHYLPHENYCARBAMATE) COATED ON SILICA IN HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

Gizo Dolidze, Iza Matarashvili, Bezhan Chankvetadze

Institute of Physical and Analytical Chemistry, Molecular Recognition and Separation Science Laboratory, School of Exact and Natural Sciences, Tbilisi State University, Tbilisi, Georgia

A molecule whose composition includes the asymmetric atom (asymmetric centre) is the chiral molecule. One enantiomer of a chiral molecule is non-superposable with its mirror image. The enantiomers have same physical and chemical properties in achiral environment and only difference between them is the sign of rotation angle of polarized light. Due to this reason and it is very difficult to separate enantiomers from each other.

Despite structural similarity of enantiomers their physiological activity may be very different. This makes enantioseparation of chiral pharmaceuticals, food additives, agrochemicals and other biologically active compounds very important.

Nowadays high-performance liquid chromatography is known as one of the useful method for separation of enantiomers. The goal of our research was the calculation of thermodynamic parameters of enantioseparation in high-performance liquid chromatography. This helps us to predict the suitable analytical conditions for the given compound on given column and to achieve the desired selectivity and enantiomer elution order.

Study was conducted on different temperature and in various mobile phases. For analyzed compounds, the difference in adsorption enthalpy and adsorption entropy were calculated using the plot of natural logarithm of the separation factor versus the reciprocal of the absolute temperature. We studied if the enantioseparation was controlled by enthalpic or entropic terms and what was the influence of temperature on retention and separation.

References :

[1] I. Matarashvili,G. Kobidze, A.Chelidze, G.Dolidze, N.Beridze, G.Jibuti, T.Farkas, B.Chankvetadze, J. Chromatogr.A, 1599, 2019, 172-179.

10th Annual Symposium on Physical and Analytical Chemistry
Tbilisi State University
January 03-04, 2020, Tbilisi, Georgia

ENANTIOSEPARATION OF SOME PHENOTIAZINE DERIVATIVES IN HIGH PERFORMANCE LIQUID CHROMATOGRAPHY USING ACETONITRILE AS A MOBILE PHASE

Sandro Gogia, Ani Rukhadze, Ana Kutchuashvili, Rusudan Kakava, Bezhan Chankvetadze

Institute of Physical and Analytical Chemistry, School of Exact and Natural Sciences, Tbilisi State University, Chavchavadze Ave 3, 179 Tbilisi, Georgia

Cyclic sulfoxides are valuable derivatives of phenothiazine intensively used in pharmaceutical and agricultural industries. The chiral centre present in the molecule causes a chirality of the compound, which affects its overall chemical and biological activity.

In this study we focused on the enantiomeric separation of racemic sulfoxides using high- performance liquid chromatography (HPLC). Thirteen different types of polysaccharide-based chiral columns were used. The racemic mixtures, previously synthesised, were first separated into two set of enantiomer solutions on i-Cellulose-5, 3u, 250 x 4.6 mm column. From obtained pure enantiomer solutions a set of spiked solutions were prepared and the samples were with the columns containing different chiral selectors. Obtained chromatograms were analysed on the interaction between the analyte and the chiral selector.

The conducted research showed, that different chiral selectors interact differently with same compounds, from which enantioselectivity derives and separation is observable.

References

[1] Chankvetadze, B. (2012). Recent developments on polysaccharide-based chiral stationary phases for liquid-phase separation of enantiomers. *J. Chrom. A 1269 (2012)* 26-51.
[2] Lämmerhofer, M. (2010). Chiral recognition by enantioselective liquid chromatography: mechanisms and modern chiral stationary phases. *J. Chrom. A 1217* (2011), 814-856.
[3] Scriba, G. K. (2016). Chiral recognition in separation science–an update. *J. Chrom. A 1467* (2016) 56-78.

10th Annual Symposium on Physical and Analytical Chemistry
Tbilisi State University
January 03-04, 2020, Tbilisi, Georgia

ENANTIOSEPARATION OF SOME PHENOTIAZINE DERIVATIVES IN HIGH PERFORMANCE LIQUID CHROMATOGRAPHY USING METHANOL AS A MOBILE PHASE

Ani Rukhadze, Sandro Gogia, Ana Kutchuashvili, Rusudan Kakava, Bezhan Chankvetadze
Institute of Physical and Analytical Chemistry, School of Exact and Natural Sciences, Tbilisi State University, Chavchavadze Ave 3, 179 Tbilisi, Georgia

Effective separation of enantiomer racemic mixtures is vital for the pharmaceutical companies for their usage in various medications. One of the separation techniques is high-performance liquid chromatography (HPLC), which makes it possible to separate otherwise indistinguishable enantiomers of the same compound. In this study, thirteen different types of polysaccharide-based chiral columns were used for HPLC separation of enantiomers of novel chiral cyclic sulfoxides. Methanol was chosen as a mobile phase. Sulfoxide samples that are listed in Table 1 were enantioseparated. This research included collecting the enantiomers on i-Cellulose-5, 3u, 250 x 4.6 mm column and preparing spiked solutions from retrieved fractions. The solutions then were used to study each enantiomer's properties on different kinds of columns and if their elution time was changed by changing specific columns.Our study showed that stationary phase has great effect not only on separating enantiomers, but also on reversing the elution order.

Table 1. List of studied phenotiazine derivatives.

Sample #	Name
44	10-(3-bromopropyl)-10H-phenothiazine-2-carbonitrile 5-oxide
45	10-(3-bromopropyl)-2-chloro-10H-phenothiazine 5-oxide
46	10-allyl-2-chloro-10H-phenothiazine 5-oxide
47	10-(3-morpholinopropyl)-10H-phenothiazine-2-carbonitrile 5-oxide
48	10-(3-bromopropyl)-2-(trifluoromethyl)-10H-phenothiazine 5-oxide
49	10-allyl-2-(trifluoromethyl)-10H-phenothiazine 5-oxide
51	10-allyl-10H-phenothiazine-2-carbonitrile 5-oxide
52	2-chloro-10-(3-morpholinopropyl)-10H-phenothiazine 5-oxide
53	10-(3-morpholinopropyl)-2-(trifluoromethyl)-10H-phenothiazine 5-oxide
55	2-(trifluoromethyl)-10H-phenothiazine 5-oxide
57	10-benzyl-2-isocyano-10H-phenothiazine 5-oxide
58	2-chloro-10-(3-(dimethylamino)propyl)-10H-phenothiazine 5-oxide
59	10-(3-(dimethylamino)propyl)-2-(trifluoromethyl)-10H-phenothiazine 5-oxide

References

[1] Chankvetadze, B. (2012). Recent developments on polysaccharide-based chiral stationary phases for liquid-phase separation of enantiomers. *J. Chrom. A, 1269*, 26-51.

[2] Lämmerhofer, M. (2010). Chiral recognition by enantioselective liquid chromatography: mechanisms and modern chiral stationary phases. *J. Chrom. A, 1217*(6), 814-856.

[3] Scriba, G. K. (2016). Chiral recognition in separation science–an update. *J. Chrom. A, 1467*, 56-78.

10th Annual Symposium on Physical and Analytical Chemistry
Tbilisi State University
January 03-04, 2020, Tbilisi, Georgia

THERMODYNAMIC STUDY OF SEPARATION KETOPROFEN ENANTIOMERS USING AMYLOSE TRIS(3,5-DIMETHYLPHENYCARBAMATE) COATED ON SILICA IN HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

Giorgi Kobidze, Iza Matarashvili, Bezhan Chankvetadze

Institute of Physical and Analytical Chemistry, School of Exact and Natural Sciences, Tbilisi State University, Tbilisi, Georgia

The goal of our research was the calculation of thermodynamic parameters of enantioseparation of ketoprofen enantiomers on polysaccharide-based chiral columns in high-performance liquid chromatography. This can help to predict the suitable analytical conditions for the given compound on given column for achieving the desired selectivity and enantiomer elution order.

We also compared thermodynamic parameters at the same stationary phase with various mobile phases. For analysed compounds, the values of adsorption enthalpy and adsorption entropy were calculated using the plot of natural logarithm of the separation factor versus the reciprocal of the absolute temperature. The goal was to evaluate if the enantioseparation was controlled by enthalpic or entropic term and what was the influence of temperature on retention and separation.

In order to calculate thermodynamic parameters this experiment was conducted on various temperatures. The results of this study have shown that temperature significantly affects chiral recognition pattern of polysaccharide phenylcarbamates. The question is if the change of chiral recognition pattern is caused by any chemical or structural change in the chiral selector, chiral analyte, both of them or, it is the result of enthalpy-entropy compensation. In order to get some idea on this regard, the enantioseparation of ketoprofen was studied on Lux Amylose-1 column in the temperature range 10-70°C when increasing the column temperature with 5° increments and afterwards, when cooling of the same column with the same increments down to 10°C.

References :

[1] I. Matarashvili, G. Kobidze, A. Chelidze, G. Dolidze, N. Beridze, G. Jibuti, T. Farkas, B. Chankvetadze, J. Chromatogr. A, 1599, 2019, 172-179.