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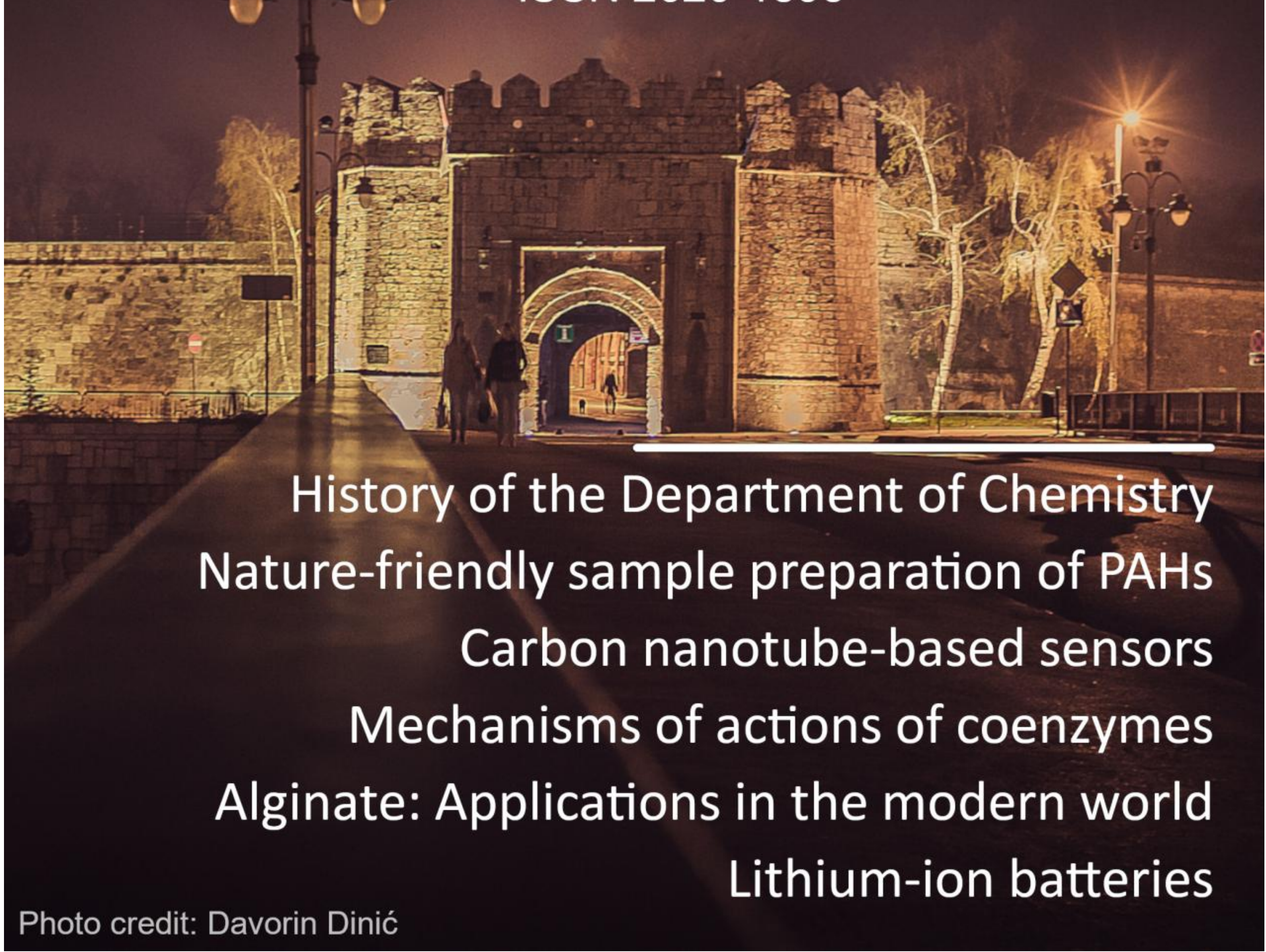

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Photo credit: Davorin Dinić

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History of the Department of Chemistry, the University of Niš, Republic of Serbia

Danijela Kostić

University of Niš, Faculty of Natural Sciences and Mathematics, Department of Chemistry,

Višegradska 33, 18000 Niš, Republic of Serbia, e-mail: danijelaaakostic@yahoo.com

ABSTRACT

Department of Chemistry was founded in 1971. In its long history, it became famous in Serbia and abroad because of the success and skills of its undergraduates, graduate students, and PhD-students. At the Department of Chemistry, since the founding, in addition to teaching, fundamental and applied researches were carried out in various fields of chemistry. Scientific activity was accomplished through many projects funded by the Republic of Serbia and international projects and within the framework of the Institute of Chemistry. Up to the end of 2017, a more than 1000 students graduated at the Department of Chemistry. Starting from the school year 2005-2006, previous Diploma of high education has been equalized with Master's degree. One hundred and ten master theses and 105 doctoral dissertations were defended (41 according to the new accredited program). Under the new Bologna program, 160 students received bachelor’s degrees and 96 master’s degrees. Graduated chemistry professors have made a great contribution to the development of education in Serbia also contributing to the development of the chemical industry in Serbia, and it is worth mentioning that many of them are very successful in working abroad. Masters and PhDs of Chemistry are employed at many faculties and colleges in Serbia and abroad. Many of them are authors of a large number of scientific papers published in renowned world scientific journals.

***Keywords**: history, Department for chemistry, University of Niš*

Teaching chemistry at the High Pedagogical School in Niš-beginning of study of chemistry on higher level

The High Pedagogical School in Niš was founded in 1948-1949 in order to educate the teaching staff (Figure 1). Chemistry was studied within three-subject (Physics-Chemistry-Mathematics) group. The group of physics-chemistry-mathematics, due to the development of the elementary education system, was transformed in 1954 into three groups: chemistry-physics,

physics-chemistry and mathematics. In accordance with this division, an adequate allocation of teaching staff was carried out within these groups.

Figure 1. Teaching staff in front of High pedagogical school in 1962 (Kerković and Ćirić, 2002).

Stanimir Arsenijević and Radmila Radovanović (Figure 2) were the first professors who were appointed in 1948/1949 for chemistry teaching. Professor Arsenijević lectured General, Inorganic, Analytical and Organic chemistry to the first generation of students, while Radmila Radovanović lectured General and Inorganic Chemistry to the second generation of students.

Stanimir Arsenijević Radmila Radovanović Čedomir Arsić

Figure 2. Chemistry professors at High Pedagogical school (Kerković and Ćirić, 2002)

In 1960, Professor Mirjana Canić was appointed, who, in addition to the theoretical teaching of General and Inorganic Chemistry, performed demonstrations and exercises and organized professional trips for students, linking theory with practice. Professor Čedomir Arsić (Figure 2) was elected in 1963 for teaching of Organic Chemistry and Methodology of Chemistry.

The initial working conditions were difficult, due to the lack of apparatus, as well as the lack of teaching and technical staff. With the efforts and enthusiasm of Prof. Stanimir Arsenijević and Radmila Radovanović, the difficulties in working within the chemistry-physics group were gradually eliminated. In the renovated premises in 1954, the first chemical laboratory was established with water and gas connections, with shelves, chemicals, well-equipped workplaces. Laboratory for experiments and exercises in chemistry contained 40 places and was an exemplary teaching base for chemistry studies and was one of the best, at that time, in the country among colleges. The first lab technician, Mihajlo Nešić, was employed in 1963.

In 1951, Stanimir Arsenijević founded the Serbian Chemical Society branch in Niš, which organized expert and scientific lectures by eminent chemistry professors.

The High pedagogical school in Niš worked from 1948 to 1971. In that period, 146 students graduated (Kerković and Ćirić, 2002).

Teaching chemistry at the Faculty of Philosophy in Niš

Chemistry at the Faculty of Philosophy began in November 1971 and was carried out in the premises and laboratories of the Higher Pedagogical School which stopped working. The chemical group thus had initial conditions for successful further development.

Lectures were conducted by temporarily employed professors, such as dr Milan Muškatirović, dr Darko Šepa and dr Ivan Stamenković. Afterwards, professors like Slobodan Vukotić and assistants Todor Pecev, Gordana Miletić, Stevan Miletić had permanent contracts. Since its founding, the Study group of chemistry consisted of three departments: the Department of Inorganic Chemistry, the Department of Analytical Chemistry and the Department of Organic Chemistry.

In 1978, postgraduate studies were introduced for the academic title of Master of Science. The courses of master's studies were: Inorganic Chemistry, Organic Chemistry, Analytical Chemistry and Course of Chemistry. For each direction, the curriculum and method of carrying out teaching and taking the exams were determined. Master's studies lasted two semesters and they were assumed to be finished after all passed exams and defending of the master's thesis, which was the result of the independent scientific work. In the period from 1978 to 1995, 119 postgraduates were enrolled, out of which 45 defended master's theses.

Specialistic studies were introduced at the Chemistry Group in 1980. There was only one direction for chemistry specialists.

A significant form of scientific research is around the creation and defense of the doctoral dissertation. At the Faculty of Philosophy in Niš, doctoral studies were introduced in 1972. At the beginning of the Chemistry Group, as it was mentioned before, there was not enough teaching staff, as well as other conditions necessary for this type of study, so the first doctoral dissertation in chemistry was defended in 1984.

At the end of 1995, 8 full professors, 3 associate professors, 2 assistant professors, 10 teaching assistants and 9 assistant trainees were working at the Department of Chemistry. From the founding until the end of 1995, 601 students of chemistry graduated, of which 238 males and 363 females. In the period from 1984 to 1995, 11 doctoral dissertations were defended at the

Faculty of Philosophy. The Institute of Chemistry was founded in 1996 and its aim is the organization of scientific research.

Research activity at the Department of Chemistry

Professors and assistants were working on 20 projects. Projects where chemists from our Department were leaders are:

1. Chemical and phytochemical investigations of herbs from the territory of the South-East Serbia (leader of the project: professor Dr Radosav Palić);
2. Application of the modern instrumental methods in natural, medical and other investigations (leader of the project: professor Dr Rangel Igov);
3. Application of physico-chemical methods for the control of waste industrial waters and input chemicals in the process of the production of leather and fur (leader of the project: professor Dr Milovan Purenović);
4. Development of current and the introduction of novel technologies into the processing of aluminum surfaces (leader of the project: professor Dr Milovan Purenović);
5. Technology of the production of the electrochemically active microalloyed aluminum (leader of the project: professor Dr Milovan Purenović);
6. Colored coatings of anodic oxidized aluminum (leader of the project: professor Dr Milovan Purenović);
7. Investigation and the development of auxiliary dyes with the aim of the replacement of imported colors (leader of the project: professor Dr Milovan Purenović);
8. Development of new methods for the characterization of tobacco raw material and main stream of cigarette smoke with the aim of the production of quality and less harmful cigarette (leader of the project: professor Dr Blaga Radovanović);
9. Balances in complex environments, within the subproject "Study of the nature, structure and origin of chemical species in natural environments” (1995-2000) funded by the Ministry of Science and Technological development, Republic of Serbia (project leader: professor Dr Pavle Premović);

10. Development of new analytical methods for the analysis in samples of natural and artificial origin in aquatic and non-aquatic environments, Ministry of Science, Technology and Development of the Republic of Serbia (1996-2000) (project leader: professor Dr Rangel Igov);
11. Development of new methods for determining low concentrations of substances in real samples (1995-2000) funded by the Ministry of Science and Technological development, Republic of Serbia (project leader: professor Dr Mirjana Obradović).

Chemists from this Department was also leaders on the following sub-projects:

1. Investigation of organic and inorganic structures in rheological materials (subproject leader: professor Dr Pavle Premović);
2. Spectroscopic investigations of any kind in natural surroundings: natural structure and the origin (subproject leader: professor Dr Pavle Premović).

The members of the chemistry group co-operated on 10 other scientific projects (Zaječaranović, 1996).

Teaching chemistry at the Faculty of Sciences and Mathematics in Niš

After the accreditation of the faculty with programmes according to Bologna declaration (http://www.bolognabergen2005.no/Docs/00_Main_doc/990719BOLOGNA_DECLARATION.PDF; http://www.parlament.gov.rs/content/lat/akta/zakoni.asp) that was completed in 2008, at the Faculty of Sciences and Mathematics in Niš, education are organized in three levels:

1) Bachelor's level (the first cycle)

This level is the beginning of a course or programme in the subject area and does not require previous studies at the university and is for beginners in higher education. The program at the bachelor's level at Department of chemistry is 3 years of full-time studies in length with 180 credits.

2) Master's level (the second cycle)

Master academic studies last 2 years. The combined total duration of a bachelor’s and a master’s studies is 5 years, or 300 ECTS. Master’s programmes always include a thesis, and unfortunately only a formal presentation. Students who complete a master's programme are awarded the degree of Master of chemistry.

The Master Chemistry program has the following directions:

- General Chemistry
- Applied Chemistry.

In the direction of General chemistry there are modules:

- Research and Development
- Professor of Chemistry

In the Applied chemistry direction there are modules:

- Applied Chemistry
- Chemistry of the Environment

3) Doctoral level (the third cycle)

The prerequisite for the studying of the doctoral level is that the candidate must complete a degree at the master's level.

Today, at the Faculty of Sciences and Mathematics, the doctoral studies last three years and are conducted under the supervision of usually one mentor. Three-year PhD program has been introduced in 2006 with 8 exams which are all picked from a list of accredited courses and 5 study researches. As mentioned before, the work on PhD theses is carried out under the guidance of a mentor selected from a pre-determined list, and dissertations are defended upon the publication of two papers in journals ranked as M20 (classification according to Ministry of Science, Education and Technological Development of Republic of Serbia).

Since 2011, the defended PhD theses are available on the faculty website in electronic form. Upon completion of the doctoral studies program, a candidate is awarded a PhD in natural science-chemistry. Until the end of 2017, 103 PhD theses have been defended, 39 of which have been defended since 2006.

Workspace

The Department of Chemistry occupies 1930.5 m^2 (811.8 m^2 classrooms, 177.2 m^2 computer rooms, and 667.4 m^2 laboratories). There are appropriate techniques for teaching: graphoscopes, video screens and laptops, and interactive board that enables contemporary teaching. For carrying out laboratory exercises and practical teaching of students, modern equipments and instruments are available. A large number of personal computers on academic networks that allows searching of chemical databases are available to the chemistry students.

The library

The Library of the Higher Pedagogical School was established in 1950 and had 19070 books and a considerable number of different journals (around 2000). The Faculty of Philosophy inherited a library from the Higher School of Pedagogy. The book fund has been increased over time and in 1995 it included 46768 books, of which 1410 books in the field of chemistry, with a large number of domestic and foreign journals. The Faculty of Sciences and Mathematics has inherited from the Faculty of Philosophy textbooks and magazines in the field of chemistry. The library fund was enriched with the purchase of contemporary editions, donations of professors and former chemistry students and editions published by professors and associates from the Department of Chemistry. The library now contains 3400 book titles from various fields of chemistry, and numerous hard copies of the journals. Today, for most subjects, there are textbooks and books of exercises whose authors are professors and associates employed at the Department of Chemistry.

Department of Chemistry publishes two scientific journals: **Chemia Naissensis**, and **Facta universitatis, series: physics, chemistry and technology**.

Teaching staff

Currently, there are 31 professors and two assistants at the chemistry department. Additionally, the students of doctoral studies are engaged in teaching, and for practicals technicians and professional associates.

Research activity at the Department of chemistry until 2011

In the period from 2000, teachers and associates of the Department of Chemistry participated in the realization of the following scientific projects, which were led by professors from the Department of chemistry.

1. Physicochemical characterization of heavy metals in structures of synthetic minerals of clay, natural minerals of clay and clay of industrial and ecological significance from the area of wider Serbia (2000-2005) funded by the Ministry of Science and Technological Development, Republic of Serbia (project leader prof. Pavle Premović);
2. Development of new and improvement of existing analytical methods for monitoring the quality of industrial products and the environment (2000-2005) funded by the Ministry of Science and Technological Development, Republic of Serbia (project leader prof. Snežana Mitić);
3. Development and application of methods for monitoring the quality of industrial products and the environment (2006-2010) funded by the Ministry of Science and Environmental Protection, Republic of Serbia (project leader prof. Snežana Mitić);
4. Investigation of chemical composition and bioactivity of secondary metabolites of plants species from genera *Achillea*, *Acinos*, *Artemisia* and *Calamintha* (2002-2005) funded by the Ministry of Science and Environment Protection, Republic of Serbia (project leader prof. Radoslav Palić);
5. Secondary metabolites: biological and antioxidant activity (2006-2010) funded by the Ministry of Science and Environmental Protection, Republic of Serbia (project leader prof. Radoslav Palić);

6. Innovation, monitoring and reconstruction of technical-technological system for refinement of alkali, cyanide and acidic wastewaters, which contain Cr, Ni, Cu, Zn, Sn and Cd, funded by: Ministry of Science and Technological Development, Republic of Serbia (project leader prof. Milovan Purenović);
7. Improvement of chemical-technological processes and system reconstruction in electronic tubes manufacture (2005-2008), funded by: Ministry of Science and Technological Development, Republic of Serbia (project leader prof. Milovan Purenović).

   International project:
8. European Union [FP7-REG-POT-2007-3-01]; KBBE: Food, Agriculture and Biotechnology project "CHROMOLAB-ANTIOXIDANT" [204756]; EU 2008-2O11 (participant)

Professors who were working at Department of Chemistry

Professors with permanent employment at Department of Chemistry were: 1) dr Slobodan Vukotić (1971-1979), professor in Analytical chemistry; 2) dr Stevan Lajšić (started 1977 with teaching in Chemistry of natural products, dean of the Faculty of Philosophy (1979-1981), and then moved to Novi Sad) (Figure 3) and 3) dr Stojan Stojković, professor in Physical Chemistry who were at University of Niš couple of years, and then moved to Belgrade.

Figure 3. Dr Stevan Lajšić (https://www.filfak.ni.ac.rs/fakultet/dekani-i-prodekani)

Because of the insufficient number of professors the following people were employed (up to 1/3 of the time): dr Bogdan Stanić, dr Srbobran Rajić, dr Lidija Pfendt, dr Bojana Grujić Injac, dr Jovan Vučetić, dr Konstantin Popov, dr Miljenko Perić, dr Slobodan Sukdolak, dr Milorad Cakić, dr Petar Ilić, dr Lazar Đorđević, dr Aleksandar Jokić, dr Milorad Jeremić, dr Slobodan Milosavljević, dr Petar Petrović, dr Mijat Malinar, dr Mile Novaković, dr Velibor Mitić and associate Dragan Lazarević.

Professors that retired:

1. Pavle Premović, full professor from 1988
2. Rangel Igov, full professor from 1989 (died)
3. Radoslav Palić, full professor from 1993
4. Miloje Rakočević, full professor from 1994
5. Todor Pecev, full professor from 1994 (died)
6. Stevan Miletić, full professor from 1995 (died)
7. Gordana Miletić, full professor from 1995
8. Milovan Purenović, full professor from 1995
9. Jasna Ursić Janković, full professor from 1999
10. Đorđe Glišin, associate professor from 1992 (died)
11. Blaga Radovanović, full professor from 1997
12. Jelica Perović, full professor from 2003 (died)
13. Ružica Nikolić, full professor from 2003

Teaching assistants and professors that were employed at The Department of Chemistry, and then left:

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1. Ivan Ivanov, teaching assistant
2. Olivera Kitanović, teaching assistant
3. Natalija Miladinović, teaching assistant
4. Nebojša Simić, associate professor
5. Anđelković Slobodan, teaching assistant
6. Miroslav Premović, teaching assistant
7. Dejan Dulanović, teaching assistant
8. Momčilo Vidaković, teaching assistant

9. Biljana Arsić, teaching assistant
10. Aleksandra Živković, teaching assistant

Unfortunately, Biljana Popović, who was working together with professor Pavle Premović died.

As associates in teaching were:

1. Drenka Zeljković, responsible for giving practical exercises in analytical chemistry to students (died)
2. Ljubomir Ignjatović, technician (died)
3. Sima Stoimenov, chemicals keeper
4. Dragica Lazarević, technician
5. Petra Cvetković, technician
6. Jovan Jovanović, technician

Conclusion

The Department of Chemistry educated over 1000 graduated chemists, 110 MSc and 64 PhDs. According to the new study program, 160 bechelor students, 96 master students and 41 doctors of science graduated from the study program. Teachers, associates and students of the Department of Chemistry participated in the realization of a large number of domestic and international scientific projects and they are authors of a large number of scientific papers. Graduated students of chemistry, masters and doctors of science have greatly contributed to the development of education and industry in Serbia and abroad.

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Istorija Departmana za hemiju, Univerziteta u Nišu, Republika Srbija

Danijela Kostić

Univerzitet u Nišu, Prirodno-matematički fakultet, Univerzitet u Nišu, Višegradska 33, 18000 Niš, Republika Srbija

SAŽETAK

Departman za hemiju osnovan je 1971. godine. U svojoj dugoj istoriji postao je poznat u Srbiji i inostranstvu po uspehu i veštini njegovih diplomiranih studenata, magistranata i doktoranata. Na Departmanu za hemiju, od osnivanja, pored nastavnog rada, vršena su osnovna i primenjena istraživanja u različitim oblastima hemije. Naučna aktivnost je realizovana kroz mnoge projekte finansirane od strane Republike Srbije, i međunarodne projekte u okviru Instituta za hemiju. Do kraja 2017. više od 1000 studenata završilo je studije na Departmanu za hemiju. Počev od školske 2005-2006. godine, prethodna diploma visokog obrazovanja izjednačena je sa diplomom master hemičar. Odbranjeno je 110 magistarskih teza i 105 doktorskih disertacija (41 po novom akreditovanom programu). Po novom Bolonjskom programu, 160 studenata je steklo diplomu osnovnih i 96 master studija. Diplomirani profesori hemije su dali veliki doprinos razvoju obrazovanja u Srbiji, takođe doprinoseći razvoju hemijske industrije u Srbiji, a treba napomenuti da mnogi od njih su veoma uspešni u inostranstvu. Magistri i doktori hemije su zaposleni na mnogim fakultetima i višim školama u Srbiji i inostranstvu. Mnogi od njih su autori velikog broja naučnih radova objavljenih u poznatim međunarodnim naučnim časopisima.

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L'histoire du Département de chimie de l'Université de Niš (République de Serbie)

Danijela Kostic

Université de Nis, Faculté des sciences et mathématiques, Département de chimie, Visegradska 33, 18 000 Niš, Serbie

RÉSUMÉ

Le Département de chimie a été fondé en 1971. Lors de sa longue histoire, le Département a connu son succès en Serbie et à l'étranger grâce à la réussite et à l'habilité de ses diplômés des programmes de licence, de DEA/master et d'études doctorales. Dès la constitution du Département de chimie, à part les activités pédagogiques, de nombreuses recherches fondamentales et appliquées ont été effectuées dans les différents domaines de la chimie. L'activité scientifique a été réalisée à travers de nombreux projets financés par la République de Serbie, ainsi qu'à travers des projets internationaux réalisés au sein de l'Institut de chimie. Jusqu'à la fin de 2017, plus de mille d'étudiants ont fini leurs-études au Département de chimie. À partir de l'année académique 2005/2006, l'ancien diplôme de l'éducation supérieure est devenu équivalent au diplôme de Master chimiste. Ainsi, au Département, cent dix mémoires de master et cent cinq thèses de doctorat (quarante-et-un, selon le nouveau programme d'études accrédité) ont été soutenus. D'après le nouveau programme de Bologne, cent soixante étudiants ont terminé leurs études en acquérant le diplôme de licence et quatre-vingt-seize étudiants acquérant celui de master. Les professeurs de chimie diplômés ont abondamment contribué au développement de l'éducation et au développement de l'industrie chimique en Serbie, mais il est à noter également que les nombreux diplômés ont de grand succès international. Aujourd'hui, les diplômés de DEA/master et d'études doctorales de chimie travaillent aux nombreuses facultés et écoles supérieures en Serbie et à l'étranger. Beaucoup parmi eux sont les auteurs d'un grand nombre d'articles scientifiques publiés dans les revues scientifiques internationales.

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История Отделения химии, Университет в Нише, Республика Сербия

Даниела Костич

Университет в Нише, Факультет естественных наук и математики, Химический департамент, Вышеградская 33, 18000 Ниш, Республика Сербия

АННОТАЦИЯ

Департамент химии основан в 1971 году. За свою долгую историю он прославился в Сербии и за рубежом успехами и умениями своих аспирантов, магистратов и докторантов. На Химическом департаменте с момента создания, в дополнение к обучению, проводились фундаментальные и прикладные исследования в различных областях химии. Научная деятельность осуществлялась в рамках многих проектов, финансируемых Республикой Сербия, и международных проектов в рамках Института химии. К концу 2017 года более 1000 студентов завершили обучение на Департаменте химии . Начиная с 2005-2006 учебного года предыдущий диплом о высшем образовании был приравнен к диплому магистра химии. Защищено 110 кандидатских и 105 докторских диссертаций (41 по новой аккредитованной программе). В соответствии с новой Болонской программой, 160 студентов приобрели степень бакалавр и 96 - степень магистра. Дипломированные преподаватели химии внесли большой вклад в развитие образования в Сербии, а также в развитие химической промышленности в Сербии, и следует отметить, что многие из них очень успешны за рубежом. Магистры и доктора химии работают на многих факультетах и в колледжах в Сербии и за рубежом. Многие из них являются авторами большого количества научных работ, опубликованных в известных международных научных журналах.

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Chair of Analytical and Physical Chemistry

Snežana Mitic, Snežana Tosic*, Aleksandra Pavlovic, Milan Mitic

University of Niš, Faculty of Sciences and Mathematics, Department of Chemistry, Višegradska 33, 18000 Niš, Serbia

ABSTRACT

The Chair for Analytical and Physical Chemistry currently consists of ten professors and two associates. A number of researchers and other associates also contribute to the work carried out within the Chair. Throughout every level of the studies (Undergraduate Academic Studies, Master Academic Studies, and Doctoral Academic Studies), the students attend a great number of courses within these scientific fields. The members of the Chair are the authors of 14 university coursebooks, workbooks, as well as practicums. The professors, associates and researchers of the Chair deal with the following fields of scientific research: the GC-MS analysis of PAHs with the optimization of the method of samples preparation, the development and validation of the ICP-~~O~~AES methods, the development and validation of kinetic spectrophotometric methods, the HPLC determination of total polyphenols, flavonoids and anthocyanins with the examination of the kinetics of their degradation, the spectrophotometric and the cyclic voltammetry determination of antioxidant activity. A large number of papers has been published in international and national journals. The research laboratories are equipped with ICP-AES, HPLC, spectrophotometers, automatic titrator, analytical balances, high purity water system, vacuum evaporator, pH-meters, conductometers, and other minor laboratory equipment. The researchers of the Chair have participated in many national scientific-research projects, as well as international projects such as Erasmus, Tempus, FP7, The Researchers' Night, and they have also attended the postdoctoral specializations and study visits abroad, which contribute to the good cooperation between the Chair and other universities in the world.

Staff of the Chair

The Chair for Analytical and Physical Chemistry includes the following professors and associates: Snežana Mitić (*Head of the Chair*), Vesna Stankov-Jovanović (*Head of the Division of Chemistry at the Center for Scientific and Professional Activities in Natural and Mathematical Sciences*), Snežana Tošić, Violeta Mitić (*Head of the Department of Chemistry*) and Aleksandra Pavlović as full professors; Sofija Rančić, Emilija Pecev-Marinković, Ivana Rašić Mišić, Milan Mitić as associate professors; Milan Stojković as an assistant professor and Jelena Cvetković and Jelena Mrmošanin as teaching assistants. Marija Ilić as a scientific associate, Marija Dimitrijević, and Ana Miletić as research associates, Slobodan Ćirić as a research assistant, professional associates and other associates in the laboratories also participate in teaching and research activities.

Figure 1. The Staff of the Chair for Analytical and Physical Chemistry

Studies

At the first level of studies (three-year undergraduate academic studies-Chemistry) students are introduced to the following courses in the field of analytical and physical chemistry: Analytical Chemistry 1, Analytical Chemistry 2, Physical Chemistry 1, Structure of Atoms and Molecules, Analytical Chemistry 3, Physical Chemistry 2, Instrumental Analytical Chemistry as obligatory courses and Statistical Data Analysis, Selected Topics in Volumetric Analysis, Complex Samples Preparation, Principles of Quality Control in Analytical Laboratory and Molecular Spectra as elective courses. At the two-year second level of master academic studies-Chemistry (modules: Research and Development, and Teacher of Chemistry) and Applied Chemistry (modules: Applied Chemistry, and Environmental Chemistry) students are introduced to the following courses: Electrochemistry, Modern Optical Methods of Analysis, Modern Electroanalytical Methods, Chemometrics, Selected Topics in Instrumental Analysis, Kinetics and Catalysis, Environmental Analytical Chemistry, Methodology of Chemistry Teaching 2 and School Practice 2 as obligatory courses, and Physico-Chemical Bases of Separation Methods in Chemistry, Selected Topics in Physical Chemistry, Physical Chemistry of Solids, Scientific Research Methodology, Working with Talented Students, Food Chemistry Analysis, Bioanalytical Chemistry, Kinetic Methods of Analysis, Analysis of Toxic Substances, and Environmental Electroanalytical Methods as elective courses. Doctoral academic studies-Chemistry in duration of three years include the following elective courses: Equilibria in Chemistry, Selected Topics in Optical and Related Methods of Chemical Analysis, Selected Topics in Electrochemical Methods of Analysis, Atomic Spectroscopy, Molecular Spectroscopy, Instrumental Analysis 1, Instrumental Analysis 2, Physical and Chemical Methods for Equilibrium Determination in Complex Media, Separation Methods, Kinetic Methods of Analysis, Selected Topics in Physical Chemistry, Selected Topics in the Applications of Organic Reagents in Chemical Analysis.

Laboratory equipment

The laboratory equipment of the Chair for Analytical and Physical Chemistry (Fig. 2) includes:

- Inductively coupled plasma atomic emission spectrometer (ICP-AES) iCAP 6300 Duo (Thermo Scientific, Cambridge, UK);
- HPLC Agilent-1200 (Agilent Technologies, Santa Clara, California, USA) with Ultra Violet-Visible–Diode Array Detection (UV-Vis DAD) detector and Fluorescence Detector (FLD);
- Spectrophotometer Agilent-8453 (Agilent Technologies, Santa Clara, California, USA);
- Spectrophotometer UV-1800 Shimadzu (Shimadzu Corporation, Kyoto, Japan);
- Spectrophotometer Spectra 2000 (LaboMed, INC., Los Angeles, California, USA);
- Lambda 15 UV/VIS Spectrophotometer (Perkin-Elmer, Waltham, Massachusetts, USA);
- Analytical balance AB204-S (Mettler Toledo Greifensee, Switzerland);
- ED5A Heating Circulator with Open Bath (Julabo, Seelbach, Baden-Württemberg, Germany);
- Rotavapor R200 (BUCHI, New Castle, USA);
- Automatic titrator 716 DMS Titrino (Metrohm, Switzerland);
- MicroMed high purity water system (TKA Wasseraufbereitungssysteme GmbH, Germany).

Figure 2. Laboratory equipment

Research Projects

Since 2000, researchers, members of the Chair for Analytical and Physical Chemistry, have been included in the following national projects:

- Ethnopharmacological study of the region of South-Eastern Serbia (2017-);
- 172047: Natural products of plants and lichens: isolation, identification, biological activity and application (2011-);
- 172051: Development of new and improvement of existing electrochemical, spectroscopic and flow injection (FIA) methods on environmental quality monitoring (2011-);
- 172061: Combinatorial libraries of heterogeneous catalysts, natural products, modified natural products, and analogs: The approach to new biologically active agents (2011-);
- 142015: Development and application of methods for industrial products and environment quality monitoring (2006-2010);
- 142054: Secondary metabolites: Biological and antioxidant activity (2006-2010);
- 1211: Development of new and improvement of existing analytical methods for industrial products and environment quality monitoring (2001-2005);
- 2812: Investigation of chemical composition and bioactivity of secondary metabolites of plants species from genera *Achillea*, *Acinos*, *Artemisia* and *Calamintha* (2001-2005);
- 02M14: Development of new analytical methods for the analysis of elements in the samples of natural and artificial origin in aquatic and non-aquatic environments (1995-2000).

They have taken part in following international projects as well:

- ERASMUS+ (Capacity building in higher education)**,** 573806-EPP-1-2016-1-RS-EPPKA2-CBHE-JP, Development of master curricula for natural disasters risk management in Western Balkan countries (NatRisk) (2016-);
- TEMPUS,544006-TEMPUS-1-2013-1-RS-TEMPUS-SMGR, FUSE-FosteringUniversity Support Services and Procedures for Full Participation in the European Higher Education Area (2013-2016);

- "RESEARCHERS' NIGHT 2018-2019", Road to Friday of Science 2.0 - "ReFocuS 2.0", 818325-ReFocuS 2.0, H2020-MSCA-NIGHT-2018;
- "RESEARCHERS' NIGHT 2016-2017", Road to Friday of Science - "ReFocuS", 722341-ReFocuS, H2020-MSCA-NIGHT-2016;
- "RESEARCHERS' NIGHT 2014-2015", 633376-SCIMFONICOM, H2020-MSCA-NIGHT-2014;
- TEMPUS, 511044-TEMPUS-1-2010-1-UK-TEMPUS-JPCR UoG "Modernisation of Post-Graduate Studies in Chemistry and Chemistry Related Programmes", MCHEM, 2011-2013;
- FP7, FP7- REG-POT-2007-3-01 "CHROMLAB-ANTIOXIDANT" (2008-2010).

Postdoctoral research and study visits

Several researchers, members of the Group for Analytical and Physical Chemistry, were on postdoctoral stays abroad supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia within the program of postdoctoral fellowships for young scientists. In 2013, Milan Mitić was on a five-month postdoctoral stay at the Laboratory of Food Science and Technology, School of Chemistry, The Aristotle University of Thessaloniki (under the supervision of Prof. Dr. Maria Tsimidou and the collaboration of Dr. Eleni Naziri). In 2008, Milan Mitić was on a three-month study visit at the National Institute for Agricultural Research Laboratory, Montpellier, INRA, France. The training was carried out under the supervision of Jean-Marc Souquet (INRA, France). Vesna Stankov Jovanović was on a six-month postdoctoral stay at University Pierre and Marie Curie (Paris, France) under the program "Research in Paris 2011" (2011-2012). In 2018, she was also on a one-month study visit at University of Natural Resources and Life Sciences (BOKU, Vienna, Austria) and in 2010 she was a visiting researcher at the Institute for Water Education at Delft University (UNESCO-IHE). Since 1986, Vesna Stankov-Jovanović has collaborated with the Department of Chemistry and Hydrogeology of the Petnica Research Center and since 2006, she has lectured various courses to school pupils.

Collaboration

Researchers at the Group for Analytical and Physical Chemistry cooperate with the following institutions: Middlesex University, London, UK; Technical University Crete, Greece; Obuda University, Budapest, Hungary; University of Messina, Messina, Italy; University "Otto Friedrich", Bamberg, Germany; Jagiellonian University, Krakow, Poland; University of Malaga, Malaga, Spain; Masaryk University, Brno, Czech Republic; University of Marseille, France; University of Poitiers, France; University of Ljubljana, Slovenia; Ondokuz Mais University, Samsun, Turkey; University of Tirana, Albania; University Alexandar Moisiu, Durres, Albania; University of Sarajevo, Bosnia and Herzegovina, and University of East Sarajevo, Bosnia and Herzegovina.

Research work

Research work includes:

- investigation of a novel sorbent to the quick, easy, cheap, effective, rugged, and safe technique for soil sample preparation for the determination of polycyclic aromatic hydrocarbons (PAHs) by GC-MS analysis;
- optimization the QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) technique, in order to establish an efficient method for the extraction of PAHs from the soil, using various sorbent and solvent system combinations, followed by GC-MS analysis;
- development and validation of the ICP-AES method for determination of elements in soil, water, plants, foods, *etc.*;
- development and validation of kinetic spectrophotometric methods for the determination of metals, amino acids, the residue of pesticides and pharmaceuticals in the soil, water, foods, and pharmaceutical preparations;
- identification and quantification of polyphenolic compounds in food and plants by HPLC chromatography;

- determination of total polyphenols, flavonoids and anthocyanins in food and plants using spectrophotometric methods;
- evaluation of food and plant antioxidant activity by spectrophotometric techniques such as 1) radical scavenging activity (2,2-diphenyl-1-picrylhydrazyl, DPPH), 2) cation decolorization activity (2,2'-azino-bis (3-ethylbenzothiazoline-6-sulphonic acid, ABTS), 3) ferric reducing antioxidant power (FRAP), 4) cupric reducing antioxidant capacity (CUPRAC), and 5) total reducing power (TRP);
- evaluation of food and plant antioxidant activity by electrochemical technique-cyclic voltammetry;
- chemometric characterization of food and plants according to their antioxidant activities, polyphenolic and metal contents;
- investigation of the kinetics of the degradation of catechins and procyanidins during food storage and preparation.

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Katedra za analitičku i fizičku hemiju

Snežana Mitić, Snežana Tošić*, Aleksandra Pavlović, Milan Mitić

Univerzitet u Nišu, Prirodno-matematički fakultet, Departman za hemiju, Višegradska 33,
18 000 Niš, Srbija

SAŽETAK

Katedru za analitičku i fizičku hemiju trenutno čini deset nastavnika i dva saradnika. U radu Katedre učestvuje i veći broj istraživača i drugih saradnika. Kroz sve nivoe studija (osnovne akademske, diplomske akademske i doktorske akademske studije) studenti pohađaju veliki broj kurseva iz ovih naučnih oblasti. Članovi Katedre su autori 14 univerzitetskih udžbenika, zbirki zadataka i praktikuma. Nastavnici, saradnici i istraživači ove katedre se u naučno-istraživačkom radu bave sledećim oblastima istraživanja: GC-MS analiza PAH-ova sa optimizacijom postupka pripreme uzoraka, razvoj i validacija ICP-AES metoda, razvoj i validacija kinetičko spektrofotometrijskih metoda, HPLC identifikacija i kvantifikacija polifenolnih jedinjenja, HPLC određivanje ukupnih polifenola, flavonoida i antocijana sa ispitivanjem kinetike njihove degradacije, određivanje antioksidativne aktivnosti spektrofotometrijski i primenom ciklične voltametrije. Publikovan je veliki broj radova u međunarodnim i nacionalnim časopisima. Istraživačke laboratorije su opremljene sa ICP-AES, HPLC, spektrofotometri, automatski titrator, analitičke vage, demineralizator, vakuum uparivač, pH-metri, konduktometri i ostala sitna laboratorijska oprema. Istraživači ove Katedre su učestvovali i učestvuju u mnogim nacionalnim naučno-istraživačkim projektima kao i međunarodnim projektima kao što su Erasmus, Tempus, FP7, Noć istraživača a takođe su odlazili na postdokorska usavršavanja i studijske boravke u inostranstvu, što između ostalog doprinosi inače dobroj saradnji sa mnogim univerzitetima u svetu.

Chaire de chimie analytique et physique

Snežana Mitic, Snežana Tosic*, Aleksandra Pavlovic, Milan Mitic

Université de Nis, Faculté des sciences et mathématiques, Département de chimie, Visegradska 33, 18 000 Niš, Serbie

L'équipe enseignante de la Chaire de chimie analytique et physique est constituée de dix professeurs et deux maîtres-assistants. Un nombre important de chercheurs et d'autres collaborateurs participent aussi aux activités de la Chaire. Dans tous les niveaux d'études (les études du premier cycle, du master et les études doctorales), les étudiants suivent des cours nombreux concernant les domaines scientifiques mentionnés. Les membres de la Chaire sont les auteurs des quatorze manuels universitaires, des cahiers d'exercices et des recueils de travaux de laboratoire. Dans leur travail scientifique, les professeurs, les maîtres-assistants et les chercheurs de la Chaire s'intéressent aux sphères de recherche suivantes : l'analyse GC-MS des HAP avec l'optimisation du processus de préparation des échantillons, le développement et la validation des méthodes ICP-OES, le développement et la validation des méthodes cinétiques spectrophotométriques, l'identification et la quantification des composés polyphénols par HPLC, la détermination du total des polyphénols, des flavonoïdes et des anthocyanes par HPLC avec l'examen de la cinétique de leur dégradation, la détermination de l'activité antioxydante par le biais de la méthode spectrophotométrique et de la voltampérométrie cyclique. Un grand nombre d'articles est publié dans des revues nationales et internationales. Les laboratoires scientifiques de la Chaire possèdent : ICP-AES, HPLC, les spectrophotomètres, le titrage automatique, les balances analytiques, les déminéralisateur, l'évaporateur rotatif, les pH-mètres, les conductomètres et d'autres appareils laboratoires. Les chercheurs de la Chaire ont participé et participent aujourd'hui aux projets scientifiques multiples au niveau national, ainsi qu'aux projets internationaux tels que : Erasmus, Tempus, FP7, La nuit des chercheurs. À l'étranger, ils ont suivi des programmes d'études postdoctorales et ont réalisé leurs séjours de recherche, ce qui contribue indubitablement à la bonne collaboration de la Chaire avec de nombreuses universités dans le monde.

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Кафедра аналитической и физической химии

Снежана Митич, Снежана Тошич *, Александра Павлович, Милан Митич

Университет в Нише, Факультет естественных наук и математики, Отдел химии, Вишеградска 33, 18 000 Ниш, Сербия

Кафедра аналитической и физической химии в настоящее время состоит из десяти преподавателей и двух сотрудников. На всех уровнях обучения (в бакалавриате, аспирантуре и докторантуре) студенты посещают большое количество курсов по этим научным областям. Члены кафедры являются авторами 14 университетских учебников, сборников задач и практикумов. Преподаватели, сотрудники и исследователи этой кафедры в научных исследованиях, проводят исследования по следующим направлениям: ГХ-МС анализ ПАУ путем оптимизации процесса пробоподготовки, разработка и валидация метода ICP-OES, разработка и валидация кинетических спектрофотометрических методов, ВЭЖХ идентификация и количественное определение полифенольных соединений, ВЭЖХ определение общего количества полифенолов, флавоноидов и антоцианов с изучением кинетики их деградации, определение антиоксидантной активности спектрофотометрически с использованием циклической вольтамперометрии. Опубликован ряд статей в международных и национальных журналах. Исследовательские лаборатории оснащены ICP-AES, ВЭЖХ, спектрофотометрами, автоматическим титратором, аналитическими весами, деминерализатором, вакуумным испарителем, pH-метрами, кондуктометрами и другим мелким лабораторным оборудованием. Исследователи этой кафедры участвовали и участвуют во многих национальных научно-исследовательских проектах, а также в международных проектах, таких как Erasmus, Tempus, FP7, Ночь исследователей, а также ездили за границу на курсы повышения квалификации, что, между прочим, способствует уже хорошему сотрудничеству со многими университетами мира.

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Chair of Organic Chemistry and Biochemistry

Gordana S. Stojanovic, Snezana C. Jovanovic*, Marija S. Gencic

University of Niš, Faculty of Sciences and Mathematics, Department of Chemistry, Višegradska Street No 33, 18000 Niš

ABSTRACT

In this presentation, the following is given briefly: an overview of courses, professors and associates at the Chair of Organic Chemistry and Biochemistry at undergraduate academic studies (bachelor), at master academic studies and at doctoral academic studies; aim and brief overview of the courses within the Chair of Organic Chemistry and Biochemistry, as well as an overview of research projects "Natural products of plants and lichens: isolation, identification, biological activity and application" and "Combinatorial libraries of heterogeneous catalysts, natural products, modified natural products and analogues: The approach to new biologically active agents", including list of researchers that are members of Chair of Organic Chemistry and Biochemistry along with their main research area and the most important achievements and/or positions.

Studies

Through numerous courses and researches, members of the Chair of Organic Chemistry and Biochemistry realize educational and scientific activity. There are ten professors, one teaching assistant and twelve PhD students which organize and carry out classes from obligatory and elective subjects in the 2017/18 academic year. Tables 1-3 display overview of courses at three different levels of study: undergraduate academic studies in Table 1 (7 obligatory and 5 elective); master academic studies in Table 2 (10 obligatory and 11 elective); and doctoral academic studies in Table 3 (13 elective). Apart from teaching, the members of the Chair are also involved in research work, which will be discussed later.

Table 1. An overview of courses, professors and associates at the Chair of Organic Chemistry and Biochemistry at undergraduate academic studies (bachelor)

N	Course	Semester	Course type [1]	L+Te+O[2]	ECTS[3]	Professor (L)	Professor/associates (Te+O)
1.	*History of Chemistry*	1.	E	2+0+0	3	Danijela Kostić	
2.	*Organic Chemistry 1*	2.	O	5+1+0	9	Gordana Stojanović	Gordana Stojanović
3.	*Experimental Organic Chemistry*	2.	O	1+0+4	3	Aleksandra Đorđević	Ivana Zrnzević
4.	*Organic Chemistry 2*	3.	O	4+1+0	8	Niko Radulović, Polina Blagojević	Dragan Zlatković
5.	*Preparative Organic Chemistry*	4.	O	1+0+5	3	Polina Blagojević	Sonja Filipović, Milica Stevanović
6.	*Chemistry of Natural Compounds*	5.	O	4+0+4	8	Danijela Kostić	Milica Todorovska
7.	*Instrumental Methods in Organic Chemistry*	6.	O	4+4+0	7	Olga Jovanović	Snežana Jovanović
8.	*Biochemistry*	6.	O	4+0+5	5	Ivan Palić	Jovana Ickovski
9.	*Nomenclature of Organic Compounds*	4.	E	2+1+0	4	Polina Blagojević	Polina Blagojević
10.	*Pharmaceutical Chemistry*	6.	E	2+0+2	5	Aleksandra Đorđević	Aleksandra Đorđević
11.	*Organic Chemistry of Food*	6.	E	2+0+2	4	Snežana Jovanović	Snežana Jovanović
12.	*Organic Chemistry in Everyday Life*	6.	E	2+2+0	4	Marija Genčić	Marija Genčić

[1] Course type: *O* – Obligatory or *E* – Elective.

[2] Active teaching hours: *L* – Lectures, *Te* –Theoretical exercises, and *O* – Laboratory work and other forms of teaching.

[3] Number of ECTS allocated.

Table 2. An overview of courses, professors and associates at the Chair of Organic Chemistry and Biochemistry at master academic studies

N	Modules[1]	Course	Semester	Course type [2]	L+Lw+O[3]	ECTS[4]	Professor (L)	Professor/associates (Lw+OMT)
1.	**Ch, Ch$_{RD}$, Ch$_{T}$**	*Dynamic Stereochemistry*	1.	O	3+2+0	7	Gordana Stojanović	Gordana Stojanović
2.	**Ch, Ch$_{RD}$, Ch$_{T}$**	*Organic Synthesis*	2.	O	3+0+4	8	Niko Radulović, Marija Genčić	Milena Živković
3.	**Ch, Ch$_{RD}$, Ch$_{T}$**	*Dynamic Biochemistry*	2.	O	2+0+2	5	Ivan Palić	Jovana Ickovski
4.	**Ch, Ch$_{RD}$**	*Selected Chapters of Organic Chemistry*	3.	O	3+2+0	7	Olga Jovanović	Olga Jovanović
5.	**Ch, Ch$_{RD}$, Ch$_{T}$**	*Chemistry of Secondary Metabolites*	2.	E	2+0+2	4	Gordana Stojanović, Aleksandra Đorđević	Gordana Stojanović, Aleksandra Đorđević
6.	**Ch, Ch$_{RD}$**	*Organic Structure Determination: An Advanced Course*	3.	E	3+0+2	5	Niko Radulović	Niko Radulović, Milan Nešić
7.	**Ch, Ch$_{RD}$**	*Advanced Organic Chemistry*	4.	E	3+0+2	5	Polina Blagojević	Polina Blagojević, Milan Nešić
8.	**Ch, Ch$_{RD}$**	*Advance Course*	4.	E	3+0+2	5	Goran	Goran Petrović, Ivan

		of Instrumental Chromatographic Methods					Petrović, Ivan Palić	Palić, Jelena Stamenković
9.	**Ch**, **Ch**$_T$	*School Experiments in Organic Chemistry*	3.	O	2+0+3	6	Danijela Kostić	Danijela Kostić
10.	**Ch**, **Ch**$_T$	*Nobel Prize in Chemistry*	4.	E	2+0+2	3	Danijela Kostić	Danijela Kostić
11.	**Ch**, **Ch**$_T$	*Everyday Life Chemistry – Atkins' molecules*	4.	E	2+0+2	3	Snežana Jovanović	Snežana Jovanović
12.	**Ch**$_A$, **Ch**$_E$	*Chemistry of Organic Polymers*	1.	O	4+0+2	7	Niko radulović	Miljana Đorđević
13.	**Ch**$_A$, **Ch**$_E$	*Applied Organic Chemistry*	2.	O	3+0+3	6	Goran Petrović	Jelena Stamenković
14.	**Ch**$_A$	*Synthesis of Macro-Quantity of Organic Compounds*	3.	O	3+0+3	7	Goran Petrović	Jelena Stamenković
15.	**Ch**$_A$, **Ch**$_E$	*Forensic Chemistry*	2.	E	2+1+2	5	Niko Radulović	Milica Stevanović
16.	**Ch**$_A$	*Medicinal Chemistry*	3.	E	3+0+2	6	Polina Blagojević	Polina Blagojević, Milan Nešić
17.	**Ch**$_A$	*Chemistry of Secondary Metabolites*	4.	E	2+0+2	4	Gordana Stojanović, Aleksandra Đorđević	Ivana Zlatanović
18.	**Ch**$_E$	*Biodegradation*	3.	E	3+0+2	5	Aleksandra Đorđević	Aleksandra Đorđević
19.	**Ch**$_E$	*Manipulation with Dangerous Organic Chemicals Substances*	4.	E	2+0+2	4	Ivan Palić	Ivan Palić
20.	**Ch**$_E$	*Organic Pollutants 1*	3.	O	2+0+1	4	Aleksandra Đorđević	Aleksandra Đorđević
	Ch$_E$	*Organic Pollutants 2*	4.	O	2+0+1	4	Polina Blagojević	Polina Blagojević, Milan Nešić

[1] This level of academic studies is organized through modules of two accredited study programmes; for *General Chemistry* program (**Ch**): *Research and Development* (**Ch**$_{RD}$) and *Chemistry Teacher* (**Ch**$_T$), and for *Applied Chemistry* program: *Applied Chemistry* (**Ch**$_A$) and *Environmental Chemistry* (**Ch**$_E$).

[2] Course type: *O* – Obligatory or *E* – Elective.

[3] Active teaching hours: *L* – Lectures, *Te* –Theoretical exercises, and *O* – Laboratory work and other forms of teaching.

[4] Number of ECTS allocated.

Table 3. An overview of courses and professors at the Chair of Organic Chemistry and Biochemistry at doctoral academic studies

N	Course	Semester	Course type [1]	L[2]	ECTS [3]	Professor
1.	*Instrumental Analysis of Selected Groups of Organic Compounds*	1.	E	4	8	Olga Jovanović, Snežana Jovanović
2.	*The Isolation of Secondary Metabolites*	1.	E	4	8	Gordana Stojanović, Aleksandra Đorđević
3.	*Chemical Microbiology*	1.	E	4	8	Aleksandra Đorđević
4.	*Physical Organic Chemistry*	1.	E	4	8	Polina Blagojević, Marija Genčić

5.	*Identification of Natural Products*	2.	E	4	8	Olga Jovanović, Goran Petrović, Ivan Palić
6.	*Contemporary Organic Synthesis*	2.	E	4	8	Niko Radulović, Goran Petrović
7.	*Chemistry of Plant Pigments*	2.	E	4	8	Danijela Kostić
	Asymmetric Organic Synthesis	3.	E	4	8	Niko Radulović
8.	*Experimental Biochemistry*	3.	E	4	8	Danijela Kostić
9.	*Two-dimensional Nuclear Magnetic Resonance Spectroscopy (2D-NMR)*	3.	E	4	8	Niko Radulović
10.	*Selected Chapters of Supramolecular Chemistry and Chemistry of Macromolecules*	4.	E	4	8	Goran Petrović
11.	*Secondary Metabolites as Biomarkers*	4.	E	4	8	Gordana Stojanović
12.	*Molecular Modeling in Organic Chemistry*	4.	E	4	8	Polina Blagojević
13.	*Conformational Analysis of Biomacromolecules*	4.	E	4	8	Ivan Palić

[1] Course type: *E* – Elective.
[2] Active teaching hours: *L* – Lectures.
[3] Number of ECTS allocated.

Table 4. The purpose and brief overview of the courses within the Group of Organic Chemistry and Biochemistry

No.	**Course**	**Purpose and brief overview**
1.	***Organic chemistry 1***	Gaining knowledge about the structural representations, systematic nomenclature, structure, properties and reactivity of hydrocarbons (alkanes, alkenes, alkynes, cycloalkanes, and aromatics) and heterocyclic aromatic compounds.
2.	***Experimental Organic Chemistry***	This course aims to introduce students to basic experimental techniques used in laboratory for organic chemistry. The main goal is developing the necessary skills to address the challenges of the experimental work.
3.	***Organic Chemistry 2***	This subject deals primarily with the basic principles to understand the structure and reactivity of organic molecules. Emphasis is on the substitution and elimination reactions and chemistry of the carbonyl group. Standard synthetic transformations are discussed from a structural, stereochemical and mechanistic points of view.
4.	***Preparative Organic Chemistry***	Upon completion of this course, students should acquire a solid foundation of essential skills and knowledge associated with organic lab techniques as well as communication and teamwork skills. Specifically, at the end of the course, students should be able to a) safely plan and carry out common organic synthetic reactions, b) work safely and effectively in an organic chemistry lab and c) write clear, concise, and correct lab reports that include appropriate citations of the relevant literature.
5.	***Chemistry of Natural Products***	This course introduces students with the most important natural products, their structure, physical and chemical properties, and their isolation and biological activities: amino acids, proteins and enzymes, carbohydrates, lipids, alkaloids, and natural phenolic compounds.
6.	***Instrumental Methods in Organic Chemistry***	This subject covers both theoretical knowledge and practical work of modern chromatographic, instrumental and combined methods for separating organic mixtures and structural analysis of different classes of organic compounds.
7.	***Biochemistry***	The course aims to introduce students with answers to questions related to biological systems at the molecular-chemical level: a) What do you mean by biomolecules? b) How do they occur? c) What and how they work?
8.	***Nomenclature of Organic Compounds***	The aim of the course is to introduce the general principles and rules for the naming of organic compounds (IUPAC nomenclature). Students will learn how to name a complex polyfunctional organic compound, or to draw its structure from the name (including stereochemistry).
9.	***Pharmaceutical Chemistry***	The aim of the course is to introduce students with the classification, nomenclature, physical and chemical properties of pharmacologically active molecules and reactivity of their functional groups.
10.	***Organic Chemistry in***	The aim of this subject is to teach students not only to memorize

	Everyday Life	chemical facts, but also to understand them and to make connections among them. A number of phenomena in our everyday life will be explained using the basic principles of organic chemistry. Upon completion of this course students will gain interesting and highly applicable knowledge of organic chemistry that allows them to observe the world around them as a large reaction vessel.
11.	***Dynamic Stereochemistry***	Acquiring knowledge about the chirality, stereoisomer nomenclature, prochirality, conformation, stereoselective and stereospecific reactions, influence of steric effects on the reactivity of organic compounds and pericyclic reactions.
12.	***Organic Syntheses***	The course introduces the student to the disconnection approach to organic synthesis, *i.e.* retrosynthetic analysis. According to this approach a chemist will start with the structure of their target molecule and progressively cut bonds to create simpler molecule; in reverse, this process gives a synthetic route to the target molecule from simpler starting materials. Lectures on the synthesis of given types of molecules alternate with strategy lectures in which the methods just learnt are placed in a wider context. The synthesis lectures cover many ways of making each type of molecule starting with simple aromatic and aliphatic compounds with one functional group and progressing to molecules with many functional groups. The strategy lectures cover questions of selectivity, protection, stereochemistry, and develop more advanced thinking *via* reagents specifically designed for difficult problems.
13.	***Dynamic Biochemistry***	This course provides students overview of those aspects of chemistry that are most significant in the understanding of biological systems. It aims to familiarize students with biochemical principles, processes and methods based on modern understanding of the structure and function of molecules as well as on the dynamics of biological systems.
14.	***Selected Chapters of Organic Chemistry***	Within this course students gain theoretical knowledge of photochemical and electrochemical reactions as well as structure, properties, procurement and reactions of organic compounds of sulfur, phosphorus and silicon. Also, the aim is acquiring of knowledge by students about properties, procurement and reactions of heterocyclic organic compounds.
15.	***Chemistry of Secondary Metabolites***	Within this course students gain knowledge about classification and biosynthesis of plant secondary metabolites as well as their biological role, physico-chemical properties, pharmacological activity and application of plant heterosides including saponosides.
16.	***Organic Structure Determination: An Advanced Course***	The purpose of this course is to provide the student with a thorough understanding of the theory and use of two spectral techniques (NMR and MS) used to identify organic compounds and to identify organic compounds by interpretation of spectral data. Proton and carbon-13 nuclear magnetic resonance spectroscopy (1D and 2D) will be studied and performed on a variety of organic compounds. The course will also cover several

		advanced NMR techniques like NOESY, ^{1}H-^{1}H COSY, HSQC, and HMQC. The goal of this course is also to emphasize the instrumental and practical nature of mass spectrometric instrumentation within the field of organic and bioanalytical chemistry. The topics of the course include fundamentals of ion motion, mass spectrometric instrumentation, applications to chemistry and biochemistry.
17.	***Advanced Organic Chemistry***	The aim of the course is to introduce the basic principles of the physical organic chemistry, *i.e.* the application of structure and theory to the study of organic reaction mechanisms: stereochemical features including conformation and stereoelectronic effects, reaction dynamics, isotope effects and molecular orbital theory applied to pericyclic and photochemical reactions, and special reactive intermediates including carbenes, carbanions, and free radicals. Upon completion of this course, students should be able to predict outcome of organic reactions, suggest reasonable reaction mechanisms and apply gained knowledge in planning organic synthesis.
18.	***Advanced Course of Instrumental Chromatographic Methods***	This course deals with the theoretical contents on HPLC and GC-MS and GC-MS-MS techniques and includes intensive practical work on the preparation and detailed analysis of the selected samples.
19.	***School Experiments in Organic Chemistry***	This subject introduces students to the principles of planning and executing school experiments in organic chemistry and biochemistry, codes of practice at work in organic chemistry laboratory, and the functional groups analysis – testing solution and characteristic chemical reactions.
20.	***Nobel Prize in Chemistry***	Introduction to the history of the development of chemistry in the 20th century, and the most important achievements in the field of chemistry. Alfred Nobel and its Foundation. Nobel Prize for Chemistry – general notes.
21.	***History of Chemistry***	History of chemistry and significant achievements in the field of chemistry.
22.	***Everyday Life Chemistry – Atkins' Molecules***	The course aims to introduce students with the molecules responsible for the experiences of our everyday life related to fabrics, drugs, plastics, explosives, detergents, fragrances, tastes, and hormones.
23.	***Organic Chemistry of Food***	This course introduces students with the chemical composition of food products and beverages, and possibilities for the determination of their physical and chemical properties using chromatographic and spectroscopic methods of analysis.
24.	***Chemistry of Organic Polymers***	This course gives a general overview of the most common types of polymers with the main focus on how they are made and how their structures govern their general properties and uses. Students will be introduced with the mechanisms and kinetics of two basic types of polymerization: (*i*) chain-reaction (or addition) and (*ii*) step-reaction (or condensation), as well as with some specific types of polymerization, and with the syntheses of elastomeric materials.
25.	***Applied Organic***	The aim of this course is the acquisition of knowledge about

	Chemistry	industrially important organic compounds and reactions (oil industry, pharmaceutical industry, production of polymers, etc.).
26.	***Synthesis of Macro Quantities of Organic Compounds***	Theoretical knowledge of the principles of industrial syntheses of organic compounds which allows students to independently choose the principle and to suggest the methodology of organic industrial syntheses.
27.	***Forensic Chemistry***	This course helps the student to develop approaches to understand, correctly use and further develop current chemical tools that are used in the forensic sciences. Upon the completion of the course, students should be able to independently investigate and solve different kind of theoretical and practical problems in forensic laboratory.
28.	***Medicinal Chemistry***	This course explores the basic principles of the design and action of drugs. Concepts presented are applied in discussing principles of drug discovery, drug development, drug/receptor interactions and structure/activity relationships. Total synthesis of selected pharmaceutical products will also be discussed.
29.	***Biodegradations***	This course helps students to understand biodegradation processes as a way nature is recycling wastes or breaking down organic matter into nutrients that can be used and reused by other organisms. The role of microorganisms and their importance in the protection of the environment from anthropogenic pollution will be discussed.
30.	***Manipulation with Dangerous Organic Chemicals***	Within this course students learn the Law on Chemicals regarding the storage, transport, safe handling and destruction of hazardous organic matter in order to make them capable to safely handle hazardous organic substances.
31.	***Organic Pollutants 1***	The aim of this course is acquiring of knowledge about the structure, physical, chemical and ecotoxicological properties of organic substances-pollutants of the environment, which belong to the group of dangerous and harmful substances.
32.	***Organic Pollutants 2***	The main purpose of this course is the introduction of students with the properties of organic compounds that are classified as environmental hazards. Upon the completion of this course student should be able to perform a rough assessment of physical, chemical and ecotoxicological properties of organic pollutants based on their structures, as well as to propose the effective way for the removal or disposal of these substances.
33.	***Instrumental Analysis of Selected Groups of Organic Compounds***	The course aims to introduce students with the latest theoretical knowledge in the field of contemporary chromatographic, instrumental and combined methods for the identification of structures of selected organic compounds from different areas of the economy and the environment. It qualifies candidates for the identification of structures of selected organic compounds from different fields of application.
34.	***The Isolation of Secondary Metabolites***	Introduction to the nature and importance of plant secondary metabolites. Screening of the plant material regarding appropriate group of secondary metabolites, choice of methods for the isolation of target group. Characteristics of selected isolation

		methods. Crystallization and other final purification methods. Production of larger quantities of natural products.
35.	***Chemical Microbiology***	This course reveals the basics of chemical microbiology: characteristics of microorganisms, microbial metabolism, ability of growing organisms to change the chemical composition of their environment by removing some compounds and excreting others as well as techniques of work in microbiological laboratory.
36.	***Physical Organic Chemistry***	This course represents an overview of the basic principles in physical organic chemistry in order to train the students to indipendenly: (*i*) disscuss the relationships among the structure, stability, reactivity and physical properties of organic compounds; (*ii*) write down all mechanistic steps of certain organic reaction; (*iii*) propose an experiment that could corroborate proposed mechanism and to discuss obtained results.
37.	***Identification of Natural Products***	This subject tells about modern methods for the identification and characterization of natural products based on chromatographic methods and combinations of chromatographic and spectroscopic methods.
38.	***Contemporary Organic Synthesis***	This course is designed to be an intensive survey of the chemical methods, strategies and controls utilized in modern synthetic organic chemistry. Upon completion of this course students should be able to propose and accomplish synthesis of a given organic molecule using herein learned contemporary synthetic methodologies.
39.	***Chemistry of Plant Pigments***	Basic ideas, concepts and results of plant pigments: classification, physiological roles, methods for the isolation and purification of plant pigments, instrumental methods for their identification, application and development of scientific and technical knowledge in the field of chemistry of plant pigments.
40.	***Asymmetric Organic Synthesis***	This course aims to give the student an overview of modern strategies and methods employed in asymmetric organic synthesis. Students will learn how it is possible to control stereochemical outcome of organic reactions either by introduction of new chiral center(s) (by use of chiral auxiliaries, reagents, catalyst, *etc.*), or by the utilization of available starting material that provide the appropriate chirality for reaching the target molecule. Upon completion of this course student should be able to plan and accomplish asymmetric synthesis of organic molecule with multiple chiral centers.
41	***Experimental Biochemistry***	Basic ideas, concepts and results of theoretical knowledge of methods for the isolation and purification of proteins and nucleic acids. Application and development of scientific and technical knowledge in the field of experimental biochemistry.
42.	***Two-dimensional Nuclear Magnetic Resonance Spectroscopy (2D-NMR)***	This course is primarily designed for PhD students who will use nuclear magnetic resonance as a routine tool in their research in order to obtain structural characterization of chemical compounds. Students will be introduced with basic 1D- and 2D-NMR techniques and trained to independently run NMR facility.
43.	***Selected Topics in***	The course covers selected theoretical knowledge (chapters) which

	Supramolecular and Macromolecular Chemistry	cover(s) and display(s) implementation of the findings from organic chemistry in materials, solid-state and polymer sciences, reflecting many and varied applications of supramolecular structures in modern chemistry.
44.	***Secondary Metabolites as Biomarkers***	The aim of this course is the use of secondary metabolites in the systematics of plants based on the distribution of alkanes, fatty acids, polyacetylenes, terpenes, aromatic and aliphatic volatile compounds, sulfur compounds, alkaloids, cyanogenic glycosides, and flavonoids.
45.	***Molecular Modeling in Organic Chemistry***	This is an introductory course in computational chemistry with emphasis on tools that enable the study of organic reactions and compounds. Students will learn: (*i*) to choose appropriate theoretical model to solve certain problems in organic chemistry; (*ii*) to optimize geometry and to simulate NMR, IR and UV-Vis spectra of organic molecules; and (*iii*) to estimate suitable physical and chemical properties of organic compounds that will enable them prediction of differences in reactivity/activity among the members of the chosen set of organic compounds.
46.	***Conformational Analysis of Biomacromolecules***	Theoretical knowledge in the field of conformational analysis of polysaccharides, proteins and nucleic acids related to their biological function in living organisms.

Reasearch

An overview of the research project "Natural products of plants and lichens: isolation, identification, biological activity and application"

Research project "Natural products of plants and lichens: isolation, identification, biological activity and application" (Project Number 172047) is financed by Ministry of Education, Science and Technological Development. It gathers researchers (professors, research assistants and PhD students) from a number of faculties and institutes (University of Niš: Faculty of Medicine, Faculty of Science and Mathematics, Faculty of Technology, Faculty of Occupational Safety, and University of Priština: Faculty of Science and Mathematics). Research Coordinate Organization is Faculty of Science and Mathematics (University of Niš). Project leader is dr Gordana Stojanović.

The total number of researchers for the period from 2011 to 2018 varied (2011-22; 2012-24; 2013-29, 2014-31, 2015-31; 2016-13; 2017-30 and 2018-31). Of the total number of researchers, the number of PhD students was 2011-9; 2012-8; 2013-8, 2014-10, 2015-9; 2016-8; 2017-8 and 2018-9. There are 15 doctoral dissertations that have an acknowledgement to the project. As shown below in Table 5, twelve researchers involved in this research project are the members of the Chair of Organic Chemistry and Biochemistry: two full professors, four associate professors, one assistant professor, and four PhD students.

Table 5. List of researchers within the frame of the Project N° 172047 that are members of the Chair of Organic Chemistry and Biochemistry alongwith their main research area and the most important achivements and/or positions

PROFESSORS	
	**Dr Gordana Stojanović** *Full Proffesor* • Main research area: Chemical analysis of essential oils and extracts of selected plant species and lichens • The most important achievements and/or positions: Head of the Chair for organic chemistry and biochemistry; Project leader

Dr Danijela Kostić

Full Proffesor

- Main research area: Chemical analysis of extracts of selected plants and their antioxidant activity, chemistry education

Dr Olga Jovanović

Associate Professor

- Main research area: Isolation, separation and chemical analysis of plant secondary metabolites

Dr Goran Petrović

Associate Professor

Dr Ivan Palić

Associate Professor

- Main research area: Chemical analysis of essential oils and extracts of selected plant species
- The most important achievements and/or positions: Deputy of Center for Chemistry; Lecturer for course of Chemical consulting

Dr Aleksandra Đorđević

Associate Professor

- Main research area: Chemical analysis of essential oils and extracts of selected plant species and examination of antimicrobial activity
- The most important achievements and/or positions: Awards for achieved success during the studies of chemistry; participant of the project "Researchers' Night"

Dr Snežana Jovanović

Assistant Professor

- Main research area: Chemical analysis of essential oils and extracts of selected plant species for chemotaxonomic purposes
- The most important achievements and/or positions: Secretary of the Department of Chemistry; Lecturer at the Pedagogical Faculty in Vranje (University of Niš)

PhD STUDENTS

Ms Jelena Stamenković

Research Assistant

Ms Ivana Zrnzević

Research Assistant

Main research area: Chemical analysis of lichen extracts and testing their biological activity

Ms Ivana Zlatanović

Research Assistant

Main research area: Analysis of lichen extracts

Ms Jovana Ickovski

Research Assistant

Ms Katarina Stepić

Research Trainee

Research within the project include the determination of composition of essential oils, extracts, head space components, biological activity and mineral composition for a selected type of plants, mushrooms, lichens and products obtained from them. By statistical processing of the results, the validity of the examined secondary metabolites as biomarkers for chemotaxonomic purposes and their correlation with biological activity have been examined. It is also being explored optimization of sample preparation and validation of the GC-MS method for the analysis of polycyclic aromatic compounds (PAH), as well as investigation of the effect of extracts or grounded samples of mushrooms on rheological characteristics and antioxidant activity of wheat flour dough.

Gas chromatography-mass spectrometry (GC-MS) analysis, High Pressure Liquid Chromatography (HPLC) analysis, isolation of extracts and/or essential oils constituents and antimicrobial activity are performed in the laboratory of the Chair of Organic Chemistry and Biochemistry.

Other assays are performed in the laboratories of our collaborators:

- Chair of Analytical Chemistry (antioxidative activity, determination of mineral composition, sample preparation and validation methods for PAH analysis);
- Department of Biology and Ecology (identification and deposition of vouchers, testing sets of chemotaxonomic markers at different taxonomic levels);
- Department of Physiology, University of Niš, Faculty of Medicine (effect of secondary metabolites on structural kidney damages);
- Faculty of Technology, University of Niš (the influence of extracts or grounded mushroom samples on the rheological characteristics and the antioxidant activity of wheat flour dough);
- Biochemical Laboratory, General Hospital, Health Center, Pirot (cholinesterase activity);
- Nuclear Objects of Serbia, Institute for Radiological Health Care, Vinča, Belgrade (cytokinesis-block micronucleus test).

The capital laboratory equipment available to the researchers refers: 7890/7000B GC-MS-MS triple quadrupole system (Agilent Technologies, USA) equipped with a Combi PAL auto sampler and a HP-5 MS fused-silica cap. column; HPLC Agilent, Zorbax Eclipse XDB-C18, equipped with a diode array detector (DAD), Alpha 1–2 LDplus freeze-dryer (CHRIST), MPLC Chromatography system (BÜCHI). The Ministry of Education, Science and Technological Development of the Republic of Serbia provides funds for all the above-mentioned equipment.

One part of the results of all performed studies was carried out within the project No 172047 and have been published in the form of chapters (monographs), original research papers, review articles, short communications in international journals and/or in national scientific journals. Furthermore, numerous papers were presented at conferences in Republic of Serbia and abroad, including plenary and invited lectures.

Table 6. An overview of research work (three selected papers, overall Nº of citations and *h*-index)

Name	**Nº of publications**[1]	**Nº of conference presentations**	**Overall Nº of Citations**[2]	***h*-index**[3]
Gordana S. Stojanović	142	113	1105	18
1. Stojanović, G. S., Đorđević, A. S., & Šmelcerović, A. A., (2013). Do Other *Hypericum* Species Have Medical Potential As St. John's Wort (*Hypericum perforatum*)? Current Medicinal Chemistry, 20, 2273-2295.				
2. Stojanović, G. S., Stojanović, I. Z., & Šmelcerović, A. A., (2012). Lichen Depsidones as Potential Novel Pharmacologically Active Compounds. Mini-Reviews in Organic Chemistry, 9, 178-184.				
3. Stojanović, G. S., Radulović, N. S., Hashimoto, T., & Palić, R. M., (2005). *In vitro* antimicrobial activity of extracts of four *Achillea* species: The composition of *Achillea clavennae* L. (Asteraceae) extract. Journal of Ethnopharmacology, 101, 185-190.				
Danijela A. Kostić	66	55	277	11
1. Kostić, D. A., Dimitrijević, D. S., Mitić, S. S., Mitić M. N., Stojanović G. S., & Zivanović A. V., (2013). A survey on macro- and micro-elements, phenolic compounds, biological activity and use of *Morus* spp. (Moraceae). Fruits, 68, 333-347.				
2. Dimitrijević, D. S., Kostić, D. A., Stojanović G. S., Mitić, S. S., Mitić M. N., & Đorđević, A. S., (2014). Phenolic composition, antioxidant activity, mineral content and antimicrobial activity of fresh fruit extracts of *Morus alba* L.. Journal of Food and Nutrition Research, 53, 22-30.				
3. Randjelović, S. S., Kostić, D. A., Arsić, B. B., Mitić, S. S., Rasić, I. D., Mitić M. N., Dimitrijević, D. S., & Stojanović G.S., (2015). Chemometric Analysis of Grapes. Open Chemistry, 13, 675-682.				
Olga P. Jovanović	21	>20	59	5
1. Jovanović, O. P., Radulović, N. S., Stojanović G. S., Palić, R. M., Zlatković, B. K., & Gudzić, B. T., (2009). Chemical Composition of the Essential Oil of *Centaurium erythraea* Rafn (Gentianaceae) From Serbia. Journal of Essential Oil Research, 21, 317-322.				
2. Jovanović, O. P., Zlatković, B. K., Simonović, S. R., Đorđević, A. S., Palić, I. R., & Stojanović G. S., (2013). Chemical composition and antibacterial activity of the essential oils isolated from leaves and fruits of *Peucedanum austriacum* (Jacq.) WDJ Koch. Journal of Essential Oil Research, 25, 129-137.				
3. Jovanović, S. Č., Jovanović, O. P., Mitić, Z. S., Golubović, T. D., Zlatković, B. K., & Stojanović, G. S., (2017). Volatile profiles of the orpines roots: *Hylotelephium telephium* (L.) H. Ohba, *H. maximum* (L.) Holub and *H. spectabile* (Boreau) H. Ohba x *telephium* (L.) H. Ohba. Flavour and Fragrance Journal, 1-5.				
Ivan R. Palić	12	29	107	6
1. Stojanović G. S., & Palić, I. R., (2008). Antimicrobial and Antioxidant Activity of *Micromeria* Bentham Species. Current Pharmaceutical Design, 14, 3196-3202.				
2. Reddy, C. M., Eglinton, T. I., Palić, R. M., Benitez-Nelson, B. C., Stojanović G. S., Palić, I. R., Đorđević, S. M., & Eglinton, G., (2000). Even Carbon Number Predominance of Plant Wax n-Alkanes: A Correction. Organic Geochemistry, 31 331-336.				
3. Palić, I. R., Ursić-Janković, J., & Stojanović G. S., (2010). Essential Oil Composition of Three Balkan *Micromeria* Species. Journal of Essential Oil Research, 22, 40-44.				
Aleksandra S. Đorđević	38	29	123	5
1. Đorđević, A. S., Lazarević, J. S., Šmelcerović, A. A., & Stojanović, G. S., (2013). The case of *Hypericum rochelii* Griseb. & Schenk and *Hypericum umbellatum* A. Kern. essential oils: Chemical composition and antimicrobial activity. Journal of Pharmaceutical and Biomedical Analysis, **77**, 145-148.				
2. Stojanović, G. S., Đorđević, A. S., & Šmelcerović, A. A., (2013). Do Other *Hypericum* Species Have Medical Potential as St. John's Wort (*Hypericum perforatum*)? Current Medicinal Chemistry, 20, 2273-2295.				
3. Jukič, M., Đorđević, A. S., Lazarević, J. S., Gobec, M., Šmelcerović, A. A., & Anderluh M., (2013). Antimicrobial activity and cytotoxicity of some 2-amino-5-alkylidene-thiazol-4-ones. Molecular Diversity, 17, 773-780.				
Snežana Č. Jovanović	16	18	9	2
1. Mitić, Z. S., Jovanović, B., Jovanović, S. Č., Mihajilov-Krstev, T., Stojanović-Radić, Z. Z., Cvetković, V. J., Mitrović, T. Lj., Marin, P. D., Zlatković, B. K., & Stojanović, G. S., (2018). Comparative study of the essential oils of four *Pinus* species: Chemical composition, antimicrobial and insect larvicidal activity. Industrial Crops & Products, 111, 55-62.				
2. Jovanović, S. Č., Jovanović, O. P., Mitić, Z. S., Golubović, T. D., Zlatković, B. K., & Stojanović, G. S., (2017). Volatile profiles of the orpines roots: *Hylotelephium telephium* (L.) H. Ohba, *H. maximum* (L.) Holub and *H. spectabile* (Boreau) H. Ohba x *telephium* (L.) H. Ohba. Flavour and Fragrance Journal, 1-5.				
3. Jovanović, S. Č., Zlatković, B. K., & Stojanović, G. S., (2016). Chemotaxonomic Approach to the Central Balkan				

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[1] According to KoBson databases

[2] Data are taken from Scopus data base (accesion date 10/04/2018). The self-citations of all authors are excluded.

[3] According to Scopus database (accesion date 10/04/2018). The self-citations of all authors are excluded.

Sedum Species Based on Distribution of Triterpenoids in Their Epicuticular Waxes. Chemistry and Biodiversity, 13, 459-465.				
Jelena G. Stamenković	5	9	9	2
1. Petrović G. M., Stamenković, J. G., Kostevski, I. R., Stojanović, G. S., Mitić, V. D., & Zlatković, B. K., (2017). Chemical composition of volatiles; antimicrobial, antioxidant and cholinesterase inhibitory activity of *Chaerophyllum aromaticum* L. (Apiaceae) essential oils and extracts. Chemistry & Biodiversity, 14(5), e1600367.				
2. Stamenković, J. G., Petrović, G. M., Stojanović, G. S. ,Đorđević, A. S., Zlatković, B. K., (2016). *Chaerophyllum aureum* L. Volatiles: Composition, Antioxidant and Antimicrobial Activity. Records of Natural Products, 10(2), 245-250.				
3. Kostevski, I. R., Petrović, G. M., Stojanović, G. S., Stamenković, J. G., & Zlatković, B. K., (2016). Essential Oil Chemical Composition and Headspace Volatiles Profile of *Achillea coarctata* from Serbia. Natural Product Communications, 11(4), 543-545.				
Ivana S. Zrzević	5	7	4	1
1. Zrnzević, I. S., Stanković, M., Stankov Jovanović, V. P., Mitić, V. D., Đorđević, A. S., Zlatanović, I. G., & Stojanović, G. S., (2017). *Ramalina capitata* (Ach.) Nyl. acetone extract: HPLC analysis, genotoxicity, cholinesterase, antioxidant and antibacterial activity. EXCLI Journal, 16, 679-687.				
2. Zrnzević, I. S., Jovanović, O. P., Zlatanović, I. G., Stojanović, I. Z., Petrović, G. M., & Stojanović, G. S., (2017). Constituents of *Ramalina capitata* (Ach.) Nyl. Extracts. Natural Product Research, 31 (7), 857-860.				
3. Stojanović, G. S., Zlatanović, I. G., Zrnzević, I. S., Stanković, M., Stankov Jovanović, V. P., & Zlatković, B. K., (2017). *Hypogymnia tubulosa* extracts: chemical profile and biological activities. Natural Product Research, 32 (3), 222-224.				
Ivana G. Zlatanović	5	5	4	1
1. Stojanović, G. S., Zlatanović, I., Zrnzević, I., Stanković, M., Stankov Jovanović, V., & Zlatković, B., (2017). *Hypogymnia tubulosa* extracts: chemical profile and biological activities, Natural Product Research, 32 (3), 222-224.				
2. Zrnzević, I. S., Stanković, M., Stankov Jovanović, V. P., Mitić, V. D., Đorđević, A. S., Zlatanović, I. G., Stojanović, G. S., (2017). *Ramalina capitata* (Ach.) Nyl. acetone extract: HPLC analysis, genotoxicity, cholinesterase, antioxidant and antibacterial activity. EXCLI Journal, 16, 679-687.				
3. Zlatanović, I. G., Stanković, M., Stankov Jovanović V. P., Mitić, V. D., Zrnzević, I. S., Đorđević, A. S., & Stojanović, G. S., (2017). Biological activities of *Umbilicaria crustulosa* (Ach.) Frey acetone extract. Journal of Serbian Chemical Society, 8, 141-150.				
Jovana D. Ickovski	1	6	12	1
1. Kostić, D. A., Dimitrijević, D. S., Stojanović, G. S., Palić, I. R., Đorđević, A. S., & Ickovski, J. D., (2015). Xanthine Oxidase: Isolation, Assays of Activity, and Inhibition. Journal of Chemistry, article ID: 294858, 8 pages.				
2. Palić, I. R., Ickovski, J. D., Đorđević, A. S., Mitić, V. D., Stankov-Jovanović, V. P., & Stojanović, G. S., (2015). Antioxidant and antimicrobial activities of the essential oil and solvent extracts of *Mentha pulegium* L.. Facta universitatis - series: Physics, Chemistry and Technology, 13(2), 109-119.				
3. **Ickovski, J. D**., Palić, I. R., Đorđević, A. S., Stankov-Jovanović, V. P., Mitić, V. D., & Stojanović, G. S., Antimicrobial activities of various extracts of *Origanum heracleoticum* L., In: Programme and Book of Abstracts of the 23rd Congress of Chemists and Technologists of Macedonia, Ohrid, Macedonia, October 8-11, 2014, BC-001.				

An overview of the research project "Combinatorial libraries of heterogeneous catalysts, natural products, modified natural products and analogues: The approach to new biologically active agents"

Research project "Combinatorial libraries of heterogeneous catalysts, natural products, modified natural products and analogues: The approach to new biologically active agents" (Project Number 172061) gathers more than 30 researchers from seven Faculties and Institutes belonging to five different Serbian Universities. Twelve researchers involved in this research project are the members of the Chair of Organic Chemistry and Biochemistry: one full professor, one associate professor, one assistant professor, one postdoctoral fellow and eight PhD students (Table 7). Principal investigator of the project is dr Niko Radulović.

Table 7. List of researchers within the frame of the Project N° 172061 that are members of the Chair for Organic Chemistry and Biochemistry along with their main research area and the most important achievements and/or positions

Professors	
	Dr Niko Radulović *Full Proffesor* **Main research area:** organic chemistry, phytochemistry, organic synthesis, NMR, mass spectrometry, biologically active compounds, structure-activity relationship, gas chromatography, chemotaxonomy **The most important achievements and/or positions:** 2017 – Member of the Editorial Advisory Board of *Chemistry & Biodiversity*; 2016 – Medal as the merit member of the Serbian Chemical Society; 2015 – Member of the permanent scientific board of the *International Symposium on Essential* Oils (ISEO); 2014 – Among the most cited researchers in Serbia in all scientific disciplines; 2012 – The award of the Outstanding Research Award of Serbian Chemical Society for the Best Young Scientist; 2011 – The Scopus Young Researcher Awards (Serbia); 2010 – Editor-in-chief *of Facta Universitatis section Physics, Chemistry and Technology*; 2001/2002 – The award for the Best Graduated Student of the University of Niš (*Silver sign* of the University of Niš)
	*Associate Professor* **Main research area:** Development of new methods for the comparison of complex mixtures of organic compounds; ^{1}H full spin analysis of natural products **The most important achievements and/or positions:** *L'Oréal-UNESCO for Women in Science* national scholarships (2011); postdoctoral stay at *Max Planck Institute for Chemical Physics of Solids* (Dresden, Germany; 2011) and *University of British Columbia*

(Vancouver, Canada; 2017); Medal of the Serbian Chemical Society for endeavour and success in science (2014)

Dr Marija Genčić
Assistant Professor
Main research area: Synthesis of bioactive ferrocene-containing molecules; Development of new methods for structure elucidation of natural products in inseparable complex mixture.
The most important achievements and/or positions: *L'Oréal-UNESCO for Women in Science* national scholarships (2017); Postoctoral stay at *Faculty of Bioscience Engineering*, *Ghent University* (Belgium, 2016); *Silver Sign* of the University of Niš, as the Best Graduate of the University in 2008/2009.

Postdoctoral fellow

Dr Marko Mladenović
Research Assistant
Main research area: Chemical composition and biological activity of essential oils; Design and synthesis of combinatorial libraries of selected natural products and their analogs.
The most important achievements and/or positions: *Special Award of the Serbian Chemical Society* for outstanding success during the studies in 2011; Prince Karađorđević Annual Award for outstanding success in high school in 2006.

PhD students

Ms Dragan Zlatković
Research Assistant
Main research area: New organic transformations of *Biginelli* and *Hantzsch*-derived compounds; New developements in iodoform reaction.
The most important achievements and/or positions: "*Ana Bjeletić i Ivan Marković*" award for the Best Graduated Student at the Department of Chemistry in 2011/2012.

Ms Miljana Đorđević
Research Assistant
Main research area: Solventless reactions in green chemistry; Biotransformations; Synthesis of iodinated analogs of natural products.
The most important achievements and/or positions: "*Ana Bjeletić i Ivan Marković*" award for the Best Graduated Student at the Department of Chemistry in 2010/2011; IUPAC Poster Prize Certificate at the *50th Meeting of the Serbian Chemical Society* (2012); EYCN poster award for the best poster at *the First Conference of Young Chemists of Serbia* (2012).

Ms Milena Živković
Research Assistant
Main research area: Chemical composition and eco-physiological role of plant surface waxes; Development of new methods for the determination of stereochemistry of natural products in inseparable mixtures; Lipidomic study of *Streptomyces* spp.
The most important achievements and/or positions: “*Ana Bjeletić i Ivan Marković*” award for the Best Graduate Student at the Department of Chemistry in 2012/2013; *Travel to Europe* grant for 70 best final-year students at the universities in Serbia in 2011 awarded by “*European movement*”.

Ms Sonja Filipović
Research Assistant
Main research area: Isolation, structure elucidation and screening of biological activities of the secondary metabolites from liverworts.
The most important achievements and/or positions: *Young Scientist Fellowship Award* at *47th International Symposium on Essential Oils* (2017).

Ms Milica Todorovska
Research Trainee
Main research area: Isolation, synthesis and biological activity testing of autolysis products from the order Brassicales.
The most important achievements and/or positions: The Best Student of integrated academic studies at pharmacy at Faculty of Medicine in Niš in 2010, 2011 and 2013; *Commendation of the Royal House of Karađorđević* for expressed extraordinary success in secondary education (2009); *Young Scientist Fellowship Award* at *47th International Symposium on Essential Oils* (2017).

Ms Milan Nešić
Teaching Assistant
Main research area: Development of new methods for the syntheses of derivatives of carbonyl compounds useful as protecting groups; Structure elucidation of components in inseparable complex mixture using NMR simulations.
The most important achievements and/or positions: *Silver Sign* of the University of Niš, as the Best Graduate of the University in Niš in 2012/2013; Annual Award of the Serbian Chemical Society for outstanding success during the studies (2013); Award – “The Best Graduated Master Student at Faculty of Science and Mathematics in 2015” given by The City of Niš.

Ms Milena Krstić
Research Trainee
Main research area: Chemical composition of essential oils from *Tordylium* species and their chemotaxonomic importance.
The most important achievements and/or positions: Award for one of the Best Students in 2015/2016 given by Youth Organisation of Leskovac.

Ms Milica Stevanović
Research Trainee
Main research area: Isolation, structure elucidation and synthesis of polyacetylene compounds in plants; Determination of stereochemically precise structures of odor-active compounds in plants.
The most important achievements and/or positions: *Special Award of the Serbian Chemical Society* for outstanding success during the studies in 2014; "*Ana Bjeletić i Ivan Marković*" award for the Best Graduate Student at the Department of Chemistry in 2014/2015; "*Dositeja*" *Scholarship for Young Talents* given by the Ministry of Youth and Sport (in 2012/2013 and 2015/2016).

The main focus of this research project is on the detailed analysis of the chemical composition of essential oils and/or extracts of plant species, lichens, liverwort species and bacteria with the aim to detect new potentially bioactive natural products (lead compounds) that might have an application in pharmacy and agriculture. Alongside the standard method based on the isolation of pure compounds by various chromatographic methods, within this project it is also friquenly applied combinatorial library approach for the identification of novel secondary methabolites. For example, if the target metabolite could not be isolated from the complex matrix and some tentative structure(s) could be inferred from available data (MS, RI, derivation reactions), the only comprehensive approach in this situation would be to create a small library of all possible compounds (in most cases isomers) that would eliminate/corroborate originally proposed structure(s). Due to the existence of detailed spectral data of all library members, the combinatorial library approach could often make possible the detection and identification of non-target compounds in the studied extracts, as well. The synthetic work also gives the desired compounds in amounts that allow the screening of biological activities of all library members in a number of assays and the establishment of structure-activity/properties relationship, thus providing important data for future investigations. Furthermore, compounds that showed the best activity/selectivity could be used as leads for the synthesis of new libraries of compounds that contained unnatural structural fragments (*e.g.* ferrocene core) that could plausible enhanced the activity/selectivity. In this way, dozens of compounds with strong antimicrobial, antioxidant, anti-inflammatory, cytotoxic, analgesic, hepato-, nephro- and gastroprotective activity (with potential application in medicine/agriculture) have been discovered within the frame of project N^o 172061 in the last seven years.

Other research work on this project is closely associated with the above described primary research interests, and includes:

(i) development of multivariate statistical approaches for the interpretation of data connecting the chemical composition and biological activities, which enable fast and impartial location of active compounds in essential oils/extracts and their mutual comparison;

(ii) investigation of *in silico*, *in vitro* and *in vivo* mechanisms of action of the most potent mixtures of natural products (*e.g.* essential oils or extracts) and newly discovered natural products and analogs;

(iii) development of new NMR based methods using lanthanide chemical shift reagent and application HiFSA-ASIS-GIAO NMR-based methodologies for the determination of the structure and the stereochemistry of metabolites directly from mixture;

(iv) discovery, optimization and mechanistic studies of new chemical reactions that could be useful in the synthesis of diverse (lead) compounds;

(v) development of new types of GC-MS, NMR and IR-derived variables, suitable for the fast and reliable comparison/characterization of complex mixtures of organic compounds, *etc*.

Results of all studies carried out within the project N^o 172061 in the last seven years have been published in over 150 peer-reviewed papers in international journals, then 17 PhD thesis were defended (7 of them at the Chair for Organic Chemistry and Biochemistry) and more than 200 abstracts were presented at conferences, including plenary and invited lectures at international level (Table 8). It is worth mentioning here that severel conference presentations have been awarded with the Best Poster Award (Table 9). Morover four PhD students, Miljana Đorđević, Milica Todorovska, Sonja Filipović, and Milan Nešić received *Young Scientist Fellowship Award* at *International Symposium on Essential Oils* (ISEO 2012 in Lisabon (Portugal) and ISEO 2017 in Pécs (Hungary)). The procurment of new capital equpment in the last few years (like 400 MHz NMR, UV-Vis, semipreparative HPLC, *etc.*), funded by the Ministry of Education, Science and Technological Development of the

Republic of Serbia, has greatly facilitated and improved the quality of the mentioned research work.

Table 8. An overview of the research work (three selected papers, overall N^{o} of citations and *h*-index)

Name	N^{o} of publications	N^{o} of conference presentations	Overall N^{o} of citations[a]	*h*- index[a]
Niko Radulović	205	more than 200	1962	19
1. Radulović, N. S., Miltojević, A. B., Stojanović, N. M., & Randjelović, P. J., (2017). Distinct urinary metabolite profiles of two pharmacologically active *N*-methylanthranilates: Three approaches to xenobiotic metabolite identification. Food and Chemical Toxicology, 109, 341-355. 2. Radulović, N. S., Blagojević, P. D., Stojanović-Radić, Z. Z., & Stojanović, N. M., (2013). Antimicrobial plant metabolites: structural diversity and mechanism of action. Current Medicinal Chemistry, 20(7), 932-952. 3. Radulović, N., Quang, D. N., Hashimoto, T., Nukada, M., & Asakawa, Y., (2005). Terrestrins A-G: *p*-Terphenyl derivatives from the inedible mushroom *Thelephora terrestris*. Phytochemistry, 66(9), 1052-1059.				
Polina Blagojević	48	more than 60	393	9
1. Radulović, N. S., & Blagojević, P. D., (2013). Average mass scan of the total ion chromatograms: A new gas chromatography-mass spectrometry derived variable for fast and reliable multivariate statistical treatment of essential oil compositional data. Journal of Chromatography A, 1301, 190-199. 2. Radulović, N. S., & Blagojević, P. D., (2012). The most frequently encountered volatile contaminants of essential oils and plant extracts introduced during the isolation procedure: Fast and easy profiling. Phytochemical Analysis, 23(2), 131-142. 3. Pejović, A., Denić, M. S., Stevanović, D., Damljanović, I., Vukićević, M., Kostova, K., Tavlinova-Kirilova, M., Randjelović, P., Stojanović, N. M., Bogdanović, G. A., Blagojević, P., D' hooghe, M., Radulović, N. S., & Vukićević, R. D., (2014). Discovery of anxiolytic 2-ferrocenyl-1,3-thiazolidin-4-ones exerting GABA$_A$ receptor interaction via the benzodiazepine-binding site. European Journal of Medicinal Chemistry, 83, 57-73.				
Marija Genčić	18	34	77	5
1. Genčić, M. S., & Radulović, N. S., (2015). Lanthanide-induced shift reagents enable structural elucidation of natural products in inseparable complex mixtures – The case of elemenal from *Inula helenium* L. (Asteraceae). RSC Advances, 5(89), 72670-72682. 2. Radulović, N. S., Denić, M. S., & Stojanović-Radić, Z. Z., (2014). Synthesis of small combinatorial libraries of natural products: Identification and quantification of new long-chain 3-methyl-2-alkanones from the root essential oil of *Inula helenium* L. (Asteraceae). Phytochemical Analysis, 25(1), 75-80. 3. Radulović, N., Đorđević, N., Denić, M., Martins Gomes Pinheiro, M., Dias Fernandes, P., & Boylan, F., (2012). A novel toxic alkaloid from poison hemlock (*Conium maculatum* L., Apiaceae): Identification, synthesis and antinociceptive activity. Food and Chemical Toxicology, 50(2), 274-279.				
Marko Mladenović	12	27	60	5
1. Mladenović, M. Z., & Radulović, N. S., (2017). The essential oil of *Achillea ageratifolia* (Sm.) Boiss. Subsp. *Serbica* (Nyman) Heimerl (Asteraceae) revisited: the stereochemical nomenclature issues, structural elucidation and synthesis of (new) sabinylesters. Flavour and Fragrance Journal, 32, 5-23. 2. Radulović, N. S., Mladenović, M. Z., Randjelović, P. J., Stojanović, N. M., Dekić, M. S., & Blagojević, P. D., (2015). Toxic essential oils. Part IV: The essential oil of *Achillea falcata* L. As a source of biologically/pharmacologically active transsabinyl esters. Food and Chemical Toxicology, 80, 114-129. 3. Radulović, N. S., Mladenović, M. Z., Stojanović-Radić, Z., Bogdanović, G. A., Stevanović, D., & Vukićević, R. D., (2014). Synthesis, characterization and antimicrobial evaluation of a small library of ferrocene-containing acetoacetates and phenyl analogs – the discovery of a potent anticandidal agent. Molecular Diversity, 18, 497-510.				
Dragan Zlatković	10	25	11	2
1. Zlatković, D. B., & Radulović, N. S., (2016). Reduction of Biginelli compounds by LiAlH$_4$: a rapid access to molecular diversity. RSC Advances, 6, 115058-115067. 2. Radulović, N., Zlatković, D., Mitić, K., Randjelović, P., Stojanović, N., (2014). Synthesis, spectral characterization, cytotoxicity and enzyme-inhibiting activity of new ferrocene-indole hybrids. Polyhedron, 80, 134-141, 3. Radulović, N. S., Zlatković, D. B., Randjelović, P. J., Stojanović, N. M., Novaković, S. B., & Akhlaghi, H., (2013). Chemistry of spices: bornyl 4-methoxybenzoate from *Ferula ovina* (Boiss.) Boiss. (Apiaceae) induces hyperalgesia in mice. Food and Function, 4, 1751-1758.				
Miljana Đorđević	5	27	5	1

1. Radulović, N. S., Đorđević, M. R., & Blagojević, P. D., (2016). Structural revision of aristol: a fresh look at the oxidative coupling of thymol under iodination conditions. RSC Advances, 6(73), 69067-69082. 2. Radulović, N. S., Đorđević, M. R., Dekić, M. S., & Blagojević, P. D., (2016). Chemical composition of the essential oil and diethyl ether extract of *Trinia glauca* (L.) Dumort. (Apiaceae) and the chemotaxonomic significance of 5-*O*-methylvisamminol. Chemistry and Biodiversity, 13(4), 403-415. 3. Radulović, N. S., & Đorđević, M. R., (2014). Chemical composition of the tuber essential oil from *Helianthus tuberosus* L. (Asteraceae). Chemistry and Biodiversity, 11(3), 427-437.				
Milena Živković	1	15	2	1
1. Ilic-Tomic, T., Genčić, M. S., Živković, M. Z., Vasiljevic, B., Djokic, L., Nikodinovic-Runic, J., & Radulović, N. S., (2015). Structural diversity and possible functional roles of free fatty acids of the novel soil isolate *Streptomyces* sp. NP10. Applied Microbiology and Biotechnology, 99(11), 4815-4833. 2. Živković, M. Z., Radulović, N. S., & Stojković, M. B. Configuration assignment of internal double bonds with almost isochronous protons *via* cyclopropanation and NMR, In: *Programme and Book of Abstracts of the 19th Central and Eastern European NMR Symposium & Bruker Users' Meeting* (CEUM 2017), Timisoara (Romania), September 5-8, 2017, pp. 26. 3. Živković, M. Z., Radulović, N. S., & Genčić, M. S., Methyl 2-methylalkanoates from the essential oil of *Humulus lupulus* L., In: *Programme and Book of Abstracts of the 47th International Symposium on Essential Oils* (ISEO 2016), Nice (France), September 11-14, 2016, pp. 128.				
Sonja Filipović	2	9	1	1
1. Radulović, N. S., Filipović, S. I., Zlatković, D. B., Đorđević, M. R., Stojanović, N. M., Randjelović, P. J., Mitić, K. V., Jevtović-Stoimenov, T. M., & Ranđelović, V. N., (2016). Immunomodulatory pinguisane-type sesquiterpenes from the liverwort *Porella cordaeana* (Porellaceae): the "new old" furanopinguisanol and its oxidation product exert mutually different effects on rat splenocytes. RSC Advances, 6(48), 41847-41860. 2. Filipović, S. I., & Radulović, N. S. The essential oil of *Myrtus communis* L. from Montenegro contains a cyclic polymethylated polyketide, In: *Programme and Book of Abstracts of the 48th International Symposium on Essential Oils* (ISEO 2017), Pécs (Hungary), September 10-13, 2017, pp. 78. 3. Radulović, N. S., Filipović, S. I., Zlatković, D. B., Đorđević, M. R., Stojanović, N. M., Randjelović, P. J., Mitić, K. V., Jevtović-Stoimenov, T. M., & Ranđelović, V. N. Structural revision of α-furanopinguisanol, In: *Programme and Book of Abstracts of the 18th Central and Eastern European NMR Symposium & Bruker Users' Meeting* (CEUM 2016), Sofia (Bulgaria), September 18-20, 2016, pp. 78.				
Milica Todorovska	1	7	-	-
1. Radulović, N. S., Todorovska, M. M., Zlatković, D. B., Stojanović, N. M., & Randjelović, P. J., (2017). Two goitrogenic 1,3-oxazolidine-2-thione derivatives from Brassicales taxa: Challenging identification, occurrence and immunomodulatory effects. Food and Chemical Toxicology, 110, pp. 94-108. 2. Todorovska, M., & Radulović, N. S. Chemical composition of *Bornmuellera dieckii* Degen (Brassicaceae) essential oil and autolyzate, In: *Book of Abstracts of the 3rd International Conference on Natural Products Utilization: from Plants to Pharmacy Shelf* (ICNPU 2017), Bansko (Bulgaria), October 18-21, 2017, pp. 325. 3. Todorovska, M., Dekić, M., & Radulović, N. S. Benzyl thiocyanate – autolysis product of glucotropaeolin or an artefact of the isolation procedure? In: *Programme and Book of Abstracts of the 12th Symposium on the Flora of Southeastern Serbia and Neighboring Regions,* Kopaonik (Serbia), June 16-19, 2016, pp. 113.				
Milan Nešić	2	8	-	-
1. Radulović, N. S., & Nešić, M. S., (2016). Diverse acetals from stoichiometric amounts of aldehydes and alcohols under very mild conditions: a new twist to PPh$_3$-CCl$_4$ reagent combination, RSC Advances, 6(95), 93068-93080. 2. Nešić, M. S., Stevanović, M. D., Filipović, S. I., & Radulović, N. S. What to do with old, auto-oxidized tetrahydrofuran? Simple, make a perfume out of it, In: *Programme and Book of Abstracts of the 47th International Symposium on Essential Oils* (ISEO 2016), Nice (France), September 11-14, 2016, pp. 78. 3. Radulović, N. S., Nešić, M. S., & Stevanović, M. D.; NMR spectra assignment of tetrahydrofuranyl acetals directly from mixtures of diastereomers by spectral simulation, In: *Programme and Book of Abstracts of the 18th Central and Eastern European NMR Symposium & Bruker Users' Meeting* (CEUM 2016), Sofia (Bulgaria), September 18-20, 2016, pp. 54.				
Milena Krstić	1	4	-	-
1. Radulović, N. S., Krstić, M. Lj., & Mladenović, M. Z. Chemotaxonomy of the genus *Tordylium* L. based on the chemical composition of the essential oils: the case of *Tordylium maximum* (Apiaceae), In: *Programme and Book of Abstracts of the 48th International Symposium on Essential Oils* (ISEO 2017), Pécs (Hungary), September 10-13, 2017, pp. 88. 2. Radulović, N. S., Krstić, M. Lj., Stojanović, N. M., & Randjelović, P. J. Cytotoxicity of octyl esters from the essential oil of *Tordylium maximum* L. (Apiaceae) towards rat peritoneal macrophages, In: *Programme and Book of Abstracts of the 47th International Symposium on Essential Oils* (ISEO 2016), Nice (France), September 11-14, 2016, pp. 129. 3. Krstić, M., Miltojević, A., & Radulović, N. Wax alkanes of *Galanthus nivalis* L. (Amaryllidaceae In: *Programme and Book of Abstracts of the 12th Symposium on the Flora of Southeastern Serbia and Neighboring Regions*, Kopaonik (Serbia), June 16-19, 2016, pp. 115-116.				

Milica Stevanović	-	5	-	-

1. Nešić, M. S., Stevanović, M. D., Fuchs, T. A. K., & Radulović, N. S. Essential-oil components of *Bupleurum praealtum* L. Synthesis and spectral characterization of a rare perillyl ester, In: *Programme and Book of Abstracts of the 48th International Symposium on Essential Oils* (ISEO 2017), Pécs (Hungary), September 10-13, 2017, pp. 121 – 121.
2. Nešić, M. S., Stevanović, M. D., & Radulović, N. S. The first report on the chemical composition of the inflorescence essential oil of *Eupatorium cannabinum* L. from Serbia, In: *Programme and Book of Abstracts of the 48th International Symposium on Essential Oils* (ISEO 2017), Pécs (Hungary), September 10-13, 2017, pp. 122.
3. Radulović, N. S., Stevanović, M. D., & Nešić, M. S. Mosher esters of α-hydroxyesters: Absolute configuration *via* NMR, In: *Programme and Book of Abstracts of the 19th Central and Eastern European NMR Symposium & Bruker Users' Meeting* (CEUM 2017), Timisoara (Romania), September 5-8, 2017, pp. 27.

[a] Data are taken from Scopus data base (accesion date 10/04/2018). The self-citations of all authors are excluded.

The scientific achievements of several researchers have been recognized at national level. Niko Radulović and Polina Blagojević were awarded with the *Medal of the Serbian Chemical Society for endeavour and success in science* in 2012 and 2014, respectively. Afterwards, in 2016 Niko Radulović was elected as an honorary member of the Society. According to Ivanović and Ho (*Scientometrics* (2014) 101:603–62) Niko Radulović is one of the seven most cited Serbian researchers in all disciplines in the period from 2006 to 2012. Polina Blagojević and Marija Genčić won *L'Oréal-UNESCO for Women in Science national scholarships* in 2011 and 2017, respectively.

The above-mentioned researchers were on several postdoctoral stays abroad supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia within the programme of postdoctoral fellowships for young scientists:

(i) Niko Radulović was for two months at *Max-Planck-Institut für Chemische Physik fester Stoffe* in Dresden (Germany, 2011) and for six months at *Institut de Chimie de Nice*, *Université de Nice-Sophia Antipolis* in Nice (France, 2017);

(ii) Polina Blagojević also spent two months at *Max-Planck-Institut für Chemische Physik fester Stoffe* in Dresden (Germany, 2011) and six months at *University of British Columbia* in Vancouver (Canada, 2017);

(iii) Marija Genčić was for six months in *SynBioC Research Group* at *Faculty of Bioscience Engineering*, *Ghent University* (Belgium, 2016).

In 2004, Niko Radulović also spent 6 months in Prof. Yoshinori Asakawa group at *Faculty of Pharmaceutical Sciences*, *Tokushima Bunri University* (Japan). Moreover, Polina Blagojević received in 2016 scholarship of the *Institute Francais* (Serbia) for short research stay in France at *Institut de Chimie de Nice*, *Université de Nice-Sophia Antipolis* in Nice. Milan Nešić spent two months at *Technical University of Ilmenau* (Germany, 2017) within IAESTE exchange program. Herein, it is worth mentioning that Milica Stevanović has been a presedent of the local IAESTE commette for the last three years promoting and coordinating the exchange of students beetween University of Niš and universities and scientific research institutions worldwide.

Since 2010, Niko Radulović is editor-in-chief of the journal *Facta Universitatis, section Physics, Chemistry and Technology* (published by University of Niš), while Polina Blagojević is the second editor in the same pre-rewied scientific journal (since 2013). Niko Radulović is also a member of the Editorial Advisory Board of the journal *Chemistry & Biodiversity* (SCIE journal published by Wiley & Sons; since 2017) and a member of the Permanent Scientific Board of the *International Symposium on Essential Oils* (ISEO; since 2015). Polina Blagojević is a participant of the international TEMPUS MCHEM programme - *Modernisation of Post-Graduate Studies in Chemistry and Chemistry Related Programmes* (4/2012 to present).

Table 9. Conference presentations awarded with the poster awards

No	Conference	Presentation	Award
1	*19th Central and Eastern European NMR Symposium & Bruker Users' Meeting*, Temisoara (Romania), September 5 – 8, 2017	Radulović, N. S., Mladenović, M. Z., & Blagojević, P. D. Having trouble with overlapped and/or second-order multiplets? Try the hybrid HIFSA-GIAO-(A)SIS approach.	Best poster award (3rd place)
2	*18th Central and Eastern European NMR Symposium and Bruker Users' Meeting*, Sofia (Bulgaria), September 18 – 20, 2016	Blagojević, P., Genčić, M., & Radulović, N. Interactions of four regioisomeric methylcamphorquinoxaline ligands with a lanthanide NMR shift reagent, $Eu(fod)_3$.	Poster prize „Prof. Valentin Dimitrov“ (3rd place)
3	*18th Central and Eastern European NMR Symposium and Bruker Users' Meeting*, Sofia (Bulgaria), September 18 – 20, 2016	Radulović, N. S., Nešić, M. S., & Stevanović, M. D. NMR spectra assignment of diastereomeric tetrahydrofuranyl acetals directly from mixture of diastereomers using spectral simulation.	Special poster prize „Prof. Valentin Dimitrov“ (1st place)
4	*2nd International Conference on Natural Products Utilization: From Plants to Pharmacy Shelf*, Plovdiv (Bulgaria), October 14-17 2015	Stojanović, N. M., Radulović, N., Ranđelović, P. J., Ilić, I., Miltojević, A. B., Mitić, K., Krstić, V., & Blagojević, P. D. Effects of methyl and isopropyl *N*-methylanthranilates from *Chosiya ternata* Kunth (Rutaceae) in rat models of different diseases.	Teva award for the best poster
5	*51th Meeting of the Serbian Chemical Society*, Niš (Serbia), June 5 – 7, 2014	Miltojević, A. B., Radulović, N. S., Živković, M. Z., Vukićević, R. D. Simple and efficient one-pot solvent-free synthesis of *N*-methyl imines of aromatic aldehydes.	IUPAC poster prize certificate
6	*1st Conference of Young Chemists of Serbia*, Belgrade (Serbia), October 19 –20, 2012	Radulović, N. S., & Đorđević, M. R. Chemical composition of the tuber essential oil from *Helianthus tuberosus* L. (Asteraceae).	EYCN poster award
7	*50th Meeting of the Serbian Chemical Society,* Belgrade (Serbia), June 14 – 15, 2012	Radulović, N. S., & Đorđević, M. R. Synthesis of mono- and diiodo-derivatives of *N*-(4-methoxyphenethyl) amide as model compounds of tyramine metabolites of marine organisms of the genus *Didemnum*.	IUPAC poster prize certificate

Alongside research work, professors and PhD students are also involved in teaching. Courses for undergraduate students aim to introduce students with the classification, structure, and reaction mechanism of organic compounds, as well as with the basic methods of their preparation and purification, and their importance in everyday life. Master's and PhD studies courses intend to broaden the knowledge of students about modern synthetic methods and NMR-based identification methods of organic compounds, as well as to introduce the students with the interdisciplinary character and applicability of chemistry in everyday lives, encompassing such as field like medicinal chemistry, forensic chemistry, organic polymers and pollutants. All courses include laboratory and/or theoretical exercises.

Since 2011, Chair members actively take part in the organization of state (and/or regional) competitions in chemistry and Serbian Chemistry Olympiad for high-school pupils, as well as in training of Serbian high-school team for the International Chemistry Olympiad (IChO). Niko Radulović is a permanent co-mentor of the Serbian teams at IChO (2012-present) and International Junior Science Olympiad (IJSO, 2011-present). In the last five years, Serbian teams won more than 20 medals in total, frequently besting teams from Germany, France and similar countries. Alongside this work with the gifted high-school pupils, members of the Chair also give efforts in the popularization of chemistry within young people through participation in science festivals and similar events.

It is noteworthy that Marija Genčić received *Nenad M. Kostić Foundation Award* for the best master's thesis in chemistry at the universities in Serbia for the 2009/2010 school year, while Milan Nešić took the second place at the mentioned contest in 2014/2015. Both master's theses were supervised by dr Niko Radulović. All of them were also awarded, in their own classes, with *Silver Sign of the University of Niš*, as the Best-Graduated Student of the University in the field of mathematics and natural sciences, and with *Annual Award of the Serbian Chemical Society*, for outstanding successes during the studies.

Katedra za organsku hemiju i biohemiju

Gordana S. Stojanović, Snežana Č. Jovanović*, Marija S. Genčić

Univerzitet u Nišu, Prirodno-matematički fakultet, Departman za hemiju, Višegradska 33, 18000 Niš, Srbija

SAŽETAK

U ovoj prezentaciji ukratko je dato sledeće: pregled kurseva, profesora i saradnika na Katedri za organsku hemiju i biohemiju na osnovnim akademskim studijama, na master akademskim studijama i na doktorskim akademskim studijama; cilj i kratak pregled kurseva na Katedri za organsku hemiju i biohemiju kao i pregled istraživačkih projekata „Prirodni proizvodi biljaka i lišaja: izolacija, identifikacija, biološka aktivnost i primena“ i „Kombinatorne biblioteke heterogenih katalizatora, prirodnih proizvoda, modifikovani prirodni proizvodi i analozi: pristup novim biološki aktivnim agensima“, uključujući i listu istraživača koji su članovi Katedre za organsku hemiju i biohemiju zajedno sa njihovim glavnim oblastima istraživanja i najvažnijim dostignućima i/ili pozicijama.

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Chaire de chimie organique et de biochimie

Gordana S. Stojanovic, Snezana C. Jovanovic*, Marija S. Gencic

Université de Nis, Faculté des sciences et mathématiques, Département de chimie, Visegradska 33, 18 000 Niš, Serbie

Dans cette présentation, nous donnons un bref aperçu des cours, des professeurs et des maîtres-assistants à la Chaire de chimie organique et de biochimie dans ses programmes d'études du premier cycle (licence), du master et du doctorat. Sont exposés également les objectifs des cours assurés au sein de la Chaire de chimie organique et de biochimie, tout comme une brève description des projets de recherche « Les produits naturels des plantes et des lichens : isolation, identification, activité biologique et application » et « Les bibliothèques combinatoires des catalyseurs hétérogènes et des produits naturels, les produits naturels modifiés et les analogues : l'approche des nouveaux agents biologiquement actifs ». De même, notre présentation contient la liste des chercheurs étant les membres de la Chaire de chimie organique et de biochimie, ainsi que leur principaux domaines de recherche et leurs résultats et/ou positions les plus importants.

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Кафедра органической химии и биохимии

Гордана С. Стојанович, Снежана Ч. Јованович *, Марија С. Генчич

Университет в Нише, Факультет естественных наук и математики, Отдел химии, Вишеградска 33, 18 000 Ниш, Сербия

В этой презентации кратко даётся следующее: обзор курсов, профессоров и сотрудников на Кафедре органической химии и биохимии в бакалавриате, магистратуре и докторантуре; цель и краткий обзор курсов на Кафедре органической химии и биохимии, а также обзор исследовательских проектов «Натуральные продукты растений и лишайников: выделение, идентификация, биологическая активность и применение» и «Комбинаторные библиотеки гетерогенных катализаторов, натуральных продуктов, модифицированные натуральные продукты и аналоги: доступ к новым биологически активным веществам» в том числе список исследователей, являющихся членами Кафедры органической химии и биохимии вместе с их основными направлениями исследований и наиболее важными достижениями и / или должностями.

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Chair of General and Inorganic Chemistry

Nikola D. Nikolić, Dragan M. Đorđević*, Maja N. Stanković, Nenad S. Krstić, Milica G. Nikolić, Vladimir D. Dimitrijević

University of Niš, Faculty of Sciences and Mathematics, Department of Chemistry, Višegradska 33, 18000 Niš, Serbia

ABSTRACT

Researchers from the Chair published over 50 scientific papers in the field of inorganic chemistry, geochemistry, bioinorganic chemistry, organometallic compounds, the chemistry of coordination compounds, tests of inorganic materials (construction materials, electrode materials, natural minerals, *etc*.), the development of chemically modified biosorbents. Also, they are participants in a number of national and international projects in the field of basic research and technological development, as well as projects for the popularization of science.

The following teachers and associates are currently working at the Chair:

Nikola Nikolić, full professor:
General chemistry
Fundamentals of inorganic chemistry
Inorganic raw materials
Applied non-metal chemistry
Chemistry in agriculture

Dragan Đorđević, full professor (Head of Chair)
The techniques and methods for the characterization of inorganic compounds
Inorganic Chemistry 2
Theoretical inorganic chemistry

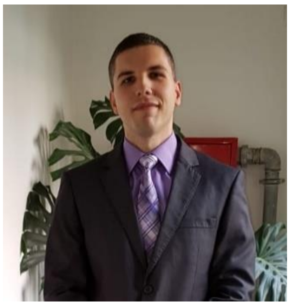
Geochemistry
Chemistry of metals in the environment
Transition metal chemistry with coordination chemistry
General and Inorganic Chemistry (Department of Biology)
Geochemistry (Department of Geography)

Maja Stanković, associate professor
General chemistry
Inorganic materials in industry
Inorganic reaction mechanism
Inorganic food chemistry
Inorganic compounds in medicine and pharmacy
Chemistry of gases

Nenad Krstić, assistant professor
Transition metal chemistry with coordination chemistry
Fundamentals of mineralogy
Inorganic compounds in medicine and pharmacy
Bioinorganic chemistry
School experiments in inorganic chemistry
Theoretical inorganic chemistry
The techniques and methods for the characterization of inorganic compounds

Milica Nikolić, teaching assistant (PhD student)

Vladimir Dimitrijević, research assistant (PhD student)



The Chair contains the following instruments:

1. Electron spin resonance (ESR) spectrometer (Bruker Optics),
2. FTIR spectrophotometer Tensor with Hyperion microscope (Bruker Optics),
3. Stereo zoom microscope (Krüss),
4. Colorimeter.

Members of the Chair participate in the realization of the following projects:

1. Project TR 34008 - *"Development and characterization of a new biosorbent for the treatment of natural and wastewater"* (associate professor Maja Stanković, assistant professor Nenad Krstić, Vladimir Dimitrijević)
2. Project ON 171025 - *"Electric breakdown of gases, surface processes and applications"* (professor Nikola Nikolić)
3. Project ON 172061 - *"Combination libraries of heterogeneous catalysts, natural products, modified natural products and their analogues: a pathway to new biologically active agents"* (Milica Nikolić)
4. Project ON 176008 – "*Development programs of revitalization of the village of Serbia*" (associate professor Dragan Đorđević)

Researchers from the Chair published over 50 scientific papers in the field of inorganic chemistry, geochemistry, bioinorganic chemistry, organometallic compounds, chemistry of coordination compounds, tests of inorganic materials (construction material, electrode material, natural minerals, *etc.*), the development of chemically modified biosorbents.

Selected publications:

1. Stanković, M. N., Krstić, N. S., Mitrović, J. Z., Najdanović, S. M., Petrović, M. M., Bojić, D. V., Dimitrijević, V. D., & Bojić, A. L., (2016). Biosorption of copper (II) ions by methyl-sulfonated *Lagenaria vulgaris* shell: kinetic, thermodynamic and desorption studies. New Journal of Chemistry, 40(3), 2126-2134.

2. Krstić, N. S., Nikolić, R. S., Stanković, M. N, Nikolić, N. G., Đorđević, D. M., (2015). Coordination compounds of M(II) biometal ions with acid-type anti-inflammatory drugs as ligands–A review. Tropical Journal of Pharmaceutical Research, 14(2), 337-349.

3. Nikolić, R. S., Krstić, N. S., Nikolić, G. M., Kocić, G. M., Cakić, M. D, Anđelković, D. H., (2014). Molecular mechanisms of beneficial effects of lipoic acid in copper intoxicated rats assessment by FTIR and ESI-MS. Polyhedron, 80, 223-227.

4. Stanković, M. N., Krstić, N. S., Đorđević, D. M., Anastasijević, N. N., Mitić, V. V., Topličić-Ćurčić, G. A., Momčilović-Petronijević, A. J., Chemical analysis of mortars of archaeological samples from Mediana locality, Serbia. Science of Sintering, accepted for the publication.

5. Premović, P. I., Đorđević, D. M., & Pavlović, M. S., (2002). Vanadium of petroleum asphaltenes and source kerogens (La Luna Formation, Venezuela): isotopic study and origin. Fuel, 81(15), 2009-2016.

6. Radulović, N. S., Stojanović, N. M., Glišić, B. Đ., Randjelović, P. J., Stojanović-Radić, Z. Z., Mitić, K. V., Nikolić, M. G., & Djuran, M. I., (2018). Water-soluble gold (III) complexes with N-donor ligands as potential immunomodulatory and antibiofilm agents. Polyhedron, 141, 164-180.

Assistant professor Nenad Krstić is the winner of the following awards and recognitions:

(1) Scholarship of the Fund for Young Talents of the Government of the Republic of Serbia (12.2006-12.2007); (2) EFG Eurobank scholarships for the best students of the final year of the state faculty (12.2007); (3) Best graduate chemist for 2007/2008 at the Faculty of Sciences and Mathematics (09.2008.); (4) Annual Award of the Serbian Chemical Society for 2008. (12.2008.); (5) Silver coin of the University of Niš for the best graduate student at the University of Niš in 2007/2008 for the group of faculties from the field of science and mathematics (06.2009.); (6) Award of the city of Vranje "Seventh September" for exceptional results in the field of education and scientific research (09.2009.).

Assistant professor Nenad Krstić was at postdoctoral studies as a scholar of the Ministry of Education, Science and Technological Development of the Government of the Republic of Serbia (10.2015.- 03.2016.) at BioMEMS Lab, University of Applied Sciences Aschaffenburg, Germany. He also went to this laboratory on two more occasions, once within a short study visit (05.12.-09.12.2016.) and the second time as a guest speaker (21.11.-01.12.2017.).

Assistant Milica Nikolić was in the Laboratory for Environmental and Life Sciences at the University of Nova Gorica, Slovenia within the exchange of master studies students

(TEMPUS project "Modernisation of Postgraduate Studies in Chemistry and Chemistry related Programmes") in the period 15.02.-15.03.2013. She is a winner of the following awards and recognitions: special recognition of the Serbian Chemical Society for outstanding success during the studies (December 2013.), the award of the fund of Nenad M. Kostić for the best master work in the field of chemistry at the Universities in Serbia (2013/2014), and "Ana Bjeletić and Ivan Marković" Fund award for the best student at the Department of Chemistry at the Faculty of Sciences and Mathematics in Niš for 2013/2014. Also, she received a scholarship of Foundation for Young Talents "Dositeja" for 2010/2011 and 2012/2013 awarded by the Ministry of Education, Science and Technological Development to the best students in the Republic of Serbia.

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Katedra za opštu i neorgansku hemiju

Nikola D. Nikolić, Dragan M. Đorđević*, Maja N. Stanković, Nenad S. Krstić, Milica G. Nikolić, Vladimir D. Dimitrijević

Univerzitet u Nišu, Prirodno-matematički fakultet, Departman za hemiju, Višegradska 33,

18 000 Niš, Srbija

SAŽETAK

Istraživači sa Katedre objavili su preko 50 naučnih radova iz oblasti neorganske hemije, geohemije, bioneorganske hemije, organometalnih jedinjenja, hemije koordinacionih jedinjenja, ispitivanja neorganskih materijala (građevinskog materijala, elektroda, prirodnih minerala itd.), razvoja hemijski modifikovanih biosorbenata. Takođe, učesnici su većeg broja nacionalnih i međunarodnih projekata iz oblasti osnovnih istraživanja i tehnološkog razvoja, kao i projekata popularizacije nauke.

Chemia Naissensis, Vol 1, Issue 1, 70

Chaire de chimie générale et inorganique

Nikola D. Nikolic, Dragan M. Đorđevic*, Maja N. Stankovic, Nenad S. Krstic, Milica G. Nikolic, Vladimir D. Dimitrijevic

Université de Nis, Faculté des sciences et mathématiques, Département de chimie, Visegradska 33, 18 000 Niš, Serbie

Les chercheurs de la Chaire de chimie générale et inorganique ont publié plus de cinquante articles scientifiques dans les domaines de la chimie inorganique, de la géochimie, de la chimie bioinorganique, des composés organométalliques, de la chimie des composés de coordination, de l’examen des matériaux inorganiques (les matériaux de construction, les matériaux d’électrodes, les minéraux naturels, etc.) et du développement des biosorbants chimiquement modifiés. Ils participent également à de nombreux projets nationaux et internationaux portant sur l’exploration et le développement technologique, ainsi qu’à des projets liés à la popularisation de la science.

Кафедра общей и неорганической химии

Никола Д. Николич, Драган М. Джорджевич *, Майя Н. Станкович, Ненад С. Крстич, Милица Г. Николич, Владимир Д. Димитриевич

Университет в Нише, Факультет естественных наук и математики, Отдел химии, Вишеградска 33, 18 000 Ниш, Сербия

Исследователи с этой кафедры опубликовали более 50 работ в области неорганической химии, геохимии, бионеорганической химии, металлоорганических соединений, химии координационных соединений, испытаний неорганических материалов (строительные материалы, электродные материалы, природные минералы и т.д.), разработки химически модифицированных биосорбентов. Они тоже принимают участие во многих отечественных и международных проектах в области исследований и технологического развития, а также в проектах по популяризации науки.

Chemia Naissensis, Vol 1, Issue 1, 72-89

Chair of Applied and Environmental Chemistry

Aleksandar Bojić, Milena Miljković, Tatjana Anđelković, Aleksandra Zarubica, Marjan Ranđelović*, Jelena Mitrović

University of Niš, Faculty of Sciences and Mathematics, Department of Chemistry, Višegradska 33, 18000 Niš, Serbia

ABSTRACT

Chair of the Applied and Environmental Chemistry was established in 1995 on the initiative of Prof. Dr. Milovan Purenović, who has been in the position of Head of the Chair since its establishment until his retirement in 2011. Prof. Dr. Aleksandar Bojić is currently Head of the Chair. Since its establishment until now, professors and associates of the Chair of Applied and Environmental Chemistry have been dedicated to the applied research, within the framework of innovative and development projects, which were realized through cooperation with industry. Also, a significant contribution has been made in the field of environmental protection, especially in the treatment of drinking and wastewater. Several operational technologies have been developed, some of them are protected by patents of the Intellectual Property Office of the Republic of Serbia. The Chair of Applied and Environmental Chemistry consists of four full professors, one associate professor, and one assistant professor.

Innovation and development projects implemented so far:

1. **Innovation project: I.3.1231, Ministry of Science of the Republic of Serbia,**
   Project title: "Development and application of catalytic reactor system for decomposition and purification of waste paints in fabric processing technology of textile factory NITEX-Niš" (1996).
2. **Innovation project: I.3.1791, "EI - Printed Circuits" - Ministry of Science of the Republic of Serbia**

Project name: " The new process of copper separation, decomposition of ammonia and other harmful substances from waste electrolytes of base ammonia complexes of copper and acid copper(I)- and copper(II)-chloride” (1997).

3. **Research and development project, Municipality of Niš**

   Project title: "Contribution to the groundwater quality in the City of Niš region", JKP Gradski vodovod- "NAISSUS-NIŠ" (1998-1999).

4. **Research and development project, "Tigar"Ltd. Pirot**

   Project title: "Contribution to the investigation of physical and chemical processes during the processing of rubber compounds by the extrusion process"(2001).

5. **Innovation project, Municipality of Medveđa**

   Project title: "Innovation of Industrial and Sewerage Water Treatment Plant Medveđa" (2001).

6. **Innovation project, “Limske hidroelektrane” Nova Varoš**

   Project title: "Solving corrosion protection problem of the internal part of pipeline in the Bistrica hydroelectric power plant"(2001).

7. **Development project: MHT 0279 - Ministry of Science of the Republic of Serbia**

   Project title: "Innovation, monitoring and reconstruction of technological systems for the purification of alkaline, cyanide and acidic wastewaters containing Cr, Ni, Cu, Zn, Sn and Cd"(2001-2004).

8. **Innovation project-JKP Gradska toplana-Niš**

   Project title: "A new procedure for the protection of boilers, hot water and heat exchangers from corrosion and scale by corrosion inhibitor protection and modifier"(2003).

9. **Innovation project: I.EE401-1007V, Ministry of Science of the Republic of Serbia**

   Project title: "High energy efficiency of boilers and heat exchangers in power plants, achieved by removing existing calcite and corrosion products and preventing calcite formation by dosing original modifiers and inhibitors in boiler water and district heating” (2005).

10. **The project of the existing process improvement: MHT 6725**

    Project title: "Improvement of chemical and technological processes and reconstruction of existing systems in the production of audio electronic tubes"(2005-2008).

11. **Innovation project: IP 8027 of the Ministry of Science of the Republic of Serbia**

    Project title: “New universal compact technology for the purification of wastewaters, municipal and drinking waters from harmful substances using novel electrochemically and chemically activated and micro alloyed materials” (2006).

12. Development project TR19031 of the Ministry of Science of the Republic of Serbia

Project title: “Development of electrochemically active micro alloyed and structurally modified composite materials” (2008-2011).

13. Innovation project no. 01501-12 Ministry of Environment-Fund for Environmental Protection

Project title: “Operational technology for decontamination of asbestos and asbestos dust with instructions for dismantling and cleaning of the machine part of the plant Fiaz-Ferode in Prokuplje” (2009-2010).

14. Innovation project no. 501-12/10-01 Ministry of Environment-Fund for Environmental Protection

Science popularization programme

Project title: "Human environment under the loupe of chemistry"; Project funding: Center for the Promotion of Science of the Republic of Serbia, 2011.

Accredited Program of Permanent Professional Development-Title: "Chemistry of gases in teaching, nature and industry"; Project duration: 2009/2010 and 2010/2011.

Accredited Program of Continuing Professional Development-Title: "Planet Earth: Minerals, Rocks, Ores-from the origin to Minerals"; Project duration: 2010-2011.

Bilateral collaboration between the University of Niš and the University Pierre and Marie Curie in Paris; Duration: 2008-2013.

Partnership for education and community development (PECD)-Niš; Title: "Development of the Chemical and Ecological Center of the City of Niš"; Project duration: 2009/2010.

Partnership for education and community development (PECD)-Niš; Title: "Eco monitoring of Niš 2011-2012"; Project duration: 2011/2012.

Promotion and popularization of science programme; Title: "Mass spectrometry, basics and applications"; Project duration: 2010.

International Meeting “Mass Spectrometry school”; Title: "Mass Spectrometry School"; Duration of the project: 10 schools from 2008 to 2018.

Teaching projects

511044-Tempus-1-2010-1-UK-Tempus-JPCR UoG "Modernization of Post-Graduate Studies in Chemistry and Chemistry Related Programs" 2010-2013.

44482-TEMPUS-1-2013-1-IT-TEMPUS-JPHES "Blending academic and entrepreneurial knowledge in technology enhanced learning" BAEKTEL 2013-2016.

573885-EPP-1-2016-1-RS-EPPKA2-CBHE-JP "ICT Networking for Overcoming Technical and Social Barriers in Instrumental Analytical Chemistry Education (NETCHEM)" 2016-2019.

Current projects

Development and characterization of new biosorbent for purification of natural and wastewaters, TR34008.

Period: 2011-2018, researchers on the project: 16

The names of the researchers engaged on the project are:

Name and surname	**Academic title**
Aleksandar Lj. Bojić	Full professor
Aleksandra R. Zarubica	Full professor
Danijela V. Bojić	Scientific Associate
Jelena Z. Mitrović	Assistant professor
Miljana D. Radović	Scientific Associate
Marjan S. Ranđelović	Associate professor
Radomir B. Ljupković	Scientific Associate
Miloš M. Kostić	Scientific Associate
Milica M. Petrović	Scientific Associate
Nena D. Velinov	Research Associate
Slobodan M. Najdanović	Research Associate

Dr Aleksandar Bojić, full professor, Head of the Chair

Teaching contributions:

Fundamentals of industrial chemistry

Corrosion and corrosion protection of metals

Industrial chemistry I

Chemistry of waters and wastewaters

Advanced water treatment processes

Remediation technologies

Publications:

University textbooks: 2

Published scientific papers: 54

Selected publications:

1. Bojic, A., Bojic, D., &Andjelkovic, T. (2009). Removal of Cu^{2+} and Zn^{2+} from model wastewaters by spontaneous reduction-coagulation process in flow conditions. Journal of Hazardous Materials,168, 813-819.
2. Milenković, D., Bojić, A., &Veljković, V. (2013). Ultrasound-assisted adsorption of 4-dodecylbenzene sulfonate from aqueous solutions by corn cob activated carbon. UltrasonicsSonochemistry, 20(3), 955–962.
3. Mitrović, J., Radović, M., Anđelković, T., Bojić, D., &Bojić A. (2014). Identification of intermediates and ecotoxicity assessment during the UV/H_2O_2 oxidation of azo dye Reactive Orange 16. Journal of Environmental Science and Health, Part A, 49, 491-502.

International collaborations:

- „1st Summer SchoolThe Mass Spectrometry Opens on the Environment and the Life“, University „Pierre and Marie Curie”–Paris (2008);

- Postdoctoral fellow at Pierre and Marie Curie-Paris, Senior research project: “Mass spectrometry analysis of UV/H_2O_2 process degradation products of organic matter in water”, 3 months: “City of Paris”, France (2009);
- “Mass spectrometry practical course in the environmental analysis of persistent organic pollutants”, University „Pierre and Marie Curie”–Paris, Funding: Ministry of Foreign Affairs of France (2010);
- “Mass spectrometry practical course in the environmental analysis of pesticides and textile dyes and their degradation products in water” at University „Pierre and Marie Curie”–Paris, Ministry of Foreign Affairs of France (2011);
- Bilateral collaboration: CNRSR. France and Ministry of Science Serbia (2011-2012);
- “Environmental Chemistry and Engineering”, Michigan State University (USA) held at the Faculty of Occupational Safety (2004).

Journal editorial boards membership:

Member of editorial board in the journal „Water SA“.

Review activities:

- Analytical Methods,
- Arabian Journal of Chemistry,
- BioResource,
- Chemical Engineering & Technology,
- Chemical Industry and Chemical Engineering Quarterly,
- Desalination,
- Desalination and Water Treatment
- Environmental Engineering and Management Journal,
- Facta Universitatis,
- Hemijska industrija,
- Journal of Applied Electrochemistry,
- Journal of Chemical & Engineering Data,
- Journal of Hazardous Materials,
- Water SA.

Dr Milena Miljković, full professor

Teaching contributions:

Food additives

Chemistry teaching methodology 1

Industrial chemistry 2

Chemistry of textile materials and industrial dyes

Surface active agents

Chemistry of dyes

Colormetrics

Research contributions:

Determination of reactive dye concentration in technological solutions and on dyed textile materials by UV/VIS spectrophotometry; 2) catalytic degradation of dyes in textile industry wastewaters; 3) analysis of the color of composite materials in dental prosthetics; 4) determination of the concentration of food colors and additives; 5) application of reflection spectrophotometry in the textile industry; 6) color metrics by CIELAB system; 7) chemical-textile technology.

Currently engaged on the project: Development of new and the improvement of already existing technological procedures to produce technical textile materials (TR 34020), Ministry of Education, Science and Technological Development, Republic of Serbia. Antioxidative and antiapoptic effect of the extract of bilberry (*Vaccinium myrtillus* L.): *in vivo* and *in vitro* experimental investigation-bilateral project (ev.no. proj. 651-03-1251/2012-09/15).

Publications:

University textbooks: 3

Published scientific papers: 21

Selected publications:

1. Miljkovic, M., Djordjevic, D. M., Miljkovic, V. M., Stamenkovic, M., &Stepanovic, J. M. (2014). The influence of pH adjusted with different acids on the dyeability of polyester fabric. Polish Journal of Chemical Technology, 16 (4), 1-5.
2. Miljkovic, M. N., Purenovic M. M., Stamenkovic M., & Petrovic M. (2012). Determination of two reactive dyes concentration in dyed cotton fabric. Hemijska Industrija, 66 (2), 243-251.
3. Miljkovic, M. N., Purenovic, M. M., Djordjevic, D. M., &Petrovic, M. (2011). Influence of different acids for adjusting the dyebath pH value on the dyeability of polyester knitwear dyed with Disperse Yellow 23. Hemijska Industrija, 65 (3), 257-261.

Dr Tatjana Anđelković, full professor

Teaching contributions:

Fundamentals of environmental chemistry

Hemodynamics of pollutants

Environmental chemistry

Pollutants and pollution control

Active learning in chemistry

The hemisphere of water and soil

Chemistry of gases

Research contributions:

Environmental Pollutants Detection; Soil analysis; Soil organic matter; Properties, isolation and characterisation of aquatic and terrestrial humic substances as well as their complexing properties, environmental analysis of water, soil and air; chemistry teaching methodologies.

Publications:

University textbooks: 3

Published scientific papers: 24

Selected publications:

1. Bojic, A. L., Bojic, D. V., & Andjelkovic, T. D. (2009). Removal of Cu^{2+} and Zn^{2+} from model wastewaters by spontaneous reduction-coagulation process in flow conditions. Journal of Hazardous Materials, 168 (2-3), 813-819.
2. Kocic, G., Pavlovic, R., Nikolic, G., Veljkovic, A., Panseri, S., Chiesa, L.M., Andjelkovic, T., Jevtovic Stoimenov, T., Sokolovic, D., Cvetkovic, T., Stojanovic, S., Kocic, H., & Nikolic R. (2014). Effect of commercial or depurinized milk on rat liver growth-regulatory kinases, nuclear factor-kappa B, and endonuclease in experimental hyperuricemia: Comparison with allopurinol therapy. Journal of Dairy Science, 97 (7), 4029-4042.
3. Andjelkovic, T., Perovic, J., Purenovic, M., Blagojevic, S., Nikolic, R., Andjelkovic, D., & Bojic, A. (2006). Spectroscopic and potentiometric studies on derivatized natural humic acid. Analytical Sciences, 22 (12), 1553-1558.
4. Milojković, D. S., Anđelković, D. H., Kocić, G. M., & Anđelković, T. D. (2015). Evaluation of method for phthalate extraction from milk related to milk fat content**.** Journal of the Serbian Chemical Society, 80 (8), 983-996.
5. Kostić, I. S., Anđelković, T. D., Anđelković, D. H., Cvetković, T. P., & Pavlović, D. D. (2016). Determination of di(2-ethylhexyl) phthalate in plastic medical devices. Hemijska industrija, 70(2), 159-164.

International collaborations:

Scholarship of French Government at the University Pierre and Marie Curie, Paris, France- Institut Parisien de Chimie Moléculaire and Laboratory L.C.H. Paris period: 14 - 29 January 2009; 6 - 11 April 2009; 6 - 24 February 2010; 8 - 26 December 2014.

Training at UPMC Pierre and Marie Curie University, Paris, France-Institut Parisien de Chimie Moléculaire in the Field of Mass Spectrometry, as project leader, CNRS/Pavle Savić, "Heavy metals geochemical modelling and speciation in groundwater and soil using soft ionization mass spectrometry" (22.11.-29.11.2011 and: 12.11 - 08.12.2012).

Several short study visits for cooperation and training at the University of Greenwich, Brno University of Technology, RWTH Aachen University, University of Nova Gorica, in the period 2010-2013 within the framework of the project 511044-TEMPUS-1-2010-1-UK-TEMPUS-JPCR, "Modernization of Post-Graduate Studies in Chemistry and Chemistry Related Programs", TEMPUS MCHEM.

Within the project 573885-EPP-1-2016-1-RS-EPPKA2-CBHE-JP, ERASMUS + NETCHEM, "ICT Networking for Overcoming Technical and Social Barriers in Instrumental Analytical Chemistry Education" several short stays for collaboration and training at the University of Greenwich, Brno, Tirana, Sorbonne University in the period 2016-2018.

Organizer and participant of 10 mass spectrometry schools “Mass Spectrometry School - The Mass Spectrometry in Environmental Pollutants Detection, Niš”, organized by Faculty of Science and Mathematics, Niš and the University Pierre and Marie Curie, Paris (France).

Postdoctoral training:

Scholarship of the Ministry of Science and Technological Development for young researchers at the Postdoctoral Training in 2011. Project title: "Oxidative metabolites of DEHP as urinary biomarkers of human exposure to phthalates from milk and milk products". Project duration: 4 months (June-September 2011). Institution in which postdoctoral training was realized: The University Pierre and Marie Curie, Paris.

Review activities:

- Water Practice and Technology
- Water Science and Technology: Water Supply
- Analytical Letters
- Journal of the Serbian Chemical Society

Awards:

Award of the Serbian Chemical Society for graduated students in 1993/94.

Dr Aleksandra Zarubica, full professor

Teaching contributions:

Fundamentals in materials engineering

Industrial chemistry

Active learning in chemistry

Materials chemistry and engineering

Green chemistry

Chemistry of surface processes

Nanostructural materials

Publications:

University textbooks: 3

Published scientific papers: 58

Selected publications:

Prekajski, M., Zarubica, A., Babić, B., Jokić, B., Pantić, J., Luković, J., & Matović, B. (2016). Synthesis and characterization of Cr^{3+} doped TiO_2 nanometric powders. Ceramics International, 42, 1862-1869.

Babic, B., Zarubica, A., Minovic-Arsic, T., Pantic, J., Jokic, B., Abazovic, N., & Matovic, B. (2016). Iron doped anatase for application in photocatalysis. Journal of the European Ceramic Society, 36(12), 2991-2996.

Zarubica, A., Vasic, M., Antonijevic, M., Randjelovic, M., Momcilovic, M., Krstic, J, & Nedeljkovic, J. (2014). Design and photocatalytic ability of ordered mesoporous TiO_2 thin films, Materials Research Bulletin, 57, 146-151.

Vukoje, I., Tomašević-Ilić, T., Zarubica, A., Dimitrijević, S., Budimir, M., Vranješ, M., Šaponjić, Z., & Nedeljković, J. (2014). Silver film on nanocrystalline TiO_2 support: Photocatalytic and antimicrobial ability. Materials Research Bulletin, 60, 824-829.

Randjelovic, M., Purenovic, M., Matovic, B., Zarubica, A., Momcilovic, M., & Purenovic, J. (2014). Structural, textural and adsorption characteristics of bentonite-based composite. Microporous and Mesoporous Materials, 195, 67-74.

Momcilovic, M., Randjelovic, M., Zarubica, A., Onjia, A., Kokunesoski, M., & Matovic, B. (2013). SBA-15 templated mesoporous carbons for 2,4-dichlorophenoxyacetic acid removal. Chemical Engineering Journal, 220, 276-283.

Randjelovic, M., Purenovic, M., Zarubica, A., Purenovic, J., Matovic, B., & Momcilovic, M. (2012). Synthesis of composite by application of mixed Fe, Mg (hydr)oxides coatings onto bentonite - A use for the removal of Pb(II) from water. Journal of Hazardous Materials, 199-200, 367-374.

Randjelovic, M., Purenovic, M., Zarubica, A., Purenovic, J., Mladenovic, I., & Nikolic, G. (2011). Alumosilicate ceramics based composite microalloyed by Sn: An interaction with ionic and colloidal forms of Mn in synthetic water. Desalination, 279 (1-3), 353-358.

Momcilovic, M., Purenovic, M., Bojic, A., Zarubica, A., & Randjelovic, M. (2011). Removal of lead (II) ions from aqueous solutions by adsorption onto pine cone activated carbon. Desalination, 276 (1-3), 53-59.

Vujicic, Dj., Comic, D., Zarubica, A., Micic, R., & Boskovic, G. (2010). KineticsofbiodieselsynthesisfromsunfloweroiloverCaOheterogeneouscatalyst. Fuel, 89 (8), 2054-2061.

Review activities:

1. Chemical Engineering Journal
2. Applied Surface Science
3. Renewable Energy
4. Reaction Kinetics and Catalysis Letters
5. Reaction Kinetics, Mechanisms and Catalysis
6. Chemical Industry and Chemical Engineering Quarterly
7. Macedonian Journal of Chemistry and Chemical Engineering
8. Processing and Application of Ceramics
9. Advanced Technologies
10. Facta Universitatis: Series-Physics, Chemistry and Technology.

Awards:

Award for the best graduated students in Study Group of Chemistry at the Faculty of Philosophy in Niš in 1994/1995.

Annual Award of the Serbian Chemical Society in 1999, for the remarkable success achieved during the academic studies.

Funding by the Government of Belgium and the Spanish Society for Analytical Chemistry for participation and presentation of scientific results at the conference "Euroanalysis XIV" (2007).

Postdoctoral training:

The postdoctoral training at the University of Technical Sciences in Berlin, Germany (from July to October 2010). Training was funded by the DAAD Foundation (A/10/05029; Section: 324).

She has been awarded by a post-doctoral degree scholarship under the EC EC BASILEUS program for 10 months at Università La Sapienza, Rome, Italy (2010). She did not use the scholarship because she was engaged and funded through DAAD Foundation in the same year.

International collaboration:

Participant of the course "Environmental Chemistry and Engineering" Michigan State University (USA) held at the Faculty of Occupational Safety (2004).

Several short study visits at the Technical Sciences University in Turin (Italy), the Technical Sciences in Coventry (United Kingdom) and Aristotle University in Thessaloniki (Greece) within the project JP 510985-2010, "Improvement of Students' Internship in Serbia", TEMPUS ISIS, period: 2011-2013, EU.

Within the project 511044-TEMPUS-1-2010-1-UK-TEMPUS-JPCR, the "Modernization of Post-Graduate Studies in Chemistry and Chemistry Related Programs", TEMPUS MCHEM, was on short study stay/training at the Faculty of Chemistry/Pharmacy, the University of Greenwich (United Kingdom).

Dr Marjan Ranđelović, associate professor

Teaching contributions:

Colloid and surface chemistry

Environmental monitoring

Industrial processes

Chemistry of surface processes

Nanostructural materials

Advanced water treatment processes

Research contributions:

Materials science, Chemical reactions in solids and on their surfaces, Functional composite materials, Electrocatalysis, Colloid chemistry, Water treatment.

Publications:

University textbooks: 1

Published scientific papers: 33

Selected publications:

1. Ranđelović, M., Purenović, M., Zarubica, A., Purenović, J., Mladenović, I., Nikolić, G. (2011). Alumosilicate ceramics based composite microalloyed by Sn: An interaction with ionic and colloidal forms of Mn in synthetic water. Desalination, 279 (1-3), 353-358.
2. Ranđelović, M., Purenović, M., Zarubica, A., Purenović, J., Matović, B., & Momčilović, M. (2012). Synthesis of composite by application of mixed Fe, Mg (hydr)oxides coatings onto bentonite - a use for the removal of Pb(II) from water. Journal of Hazardous Materials, 199-200, 367-374.

3. Ranđelović, M., Purenović, M., Matović, B., Zarubica, A., Momčilović, M., Purenović, J. (2014). Structural, textural and adsorption characteristics of bentonite-based composite. Microporous and Mesoporous Materials, 195, 67-74.
4. Ranđelović, M., Momčilović, M., Matović, B., Babić, B., & Barek, J. (2015). Cyclic voltammetry as a tool for model testing of catalytic Pt- and Ag-doped carbon microspheres. Journal of Electroanalytical Chemistry, 757, 176–182.
5. Ranđelović, M., Momčilović, M., Nikolić, G., Đorđević, J. (2017). Electrocatalitic behaviour of serpentinite modified carbon paste electrode. Journal of electroanalytical chemistry, 801, 338-344.

International collaboration:

Three short research stays at the Faculty of Chemistry and Mineralogy of the University of Leipzig, Germany (7-28 days).

Short research stay at the Faculty of Chemistry and Chemical Engineering, Babes-Bolyai University, Cluj-Napoca, Romania (7 days).

Short research stay at the Faculty of Natural Sciences and Mathematics, Ss. Cyril and Methodius University, Skopje (5 days).

Short research stays at the UNSW Sydney, Faculty of Science, School of Materials Science and Engineering, Australia (21 days).

Short research stays at the Faculty of Science, Charles University in Prague, Czech Republic (5 days).

Short study stay at the University of Ljubljana, Slovenia (6 days).

Peer review activity:

Microporous and Mesoporous Materials

Journal of Hazardous Materials

Journal of Chemical Engineering

Desalination

Awards:

Special award of the Serbian Chemical Society for 2007 for outstanding success during the academic study of chemistry.

Dr Jelena Mitrović, assistant professor

Teaching contributions:

Fundamentals of industrial chemistry

Environmental monitoring

Water and wastewater treatment technologies

Selected chapters in purification and disinfection of waters

Selected publications:

1. Mitrović, J., Radović, M., Anđelković, T., Bojić, D., & Bojić, A. (2014). Identification of intermediates and ecotoxicity assessment during the UV/H_2O_2 oxidation of azo dye Reactive Orange 16. Journal of Environmental Science and Health, Part A, 49, 491-502.
2. Radović, M. D., Mitrović, J. Z., Bojić, D. V., Antonijević, M. D., Kostić, M. M., Baošić, R. M., & Bojić, A. Lj. (2014). Effects of system parameters and inorganic salts on the photodecolourisation of textile dye Reactive Blue 19 by UV/H_2O_2 process. Water SA, 40(3) 571-578.
3. Mitrović, J., Radović, M., Bojić, D., Anđelković, T., Purenović, M., & Bojić, A. (2012). Decolorization of textile azo dye Reactive Orange 16 with UV/H_2O_2 process. Journal of the Serbian Chemical Society, 77(4), 465 – 481.

International collaboration:

„1st Summer School: The Mass Spectrometry Opens on the Environment and the Life“, the University „Pierre and Marie Curie”–Paris (2008).

Peer review activity:

- Water SA

- Chemical Industry and Chemical Engineering Quarterly
- Environmental Technology
- Water Environment Research

Available equipment in the laboratory for Applied Chemistry:

- AAS Perkin Elmer A300 with graphite cuvette and the system for gaseous hydrides, AAnalyst 300 (Perkin Elmer, USA),
- HPLC, Dionex Ultimate 3000, Thermo Fisher Scientific, MA USA with Diode Array Detector and Dionex Corona Veo Charged Aerosol Detector,
- Ion Trap MS model LCQ DECA (Thermo Finnigan, USA),
- Ion Trap MS model LCQ Advantage (Thermo Finnigan, USA),
- GC-MS model 6890/5973 (Hewlett Packard, USA),
- UV-vis, UV-1800 (Shimadzu, Japan),
- Potentiostat, Amel 510 DC (Materials Mates, Italy) controlled by VoltaScope software package,
- Potentiostat, EmStat Blue (PalmSence, Netherlands),
- Colorometer, MultiDirect, Lovibond-Tintometer (Germany),
- Turbidimeter, Turb 355 IR/T, WTW (Germany),
- Conductometer, sension5, HACH, Colorado (USA),
- Water Purification System, Smart2Pure, Thermo Fisher Scientific (MA USA),
- Vacuum evaporator, RV 10 D, IKA (Germany),
- Recirculating Water Vacuum Pump, JPV, Velp Scientifica (Italy),
- Muffle furnace, Sel-Horn R-3 L (J.P. Selecta s.a., Spain),
- Muffle furnace (Vims elektriks, Serbia),
- Drying oven (Raypa, Spain),
- Incuterm (Raypa, Spain),
- Thermostat, F 12 (Julabo, Germany),
- Air sampler, 4G 2R (ASV Co d.o.o., Serbia),
- Digital bireta, solarus (Hirschman Laborgerate, Germany),
- Power Supply, Model 1786B (BK Precision, USA),
- Digital microscope Motic,
- Heating mantle with controller (Witeg, Germany) – 2x,
- Peristaltic pump, SP 311 (Velp Scientifica, Italy),

- Peristaltic pump, PLP 380 (Dülabo, Germany),
- Ultrasonic bath, Sonic (Vims Elektrik, Serbia),
- Ultrasonic bath, Sonic 4.5 G (Vims Elektrik, Serbia),
- Hot plate, HP-20D (Witeg, Germany),
- Advanced Vortex Mixer, Zx3 (Velp Scientifica, Italy),
- Shaker, KS 130 control (IKA®-Werke, Germany) – 2x,
- Heating Magnetic Stirrer, Aluminum Hot Plate Stirrer, ARE (Velp Scientifica, Italy),
- Overhead Stirrer, Stirrer type PW (Velp Scientifica, Italy),
- Magnetic Stirrer, MULTISTIRRER 6 (Velp Scientifica, Italy),
- Magnetic Stirrer, AGE (Velp Scientifica, Italy) – 2x,
- BOD_5, oxiTOP IS6 (WTW, Germany),
- pH meter with ion-selective electrodes, sension3 (HACH, Colorado, USA),
- pH meter, H260G (HACH, Colorado, USA),
- pH meter, Orion Star A214 (Termo Scientific, USA),
- Analytical scale, ALS 220-4 (KERN, Germany),
- Analytical scale (Sartorius, Serbia),
- Technical scale, 440-33 (KERN, Germany),
- UV reactor
- UV/Vis reactor
- UV meter, solarmeter, model 8.0 UVC (Solartech Inc, USA),
- Infrared Thermometer, No. 201311007089
- Test screening machine, JEL 200 (Germany),
- Laboratory blender, Waring commercial (USA),
- Micropipettes.

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Katedra za primenjenu hemiju i hemiju životne sredine

Aleksandar Bojić, Milena Miljković, Tatjana Anđelković, Aleksandra Zarubica, Marjan Ranđelović[*], Jelena Mitrović

Univerzitet u Nišu, Prirodno-matematički fakultet, Departman za hemiju, Višegradska 33, 18000 Niš, Srbija

SAŽETAK

Katedra za primenjenu hemiju i hemiju životne sredine je osnovana 1995. godine na inicijativu Prof. Dr Milovana Purenovića, koji je bio na poziciji Šefa katedre od njenog osnivanja pa sve do svog penzionisanja 2011. godine. Prof. Dr Aleksandar Bojić je aktuelni Šef katedre. Od svog osnivanja pa do danas, profesori i saradnici Katedre za primenjenu hemiju i hemiju životne sredine su usmereni ka primenjenim istraživanjima u okviru inovacionih i razvojnih projekata, koji su realizovani u saradnji sa industrijom. Takođe, značajan naučni doprinos je dat na polju zaštite životne sredine, posebno u tretmanu pijaćih i otpadnih voda. Razvijen je veliki broj operativnih tehnologija, pri čemu su neke od njih zaštićene patentima u Zavodu za intelektualnu svojinu Republike Srbije. Katedru za primenjenu hemiju i hemiju životne sredine čine četiri redovna profesora, jedan vanredni profesor i jedan docent.

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Chaire de chimie appliquée et chimie de l'environnement

Aleksandar Bojic, Milena Miljkovic, Tatjana Andjelkovic, Aleksandra Zarubica, Marjan Randjelovic*, Jelena Mitrovic

Université de Nis, Faculté des sciences et mathématiques, Département de chimie, Visegradska 33, 18 000 Niš, Serbie

La Chaire de chimie appliquée et chimie de l’environnement a été créée en 1995 à l’initiative du professeur des universités Milovan PurenoviC qui en était le directeur depuis la création de la Chaire jusqu’à sa retraite en 2011. Le directeur actuel de la Chaire est le professeur des universités Aleksandar Bojic. Depuis la formation de la Chaire de chimie appliquée et chimie de l’environnement jusqu’aujourd’hui, les professeurs et les maîtres-assistants sont orientés vers les recherches appliquées dans le cadre des projets innovateurs et développementaux qui se réalisent en collaboration avec l’industrie. Une contribution importante a été apportée dans la sphère de la protection de l’environnement et en particulier celle du traitement de l’eau potable et des eaux usées. Un nombre considérable de technologies opérationnelles a été développé, certaines d’entre elles étant protégées par des brevets de l’Institut de la propriété intellectuelle de la République de Serbie. Aujourd’hui, l’équipe pédagogique de la Chaire de chimie appliquée et chimie de l’environnement compte quatre professeurs des universités, un professeur associé et un maître de conférences.

Кафедра прикладной химии и химии окружающей среды

Александар Бойич, Милена Милькович, Татьяна Анджелькович, Александра Зарубица, Марьян Ранджелович *, Елена Митрович

1-Университет в Нише, Факультет естественных наук и математики, Отдел химии, Вишеградска 33, 18 000 Ниш, Сербия

Кафедра прикладной и химии окружающей среды была основана в 1995 году по инициативе проф. доктора Милована Пуреновича, возглавлявшего кафедру с момента её основания до выхода на пенсию в 2011 году. Нынешний заведующий кафедрой – профессор доктор Александар Бойич. С момента создания до сегодняшнего дня, профессора и сотрудники Кафедры прикладной и химии окружающей среды ориентированы на прикладные исследования в рамках иновационных проектов и проектов развития, которые были реализованы в сотрудничестве с промышленностью. Кроме того, значительный научный вклад внесён в области охраны окружающей среды, особенно касательно очистки питьевой и сточных вод. Разработано большое количество операционных технологий, некоторые из которых защищены патентами в Ведомстве по интеллектуальной собственности Республики Сербии. Кафедра прикладной и химии окружающей среды состоит из четырёх ординарных профессоров, одного экстраординарного професора и одного доцента.

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Recent developments in sorbent based water samples treatments prior GC-MS analysis of polycyclic aromatic hydrocarbons

Slobodan A. Ćirić[1*], Violeta D. Mitić[1], Jelena S. Nikolić[1], Marija D. Ilić[1], Marija V. Dimitrijević[1], Strahinja R. Simonović[2], Vesna P. Stankov Jovanović[1]

1- *University of Niš, Faculty of Science and Mathematics, Department of Chemistry, Višegradska 33, 18000 Niš, Serbia*

2- *University of Priština (with contemporary seat at Kosovska Mitrovica), Faculty of Science and Mathematics, Department of Chemistry, Lole Ribara 29, 38220 Kosovska Mitrovica, Kosovo, Serbia*

[*]Corresponding author: Slobodan A. Ćirić- slobodan.ciric@pmf.edu.rs, University of Niš, Faculty of Science and Mathematics, Department of Chemistry, Višegradska 33, 18000 Niš, Serbia

ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are omnipresent contaminants of the environment, with evidenced harmful effects to human health. Especially endangered are waters, which may affect biota directly or by enabling transport through all environmental compartments. Therefore, constant monitoring of PAHs content in waters is of essential importance. Before most of the analysis, sample preparation is compulsory. Conventional extraction techniques are often time and reagents consuming and not following the rules of “green analytical chemistry”. Thus, miniaturization of classic extraction methods is of high importance to reduce solvent volumes, waste, time of treatment and cost. Recent sample preparation techniques, such as solid phase extraction (SPE), microextraction by packed sorbent (MEPS), solid phase microextraction (SPME), stir bar sorptive extraction (SBSE), dispersive solid phase extraction (dSPE) and dispersive micro-solid phase extraction (D-µ-SPE) were proven as suitable for the extraction of polycyclic aromatic hydrocarbons (PAHs) from water samples and their determination by gas chromatography-mass spectrometry. These sample pretreatments are following “green chemistry” principles, offering the simplicity of operation, reducing costs and time of preparation, without compromising the general analytical parameters of the applied analytical method.

***Keywords**: PAHs, water samples, sample preparation, sorbents, GC-MS*

Introduction

Analytical procedures typically consist of several equally important steps - sampling, sample treatment, isolation of the target compounds, identification, quantification, and data handling. All operations carried out with samples before the instrumental determination of target compounds are considered to be part of the sample preparation step. Sample preparation includes sampling, labeling, mechanical processing and homogenization of the studied matrix. Also, any gravimetric or volumetric determination in order to characterize the matrix structure could be considered as a sample preparation step. Fractionation, isolation, and enrichment of the target compounds from potential interferences are crucial in every analysis. Nevertheless, the term sample preparation has typically been associated with the latter group of chemical operations, all earlier mechanical and basic treatments being named as sample pre-treatment (Koning et al., 2009). Also, sample preparation is the most important procedure to remove the matrix interferences and enrich the analytes, especially for environmental water analysis. Furthermore, sampling and sample preparation procedures are the most crucial steps in all analytical techniques applied for the analysis of heterogeneous materials.

Nowadays, sample preparation procedures are more than ever linked with the protection of the environment following the philosophy of Green Analytical Chemistry (GAC). GAC was introduced in 2000 in order to reduce or to remove the side-effects of analytical practices on operators and the environment. Even though it is a relatively new area of activity within green chemistry, GAC has attracted a great deal of interest among chemists. It concerns the role of analytical chemists in making laboratory practices more environmentally friendly (Armenta et., al 2008). GAC is focused on developments in instrumentation and methodologies that generate less hazardous waste and therefore are more secure for utilization and more environmentally friendly, enabling analytical laboratories to be sustainable regarding costs and energy. Despite the concept of GAC providing ideology, it also poses many challenges associated with reaching a compromise between the increasing quality of the results and the improving environmental friendliness of analytical methods. As a result, the guidelines and the principles of green chemistry have been introduced to provide a framework for GAC (Gałuszka et al., 2013).

There are different ways to make sample preparation “green” (Płotka et al., 2013). First, it is necessary to eliminate, or at least reduce, the amounts of solvents and reagents used in the analysis. Otherwise, solvent recovery and reuse are recommended. Furthermore, green media, such as agro-solvents, ionic liquids (ILs), supercritical fluids or superheated water, are preferable, rather than petrol-based solvents. The scale of analytical operations should be reduced, and instruments should be miniaturized. Integration of operations and automation of sample preparation are also important. Moreover, application of factors enhancing the effectiveness of sample preparation (e.g., high temperature and/or pressure, microwave and UV radiation, and ultrasound energy) also impact on the “green” character of the whole procedure. There are many review papers focused on different aspects of “green” sample preparation for chromatographic analysis (Armenta et al., 2008; Pawliszyn et al., 2010; Welch et al., 2010).

Pollutants analysis is a challenge for researchers because their concentrations in samples are usually very low. Also, the extreme complexity of environmental samples requires instate and delicate procedures. Besides, many structural isomers are often present in environmental samples (Poster et al., 2006). Because of that, it is necessary to establish extraction and clean up technique that meets the requirements that analytical method must satisfy in term of accuracy and precision, but also simplicity and cost.

PAHs in water

Polycyclic aromatic hydrocarbons (PAHs) represent a very significant group of environmental pollutants due to their potentially harmful effects on health exerting carcenous, mutagenous and teratogenous actions (EPA, 1987). Because of the listed characteristics, but also of their conspicuous to degradation in nature, they have been listed by the US-EPA as priority pollutants, but also by the European Environment Agency (ATSDR, 2006).

The definition of PAHs implied numerous groups of organic compounds containing two or more fused rings, of aromatic character and made up of carbon and hydrogen atoms. They can be produced naturally or by anthropogenic activities, and high amounts of PAHs are emitted from incomplete combustion or high-temperature pyrolytic processes involving fossil fuels, forest fires, volcanoes or hydrothermal processes, usage of coal and from motor vehicle exhaust (Poster et al., 2006; Wenzl et al., 2006). Due to a large number of sources PAHs have been registered in water, air, soil, agricultural products and nearly everywhere in the environment (Khalili – Fard et al., 2012). The possible sources of PAHs in water may be through atmospheric deposition (*via* wet and dry particle deposition and gross gas absorption), wastewater treatment plant discharges, tributaries, stormwater runoff, oil spills, groundwater discharges from underground water and runoff of PAHs from contaminated sites. (Rodenburg et al., 2010)

Long-term data on POPs in water provide important information that can be used to appraise the powerfulness of actions taken to diminish emissions. Concentrations of POPs (including PAHs) in surface water are directly linked to their bioaccumulation in the food chain (Hu et al., 2007).

Trends in sample preparation as a most critical step in PAH analysis, are aimed to avoid disadvantages of existing techniques. Conventional techniques, such as liquid-liquid extraction (LLE), solid-liquid extraction (SLE) and Soxhlet extraction, are still widely accepted and used for routine applications and/or reference purposes. However, in recent years, some of these techniques have been revisited, and upgraded versions in which their most pressing shortcomings have been solved, are now available. The studies in this field have also led to the development of new faster and more powerful and/or versatile extraction and preconcentration techniques (Dean, 2009).

As an alternative to LLE, solid-phase extraction (SPE) has become more popular than LLE for analyte preconcentration and matrix removal, due to its simplicity and economy regarding time and solvent save. SPE has gained wide acceptance because of the inherent disadvantages of LLE, whose drawbacks include (Picó et al., 2007):

- inability to extract polar compounds;
- being laborious and time-consuming;
- expense;
- the tendency to form emulsions;
- need for evaporation of large volumes of solvents; and,

- disposal of toxic or flammable chemicals.

Due to increasing demand for simple, rapid, and accurate sample preparation procedures new techniques have been developed. The following sections provide an overview of sorbent-based sample pretreatment techniques such as SPE, microextraction by packed sorbent (MEPS), solid phase microextraction (SPME), stir bar sorptive extraction (SBSE), dispersive solid phase extraction (dSPE) and dispersive micro solid phase extraction (D-µ-SPE) with mention of their general application in various contaminants analysis and the analysis of PAHs in water.

Sorbent based sample pretreatment techniques

Many techniques currently used for pretreatment of gaseous, fluid or liquid samples are based on trapping the investigated analytes on or in a suitable sorbent. Preconcentrated target compounds are subsequently desorbed, in a selective fashion, by elution with a relatively small amount of solvent either in a vial or in an appropriate interface; or by thermal desorption, typically in the injection port of the instrument selected for the final determination. The latter approach avoids dilution but is limited to (semi-)volatile thermally stable compounds. In general, techniques based on sorption extraction can nowadays be considered well established and accepted. As expected for sophisticated techniques, in most instances no significant conceptual changes have been introduced during the last decade, and as with other techniques, instrumental developments have mainly been orientated to increase automation and integration of the techniques with final instrumental analysis (a field where miniaturization has again played a relevant role). Thereby, the most active research topics concerning these techniques have been the synthesis of new sorbent phases that solved the remaining practical problems in this research field and the development of novel application studies (Ramos, 2012).

Solid phase extraction (SPE)

SPE as a physical extraction process was first introduced in the mid-1970s (Chen et al., 2010) and today is the most popular technique for environmental and food samples. The SPE procedure, due to its high versatility is used for many purposes (purification, trace enrichment, desalting, derivatization, and class fractionation) (Andrade-Eiroa et al., 2015). The principles of SPE and liquid-liquid extraction are similar. The problems associated with LLE (incomplete phase separations (emulsion); use of expensive, breakable specialty glassware; less-than-quantitative recoveries; disposal of large quantities of organic solvents), can be overcome using SPE procedure. SPE procedure consists of 1) loading a sample on a cartridge containing sorbent that binds target compounds, 2) washing undesirable compounds, and 3) eluting target compounds.

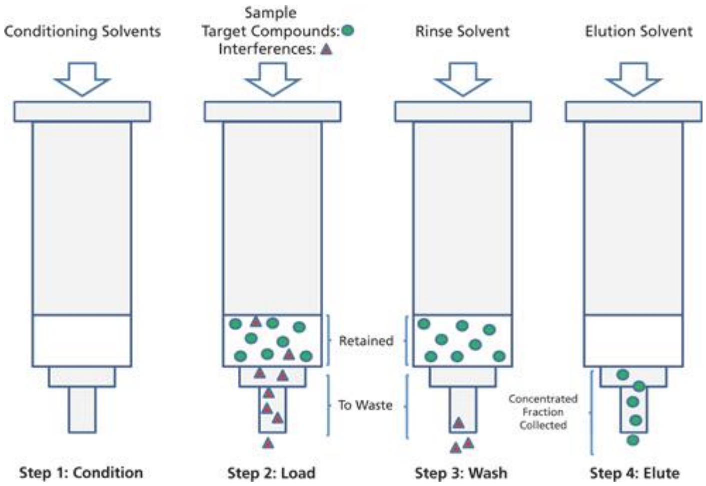

Figure 1. Illustration of solid-phase extraction (SPE) procedure (Zdravkovic, 2017)

Also, SPE has proved more efficient than LLE because of higher recovery, it is easy to perform, rapid, and can be automated (Gilar et al., 2001; Titato and Lanças, 2005).

To get optimal SPE extraction conditions, the choice of sorbent is a crucial factor because it can control parameters of primary importance (selectivity, sensitivity, affinity, and capacity) (Nováková and Vlcková, 2009). The choice of sorbent depends on the nature of the analytes and their physical and chemical properties, which define the interaction with the chosen sorbent. The selectivity of the sorbent depends on the attractive forces between the analytes and the functional groups on the surface of the sorbent. The interactions with analytes can be achieved by hydrophobic, hydrophilic, cationic-anionic and selective antigen-antibody contacts.

The sorbents widely used for SPE packing can be classified into (Lucci et al., 2012):

- polar phases (normal phase), (underivatized silica material (SPE-Si), magnesium silicate (SPE- Florisil) and aluminum oxide materials (SPE-alumina)
- non-polar phases (reversed phase), (alkyl or aryl silica and polymer-based materials - cyano (SPE-CN), octyl (SPE-8), octadecyl (SPE-18) and phenyl (SPE-Ph), copolymers of styrene-divinylbenzene (SPE-PSDVB))
- ion exchange is based on positively or negatively charged groups that are bonded to the silica surface
- immunoaffinity adsorbents (antibody materials bonded onto silica gel support).

A large variety of sorbents commercially available makes this technique suitable for the determination of analytes with divergent chemical structures and polarities. Current research is focused mainly on the development of novel sorbents allowing higher loading capacities, increased retention efficiency of vastly polar analytes from water samples. Application of molecularly imprinted polymers (MIPs) and selective immuno-sorbents (ISPEs) enables improved selectivity during the retention process and so contributing to the simplification of the subsequent clean-up and/or detection steps (Fontanals et al., 2007). In a little while back published paper, five ionic liquid-modified porous polymers with different imidazolium-based functional groups were obtained, and a new molecular imprinting technique was introduced to form the ordered functional groups in the porous structure (Tian et al., 2011).

The progress in sorbent materials synthesis has enabled pure sorbents with small particles. These small particles (ca. 40 μm) provided higher retention capacities than conventional-size ones, and promoted the use of smaller SPE cartridges, without a significant loss of retention efficiency. Reducing the size of the conventional 1–6 mL SPE syringe barrels to the 10 mm × 1–2 mm i.d. of the Prospeckt type cartridges used in the hyphenated systems led to a reduction of sample volumes from 0.5–1.0 L to less than 50–100 mL. Quite often, even 5–10 mL suffices to obtain similar LODs of 0.01–0.1 μg L^{-1} with SPE-LC and 1000-fold lower with SPE-GC that previously required 100- fold larger volumes. More importantly, quantitative elution of the analytes can be achieved with 50–100μL of the appropriate solvent, *i.e.*, with a volume small enough to allow complete transfer to the instrument selected for final determination. This fact promoted the development of hyphenated and automated systems for unattended, green and fast (ca. up to 20 min) treatment of aqueous samples with the minimal sample and solvent consumption and significant reduction of waste generation (Bagheri et al., 1993).

Graphene has also been used as the sorbent in the sample preparation because of its ultra-high specific surface area, superior chemical stability, and excellent thermal stability (Liu et al., 2011; Liu et al., 2012; Wang et al., 2013).

Besides the development of new sorbents, a number of modifications based on miniaturization and automation resulted in the development of new extraction techniques - solid-phase dynamic extraction (SPDE), microextraction by packed sorbent (MEPs), matrix solid-phase dispersion (MSPD), stir-bar sorptive extraction (SBSE), solid-phase microextraction (SPME), automated headspace dynamic solid-phase extraction, and dispersive solid-phase extraction (d-SPE) (Andrade-Eiroa et al., 2015).

Due to the usual low levels of PAHs in water samples, a pre-concentration step before analysis is required and owing to the trend for decreasing the use of organic solvents in the laboratory. Solid-phase extraction (SPE) is preferred over liquid-liquid extraction (LLE), where classical extraction sorbents used for the extraction of PAHs from water are C8, C18 or polymers of styrene-divinylbenzene (Marce´ and Borrull, 2000; Martinez et al., 2004), where sorbents are packed in cartridges or disks. Solid-phase extraction (SPE) is a conventional extraction and preconcentration method for PAHs from aqueous samples (Li and Lee, 2001; Bruzzoniti et al., 2010). The main drawbacks of the SPE technique are its high organic solvent consumption and sample consumption.

Sargenti et al. (1998) compared four different extraction techniques (solid-phase extraction, supercritical fluid extraction (SFE), solid-phase extraction followed by supercritical fluid extraction (SPE/SFE) and liquid-liquid extraction (LLE)) for the extraction of 16 PAHs from drinking water. The results showed that recoveries were good for SPE and SPE/SFE for all compounds, recoveries for SFE were worse than SPE/SFE, and LLE had the worst recovery and reproducibility.

Microextraction by packed sorbent (MEPS)

New novelty in the area of sample preparation is microextraction by packed sorbent (MEPS) originally designed and patented by Astra Zeneca, Sweden (Abdel-Rehim, 2003; Abdel-Rehim, 2004). MEPS is a miniaturized SPE technique in which sorbent packing material (ca. 1 mg) is placed at the top of the syringe needle (Moein et al., 2015). MEPS can be fully automated, the sample preparation procedure is performed online using the same syringe, and the whole extract is injected into a chromatographic system (Abdel-Rehim, 2010). The difference between MEPS and SPE is that, in SPE, the solution flow is in one direction (up to down) but in MEPS it is in two directions (up and down) (Yang et al., 2017).

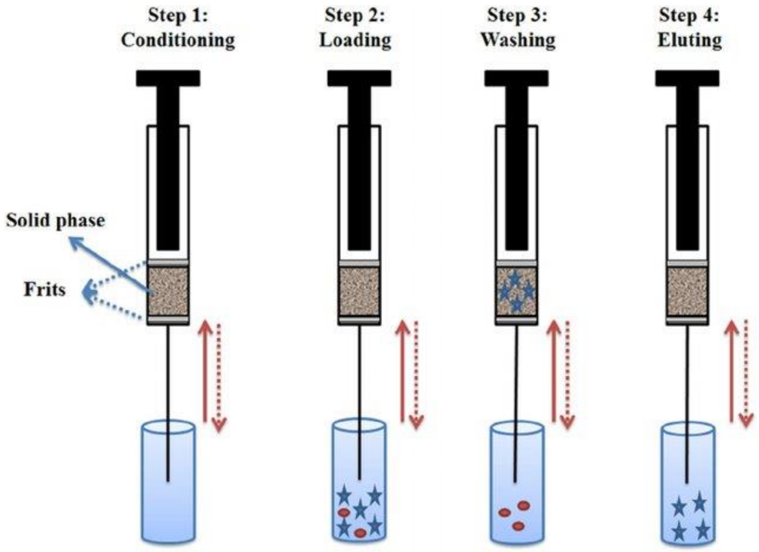

Figure 2. Illustration of microextraction by packed sorbent (MEPS) (Moein et al., 2015)

For extraction, 10-250 µL of an aqueous sample is successively withdrawn and ejected, allowing preconcentration of the analytes on the selected sorbent. Commercially available MEPS uses the same sorbents as regular SPE columns. Analytes elution is typically accomplished with 20–50 μL of an appropriate solvent, which can directly be transferred to the GC/LC (gas chromatography or liquid chromatography) port. Compared to other sample preparation techniques, MEPS provides significantly shorter extraction times and significantly less sample capacity and solvent use (about 10 μL) than classical SPE (Fu et al., 2012).

MEPS applications include the determination of PAHs in water (El-Beaqqali et al., 2006; Fu et al., 2012). MEPS procedure reported by Fu et al. (2012) for PAH analysis is performed with a MEPS system containing a syringe equipped with C18 sorbent incorporated in the needle. Before each sample extraction, MEPS sorbent was conditioned using 80 μL of methanol and 100 μL of ultrapure water. Both methanol and water were discarded into waste vials. The water sample (50 μL each) was pulled/pushed through the syringe 40 times at a speed of 5 μL s^{-1} by the autosampler. Then sorbent was washed using 100 μL pure water to reduce interference absorption and was dried by ten cycles of drawing and pressing air. Finally, analytes were eluted with 50 μL methanol directly into the GC large volume injector. To get rid of any carryover effect, eight 80 μL portions of methanol were used to clean the sorbent after the extraction/elution step. MEPS showed similar recovery results compared to the SPE method. However, a better sensitivity was obtained using the proposed MEPS method. Furthermore, MEPS minimized the volume of organic solvent used for the elution, as well as sample volumes. The proposed MEPS–GC–MS method could be used as a screening method for monitoring PAHs in environmental waters (Fu et al., 2012).

Solid phase microextraction (SPME)

The research of solid-phase microextraction processes (SPME) started 30 years ago (Arthur and Pawliszyn, 1990; Pawliszyn, 1997). This method was adopted as an alternative, to the until then applied sample preparation techniques, but nowadays it has diverse applications with the purpose to extract various analytes. SPME represent fast and cost-effective sample preparation method for GC and LC that does not require any solvent. SPME is composed of two basic steps: (1) partitioning of analytes between the extraction phase and the sample matrix and (2) desorption of concentrated extracts into an analytical instrument.

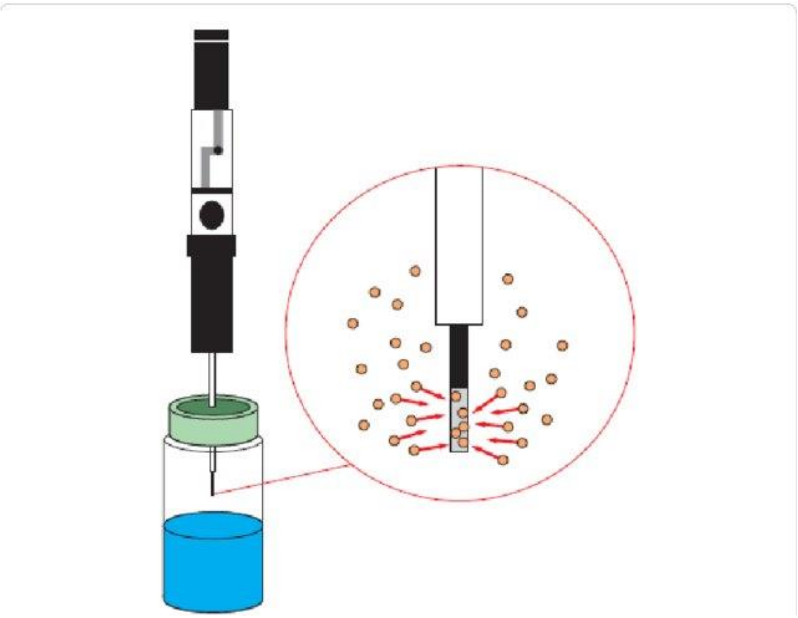

Figure 3. Illustration of solid phase microextraction (SPME) (Schmidt and Podmore, 2015)

A few factors, such as temperature, pH, stirring, and concentration of salt may affect the time of equilibration and the equilibrium constant (Pawliszyn, 1997). By changing pH, the neutrality of the target compound can be achieved. Basic pH promotes recoveries of basic analytes, while acidic analytes are recovered in greater extent at acidic pH. Recovery may be equally improved by salt addition, *e.g.*, NaCl, which provokes evident ionic effects. Many of the target analytes are polar and firmly bound to the matrix. To make these analytes inclinable to thermal desorption from SPME fiber, during GC analysis, derivatization may be required. Proper few derivatization techniques have been employed and reported in previous papers (Pan and Pawliszyn, 1997). The process of derivatization implies the addition of appropriate reagents to the sample matrix and extraction/derivatization on the fiber. The high potential for derivatization exists in SPME, allowing enhanced analysis, but unfortunately, this potential has not been studied enough. Notwithstanding several studies of SPME deal with drugs and their metabolites in body fluids (plasma and urine), (Fritz, 1999), only minority of them treat SPME optimization for analysis of drugs in plasma. In the majority of uses, SPME is coupled on-line with GC/MS, while LC/MS is applied rarely.

There are two configurations of SPME: fiber SPME and in-tube SPME (Kataoka, 2003; Hinshaw, 2003). The theories behind fiber and in-tube SPME methods are similar. With fiber SPME, analytes are adsorbed on the outer surface of the fiber from an agitated sample solution; while with in-tube SPME, they are adsorbed on the inner surface of the capillary column from a flowing sample solution. Therefore, with in-tube SPME, it is necessary to prevent plugging of the capillary column and flow lines by filtering the sample solution before an extraction. On the other hand, the fiber SPME should be handled carefully during insertion and agitation because the fiber is fragile and may break easily (Pawliszyn, 1997; Lord and Pawliszyn, 2000). However, a fiber SPME is generally limited to the analysis of volatile and thermally stable compounds. It tends to encounter complexity in coupling with LC. Thus, a fiber SPME associated with LC was usually introduced to analyze weakly volatile and thermally labile compounds not amenable to GC (Lord and Pawliszyn, 2000; Zambonin, 2003).

The volume of the sorbent is very small (< 0.7 µl) in SPME, and this limits the amount of extracted analyte and hampers the usefulness of the technique for ultra-trace analysis (Baltussen et al., 1999). Besides, the extraction efficiency is low, even in cases of analytes with fairly high partition coefficient between the gas and liquid phases, and this makes quantification vulnerable to matrix effects. Because of these reasons, quantitative analysis by SPME is not straightforward, but the simplicity and easiness of the use make the technique very suitable as a screening tool (Baltussen et al., 1998; Mol et al., 1995). Differences between SPE, MEPS, and SPME are presented in Table 1 (Abdel –Rehim, 2011).

Table 1. Overview of SPE, MEPS and SPME characteristics

	SPE	**MEPS**	**SPME**
Sorbent amount	50 – 2000 mg	2 – 4 mg	thickness 150 µm
Time	15 min	1 min	20 – 40 min
Recovery	good	good	low
Sensitivity	good	good	low
Cartridge re-use	1 extraction	100 extractions	50 extractions

In SPME procedure for PAHs analysis in water, the polydimethylsiloxane (PDMS) fibers (100 µm film thickness) were put in the injection port of the instrument for 3 h, at 270 °C. The volume of water sample (8 mL), was placed in a vial and capped with PTFE coated septa (10 mL). The fibers are submerged in water samples with agitation at 250 rpm for 60 minutes; afterward, the fiber was thermally desorbed for 10 min into the injection system (Rami et al., 2012). Various experiments have been performed to define the optimal conditions for SPME application in PAHs analysis in water such as temperature, equilibration time, salinity and compound concentration (King et al., 2003). Report of Chen (2004) showed that under optimized conditions, SPME demonstrates to be a very simple, rapid, sensitive and accurate technique for the extraction of polycyclic aromatic hydrocarbons from water samples where high recovery and good reproducibility were obtained by using PDMS fiber.

Stir bar sorptive extraction (SBSE)

SBSE was introduced in 1999 by Baltussen et al. This technique was developed to extract organic analytes from liquid samples and is based on the sorption of analytes onto a thick film of polydimethylsiloxane (PDMS) coated on an iron stir bar (Popp et al., 2001). It consists of two steps: (1) extraction of an analyte from sample to the PDMS polymer and (2) desorption of analyte from sorbent to chromatographic system.

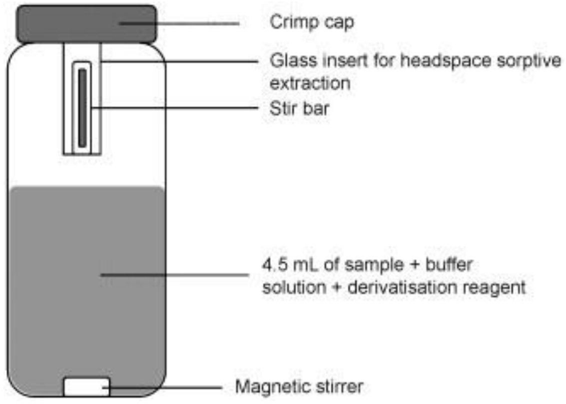

Figure 4. Illustration of stir bar sorptive extraction (SBSE) (Prieto et al., 2008)

The liquid sample is stirred with a stir bar, and after extraction, the stir-bar is removed and dried with soft tissue. The analytes are desorbed either thermally (for GC analysis) or with liquid (mainly for LC analysis). In contrast to SPME, a particular interface is required for thermal desorption. The desorption process is relatively slow, owing to a large amount of coating. Typical desorption times are 10 min, which means that the desorbed analytes must be re-concentrated before the GC separation. This procedure is usually done in a programmed temperature vaporizer (PTV) with cryogenic cooling. For semi-volatile analytes with boiling points above 200 °C, ambient temperature is sufficient for focusing, while for volatile analytes temperatures as low as - 150 °C can be used with liquid nitrogen cooling (Kawaguchi et al., 2006).

Several studies have demonstrated the practicability of SBSE where this technique has been applied for the extraction of different types of organic compounds in aqueous solutions (Kolahgar et al., 2002) and wine (Sandra et al., 2001). However, the technique has not been as widely accepted as could be anticipated, probably due to the limited number of coatings materials commercially available and the difficulty of full automation. At present, efforts in this field focuses on the development of dual phase/ hybrid twisters, in which the conventional PDMS phase is combined with another sorbent to increase the selectivity and/or efficiency of the extraction process (Ibrahim et al., 2011), as well as in the development of alternative new coating materials with improved analytical features (Faraji et al., 2011). Matrix effect is one of the major limitations of SBSE. Samples with high organic matter or suspended solid components, such as environmental samples, biological fluids or foods, are very tough to extract with SBSE. Taking into account that stir-bars are expensive and must be reused for several extractions as long as the coating is in appropriate conditions, SBSE has not the best precisions when compared to other extraction techniques such as SPE. Therefore, SBSE may be the best choice for ultra-trace analysis, but probably not the best technique for small sample volumes or when high precision is required. (Camino-Sánchez et al., 2014).

SBSE has been successfully applied to preconcentrate trace amounts of volatile organic compounds, organochlorine compounds, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyl (PCBs), pesticides, hormones, alkylphenol, and bisphenol A (Rykowska and Wasiak, 2013).

The SBSE method exerted an enormous capability to extract PAHs from water (Popp et al., 2001; Hauser et al., 2002). Procedure for SBSE of PAHs from water described by Popp et al. (2001) consists of using new or used stir bars which were conditioned as follows: the stir bars were placed into a vial containing 1 mL of a 1:1 mixture of methylene chloride and methanol, and treated for 5 min with sonication. Then the solvent mixture was rejected, and the procedure was repeated three times. The twister was dried in a desiccator at room temperature and heated for 90 minutes at 280 °C with a nitrogen stream of about 100 mL min^{-1}. To enrich the PAHs, a 10 mL water sample was placed in a 10 mL glass vial and then extracted for 60 min at a stirring speed of 1000 rpm. After extraction, the stir bar was removed with clean tweezers and dried with a lint-free tissue. Then the stir bar was placed into the insert (250 μL glass flat bottom) of a 2 mL vial. The insert was filled with 150 μL acetonitrile (ACN) or with an ACN-water mixture (4:1). Desorption of the PAHs was performed with an ultrasonic device for 10 min. After desorption, the stir bar was removed by a magnetic rod, and the vial with the 250 μL insert was placed into the autosampler of the LC instrument used. Time of extraction and time od desorption was optimized, and ACN was chosen as the solvent in order to enable sensitive determination of PAHs in water samples.

Dispersive solid-phase extraction (dSPE)

Most likely, the most powerful method introduced lately in the field of SPE has been the method known as QuEChERS. The acronym applies for Quick, Easy, Cheap, Rugged, Effective and Safe; they are the most important properties of the analytical method used for the determination of pesticides in vegetables and fruits (Anastassiades et al., 2003). The method is a multi-step procedure based on solvent extraction of the target compound and extracts clean up using dispersive solid-phase extraction (d-SPE). Instead of adding sample extract to packed sorbent materials, like in SPE, the extract is added to a tube containing powder form of sorbent.

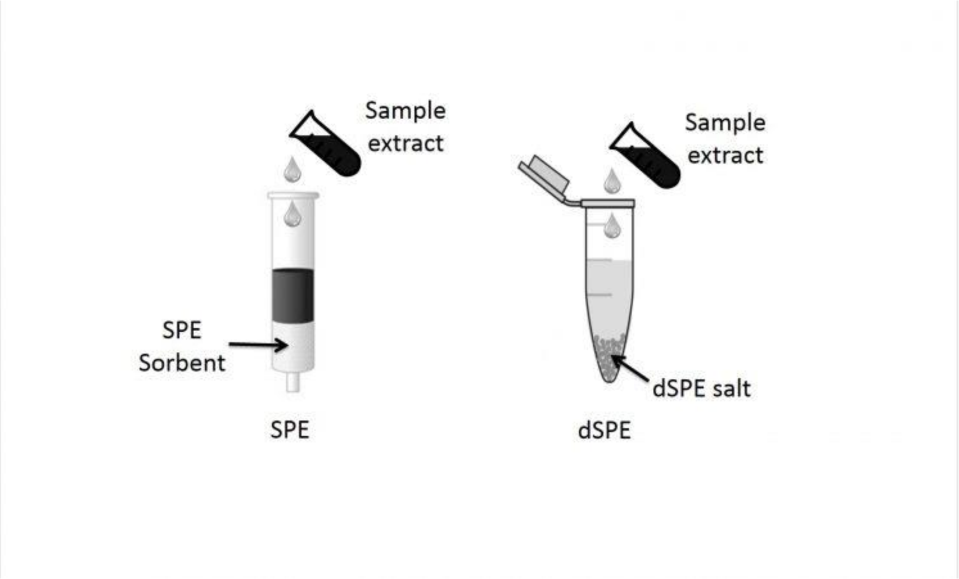

Figure 5. The difference between SPE and dSPE procedure (Lam, 2016)

The procedure starts with the addition of magnesium sulfate to secure water removal from an organic solvent, continuing with primary secondary amine (PSA) sorbent addition, to eliminate polar compounds, (mostly organic acids, sugars, and polar pigments). In some other procedures, graphitized carbon black is added to the sample to eliminate sterols and pigments like chlorophyll. The usefulness of dSPE was established after being recognized by the Association of Official Analytical Chemists (AOAC) as an international method for multiclass pesticide determination in fruits and vegetables (Lehotay, 2007). The primary objective of the sorbent is the retention of the matrix components while the analytes remain in the liquid phase. This balance between selectivity and sensitivity is achieved by adding low amounts of sorbent. More than 50 sorbents were tested for dSPE, but four types of sorbents are commonly employed in dSPE, namely: primary–secondary amine (PSA), graphitized carbon black (GCB), RP-C18 and alumina (Anastassiades, 2006). The sorbent selection is usually carried out taking into account the nature of the interferences to be eliminated. Thus, PSA is used for polar organic acids, sugars, pigments, and fatty acids while GCB is more appropriate to retain aromatic and polar compounds; RP-C18 is more convenient for starch, sugars, and lipophilic compounds, alumina retains vitamins, glycosides and plant sterols (Lagana et al., 2002; Lagarda et al., 2006). PSA in combination with GCB gives excellent results for samples with high contents of carotenoids or chlorophyll (Anastassiades, 2006).

QuEChERS technique including dSPE was used for PAH analysis in various matrices. Some publications describe analysis if 16 priority PAH (Cvetkovic et al., 2016; Kao et al., 2014; Madureira et al., 2014; Ramalhosa et al., 2009), while some describe analysis only of some of them (Sadowska-Rociek et al., 2014; Surma et al., 2014; Yoo et al., 2014).

Dispersive micro-solid phase extraction (D-μ-SPE)

D-μ-SPE is a very efficient procedure to increase the selectivity of analytical processes. It is a sample preparation technique where the solid sorbent in the μg range is dispersed in the solution being analyzed (Kocot et al., 2013a). After centrifuging the suspension, the solid-phase sediments are at the bottom of the test tube. Next, an appropriate organic solvent is used to elute the analytes of interest from the solid sorbent before analysis of the organic extract. After elution of adsorbed analytes, they are thermally desorbed or directly determined by a suitable technique (Khezeli and Daneshfar, 2017).

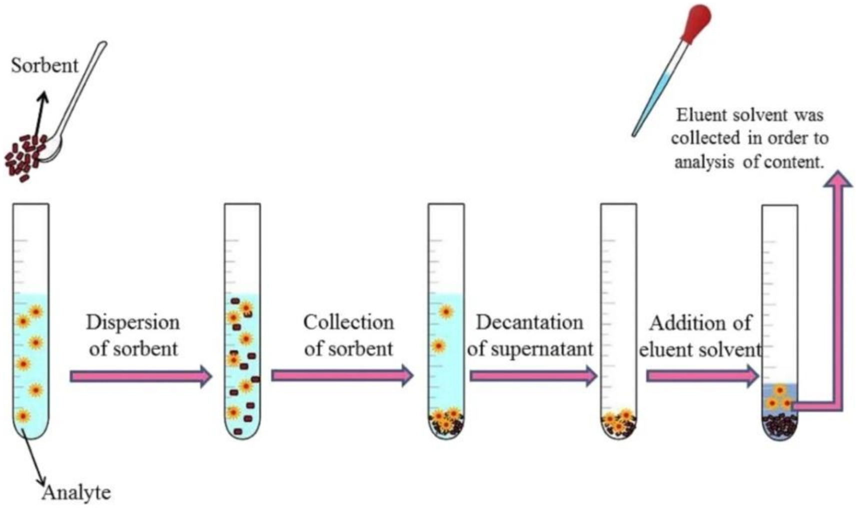

Figure 6. Illustration of dispersive micro-solid phase extraction (D-μ-SPE) (Khezeli and Daneshfar, 2017)

Due to the immediate reaction between analytes of interest and the sorbent, sample-preparation time is shortened (Kocot et al., 2013b). Moreover, because the contact between the target analytes and the support is higher than in traditional SPE, it increases the equilibrium rate and provides higher extraction yields. Generally, the simplicity of operation and the flexibility of the working conditions of SPE methods greatly depend on the proper choice of sorbent materials. The solid sorbents used in D-μ-SPE need to have high capacity and large surface area, to guarantee fast, quantitative sorption and elution, and to be characterized by high dispersibility in liquid samples (Kocot et al., 2013c).

The advantages of D-μ-SPE over conventional methods are that D-μ-SPE allows the direct contact between the analytes/interferes with the adsorbent thank to the homogeneous dispersion of the solid in the liquid matrix sample. Although it was initially proposed to increase the method selectivity, it can also be used to increase the sensitivity by retaining the target analytes on the appropriate sorbent material (Alcudia-León et al., 2008), uses smaller quantities of sorbents and solvents. Furthermore, it is simple and uses inexpensive equipment. For PAHs analysis in water samples there are variety of sorbents applicated in D-μ-SPE, for example, magnetic nanoparticles-nylon 6 composites (Reyes-Gallardo et al., 2014), magnetic graphitic carbon nitride (g-C_3N_4/Fe_3O_4) (Rajabi et al., 2016), biocompatible calcium carbonate vateritic polymorph was recrystallized from eggshell waste (Nuhu et al., 2012).

The main differences between SPE and D-μ-SPE as extraction methods are:

a) Sorbent type - there are several types of sorbents for SPE (normal-phase, reversed-phase, ionic and other special sorbents). In contrast, the number of solid sorbents in D-μ-SPE is much more in progress, and an increased interest in the development of synthetic new sorbents is present. However, in SPE method due to the unsatisfactory selectivity of traditional sorbents, they usually can´t separate analytes efficiently in complex biological or environmental samples (He et al., 2007);

b) The difference in extraction procedure - in SPE liquid sample is passed through a column containing sorbent that retains the target analytes. Sample loading step for cartridge SPE requires a relatively long period. In the case of D-μ-SPE, a small amount of a solid sorbent (μg or mg range) is dispersed in the sample solution to extract the target analytes.

c) Extraction time -SPE as a well-known method of separation and pre-concentration has been developed and widely used in different fields, but it is a time-consuming method. In D-μ-SPE, extraction is not carried out in the SPE cartridge, but it is performed in the bulk solution. Compared with SPE, D-μ-SPE enables the analytes to interact equally with all of the dispersed sorbent particles, to achieve higher capacity per amount of sorbent and to avoid common problems of conventional SPE method such as channeling or blocking of cartridges or discs. D-μ-SPE has the following advantages: less organic solvent and sorbent consumption, high extraction efficiency and short time requirement.

d) Applicability of nano-materials - Application of the nano-materials packed into a cartridge of SPE can be hampered because these materials can cause high back pressure and long sample loading time (Asgharinezhad et al., 2015). Nano-materials possess large surface area and short diffusion route, which may result in high extraction efficiency and rapid extraction dynamics of D-μ-SPE. As previously reported by Jeannot and Cantwell (1996) the extraction rate constant is a function of the mass-transfer coefficient of analytes, interface area between the aqueous phase and extraction phase. Therefore, compared to the traditional micrometer-sized sorbents used in SPE, nano-materials offer a significantly larger surface area and a shorter diffusion route causing the rapid extraction dynamics and high extraction capacity in D-μ-SPE (Huang et al., 2013).

Conclusion

Industrial or naturally produced PAHs can accumulate in the environment, in surface and ground water, soil, food, and food products. They are usually present at ultra-trace amounts and in matrices of high complexity. Sample preparation is a crucial step in the development of an analytical method for environmental and food analysis. Determination of analytes present in complex samples at a very low concentration level usually requires analytical procedures that include isolation and/or enrichment of target analytes before their quantification. SPE offers an excellent alternative to classical LLE. Miniaturization based on the classic SPE method is of high importance in order to reduce solvent volumes, wasted material, time and cost. Recent sample preparation techniques presented here, such as SPE, MEPS, SPME, SBSE, dSPE, and D-μ-SPE are suitable for determination of various contaminants in the environment. A vast number of extraction methods have been used for PAHs extraction from water samples, and this review suggests sorbent based sample pretreatment techniques, which offer green extraction options, the simplicity of operation, relatively low costs of instrumentation, easy coupling to chromatographic systems and shortening the time of extraction.

Conflict of interest

Declarations of interest: none.

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Chemia Naissensis, Vol 1, Issue 1, 124-125

Nedavni razvoj u tretmanima uzoraka vode sorbensom pre GC-MS analize policikličnih aromatičnih ugljovodonika

Slobodan A. Ćirić[1*], Violeta D. Mitić[1], Jelena S. Nikolić[1], Marija D. Ilić[1], Marija V. Dimitrijević[1], Strahinja R. Simonović[2], Vesna P. Stankov Jovanović[1]

1- *Univerzitet u Nišu, Prirodno-matematički fakultet, departman za hemiju, Višegradska 33, 18 000 Niš, Srbija*

2- *Univerzitet u Prištini (sa privremenim sedištem u Kosovskoj Mitrovici), Prirodno matematički fakultet, Departman za hemiju, Lole Ribara 29, 38220 Kosovska Mitrovica, Kosovo, Srbija*

SAŽETAK

Policiklični aromatični ugljovodonici (PAHs) su sveprisutni zagađivači životne sredine, sa evidentiranim štetnim efektima na ljudsko zdravlje. Posebno su ugrožene vode što može direktno uticati na biotu ili putem transporta kroz sve delove životne sredine. Zbog toga je konstantno praćenje sadržaja PAH-ova u vodama od suštinskog značaja. Pre većine analiza priprema uzoraka je obavezna. Konvencionalne tehnike ekstrakcije uglavnom dugo traju i njihovom primenom se troši velika količina rastvarača, što nije u skladu sa pravilima "zelene analitičke hemije". Prema tome, minijaturizacija klasičnih metoda ekstrakcije je od velike važnosti zbog smanjenja količine rastvarača, otpada, vremena tretmana i troškova. Nedavne tehnike pripreme uzoraka, kao što su ekstrakcija čvrstom fazom (eng. solid phase extraction - SPE), mikroektrakcija sa upakovanim sorbentom (eng. microextraction by packed sorbent - MEPS), mikroektrakcija čvrstom fazom (eng. solid phase microextraction - SPME), sorpciona ekstrakcija mešanjem (eng. stir bar sorptive extraction - SBSE), disperzivna ekstrakcija čvrstom fazom (eng. dispersive solid phase extraction - dSPE) i disperzivna mikroekstrakcija čvrstom fazom (eng. dispersive micro-solid phase extraction - D-µ-SPE) su se pokazale pogodnim za ekstrakciju

policikličnih aromatičnih ugljovodonika iz uzoraka vode za njihovo određivanje gasnom hromatografijom sa masenom spektrometrijom. Ove tehnike pripreme su u skladu sa principima “zelene hemije” i pružaju jednostavnost pri radu pri čemu su smanjeni troškovi i vreme pripreme bez ugrožavanja analitičkih parametara primenjene metode.

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Le développement récent au sein des traitements des échantillons de l’eau à l’aide de sorbant avant l’analyse GC-MS des hydrocarbures aromatiques polycycliques

Slobodan A. Ciric[1] *, Violeta D. Mitic[1], Jelena S. Nikolic[1], Marija D. Ilic[1], Marija V. Dimitrijevic[1], Strahinja R. Simonovic[2], Vesna P. Stankov Jovanovic[1]

1- Université de Nis, Faculté des sciences et mathématiques, Département de chimie, Visegradska 33, 18 000 Niš, Serbie

2- Université de Pristina (avec siège temporaire à Kosovska Mitrovica), Faculté des sciences et mathématiques, Département de chimie, Lole Ribara 29, 38220 Kosovska Mitrovica, Kosovo, Serbie.

RÉSUMÉ

Les hydrocarbures aromatiques polycycliques (HAP) représentent des polluants omniprésents dans l’environnement, qui ont des effets nocifs sur la santé humaine. Les eaux sont particulièrement menacées, ce qui peut affecter directement le biota ou au moyen du transport à travers toutes les parties de l’environnement. De ce fait, il est d’une importance impérative de surveiller le contenu des HAP dans les eaux. Avant la plupart des analyses, la préparation des échantillons est obligatoire. Les techniques conventionnelles d’extraction prennent souvent beaucoup de temps et elles exigent la dépense d’une grande quantité des réactifs, le fait qui n’est pas conforme aux règles de la « chimie analytique verte ». En conséquence, la diminution de l’application des méthodes classiques d’extraction s’avère d’une grande importance en vue de la réduction de la quantité des réactifs utilisés et des pertes, de la réduction du temps de traitement et des moyens financiers. Les techniques de préparation des échantillons récentes, telles que l’extraction en phase solide (SPE), la micro-extraction par un sorbant (MEPS), la micro-extraction en phase solide (SPME), l’extraction par sorption sur barreau-agitateur (SBSE),

l'extraction dispersive en phase solide (dSPE) et la micro-extraction dispersive en phase solide (D-µ-SPE) se sont montrées adéquates pour l'extraction des hydrocarbures aromatiques polycycliques (HAP) des échantillons d'eau pour leur détermination par la chromatographie en phase gazeuse-spectrométrie de masse. Ces techniques préparatives sont conformes aux principes de la « chimie verte » et elles offrent une simplicité dans le fonctionnement en réduisant le coût et le temps de préparation, sans compromettre les paramètres analytiques généraux de la méthode analytique appliquée.

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Последние разработки в обработке образцов воды сорбентом перед ГХ-МС анализом полициклических ароматических углеводородов

Слободан А. Чирич[1] *, Виолета Д. Митич[1], Jелена С. Николич[1], Марија Д. Илич[1], Марија В. Димитриjевич[1], Страхиња Р. Симонович[2], Весна П. Станков Jованович[1]

1-Университет в Нише, Факультет естественных наук и математики, Отдел химии, Вишеградска 33, 18 000 Ниш, Сербия

2-Университет в Приштины (с временной штаб-квартирой в Косовской Митровице), Факультет естественных наук и математики, Отдел химии, Лоле Рибара, 29, 38220 Косовская Митровица, Косово, Сербия

АННОТАЦИЯ

Полициклические ароматические углеводороды (PAHs) являются вездесущими загрязнителями окружающей среды, с зарегистрированными вредными воздействиями на здоровье человека. Особенно под угрозой воды, что может напрямую влиять на биоту или путём транспорта через все части окружающей среды. Поэтому постоянный мониторинг содержания ПАУ в водах имеет существенное значение. Перед большинством анализов необходима подготовка образцов. Обычные методы экстракции, как правило, занимают много времени и их использованием расходуется большое количество растворителей, что не соответствует правилам «зелёной аналитической химии». Следовательно, миниатюризация классических методов экстракции имеет большое значение для уменьшения количества растворителей, отходов, времени обработки и затрат. Последние методы подготовки образцов, такие как твёрдофазная экстракция (eng. solid phase

extraction - SPE), микроэкстракция с помощью сорбента (eng. microextraction by packed sorbent - MEPS), твёрдофазная микроэкстракция (eng. solid phase microextraction - SPME), сорбционная экстракция с перемешиванием (eng. stir bar sorptive extraction - SBSE), дисперсионная твёрдофазная экстракция (eng. dispersive solid phase extraction - dSPE) и дисперсионная микротвёрдофазная экстракция (eng. dispersive micro-solid phase extraction - D-μ-SPE) оказались пригодными для извлечения полициклических ароматических углеводородов из образцов воды для их определения методом газовой хроматографии с масс-спектрометрией. Эти методы подготовки соответствуют принципам «зелёной химии» и обеспечивают простоту использования, снижая затраты и время приготовления без ущерба для аналитических параметров применяемого метода.

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Carbon nanotube-based electrochemical sensors for pesticide determination in aqueous solutions: a review

Jelena Čović, Aleksandra Zarubica, Aleksandar Bojić, Marjan Ranđelović*

University of Niš, Faculty of Sciences and Mathematics, Department of Chemistry,
33 Višegradska Str., 18000 Niš, Serbia

*Corresponding author: Marjan Ranđelović-hemija@gmail.com, University of Niš, Faculty of Sciences and Mathematics, Department of Chemistry, Višegradska 33, 18000 Niš, Serbia

ABSTRACT

Excellent mechanical, electrical and magnetic properties of carbon nanotubes (CNT) make CNTs a promising material for the development of electrochemical sensors. Pesticides are very important for an increase in crop yields. However, the intensive use of pesticides can lead to the accumulation of their remains, thus creating a severe problem and risk to human and environmental health. Those are the reasons why the monitoring of pesticides in the environment is extremely important. For that purpose, electrochemical sensors based on carbon nanotubes were designed, and their main aim is pesticide monitoring at environmental samples. A review of the recent studies of environmental monitoring of pesticides using electrochemical sensors based on carbon nanotubes is presented.

Keywords: *electrochemical sensors, pesticides, carbon nanotubes*

Introduction

Carbon nanotubes (CNTs) are officially mentioned in 1991 when Sumio Iijima discovered the existence of multi-walled CNTs (MWCNTs) as a byproduct in the synthesis of phularen (Iijima, 1991). Two years later, two groups of scientists, one led by Iijima et al. (Iijima and Ichihashi, 1993) and the other by Bethune (Bethune et al., 1993), experimentally came to the discovery of single-walled CNTs (SWCNTs).

Single-walled carbon nanotubes (Fig. 1) can be considered as long, trained layers of graphene. Their diameter is nanometer dimensions (typically between 0.7 and 1.4 nm), and the length is several thousand times greater than the diameter (Cvetićanin, 2013). Several concentric cylinders inserted into each other with a layer spacing of 0.3–0.4 nm are created multi-walled carbon nanotubes (Fig. 1) (Andrews et al., 2002).

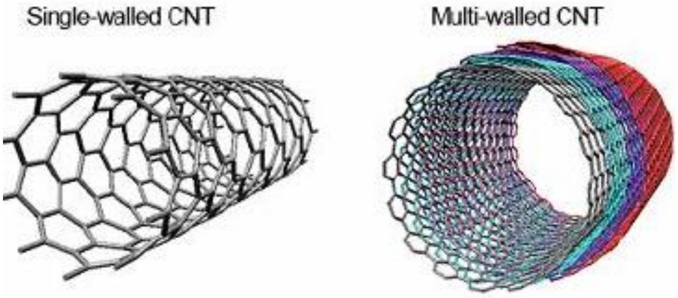


Figure 1. Single-walled carbon nanotube (SWCNT) and multi-walled carbon nanotube (MWCNT)

There are three main techniques for synthesis MWCNTs and SWCNTs: arc-discharge, laser-ablation, and catalytic growth. SWCNTs have higher specific stiffness and strength than MWCNTs (Batra and Sears, 2007). Due to excellent physical and elastic characteristics, high electrical conductivity (Demczyk et al., 2002; Hong and Myung, 2007; Peng et al., 2008) CNTs are a unique material.

The advantages of carbon nanotubes compared to other materials are small size, high strength, high electrical and thermal conductivity, specific shape. Due to all these properties, carbon nanotubes can be used in electroanalytical applications. The superficial incorporation of metallic nanoparticles (Yang et al., 2015), organic (Eguílaz et al., 2016) and inorganic molecules (Husmann and Zarbin, 2016) is very important because it can increase the field of electroanalytical applications. Carbon nanotubes are raw materials for the development of electrochemical sensors to detect dyes, ions, phenols, drugs, and pesticides (Govindhan et al., 2015; Wang et al., 2014; Zhang et al., 2009).

The recent advances in the creation of electrochemical sensors on the basis of carbon nanotubes for the determination of pesticides in real samples are described here.

Pesticides

Pesticides are products of natural or chemical origin whose application is protection plants against weeds, diseases, harmful insects, mites and other harmful organisms. Although the use of pesticides leads to an increase in crop yields, the intensive use of pesticides can lead to the accumulation of their remains, thus creating a serious problem and risk to human and environmental health (Damalas and Eleftherohorinos, 2011). Also, these compounds are widely distributed in the environment, and their existence in water, soil, sewage sludge, sediment has been discovered (Domínguez et al., 2016). In the human body, they may increase the risk of numerous disorders, even in low concentrations. Those are the reasons why the monitoring of pesticides in the environment is extremely important.

Classification of pesticides

Pesticides can be classified in several ways and, one of the ways is classification according to purpose, which includes acaricides, algicides, bactericides, fumigants, fungicides, herbicides, insecticides, rodenticides, *etc*. Pesticides can be also classified according to the way of entering the organism: abdominal (digestive), contact, fumigant. According to the chemical composition, all pesticides can be divided into three groups: inorganic compounds, organic compounds, and pesticides of natural origin.

Pesticides of inorganic origin are compounds of mercury, fluorine, barium, sulfur, copper, as well as chlorates and borates. Pesticides of natural origin (for example pyrethrins, antibiotics or phytocides) are compounds which are the result of biosynthesis of living organisms (plants, bacteria, and fungi). The largest group of pesticides are organic compounds, and they include organochloric, organophosphorus compounds, derivatives of carbon, thio- and dithiocarboxylic acids, nitro derivatives of phenol, phthalimides, mineral oils, etc. (Gruzdyev, 1988).

There are several methods for the detection of pesticides. Some of them are fluorescence spectrophotometry, gas chromatography with mass spectrometry detection, high-performance liquid chromatography (HPLC) with fluorescence detection and HPLC coupled to mass spectrometry (Chen et al., 2015; Lemos et al., 2016; López et al., 2016; Mol et al., 2016). Unlike the expensive spectroscopic and chromatographic methods, electrochemical methods are cheap, sensitive, selective and simple methods for the determination of pesticides.

Electrochemical sensors based on carbon nanotube for determination of pesticides

Here, we present a general overview of the recent researches on the topic of environmental monitoring of pesticides using sensors based on a carbon nanotube, glassy carbon electrode (GCE) and carbon paste electrode (CPE) (Tables 1 and 2). As can be seen, different electrodes for the detection of various pesticides were used. Electrochemical sensors can be designed with pristine carbon nanotubes or carbon nanotubes which are modified by other compounds.

Table 1. Electrochemical sensors based on modified GCE for determination various pesticides

Electrode	Pesticide	Limit of detection (mol/L)	Linear range (mol/L)	Reference
FMWCNTs/GCE	Carbendazim	5.2×10^{-11}	5.2×10^{-11} - 2.6×10^{-4}	Sundari et al., 2010
Fullerene/MWCNT/ Nafion/GCE	Carbendazim	1.7×10^{-8}	2.0×10^{-8} - 3.5×10^{-7}	Teadoum et al., 2016
MWCNT/Pd-Ir with MB	Carbofuran	1.7×10^{-12}	4×10^{-11} - 4×10^{-9}	Li et al., 2016
MWCNTs/TiO_2NPs	Diazinon	3×10^{-9}	11×10^{-9} - 8.36×10^{-6}	Ghodsi and Rafati, 2017
β–CDs/MWCNTs/GCE	Dichlorophen	1.4×10^{-8}	5.0×10^{-8} - 2.9×10^{-6}	Sipa et al., 2018
MWCNTs/GCE	Fenitrothion and Bifenox	8×10^{-8}	2×10^{-7} - 6×10^{-5}	Salehzadeh et al., 2016
β-CD-rGO/GCE	Paichongding	1.1×10^{-6}	1×10^{-6} - 1×10^{-5} 1×10^{-5} - 5.5×10^{-5}	Zhang M. et al., 2016
AuNPs/CNT/GCE	Parathion	1.0×10^{-7}	5.0×10^{-7} - 6.0×10^{-5}	Zhang Y. et al., 2009
GCE/MWCNTs	Propham	3.65×10^{-7}	2×10^{-6} - 4.78×10^{-5}	Leniart et al., 2016
IL-MWCNT/GCE	Pyrimethanil	1.6×10^{-8}	1×10^{-7} - 1×10^{-4}	Yang et al., 2015
C_{60}–MWCNTs/GCE	Vinclozolin	9.1×10^{-8}	2.5×10^{-6} - 8.8×10^{-6}	Rather et al., 2012

Table 2. Electrochemical sensors based on carbon paste electrode (CPE) for determination various pesticides

Electrode	Pesticide	Limit of detection (mol/L)	Linear range (mol/L)	Reference
ZXCPE	Carbamyl	3×10^{-7}	$1\times10^{-6} – 1\times10^{-4}$	Salih et al., 2017
MIP/CPE	Dicloran	4.8×10^{-10}	1×10^{-6} - 1×10^{-9}	Shahtaheria et al., 2017
MWCNPE	Methiocarb	2.0×10^{-6}	6.7×10^{-6} - 2.6×10^{-4}	Inam and Bilgin, 2013

Sensors based on carbon nanotubes

There are many pieces of research based on carbon nanotubes using as bare electrode, such as CPE or modified GCE.

Carbon paste electrode is a composite electrode constructed using carbon materials such as graphite, carbon nanotubes (CNPE) or products from the combination of at least two materials. CNPE is a mixture of carbon nanotubes and a hydrophobic organic liquid (mineral oil, paraffin oil, or silicone oil) placed on a plastic or glass tube of a specific diameter (Apetrei et al., 2011).

Inam and Bilgin (2013) detected the insecticide methiocarb using a multi-walled carbon nanotube paste electrode by square-wave voltammetry (SWV). The preparation of the used electrode (CNPE) was performed by mixing the carbon nanotube powder with mineral oil (0.15:0.85 w/w ratio). Methiocarb electrochemical characterization in 0.1 mol/L H_2SO_4 presented an irreversible anodic peak at + 1.3 V vs. Ag/AgCl. The results showed a linear dynamic range between 6.7×10^{-6} and 2.6×10^{-4} mol/L and a detection limit of 2.0×10^{-6} mol/L, with recoveries of (98.5±0.3)% in river water samples, respectively.

A rigid and flat surface is a characteristic of a glassy carbon electrode (GCE). Before any experiment, the surface of the electrode should be cleaned by polishing with alumina, followed by sonification in ethanol and ultrapure water. After purification, the electrode can be modified by homogenous reagent dispersion prepared in ultrapure water or an organic solvent (acetonitrile, ethanol). An aliquot of dispersion is added to the surface of the electrode (μL) and left to dry at room temperature. As a result, a homogeneous film on the surface of the electrode is obtained (Li et al., 2013).

Sundari et al. (2010) detected the pesticide carbendazim using a GCE modified with functionalized multi-walled carbon (FMWCNTs/GCE) by differential pulse adsorptive stripping voltammetry. The sensor showed a linear concentration range between 5.2 x 10^{-11} and 2.6 x 10^{-4} mol/L, with recovery percentages between 84.5% and 93.7% in water samples.

Hamid et al. (2016) investigated the electrochemical behavior of fenitrothion (FT) and bifenox (BF) using a GCE modified with multi-walled carbon nanotube by square wave voltammetry (SWV). Fig. 2 shows the SEM image of the surface GCE modified with MWCNTs (MWCNTs/GCE). Typical square wave voltammograms for a solution containing FT and BF (pH 5.0) are shown in Fig. 3. Quantification determination of FT and BF based on the cathodic peaks C_0 and C_0' is not possible. Anodic peak A_1 (at -0.061 V vs. Ag/AgCl) is related to the oxidation of FT_{red} resulting from the reduction of FT. Anodic peak A_2 (at 0.063 V vs. Ag/AgCl) is related to the oxidation of BF_{red} resulting from the reduction of BF. The detection limit for both FT and BF was found to be 0.08 μM and linear response over the range 0.2-60 μM. The method revealed recovery percentages of FT and BF in the range of 96.6-104% in river water samples.

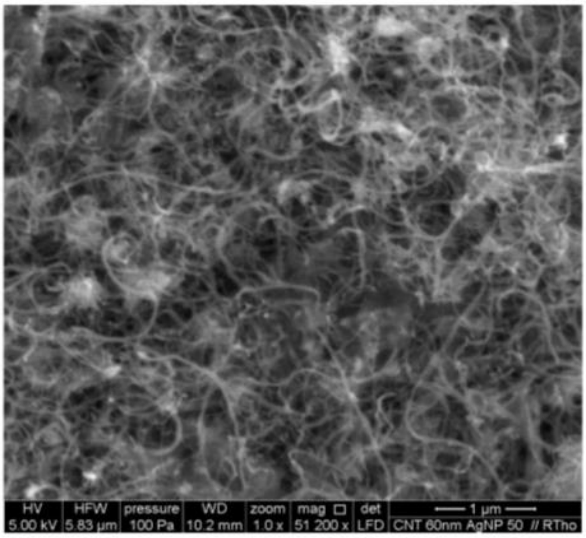


Figure 2. SEM image of MWCNTs/GCE (Hamid et al., 2016)

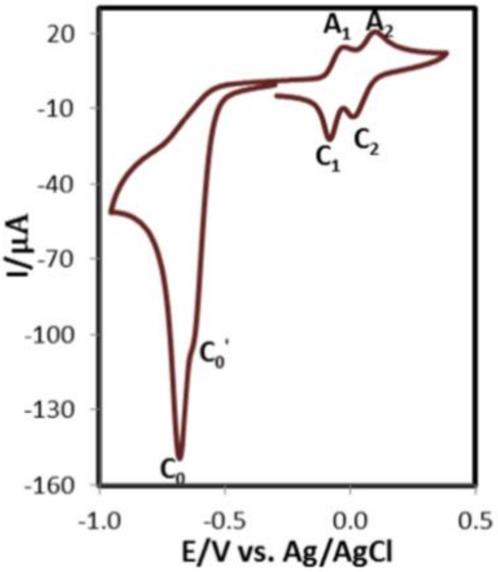


Figure 3. Cyclic voltammogram of 1.0 mM FT and 1.0 mM BF in aqueous solution containing acetate buffer (pH = 5.0, 0.2 M) and 20% ethanol (v/v) at the glassy carbon electrode. Starting potential −0.3 V, first switching potential −0.9 V and second switching potential 0.35V vs. Ag/AgCl. Scan rate 100 mV/s (Hamid et al., 2016)

Leniart et al. (2016) studied electrochemical oxidation of herbicide propham on a glassy carbon electrode modified with multi-walled carbon nanotubes (GCE/MWCNTs) by square wave adsorptive stripping voltammetry (SWAdSV). The best signal at +1.49 V vs. Ag/AgCl was recorded in 0.5 mol/L sulphuric acid. A limit of detection (LOD) and a limit of quantification (LOQ) were 3.65×10^{-7} and 1.09×10^{-6} mol/L, respectively. The determination of propham was performed using the developed method in spiked Bzura River water samples. Fig. 4 presents SWAdS voltammograms for the determination of propham in water samples using the standard addition method: 0) blank, (1) river water sample spiked with propham, (2) as (1) $+5.00\times10^{-6}$ mol/L, (3) as (1) $+9.09\times10^{-6}$ mol/L, (4) as (1) $+1.54\times10^{-5}$ mol/L, (5) as (1) $+2.00\times10^{-5}$ mol/L.

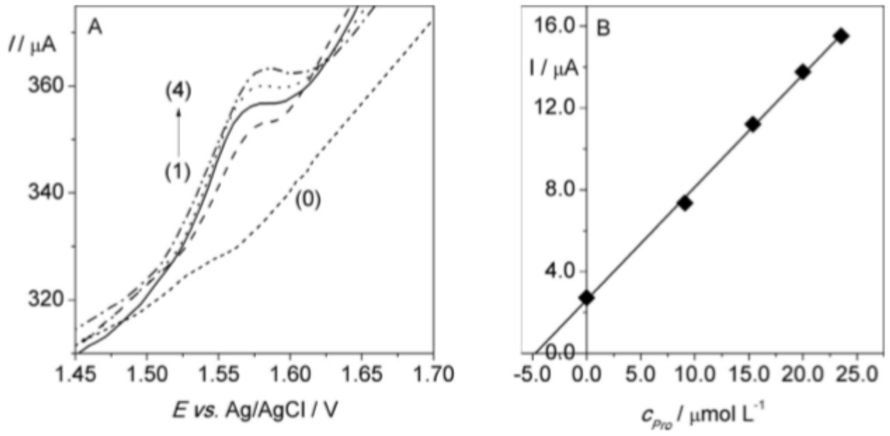


Figure 4. SWAdS voltammograms for the determination of propham in water samples using the standard addition method (Leniart et al., 2016)

Sensor based on GCE modified with MWCNTs/ TiO_2 nanoparticles

Ghodsi and Rafati (2017) developed a voltammetric sensor for diazinon pesticide determination based on glassy carbon electrode (GCE) surface modified with multi-walled carbon nanotubes covered by TiO_2 nanoparticles (MWCNTs/TiO_2NPs). The voltammetric probes were carried out by cyclic voltammetry (CV), linear sweep voltammetry (LSV), differential pulse voltammetry (DPV) and square wave voltammetry (SWV). Prepared MWCNTs/TiO_2NPs was characterized with scanning electron microscopy (SEM), X-ray diffraction (XRD) and energy dispersive X-ray analysis (EDX) techniques (Fig. 5). The sensors showed a linear range between 11-8360 nM, a limit of detection 3 nM and a limit of quantification 10 nM. The developed sensor showed good sensitivity and was successfully examined for diazinon determination in real water samples. The sensor showed the highest sensitivity when SWV technique was applied (Fig. 6). Therefore next diazinon determination in real samples was obtained using SWV technique.

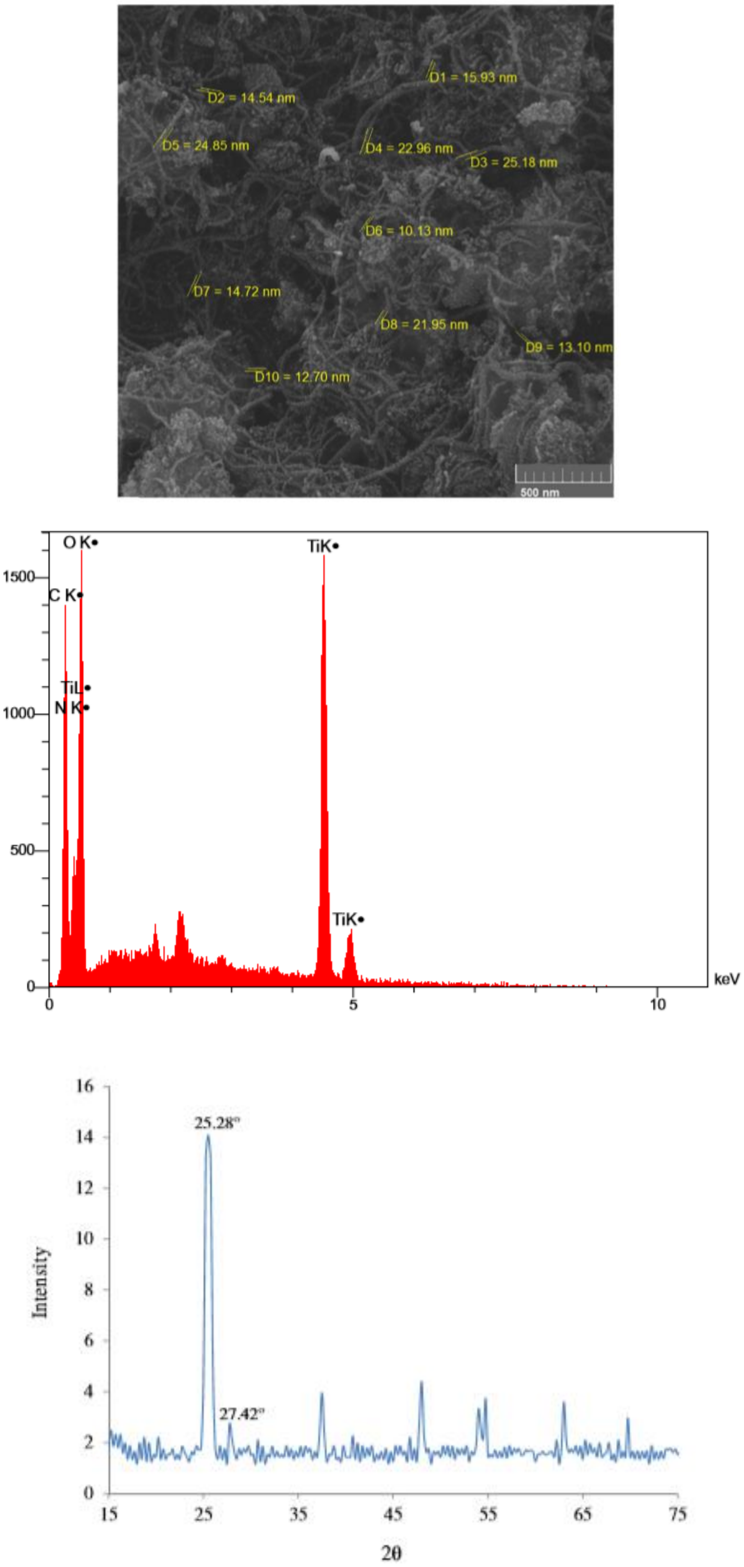


Figure 5. a) SEM image; b) EDX analysis;

c) XRD pattern of MWCNTs/TiO_2NPs nanocomposite on GCE surface (Ghodsi and Rafati, 2017)

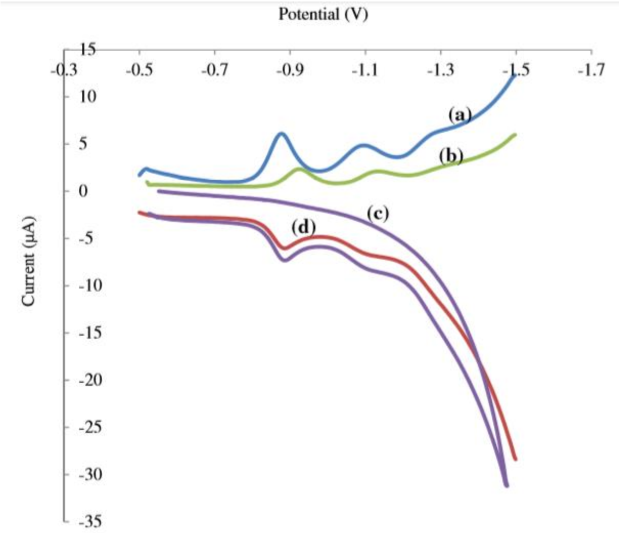
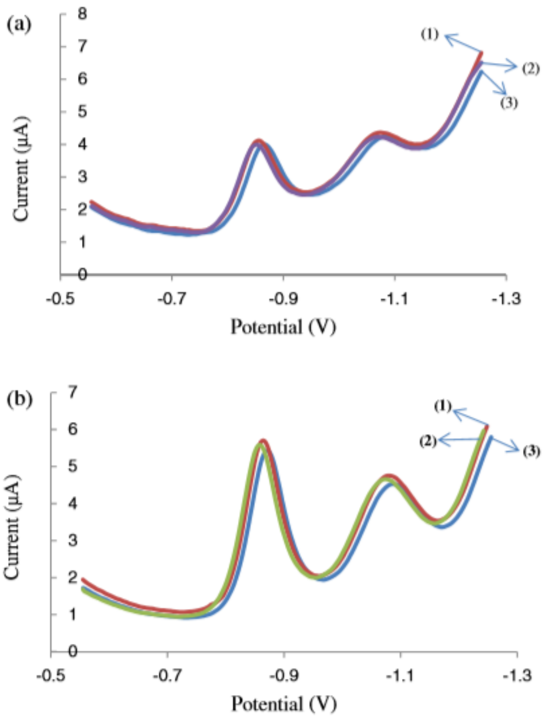


Figure 6. (a) SWV, (b) DPV, (c) CV and (d) LSV response of the developed sensor to 2 μM diazinon (Ghodsi and Rafati, 2017)

Fig. 7 represents a) SWV voltammograms of 1) a sample from well water spiked with 1 μM of diazinon, 2) a sample from tap water spiked with 1 μM of diazinon and 3) phosphate buffer containing 1 μM of diazinon obtained by GCE/MWCNTs/TiO_2NPs. Fig. 7 b) and c) represent the same SWVs with 2 μM and 3 μM of diazinon, respectively.



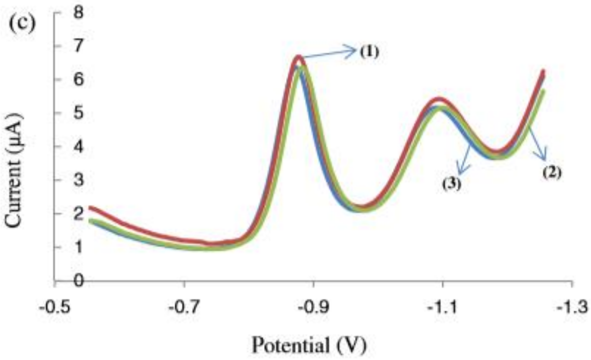


Figure 7. SW voltammograms of 1) a sample from well water spiked with 1 µM of diazinon, 2) a sample from tap water spiked with 1 µM of diazinon and 3) phosphate buffer containing 1 µM of diazinon obtained by GCE/MWCNTs/TiO_2NPs. Panels b and c show same SWVs with 2 µM and 3 µM of diazinon respectively (Ghodsi and Rafati, 2017)

Sensor based on low silica X zeolite modified carbon paste electrode

The team of scientists worked on the development of an electrochemical sensor for the detection of carbamyl pesticides, which is based on low silica X (LSX) zeolite modified carbon paste electrode. For characterization of synthesized LSX zeolite was used XRD analysis. Fig. 8. shows intense diffractions peaks at 2θ values equal to 6.12°, 13.96°, 24.31°, 26.69° and 30.97° which corresponds to the characteristic peaks of zeolite X.

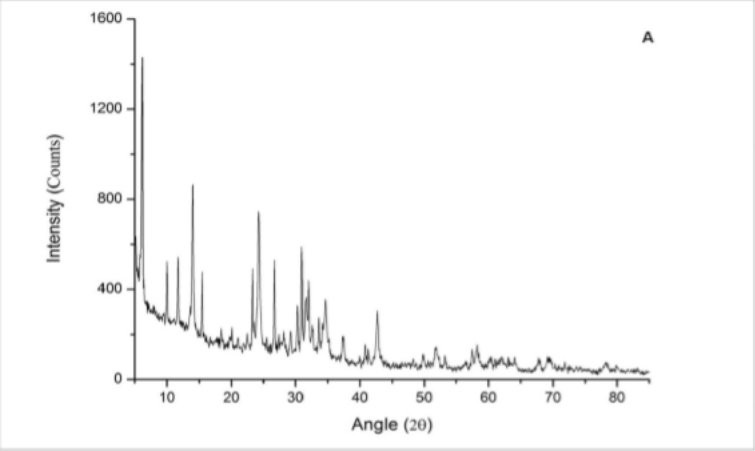


Figure 8. X-ray diffraction patterns of Low Silica X Zeolite (LSXZ) (Salih et al., 2017)

The electrochemical behavior of the ZXCPE in potassium hexacyanoferrate III/II solution was investigated by cyclic voltammetry (CV). Fig. 9. represents the responses obtained by CV between -0.2 and +0.7 V (vs. SCE) at CPE and ZXCPE in 0.1 M KCl solution containing 1 mM $[Fe(CN)_6]^{3-/4-}$ (1:1) at 50 mV/s. At CPE (curve b), the values of current Ipa = 18 µA, Ipc = - 19 µA were recorded, while the modified electrode of ZXCPE showed an evident increase in current value (Ipa = 26 µA, Ipc = - 26 µA). This implies that the electron transfer rate at ZXCPE is improved (Salih et al., 2017).

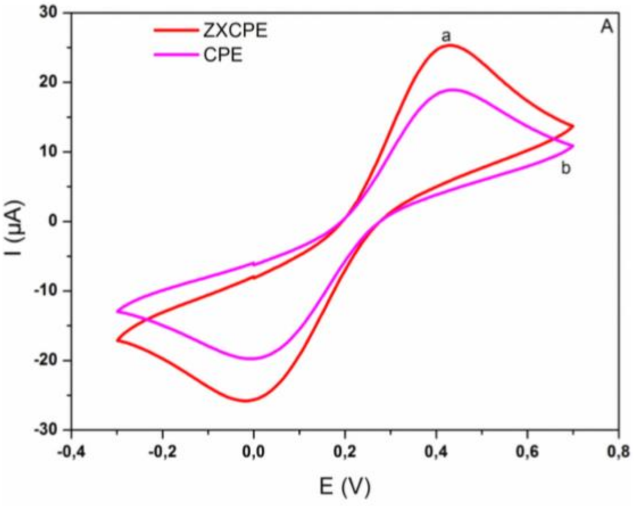


Figure 9. Cyclic voltammograms of ZXCPE and CPE in 1 mM $[Fe(CN)_6]^{3-/4-}$/0.1 M KCl at 50 mv/s (Salih et al., 2017)

Sensors based on metallic nanoparticles and carbon nanotubes

Metallic nanoparticles are important, because, in combined use with carbon nanotubes, they improve the electrochemical characteristic of electrodes, more precisely higher analytical sensitivities and lower detection limits.

Zhang et al. (2009) developed a voltammetric sensor for parathion pesticide determination based on glassy carbon electrode (GCE) surface modified with AuNPs/CNT. Firstly, modification of the GCE surface was performed with 5 µL of a 0.5% m/m Nafion aqueous dispersion containing CNTs. After that, the AuNPs were electrodeposited on the CNTs/GCE in 0.2 mol/L H_2SO_4 solution containing 5 mmol/L $HAuCl_4$. Electrodeposition is performed by cyclic voltammetry between −0.2 V and +1.0 V (vs. SCE). The analytical curve shows linearity in the range 5.0×10^{-7}-6.0×10^{-5} mol/L and a LOD of 1.0×10^{-7} mol/L, with recovery percentages between of 104.3% in water samples. In Fig. 10. are shown the SEM images obtained for the CNTs (Fig. 10a), AuNPs deposited on GCE (Fig. 10b) and AuNPs deposited on CNTs/GCE (Fig. 10c).

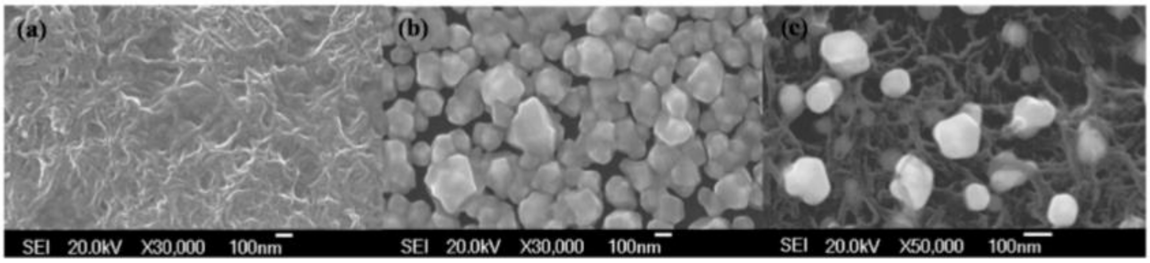


Figure 10. a) SEM image of the CNTs, b) Au nanoparticles on GCE, c) Au nanoparticles combined with CNTs on GCE (Zhang et al., 2009)

Sensors based on β-cyclodextrin and carbon nanotubes

Sipa et al. (2018) successfully developed an electrochemical sensor based on a glassy carbon electrode modified with β–cyclodextrins and multi-walled carbon nanotubes (β–CDs/MWCNTs/GCE) for detection of the pesticide dichlorophen (Dcp). The voltammetric measurements carried out by square-wave adsorptive stripping voltammetric (SWAdSV) and in phosphate buffer (PBS) (pH=6.5) as a supporting electrolyte (Fig. 11). The results showed a linear concentration range from 5.0×10^{-8} mol/L to 2.9×10^{-6} mol/L and a limit of detection 1.4×10^{-8} mol/L. The determination of Dcp in river water was performed using this sensor.

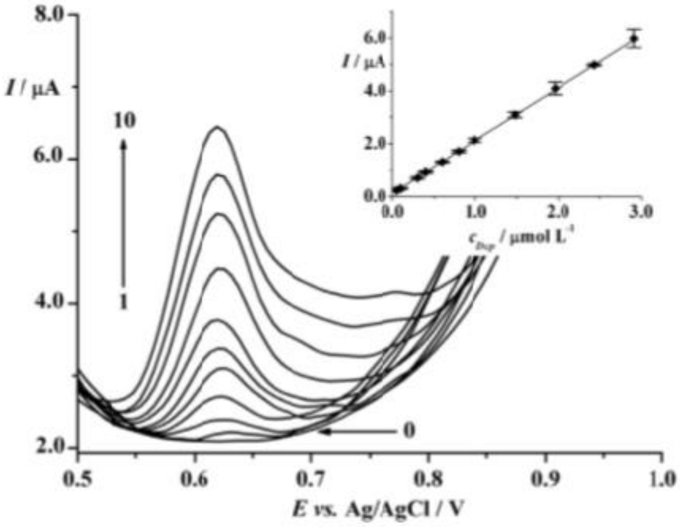


Figure 11. SWAdSV responses at β–CDs/MWCNTs/GCE in PBS (pH 6.5) containing different concentrations of Dcp: (0) supporting electrolyte, (1) 5.0×10^{-8}, (2) 1.0×10^{-7}, (3) 3.0×10^{-7}, (4) 6.0×10^{-7}, (5) 8.0×10^{-7}, (6) 1.0×10^{-6}, (7) 1.5×10^{-6}, (8) 2.0×10^{-6}, (9) $2.4 \times$

10^{-6}, and (10) 2.9 × 10^{-6} mol/L. The inset show the corresponding calibration graph of Dcp. The error bars were constructed as confidence level (p) of 95% (n = 4) (Sipa et al., 2018)

Sensors based on molecularly imprinted polymer and carbon nanotubes

High selective sensor based on a molecularly imprinted polymer (MIP) and carbon nanotubes modified carbon paste electrode for detection of dicloran pesticide were designed by Shahtaheria et al. (2017). Beside a MIP, a non-imprinted polymer (NIP) was also synthesized and applied in the carbon paste electrode. The MIP-CP electrode was very selective for dicloran and showed very high recognition ability in comparison to NIP-CP. There was a significant difference between the ability of MIP and NIP to adsorb dicloran. Fig. 12 presents the square wave voltammograms related to the determination of the defined concentration of dicloran by MIP-CP, NIP-CP, and bare CP.

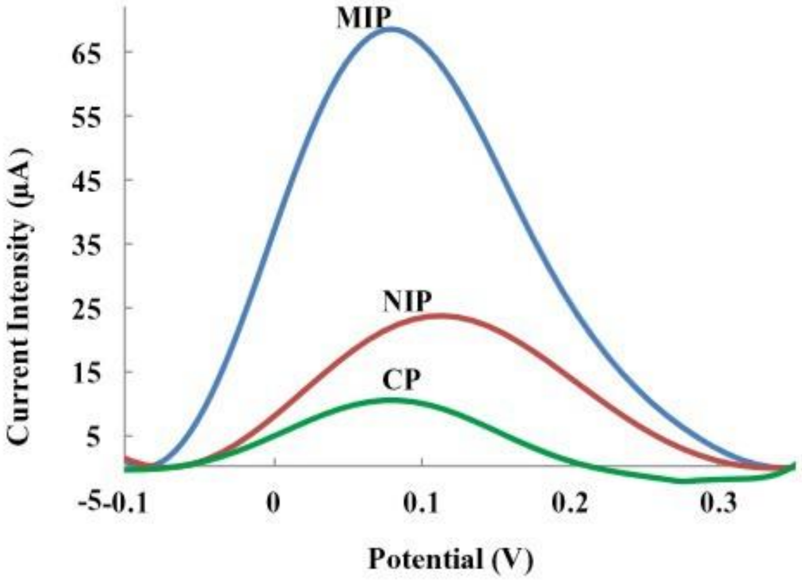


Figure 12. The voltammograms of MIP-CP, NIP-CP, and CP for the defined concentration of dicloran (5×10^{-7} mol/L) (Shahtaheria et al., 2017)

The obtained calibration curve was linear from 1×10^{-6} to 1×10^{-9} mol/L, and LOD and LOQ were 4.8×10^{-10} and 9.4×10^{-10} mol/L, respectively. The designed sensor was successfully used for the determination of dicloran in real samples, such as tap water, river water.

Conclusion

All these studies, as well as a large number of studies not mentioned in this review, have shown that pesticides from different groups can be quantified using electrochemical sensors based on carbon nanotubes. Carbon nanotubes have provided electrochemical sensors with the relatively good analytical performance required for the detection of pesticides. Either they were used alone or in combination with different types of modifiers. Some of the modifiers used are metal particles, TiO_2 nanoparticles, LSX zeolites, β-cyclodextrins, molecularly imprinted polymer, *etc*. The aim of modifying the electrode from the carbon paste and the glassy carbon electrode is to achieve a well expressed analytical signal and to shift the working potential closer to zero. Both of these effects are desirable in order to achieve high sensitivity and good selectivity.

It means that the use of carbon nanotubes as electrode modifiers, for the preparation of electrochemical sensors used to track pesticides, had a positive effect. It is undoubtedly necessary to continue research in order to overcome all the challenges for progress in this area.

An interesting approach to future research is the ability to design devices by which different analytes will be simultaneously determined at different points of the sensor. This challenge is related to the current goals, relating to the miniaturization of analytical devices, the minimal consumption of chemical reagents and the generation of waste, and the ability to carry instruments outside the laboratory. Regarding material synthesis, which will be suitable for making the sensor, currently, the preparation of composites of carbon nanotubes with other allotropic carbon modifications is a trend, such as carbon black, diamond or graphene.

Acknowledgment

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Conflict-of-Interest Statement

Declarations of interest: none.

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Chemia Naissensis, Vol 1, Issue 1, 150

Elektrohemijski senzori na bazi ugljeničnih nanocevi za određivanje pesticida u vodi: pregled

Jelena Čović, Aleksandra Zarubica, Aleksandar Bojić, Marjan Ranđelović*

Univerzitet u Nišu, Prirodno-matematički fakultet, Departman za hemiju, Višegradska 33, 18000 Niš, Srbija

SAŽETAK

Izvanredne mehaničke, električne i magnetne karakteristike ugljeničnih nanocevi čine ih materijalom koji obećava za razvoj elektrohemijskih senzora. Pesticidi su veoma važni za povećanje prinosa useva. Međutim, prekomerna upotreba pesticida može dovesti do akumulacije ostataka njihove razgradnje, tako stvarajući ozbiljan problem i rizik za ljude i životnu sredinu. Ovo su razlozi zbog čega je monitoring pesticida u životnoj sredini izuzetno važan. U ovu svrhu elektrohemijski senzori bazirani na ugljeničnim nanocevima su dizajnirani, i njihov glavni cilj je monitoring pesticida u realnim uzorcima. Pregledni rad o najnovijim istraživanjima za monitoring pesticida korišćenjem elektrohemijskih senzora baziranih na ugljeničnim nanocevima je prezentovan.

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Capteurs électrochimiques à base de nanotubes de carbone pour la détermination des pesticides dans l'eau : aperçu

Jelena Čović, Aleksandra Zarubica, Aleksandar Bojić, Marjan Ranđelović*

Université de Nis, Faculté des sciences et mathématiques, Département de chimie, Visegradska 33, 18 000 Niš, Serbie

RÉSUMÉ

Les excellentes propriétés mécaniques, électriques et magnétiques rendent les nanotubes de carbone (NTC) un matériau prometteur dans le domaine du développement de nouveaux capteurs électrochimiques. Au sein de l'agriculture, les pesticides sont très importants pour l'augmentation des rendements. Cependant, leur utilisation intensive peut entraîner l'accumulation de leurs restes et des effets nocifs sur l'environnement et la santé des hommes. Ce sont les raisons principales pour lesquelles la surveillance des pesticides dans l'environnement est extrêmement importante. La surveillance des pesticides peut être effectuée à l'aide des capteurs électrochimiques. Cet article révèle les plus récents résultats dans le champ de développement des nouveaux capteurs électrochimiques dont le but est la surveillance du niveau des pesticides dans l'eau.

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Электрохимические сенсоры на основе углеродных нанотрубок для определения пестицидов в пустоте: обзор

Елена Чович, Александра Зарубица, Александар Божич, Марьян Ранджелович *

Университет в Нише, Факультет естественных наук и математики, Отдел химии, Вишеградска 33, 18 000 Ниш, Сербия

АННОТАЦИЯ

Исключительные механические, электрические и магнитные свойства углеродных нанотрубок делают их важным материалом в области разработки новых электрохимических сенсоров. Пестициды очень важны для сельскохозяйственного производства и выращивания сельскохозяйственных культур, но их чрезмерное использование может привести к накоплению остатков их деградации и негативному воздействию на окружающую среду и здоровье человека. Это основные причины, по которым мониторинг пестицидов в окружающей среде является важным и может быть очень успешно выполнен с использованием электрохимических датчиков. В этой обзорной статье представлены новейшие достижения в области разработки новых электрохимических датчиков для мониторинга пестицидов в водах.

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Mechanisms of actions of coenzymes

Biljana Arsić

*University of Niš, Faculty of Sciences and Mathematics, Department of Chemistry, Višegradska 33,
18000 Niš, Republic of Serbia*, e-mail: ba432@ymail.com

ABSTRACT

Each living species uses coenzymes in numerous important reactions catalyzed by enzymes. There are two types of coenzymes depending on the interaction with apoenzymes: coenzymes frequently called co-substrates and coenzymes known as prosthetic groups. Main metabolic roles of co-substrates (adenosine triphosphate (ATP), *S*-adenosyl methionine, uridine diphosphate glucose, nicotinamide adenine dinucleotide (NAD^+) and nicotinamide adenine dinucleotide phosphate ($NADP^+$), coenzyme A (CoA), tetrahydrofolate and ubiquinone (Q)) and prosthetic groups (flavin mononucleotide (FMN) and flavin adenine dinucleotide (FAD), thiamine pyrophosphate (TPP), pyridoxal phosphate (PLP), biotin, adenosylcobalamin, methylcobalamin, lipoamide, retinal, and vitamin K) are described in the review.

Keywords: *Coenzyme, Co-substrates, Prosthetic groups, Mechanisms.*

Introduction

Coenzymes can be classified into two groups depending on the interaction with apoenzyme. The coenzymes of the first type-often called co-substrates are substrates in the reactions catalyzed by enzymes. Co-substrate is changing during the reaction and dissociating from the active center. The original structure of co-substrate is regenerating in the next reaction catalyzed by other enzymes. Therefore, co-substrates cover mobile metabolic group between different reactions catalyzed by enzymes (http://www.uwyo.edu/molecbio/courses/molb-3610/files/chapter%207%20coenzymes%20and%20vitamines.pdf).

The second type of the coenzymes is called the prosthetic groups. The prosthetic group remains bonded for the enzyme during the reaction. In some cases, the prosthetic group is covalently bound for its apoenzyme, while in other cases it is weakly bound to the active center by numerous weak interactions. Similarly to ionic amino acid residues of the active site, the prosthetic group must return to its original form during the whole catalytic event or holoenzyme will not remain catalytically active (http://www.uwyo.edu/molecbio/courses/molb-3610/files/chapter%207%20coenzymes%20and%20vitamines.pdf).

Every living species uses coenzymes in a different number of the important reactions catalyzed by enzymes. Numerous species can synthesize their coenzymes from simple precursors. This ability is particularly important in four out of five kingdoms: prokaryotes, protozoa, fungi, and plants. Animals, generally, lost their ability to synthesize some coenzymes. Mammals (including humans) have the ability for the source coenzymes, or their direct precursors in order to survive. Final vitamin sources are usually plants and microorganisms, although carnivores can get vitamins from meat. Majority of vitamins must be transformed enzymatically into their corresponding coenzymes (Arsic et al., 2016).

The illnesses emerged due to the deficiency, *i.e.*, when there is a lack of vitamins, or it is absent in the food nutrition (Arsic et al., 2016). Majority of vitamins are converted into coenzymes, most often after the reaction with ATP (Huennekens et al., 1974). A portion of ATP molecule which is transferred to the vitamin is the group which binds the coenzyme for the enzyme active centers. Vitamins soluble in water are necessary in small quantities because they are excreted by urine, and cell depots of their coenzymes are unstable (Schellack et al., 2015).

On the other side, lipid vitamins, like vitamins A, D, E, I, K are stored in animals, and increased intake can cause toxic states known as hypervitaminoses (Engelking, 2015).

The most important enzymes are listed in Table 1 together with their roles in metabolism and their vitamin sources.

Table 1. The most important coenzymes (Horton et al., 2006)

Coenzyme	**Vitamin**	**Main metabolic role**	**Mechanistic role**
Adenosine triphosphate (ATP)	-	Transfer of phosphoryl or nucleotidyl groups	Co-substrate
S-Adenosyl methionine	-	Transfer of metal groups	Co-substrate
Uridine diphosphate glucose	-	Transfer of glycosyl groups	Co-substrate
Nicotinamide adenine dinucleotide (NAD^+) and nicotinamide adenine dinucleotide phosphate ($NADP^+$)	Niacin	Oxidation-reduction reactions involving 2-electron transfers	Co-substrate
Flavin mononucleotide (FMN) and flavin adenine dinucleotide (FAD)	Riboflavin (B_2)	Oxidation-reduction reactions including one and two electron transfers	Prosthetic group
Coenzyme A (CoA)	Pantothenate (B_3)	Transfer of acyl groups	Co-substrate
Thiamine pyrophosphate (TPP)	Thiamine (B_1)	Transfer of fragments from two carbons containing carbonyl group	Prosthetic group
Pyridoxal phosphate (PLP)	Pyridoxine (B_6)	Transfer of groups from and to amino	Prosthetic group

		acids	
Biotin	Biotin	ATP dependent carboxylation of substrate or transfer of carboxylic groups between substrates	Prosthetic group
Tetrahydrofolate	Folate	Transfer of substituents with one carbon, particularly formyl and hydroxymethyl groups; giving methyl group for thiamine in DNA	Co-substrate
Adenosylcobalamin	Cobalamine (B_{12})	Intramolecular rearrangement	Prosthetic group
Methylcobalamin	Cobalamine (B_{12})	Transfer of methyl groups	Prosthetic group
Lipoamide	-	Oxidation of hydroxyalkyl group from TPP and the next transfer as an acyl group	Prosthetic group
Retinal	Vitamin A	Eyesight	Prosthetic group
Vitamin K	Vitamin K	Carboxylation of some glutamic residues	Prosthetic group
Ubiquinone (Q)	-	Electron carrier soluble in fats	Co-substrate

ATP and other nucleotide co-substrates

There are many nucleoside triphosphates which behave as coenzymes. Among them, adenosine triphosphate (ATP) is the most abundant. Other frequent examples are GTP, *S*-adenosyl methionine and nucleotide sugars such as uridine diphosphate glucose (UDP-glucose). ATP (Figure 1a) can donate phosphoryl, pyrophosphoryl, adenylyl (AMP), or adenosyl groups in reactions of group transfers.

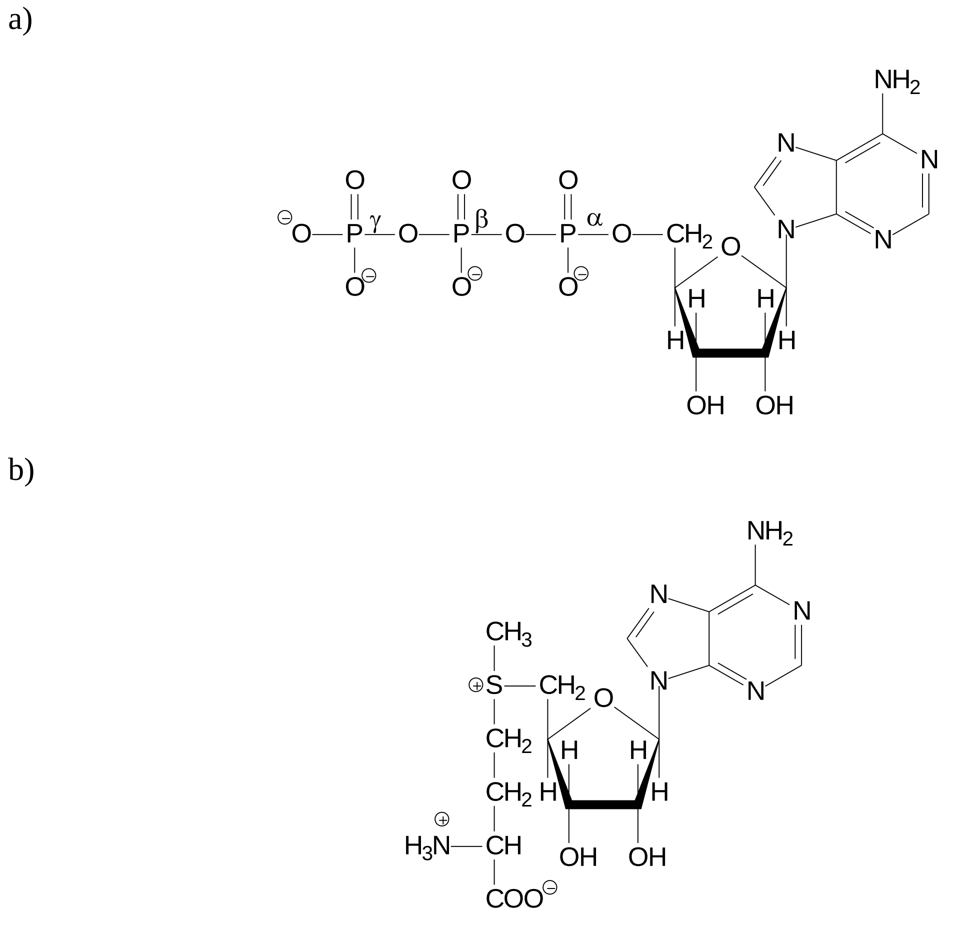


Figure 1. a) Nitrogen base adenine is connected to the ribose which carries three phosphoryl groups. Transfer of the phosphoryl group gives ADP, and the transfer of nucleotidyl group (AMP) gives pyrophosphate; b) *S*-adenosyl methionine

The most usual reaction involving ATP is the transfer of the phosphoryl group. In the reactions catalyzed by enzymes, for example, γ-phosphoryl group ATP is transferred to the nucleophile, leaving ADP. The second most usual reaction is a transfer of the nucleotidyl group (transfer of AMP part), leaving pyrophosphate (PP_i).

S-adenosyl methionine (Figure 1b) is synthesized in the reaction of methionine with ATP. Different from a thiomethyl group of methionine, positively charged sulfonium *S*-adenosyl methionine is highly reactive, so it reacts readily with nucleophilic acceptors, and practically it is a donor of all methyl groups used in biosynthetic reactions (*e.g.*, conversion of hormone norepinephrine into epinephrine). Methylation reactions which require *S*-adenosyl methionine involve methylation of phospholipids, proteins, DNA, and RNA. In plants, *S*-adenosyl methionine is involved in the regulation of fruit ripening as a precursor of plant hormone ethylene (Chiang et al., 1996).

Nucleotide-sugar coenzymes are involved in the metabolism of carbohydrates. The most common nucleotide sugar, uridine diphosphate glucose (UDP-glucose) is formed in the reaction of glucose 1-phosphate with uridine triphosphates (UTP) (Figure 2). UDP-glucose can donate its glycosyl group to the corresponding acceptor releasing UDP. UDP-glucose is regenerated when UDP accepted phosphoryl group from ATP and obtained UTP reacts with another molecule of glucose-1-phosphate.

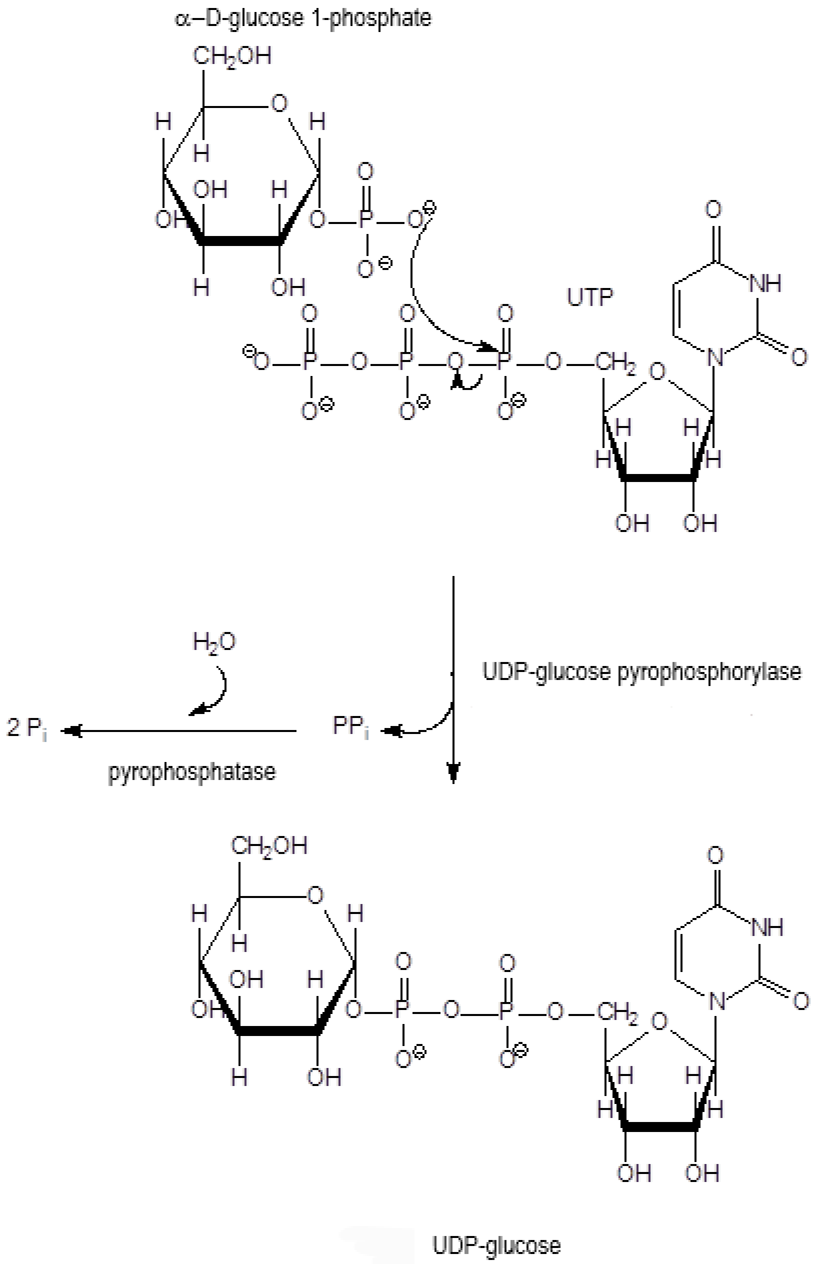


Figure 2. The formation of UDP glucose catalyzed with UDP-glucose phosphorylase (Horton et al., 2006)

In the mechanism of the formation of UDP glucose, the oxygen of the phosphoric group of α-D-glucose 1-phosphate attacks α-phosphorus of UTP. The released PP_i is hydrolyzed fast to 2 P_i by the action of pyrophosphatase. This hydrolysis enables the occurring of the reaction catalyzed by pyrophosphorylase.

NAD$^+$ and NADP$^+$

Nicotinamide coenzymes are nicotinamide adenine dinucleotide (NAD$^+$) and nicotinamide adenine dinucleotide phosphate (NADP$^+$). The both contain nicotinamide (Figure 3a).

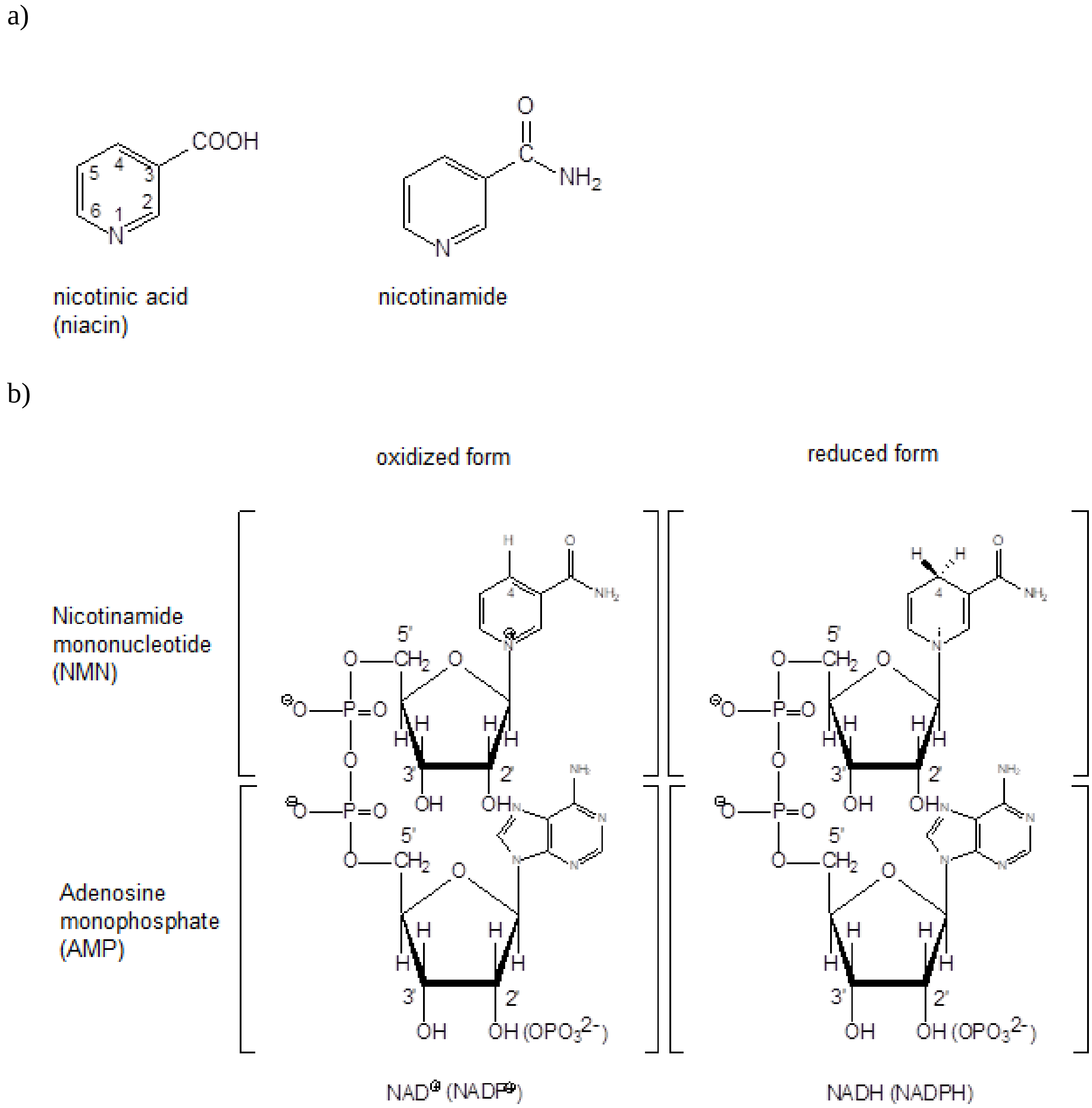


Figure 3. a) Nicotinic acid (niacin) and nicotinamide; b) Oxidation and reduction forms of NAD (and NADP)

The deficiency of nicotinic acid (niacin) causes the pellagra disease. Nicotinic acid or nicotinamide is essential as a precursor of NAD^+ and $NADP^+$ (pyridine nucleotide coenzymes) (Figure 3b) (Sorci et al., 2010). Nicotinamide coenzymes play a role in numerous oxidation-reduction reactions in the form of electron transfers from and to the metabolite. Pyridine ring NAD^+ is reduced by the addition of hydride ion onto C-4 when NAD^+ is transformed into NADH (and when $NADP^+$ is transformed into NADPH) (Sorci et al., 2010).

NAD^+ and $NADP^+$ almost always behave as dehydrogenase substrates (Bellamacina, 1996). Dehydrogenase catalyzes the oxidation of the substrate by transferring two electrons and proton in the form of hydride ion (H^-) onto C-4 of nicotinamide group NAD^+ and $NADP^+$. In this way, the reduced forms are formed (NADH and NADPH), where new C-H bond is created on C-4 (Bellamacina, 1996).

NADH and NADPH (stable in solutions containing oxygen) possess reductive power (Kukielka and Cederbaum, 1990). The stability of reduced pyridine nucleotides allows them to carry their reduction potential from one enzyme to another; the characteristics not owned by flavin coenzymes. The majority of reactions in which NADH and NADPH are formed are catabolic reactions. The oxidation of NADH in mitochondria is coupled with ATP synthesis. The most significant part of NADPH is used as a reduction agent in biosynthetic reactions (Kukielka and Cederbaum, 1990).

NADH and NADPH show a maximum in ultraviolet region at 340 nm caused by dihydropyridine ring, while NAD^+ and $NADP^+$ do not absorb the light at this wavelength. The appearance and disappearance of the absorbance at 340 nm are useful for the measurement of the rate of the oxidation (McComb et al., 1976).

In the mechanism of the oxidation of lactate to pyruvate catalyzed by lactate dehydrogenase (Figure 4), the coenzyme accepts the hydride ion on C-4 in nicotinamide group. This phenomenon leads to the bond rearrangement in the ring when electrons are moving to the positively charged nitrogen atom. The enzyme represents acid-base catalyst and the suitable place for binding coenzyme, and the substrate as well. Two hydrogens are moving from the lactate to produce pyruvate. One of these hydrogens are moving to NAD^+ as a hydride ion bearing two electrons, and the another is transferring to His-195 as a proton. The second hydrogen is then releasing as H^+ to regenerate the base catalyst (His-195) (Kane, 2014; Speers and Reguera, 2012).

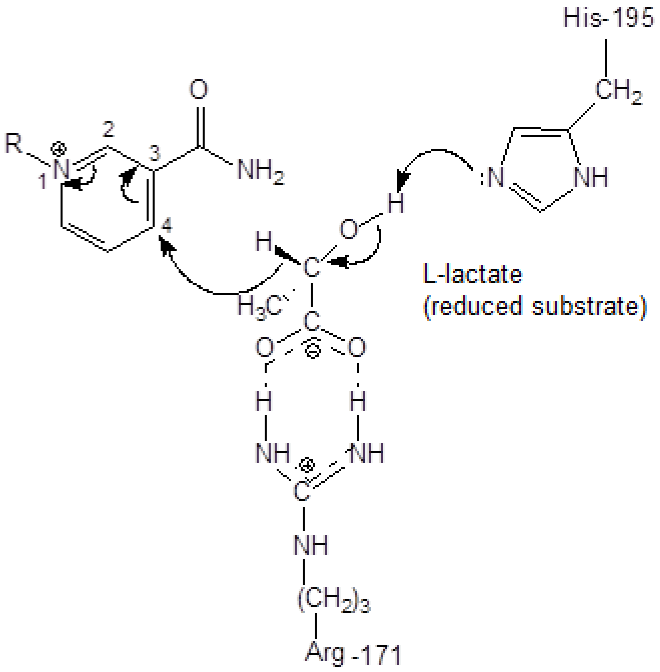


Figure 4. The mechanism of lactate dehydrogenase (Speers and Reguera, 2012)

FAD and FMN

Coenzymes flavin adenine dinucleotide (FAD) and flavin mononucleotide (FMN) are derived from riboflavin or vitamin B_2. Riboflavin is synthesized by bacteria, protozoa, fungi, plants and some animals. Mammals are getting riboflavin from food. Riboflavin consists from ribitol connected to N-10 atom of heterocyclic ring system called isoalloxazine (Figure 5a). Similarly to NAD^+ and $NADP^+$, FAD contains AMP and pyrophosphate bond (Figure 5b).

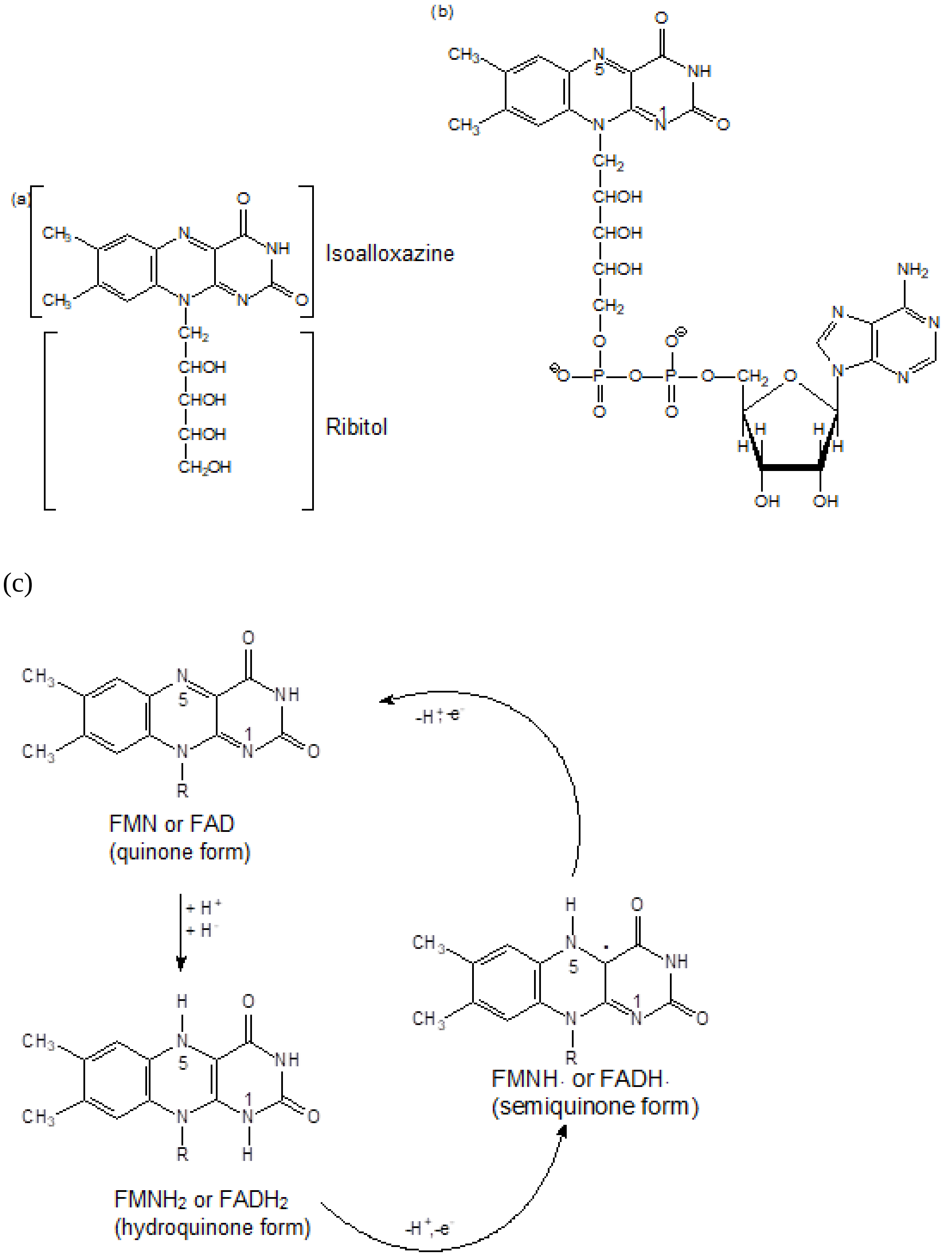


Figure 5. Riboflavin and its coenzymes. (a) Riboflavin; (b) Flavin mononucleotide (FMN) and flavin adenine dinucleotide (FAD); (c) Reduction and reoxidation of FMN or FAD

FAD or FMN are necessary as prosthetic groups for many oxidoreductases. Reduced flavin coenzymes can be easily oxidized in the presence of oxygen. FAD and FMN are reduced to $FADH_2$ and $FMNH_2$ by taking proton and two electrons in the form of hydride ion (Figure 5c). Oxidized enzymes are light yellow as a result of the system of conjugated double bonds of the isoalloxazine cyclic system. Different from NADH and NADPH, which exclusively participate in two-electron systems, $FMNH_2$ and $FADH_2$ are donated electrons (one (FADH· or FMNH· are formed) or two). The intermediates are relatively stable free radicals called semiquinones. Oxidation of $FADH_2$ and $FAMNH_2$ is often coupled with the reduction of metalloproteins containing Fe^{3+} (in [Fe-S] cluster). Since iron-sulfur cluster can accept only one electron, reduced flavin must be oxidized into two one-electron steps *via* semiquinone intermediate (Ghisla and Massey, 1989).

Coenzyme A

Numerous metabolic processes depend on coenzyme A (CoA, or HS-CoA), including the oxidation of fuel molecule and biosynthesis of some carbohydrates and fats. The coenzyme is involved in the reactions of acyl group transfers (Leonardi et al., 2005). It has three main components: 2-mercaptoethylamine unit with free -SH group, pantothenate vitamin (vitamin B_3), and ADP part (Figure 6a). Acetyl CoA is energetically rich compound because of the high energy of thioester bond.

Phosphopantetheine, phosphate ester which contains 2-mercaptoethylamine and pantothenate parts of coenzyme A, is a prosthetic group of a small protein (77 amino acid residues), known as an acyl carrier protein (ACP). The prosthetic group is esterified to ACP *via* oxygen in the side chain of a serine residue (Figure 6b). The intermediates acetylate SH of the prosthetic group ACP in the fatty acids' biosynthesis (Leonardi et al., 2005).

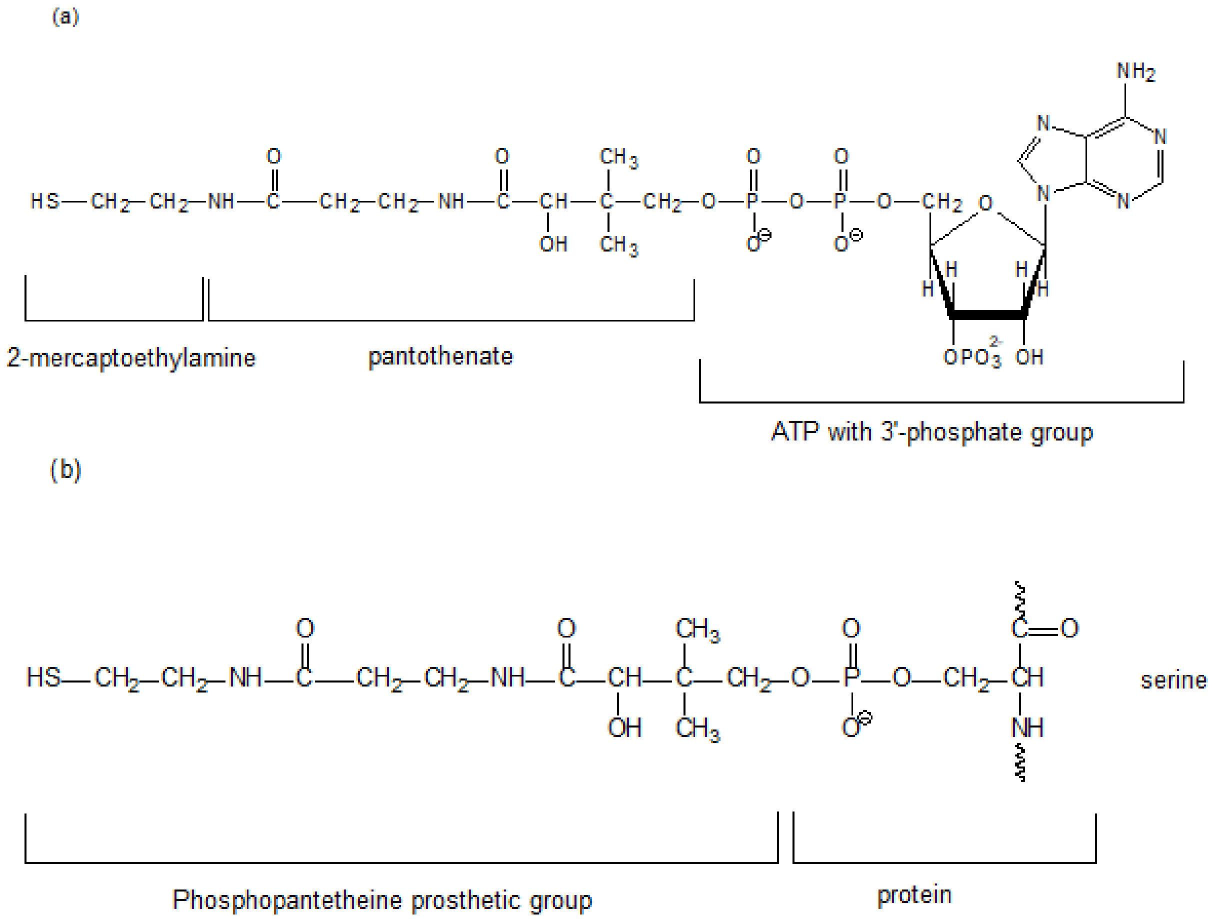


Figure 6. (a) Coenzyme A; (b) Acyl carrier protein (ACP)

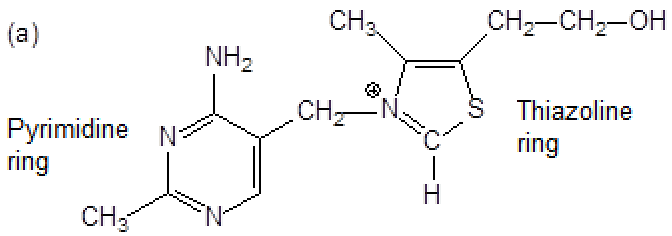
Thiamine pyrophosphate

Thiamine (or vitamin B$_1$) contains pyrimidine ring and positively charged thiazoline ring (Figure 7a). In mammals, thiamine is the essential vitamin, wide-spread in the rice peel and other wheat. Its deficiency causes beriberi. Coenzyme is the thiamine pyrophosphate (TPP) (Figure 7b). TPP is synthesized from thiamine by the enzymatic transfer of pyrophosphoryl group from ATP (Shepard and Broderick, 2010).

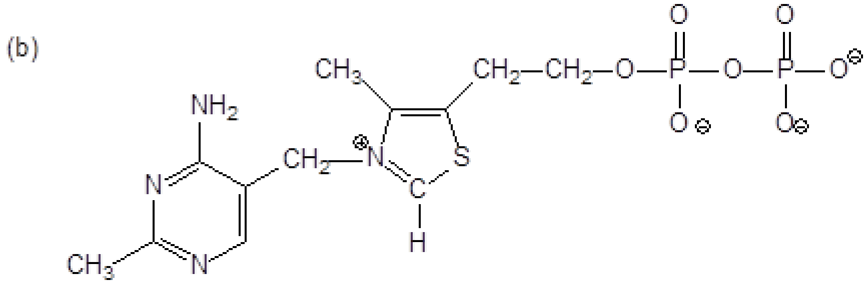
Numerous decarboxylases (carboxylases) require TPP as a coenzyme (*e.g.*, pyruvate decarboxylase of the yeast) (Figure 7c).

TPP is also the coenzyme involved in oxidative decarboxylation of α-keto acids, except for pyruvates. The first steps in these reactions are occurring according to the mechanism shown in

Figure 7c. Besides, TPP is a prosthetic group for the enzymes known as transketolases, which catalyze the transfer between the sugar molecules of two carbon groups containing keto group.



Thiamine (vitamin B_1)



Thiamine pyrophosphate (TPP)

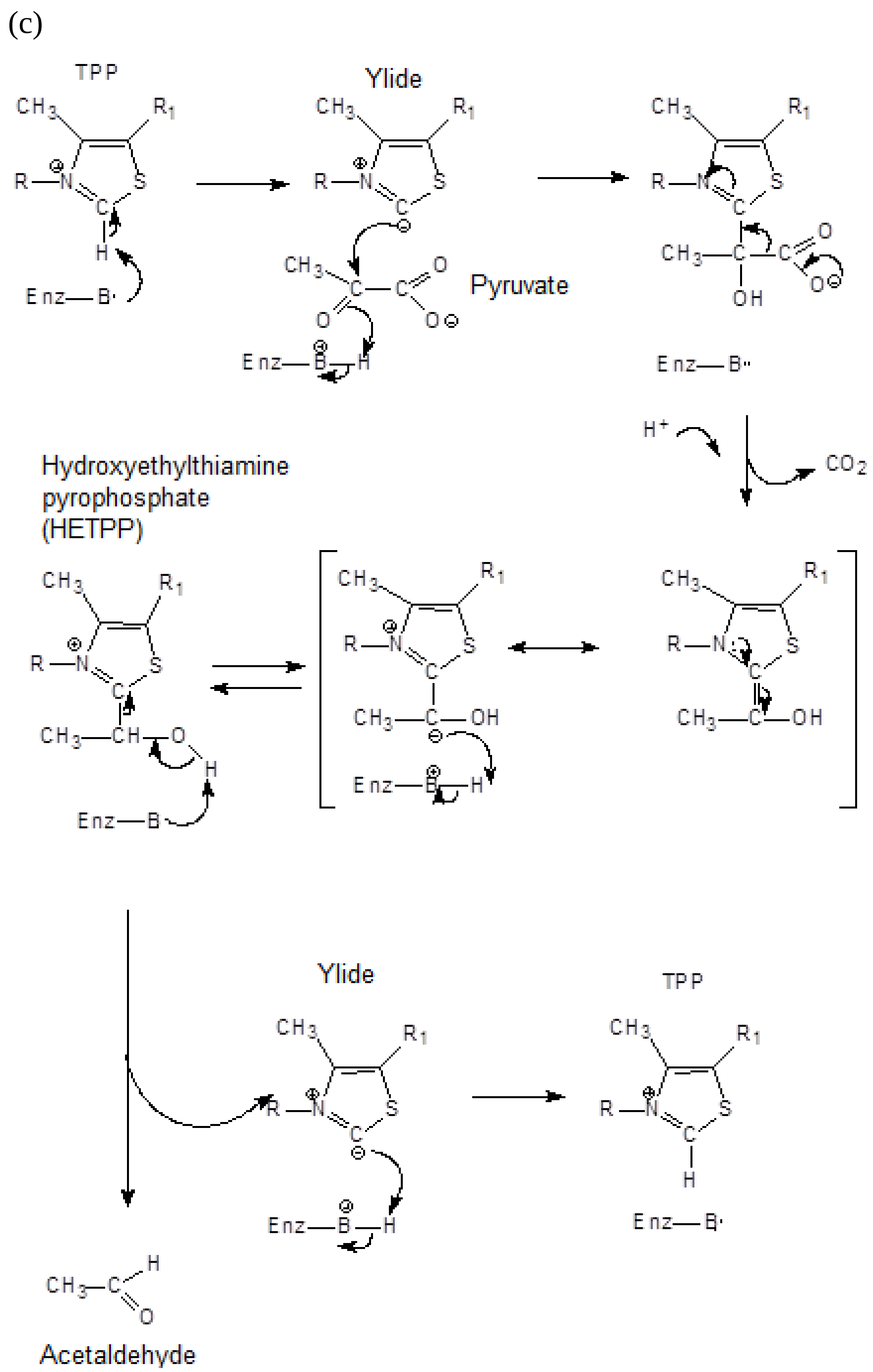


Figure 7. (a) Thiamine (vitamin B_1); (b) Thiamine pyrophosphate (TPP); (c) The mechanism of pyruvate decarboxylase from the yeast

Thiazoline ring of the coenzyme contains the reactive center. C-2 of TPP has unusual activity; it is acidic despite high pK_a in aqueous solution. Experiments show that pK_a value for the ionization of hydroxyethylamine pyrophosphate (HETPP) (*i.e.*, forming of dipolar carbanion) changes from 15 in water to 6 on the active center of pyruvate decarboxylase. This increased acidity is ascribed to low polarity of active center, which is also responsible for the increased reactivity of TPP itself. The positive charge of thiazoline ring of TPP attracts electrons, weakening the bond between C-2 and hydrogen. The proton is mostly removing by base part of the enzyme. Ionization gives resonantly stable dipolar carbanion known as ylide. Negatively charged C-2 attacks electron-deficit carbonyl carbon of pyruvate substrate, and the first product (CO_2) is releasing. Two carbons of pyruvate are now attached to thiazoline ring as a part of resonance-stabilized carbanion. In the next step, the protonation of carbanion gives hydroxyethylamine pyrophosphate (HETPP). HETPP is separating, releasing acetaldehyde (the second product). TPP is forming again when ylide is protonating from the side of the enzyme (Figure 7c) (Shepard and Broderick, 2010).

Pyridoxal phosphate

The family of B_6 vitamins soluble in water consists of three closely connected molecules differing only in the state of the oxidation or amination of the carbon bound to the position 4 of the pyridine ring (Figure 8a). Induced deficiency of vitamin B_6 in mice causes dermatitis and various disorders connected to the metabolism of proteins; deficiencies of vitamin B_6 in humans are rare. Once B_6 enters the cell, enzymatic transfer of γ-phosphoryl group from ATP forms coenzyme pyridoxal 5’-phosphate (PLP) (Figure 8b) (Hayashi et al., 1990).

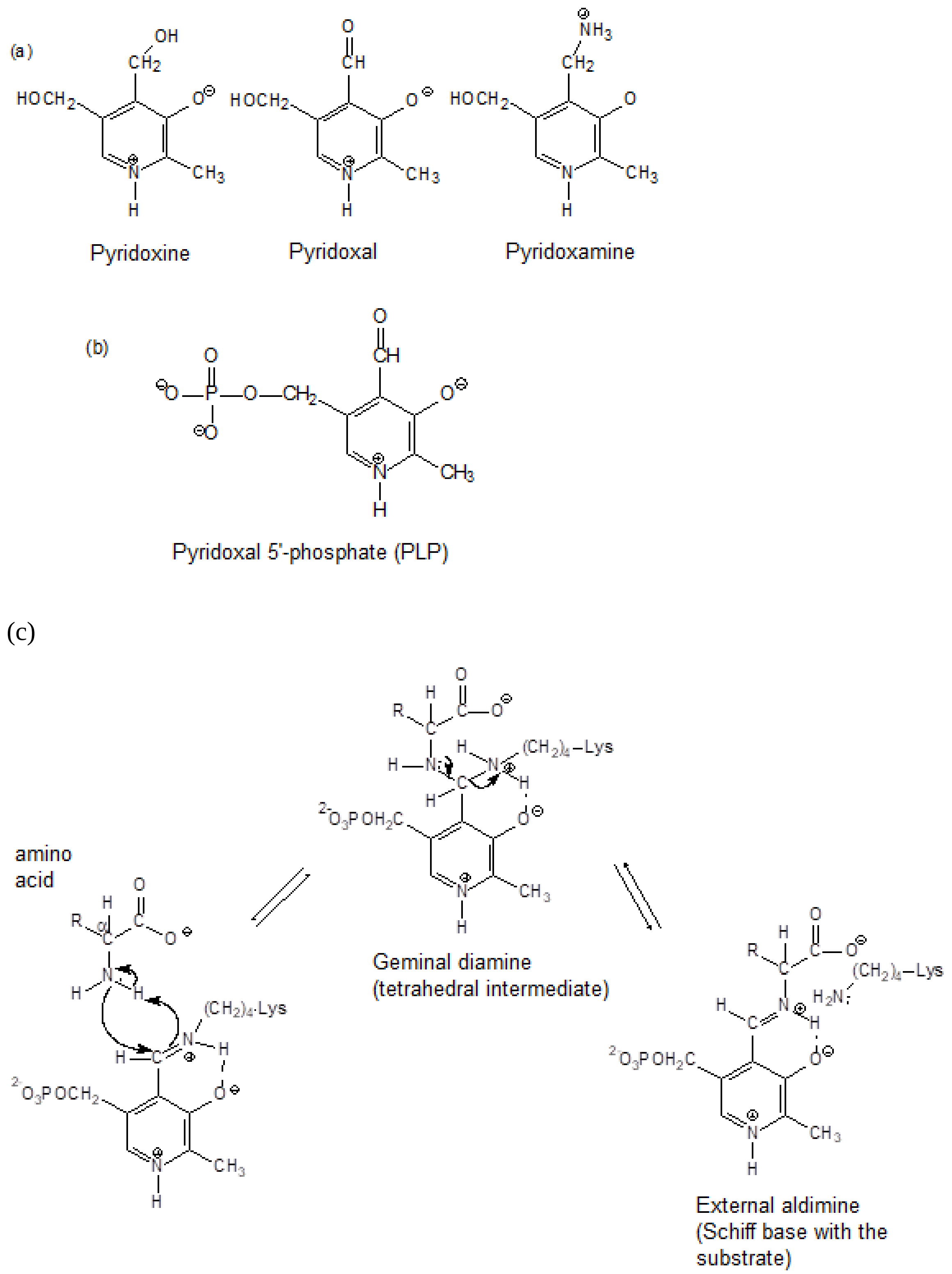


Figure 8. (a) Vitamins of B_6 family: pyridoxine, pyridoxal, and pyridoxamine; (b) Pyridoxal 5'-phosphate (PLP); (c) The binding of the substrate to the PLP-dependent enzyme

Pyridoxal phosphate is a prosthetic group for many enzymes which catalyze different reactions, including isomerizations, decarboxylations, and eliminations in side chain or substitutions. In enzymes dependent on PLP, the carbonyl group of the prosthetic group is binding as Schiff base (imine) for ε-amino group of a lysine residue in the active center (Figure 8c) (Hayashi et al., 1990; Horton et al., 2006).

Transamination is most frequently dependent reaction on PLP, and the mechanism of this type of the reaction is presented in Figure 9.

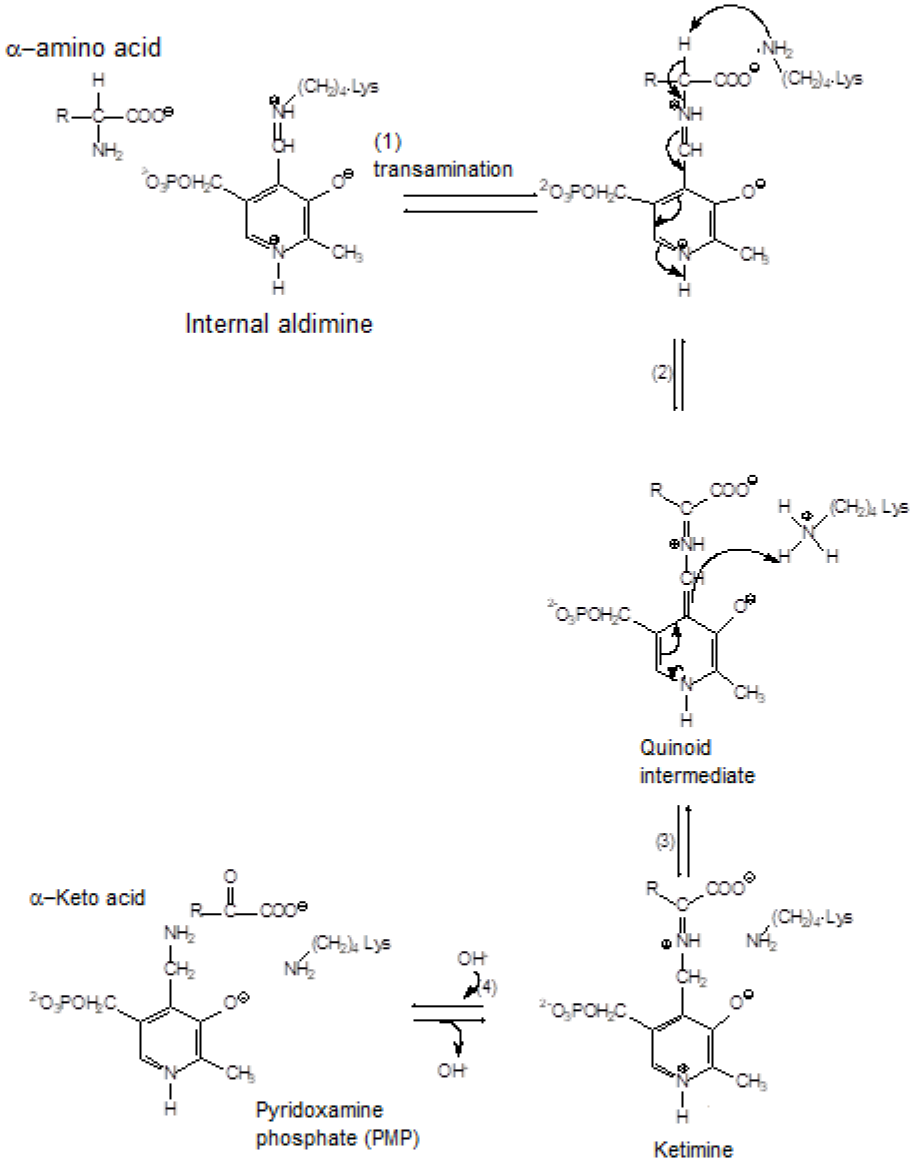


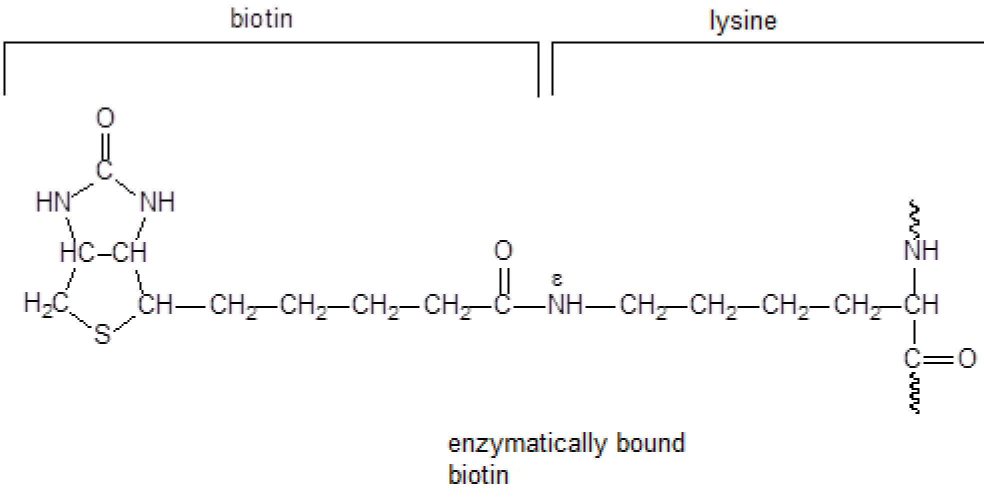
Figure 9. The mechanism of transaminase (Horton et al., 2006)

In the first step of the mechanism, amino acid replaces lysine from internal aldimine which binds PLP for the enzyme forming the external aldimine. In the second step, α-hydrogen of the amino acid is taken with the base catalyst by the same lysine residue. Electronic rearrangement leads to the quinoid intermediate. In the third step, the protonation of the intermediate with the lysine residue gives ketoimine. In the fourth step, hydrolysis of the ketoimine gives α-keto acid, which dissociates, and PMP remains bound to the enzyme. If another α-keto acid enters, each step goes in reverse. The amino acid is transferred to α-keto acid, giving new amino acid and regenerates the original PLP form of the enzyme (Figure 9) (Hayashi et al., 1990; Horton et al., 2006).

Biotin

Biotin is a prosthetic group for enzymes which catalyze the reactions of the transfer of carboxyl group and the reaction of carboxylation dependent on ATP. It is covalently bound to the active center of its enzyme host by amide bond for ε-amino group of a lysine residue (Figure 10a).

(a)



(b)

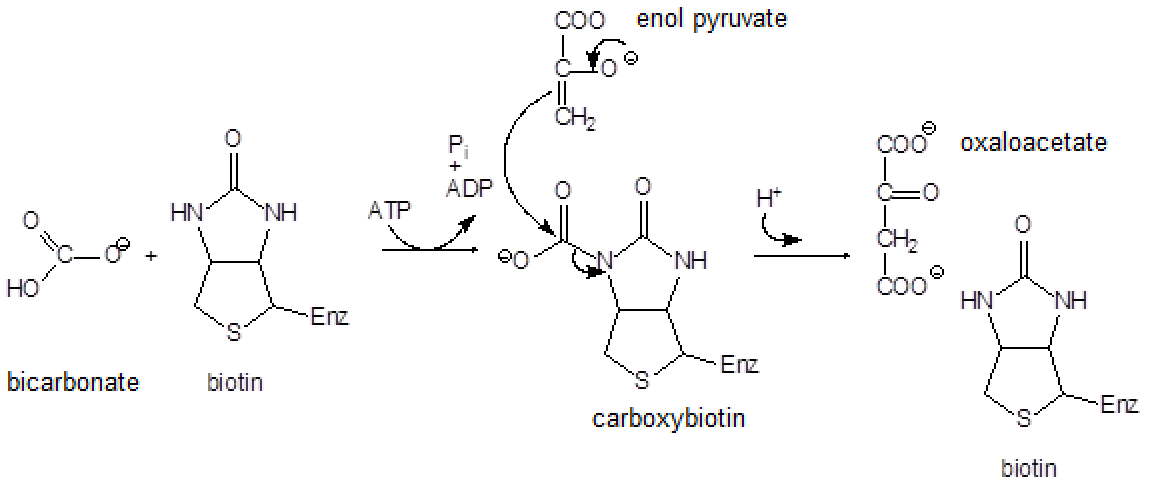


Figure 10. (a) Enzymatically bound biotin. (b) The reaction catalyzed by pyruvate carboxylase (Knowles, 1989)

The reaction of pyruvate carboxylase demonstrates the role of biotin as a carrier of carbon dioxide (Figure 10b). Firstly, bicarbonate and ATP react forming carboxybiotin. Carboxybiotinyl-enzyme complex gives stable activated form CO_2 which can be transferred to the pyruvate. Then the enolate form of the pyruvate attacks carboxyl group of carboxybiotin, forming oxaloacetate and regenerated biotin (Figure 10b).

The biotin is synthesized in intestine bacteria, and it is necessary in micrograms daily, so the deficiency of biotin is rare in humans or animals with regular feeding.

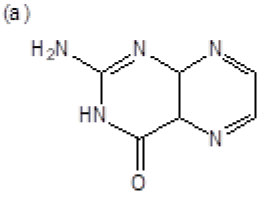
Different laboratory techniques use high affinity of avidin for biotin. For example, the substance for which biotin is covalently bound can be extracted from the complex mixture by affinity chromatography on the column immobilized with avidin (Hsu, 1985).

Tetrahydrofolate

Vitamin folate is isolated for the first time in the early 1940s from green leaves, liver, and yeast. Folate has three main components: pterin (2-amino-4-oxopteridine) (Figure 11a), the residue of *p*-aminobenzoic acid, and residue of the glutamate. Humans need folate in nutrition because they are not in the position to synthesize pterin-*p*-aminobenzoic acid intermediate (PABA) (Wallig and Keenan, 2013).

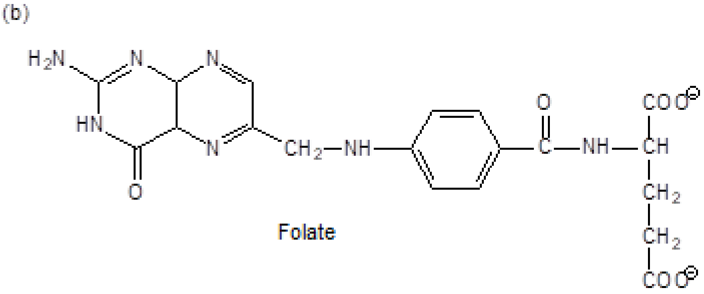
Coenzyme formed from the folate (Figure 11b) is known as tetrahydrofolate (Figure 11c) (Wallig and Keenan, 2013).

(a)

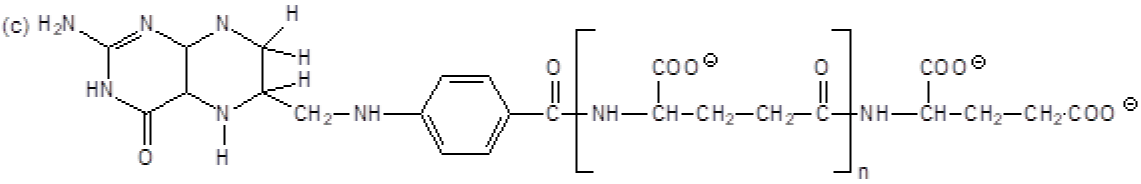


Pterin
(2-amino-4-oxopteridine)

(b)



Folate



Tetrahydrofolate (tetrahydrofolyl polyglutamate)

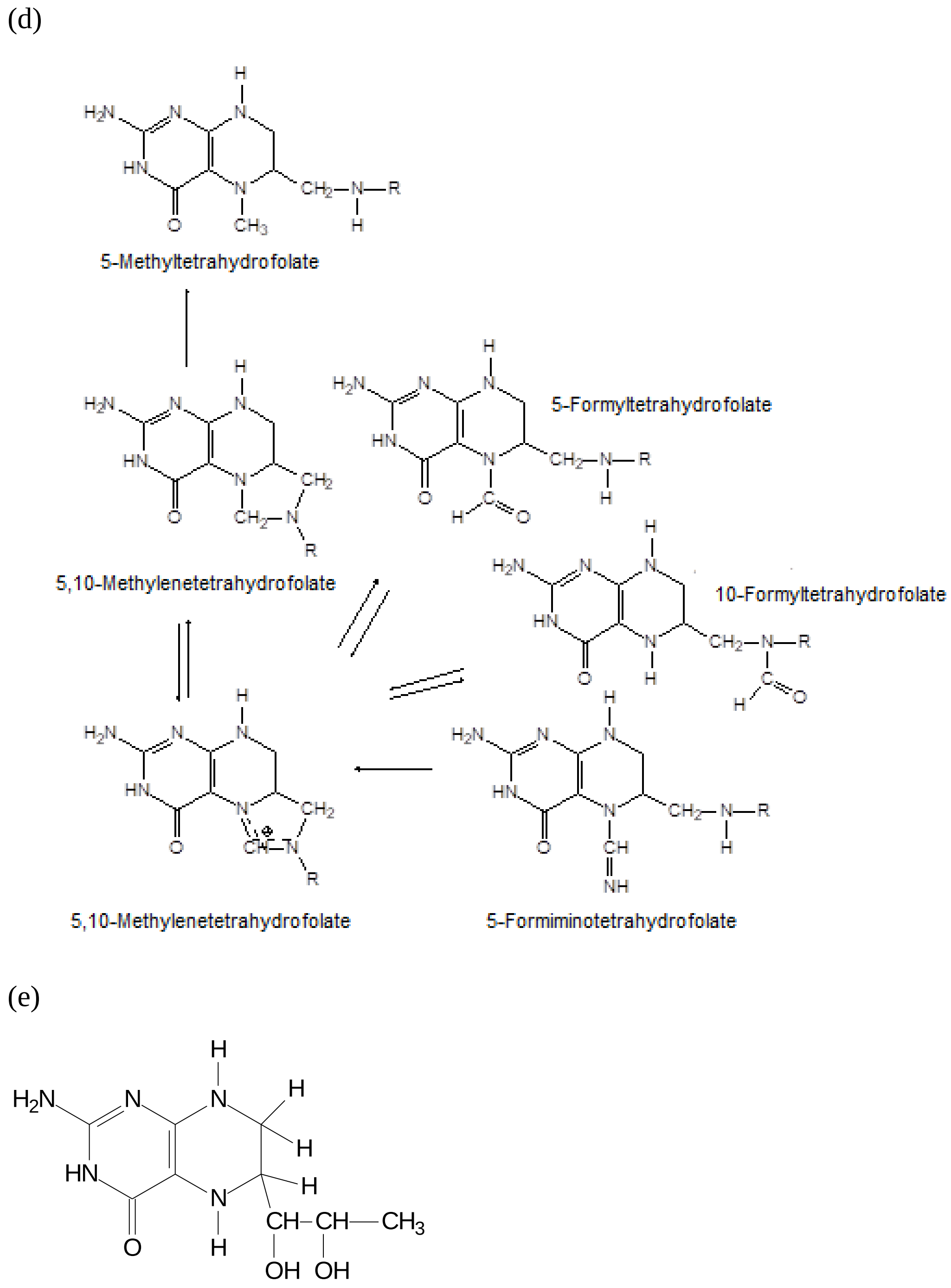


Figure 11. (a) Pterin; (b) Folate; (c) Tetrahydrofolate; (d) Monocarbonic derivatives of tetrahydrofolates; (e) 5,6,7,8-tetrahydrobiopterin

The anionic polyglutamic residue, usually five to six residues long, takes part in the binding of coenzymes for enzymes (Wallig and Keenan, 2013).

Tetrahydrofolate is formed by the addition of hydrogens into positions 5, 6, 7 and 8 of pterin cyclic system.

The reduction of dihydrofolate obtained during the formation of the methyl group of thymidylates (dTMP) is the primary metabolic function of dihydrofolate reductase. This reaction which uses derivative of tetrahydrofolate is the essential step in the synthesis of DNA. Because the cell division cannot be achieved when DNA synthesis is stopped, dihydrofolate reductase is intensively studied as an aim in chemotherapy for cancer treatment (Horton et al., 2006).

5,6,7,8-tetrahydrofolate is necessary to enzymes which catalyze biochemical transfers of several monocarbon units. The groups bound to tetrahydrofolate are methylene, methyl, and formyl. Figure 11d shows the structure of several monocarbon derivatives of tetrahydrofolate and enzymatic interconversion happens between them (Horton et al., 2006).

Monocarbonic metabolic groups are covalently bound for the secondary amine N-5 or N-10 of tetrahydrofolates, or both in cyclic form. 10-Formyltetrahydrofolate is a donor of formyl groups, and 5,10-methylenetetrahydrofolate is the donor of hydroxymethyl groups (Figure 11d).

The second pterin coenzyme, 5,6,7,8-tetrahydrobiopterin has a side chain with three carbons on C-6 pterin part instead of long side chain which is situated in tetrahydrofolate (Figure 11e) (Wallig and Keenan, 2013). This coenzyme is not derived from vitamin; it is synthesized by animals alone and by other organisms. Tetrahydrobiopterin is a cofactor for several hydroxylases, and it is a reducing agent in the conversion of phenylalanine to tyrosine. Also, it is necessary to the enzyme which catalyzes the synthesis of nitrogen oxide from arginine.

Cobalamin

Cobalamin (vitamin B_{12}) is the biggest B vitamin, and it is last isolated. The structure of cobalamin includes corrin ring system which is similar to the porphyrinic cyclic system of heme. Cobalamin contains cobalt instead of iron which is situated in heme. In coenzyme form of cobalamin, R group is either methyl group (in methyl-cobalamin) or 5’-deoxyadenosyl group (in adenosylcobalamin) (Banerjee and Ragsdale, 2003).

Cobalamin is necessary as a micro substance to all animals and some bacteria and algae, but it is not necessary for plants, and they are not synthesizing them. Thus, humans will generally get vitamin B_{12} from food of animal origin. Vegetarians are getting appropriate quantity from microorganisms. The cobalamin deficiency can cause anemia, potentially fatal diseases in which there is decreasing in the production of blood cells by bone marrow. This type of anemia can lead to neurological disorders. Majority of victims of this anemia do not excrete necessary glycoprotein (called internal factor) (Arsic et al., 2016).

The role of adenosylcobalamin reflects the reactivity of C-Co bond. The coenzyme takes part in several intramolecular rearrangements catalyzed by enzymes where hydrogen atom and another group bound to the neighboring carbon atoms inside the substrate, by exchanging places (Figure 12a). The example is methyl malonyl-CoA mutase reaction (Figure 12b), important in the fatty acids' metabolism containing an odd number of carbon atoms, which leads to the formation of succinyl CoA, intermediate in the chain of citric acid (Banerjee and Ragsdale, 2003).

Methylcobalamin takes part in the transfer of methyl groups and the regeneration of methionine from homocysteine in mammals. In this reaction, the methyl group of 5-methyltetrahydrofolate transits into reactive, reduced form of cobalamin creating methylcobalamin, which can transfer a methyl group to thiol chain of homocysteine.

The third group of cobalamin enzymes is reduced dehalogenase dependent on vitamin B_{12}. They are bacterial enzymes making detoxication of chlorinated organic molecules including PCB (Banerjee and Ragsdale, 2003; Horton et al., 2006).

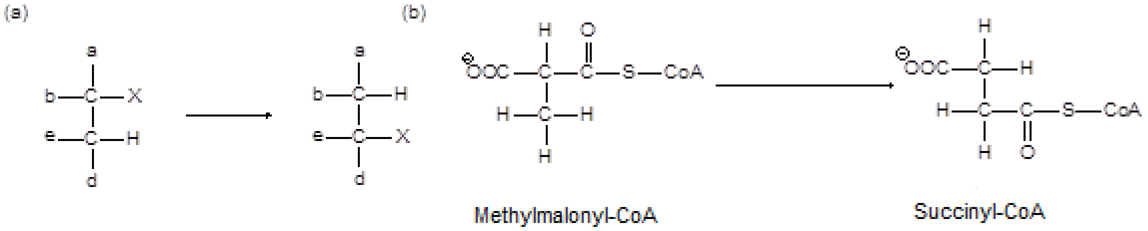


Figure 12. (a) The rearrangement in which hydrogen atom and the substituent on a neighboring carbon atom are exchanging places; (b) The rearrangement of methyl malonyl CoA in succinyl CoA, catalyzed with methyl malonyl-CoA mutase (Horton et al., 2006)

Lipoamide

Coenzyme lipoamide is a protein binding form of lipoic acid. Although lipoic acid is often described as vitamin B, it seems that the animals are capable of synthesizing it. It is necessary for particular bacteria and protozoa to grow (Figure 13) (Shen et al., 2011).

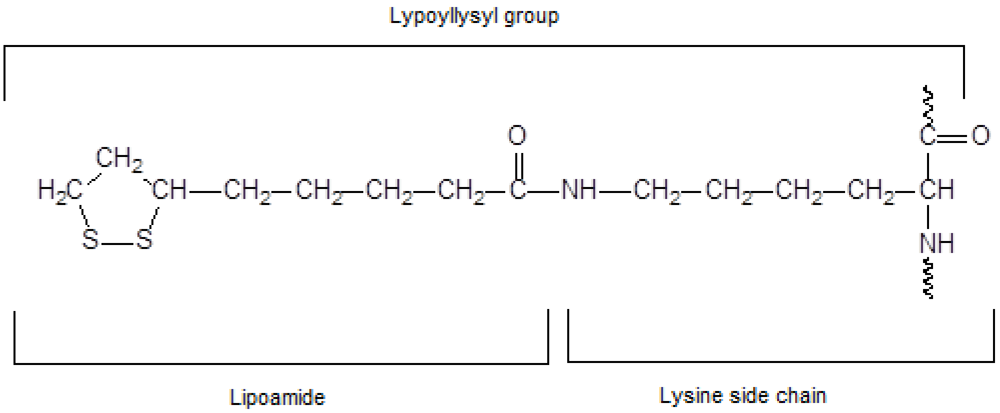


Figure 13. Lipoamide

It is believed for lipoamide to function as a pendulum which carries acyl groups between active centers in multi-enzymatic complexes. For example, in complex of pyruvate dehydrogenase, disulfide ring of lipoamide prosthetic group reacts with HETPP, binding its acetyl group on sulfur atom attached to C-8 of lipoamide and creating thioester. Then, the acyl group is moved to the sulfur atom of coenzyme A giving reduced (dihydrolipoamide) form of prosthetic group.

The last step catalyzed by pyruvate dehydrogenase complex is the oxidation of dihydrolipoamide. In this reaction, NADH is formed by the action of the flavoprotein component of the complex. The actions of multiple coenzymes of pyruvate dehydrogenase complex show how coenzymes supplying reactive groups and thus increasing catalytic diversity of proteins are used for storing energy and carbon building blocks (Horton et al., 2006; Shen et al., 2011).

Ubiquinone

Ubiquinone (coenzyme Q) (Figure 14a) is a coenzyme soluble in fats synthesized by all species. In the membrane, ubiquinone transports electrons between enzymatic complexes situated in the membrane. Some bacteria use menaquinone instead of ubiquinone. Ubiquinone analog called plastoquinone (Figure 14b) has a similar function in the photosynthetic transport of electrons in chloroplasts (DiNicolantonio et al., 2015).

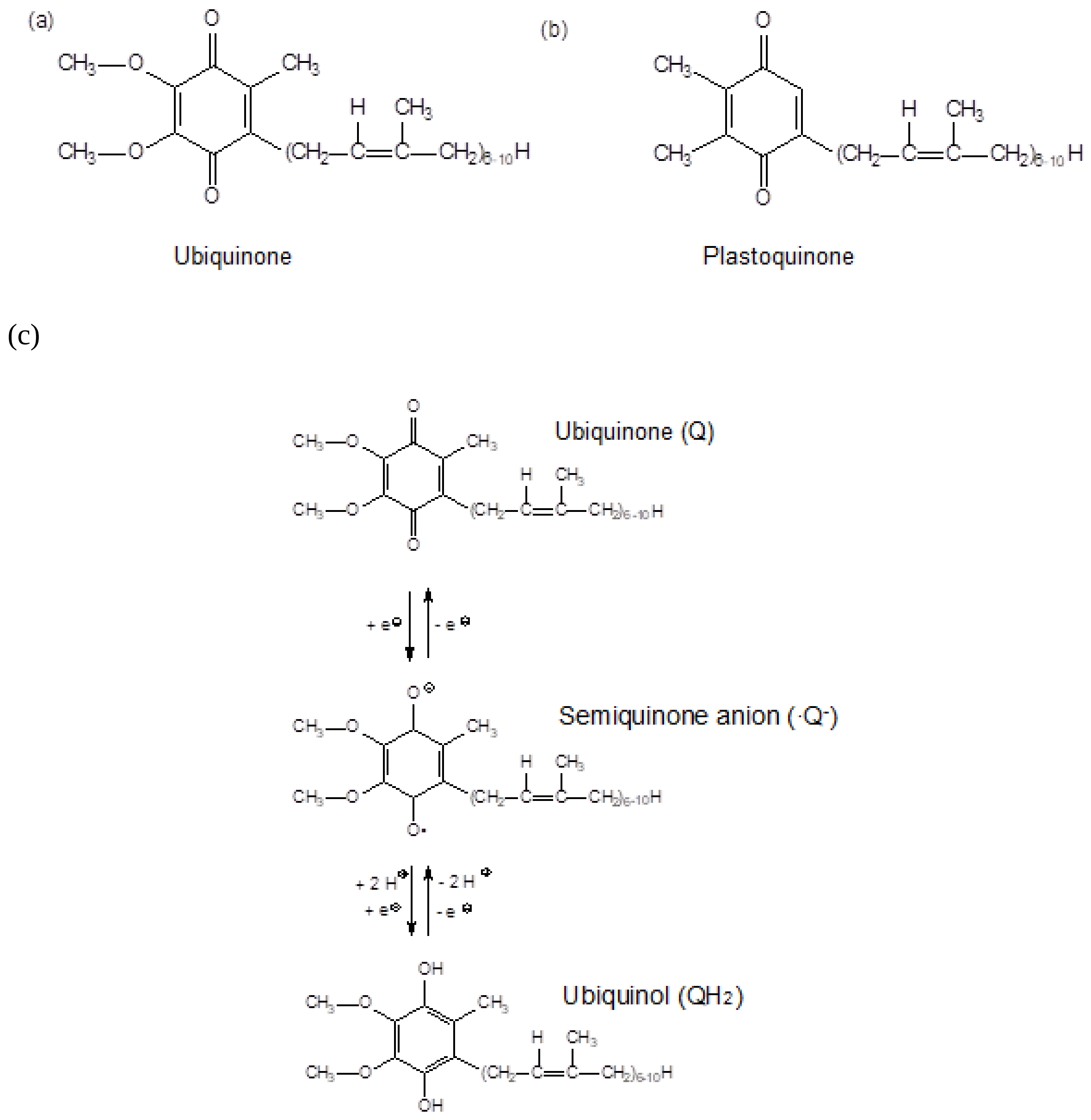


Figure 14. (a) Ubiquinone; (b) Plastoquinone; (c) Three oxidation states of ubiquinone

Ubiquinone is a stronger oxidation reagent than both NAD$^+$ and flavin coenzymes. Similarly to FMN and FAD, ubiquinone can accept or donate electrons (one or two) because it has three oxidation states: oxidized Q, partially reduced semiquinone free radical and completely reduced QH_2 (ubiquinol) (Figure 14c) (Sohal, 2004).

Coenzyme Q plays the leading role in the electron transport connected to the membrane. It is responsible for the moving of protons from one side of the membrane to another by the process known as cycle Q. The created protein gradient leads to ATP synthesis (Lenaz et al., 2007).

Protein coenzymes

Some proteins behave as coenzymes. They do not catalyze reactions, but they are necessary from specific enzymes. These enzymes are called either protein for groups transfer or protein coenzymes. They contain functional group either as a part of their protein skeleton or as a prosthetic group (Horton et al., 2006).

Metal ions, iron-sulfur clusters, and heme groups are reactive centers usually found in these protein coenzymes. Several protein coenzymes have two reactive centers. Thioredoxins are observed as reduction agents (cycle of citric acid, photosynthesis, and synthesis of deoxyribonucleotides). Disulfide reactive center of thioredoxin is on the surface of the protein, so it is available to the active centers of corresponded enzymes (Horton et al., 2006; Johnson et al., 2014).

Cytochromes

Cytochromes are protein coenzymes containing heme where Fe (III) atoms undergo reversible one-electron reduction. They are classified as *a*, *b* and *c* based on their visible absorption spectra. Heme of cytochrome *b* type is the same as that of hemoglobin and myoglobin. Heme of cytochrome *a* has a hydrophobic chain of 17 carbons on C-2 porphyrin ring and formyl group on C-8, while heme of type *b* has a vinyl group attached on C-2 and methyl group on C-8. In cytochromes of type *c*, the heme is covalently bound to apoprotein with two thioester bonds formed by the addition of thiol groups of two cysteine residues for vinyl groups of the heme (Heldt and Piechulla, 2011).

The tendency to transfer an electron to another substance, measured as a reductive potential, also varies among cytochromes. The range of reduction potentials among prosthetic groups is an essential property of membrane-connected electron transferred cycles and biosynthesis (Heldt and Piechulla, 2011).

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Mehanizmi delovanja koenzima

Biljana Arsić

Univerzitet u Nišu, Prirodno-matematički fakultet, Departman za hemiju, Višegradska 33, 18000 Niš, Republika Srbija, e-mail: ba432@ymail.com

SAŽETAK

Svaka živa vrsta koristi koenzime u brojnim važnim reakcijama katalizovanih enzimima. Postoje dva tipa koenzima u zavisnosti od interakcije sa apoenzimima: koenzimi često nazivani kosupstratima i koenzimi poznati kao prostetične grupe. Glavne metaboličke uloge kosupstrata (adenozin trifosfata (ATP), *S*-adenozil metionina, uridin difosfat glukoze, nikotinamid adenin dinukleotida (NAD^+) i nikotinamid adenin dinukleotid fosfata ($NADP^+$), koenzima A (CoA), tetrahidrofolata i ubihinona (Q)) i prostetičnih grupa (flavin mononukleotid (FMN) i flavin adenin dinukelotida (FAD), tiamin pirofosfata (TPP), piridoksal fosfata (PLP), biotina, adenozilkobalamina, metilkobalamina, lipoamida, retinala, i vitamina K) su opisane u ovom revijalnom radu.

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Mécanismes d'action des coenzymes

Biljana Arsic

Université de Nis, Faculté des sciences et mathématiques, Département de chimie, Visegradska 33, 18 000 Nis, Serbie

RÉSUMÉ

Chaque espèce vivante utilise des coenzymes dans de nombreuses réactions importantes catalysées par des enzymes. Il existe deux types de coenzymes en fonction de leur interaction avec les apoenzymes : les coenzymes fréquemment appelés les co-substrats et les coenzymes connus comme les groupes prosthétiques. Dans cet article, nous proposons la description des rôles essentiels métaboliques des co-substrats (adénosine triphosphate (ATP), *S*-adénosyl méthionine, uridine diphosphate glucose, nicotinamide adénine dinucléotide (NAD^+) et nicotinamide adénine dinucléotide phosphate ($NADP^+$), coenzyme A /CoA/, tétrahydrofolate et ubiquinone (Q)) et des groupes prosthétiques (flavine mononucléotide (FMN) et flavine adénine dinucléotide (FAD), thiamine pyrophosphate (TPP), phosphate de pyridoxal (PLP), biotine, adénosylcobalamine, méthylcobalamine, lipoamide, rétinal et vitamine K).

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Механизмы действия коферментов

Биляна Арсич

Университет в Нише, Факультет естественных наук и математики, Химический департамент, Вышеградская 33, 18000 Ниш, Республика Сербия

АННОТАЦИЯ

Каждый живой вид использует коферменты во многих важных реакциях, катализируемых ферментами. Существует два типа кофермента в зависимости от взаимодействия с апоферментами: коферменты, часто называемый ко-субстратами, и коферменты, известные как простетические группы. Основные метаболические роли ко-субстратов (аденозинтрифосфатов АТФ), *S*-аденозилметионина, уридиндифосфат глюкозы, никотинамидадениндинуклеотида (NAD^+) и никотинамидадениндинуклеотидфосфата ($NADP^+$), коэнзима А (CoA), тетрагидрофолатина и убихинона (Q)) и простетических групп (флавин мононуклеотид (FMN) и флавин-адениндинуклеотида (FAD), тиаминпирофосфата (TPP), пиридоксальфосфата (PLP), биотина, аденозилкобаламина, метилкобаламина, липоамида, ретиналя, и витамина К) описаны в этой работе.

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Alginate: Applications in the modern world

Lazar N. Kulašević

University of Nis, Faculty of Science and Mathematics, Department of Chemistry, Višegradska 33, 18000 Niš, Serbia, e-mail: lazar.kulasevic@gmail.com

ABSTRACT

Alginate is a natural polysaccharide extracted from the cell walls of brown algae. Thanks to its biocompatibility, biodegradability, nontoxicity, and low cost, this biopolymer is widely applicable across various fields of biomedical science and bioengineering. Alginates are used as a gelling agent in food industry. Alginate hydrogels are an appealing scaffold material because of their resemblance with natural tissues. Consequently, alginates are widely used in tissue engineering and alginate gel beads as transport vehicles in drug delivery systems. Nonetheless, alginate hydrogels are used in nanotechnology to build artificial capillary blood vessels.

Keywords*: alginate, biopolymer, hydrogel, gel beads, drug delivery, tissue engineering*

Introduction

Alginate (ALG), a naturally occurring biopolymer commercially extracted from brown seaweeds (*Phaeophyceae* such as *Fucus*, *Laminaria*, *Ascophyllum*) (Rinuado, 2014), has a variety of applications in the modern world of which some will be discussed in this short review. ALG polymers are a family of linear unbranched polysaccharides made up of (1→4)-linked β-D-mannuronic acid (M) and α-L-guluronic acid (G) (Fig. 1a) residues. The fact that M and G are C5 epimers results in a switch-over of the monomer chair conformation, giving rise to all four possible glycosidic linkages (Draget, 1997). Therefore, three types of building blocks appear in polymer: MM, GG, and MG (Fig. 1b). When ALG is added to an aqueous solution of multivalent cations (*e.g.*, Ca^{2+}, Ba^{2+}, Cu^{2+}), chelation occurs and ionic hydrogel forms. The selective binding of multivalent cations is one of the most important properties of ALG, which is the basis for gel formation, and the fact that sol–to–gel conversion of alginates is not peculiarly influenced by temperature. In the most commonly used hydrogel, calcium alginate (Ca-ALG), the strong interaction between calcium ions and sugar residues create junction zones in the ALG network, in which, calcium is embedded into the GG blocks forming so-called egg-box model (Fig. 1c). Thus, the G/M ratio often determines the physicochemical properties of the hydrogel (Balać et al., 2010; Tønnesen and Karlsen, 2002; Tønnesen and Karlsen, 2011).

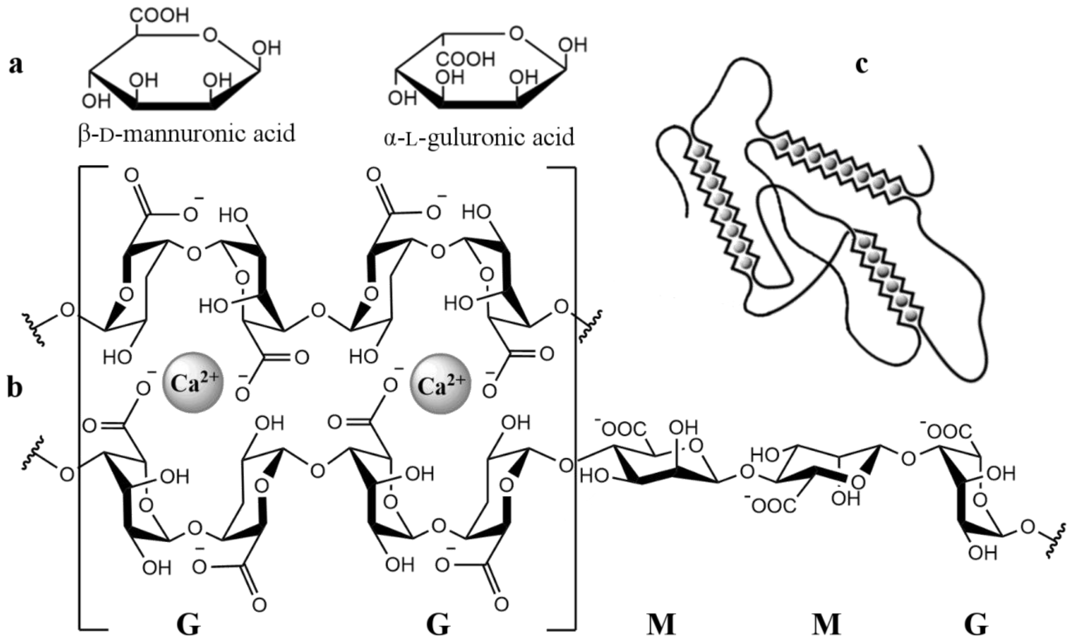

Figure 1. Monosaccharides (a), building blocks: GG, MM, and MG (b), and schematic crosslinking of Ca-ALG including the egg-box model (c).

Considering that ALG is generally regarded as safe by the U.S. Food and Drug Administration (FDA), it has been used commercially as a gelling agent in the food industry (Brownlee et al., 2009), pharmaceutical (Tønnesen and Karlsen, 2002), biomedical (Lee and Mooney, 2012), and personal care.

Preparation of alginate hydrogel

ALG gel beads are generally prepared by adding Na-ALG solution dropwise into an aqueous solution of $CaCl_2$. Gel strength and volume reduction of the beads increases with increasing concentration of the $CaCl_2$ solution up to 0.02M. For higher concentration of Ca^{2+}, the gel strength and volume reduction are approximately constant. The size of gel beads depends upon the type of ALG and the gelling conditions (Martinsen et al., 1989). Additionally, gelation could be activated by UV irradiation, as well. The approach involves a combination of an insoluble salt of the cation (*e.g.*, calcium carbonate, $CaCO_3$), an aqueous solution of ALG, and a photoacid generator. Upon exposure to UV light, the photoacid generator dissociates to release H^+ ions, which react with $CaCO_3$ to generate free Ca^{2+}. Photogellable ALG solutions are used for encapsulation of cells and calcium-sensitive biomolecules. Plus, the light-triggered gelation can be achieved in a local manner (Javvaji et al., 2011).

Alginate in drug delivery systems

ALG hydrogels are insoluble but swellable in an aqueous medium. Due to its moisture and resemblance with natural tissues, ALG hydrogel is an excellent candidate for drug delivery and tissue engineering (Ratner and Bryant, 2004; Tønnesen and Karlsen, 2002). ALG, being a polyanion, has the increased charge density giving rise to a greater mucoadhesion. In addition, ALG has the highest mucoadhesive strength in comparison to polymers such as polystyrene, chitosan, carboxymethylcellulose, and polylactic acid (George and Abraham, 2006).

The biocompatibility of ALG hydrogels heavily depends on the G/M ratio and the inner viscosity of the prepared hydrogel. ALG hydrogels, especially ALG beads, are being used as delivery systems for bioactive peptides and proteins, genes, and a variety of drugs (Li et al., 2012).

Spherical beads are formed instantaneously when droplets of Na-ALG solution get in contact with the $CaCl_2$ solution. ALG beads have the ability to reswell. This property is responsive to the pH of the environment, so acid-sensitive drugs, taken orally, would be protected from gastric juice (pH = 1.5 – 2.0), but once dried particles enter the small intestine (pH = 7.4), the beads reswell to their original size and function as matrices for controlled release of encapsulated drugs (Yotsuyanagi et al., 1987). Due to the adherence of ALG particles to the mucosal tissues, protein transport time is prolonged and the drug is localized, which improves drug bioavailability and effectiveness (George and Abraham, 2006).

ALG scaffolds are able to release encapsulated proteins by two mechanisms: (1) diffusion of the protein through the porous ALG matrice (Fig. 2) (pores being 5–200 nm in diameter), and (2) degradation of the polymer network. The increase of the abundance of alginate in the beads lowers the rate of diffusion of the proteins from the matrix. However, small molecules such as glucose and ethanol diffuse uninterrupted from the gel. Therefore, cell encapsulation methods began to thrive, especially the encapsulation of hormone-producing cells or recombinant cells for the treatment of diabetes mellitus, liver diseases, parathyroid disorders, and various neurological disorders (Gambotz and Wee, 1998).

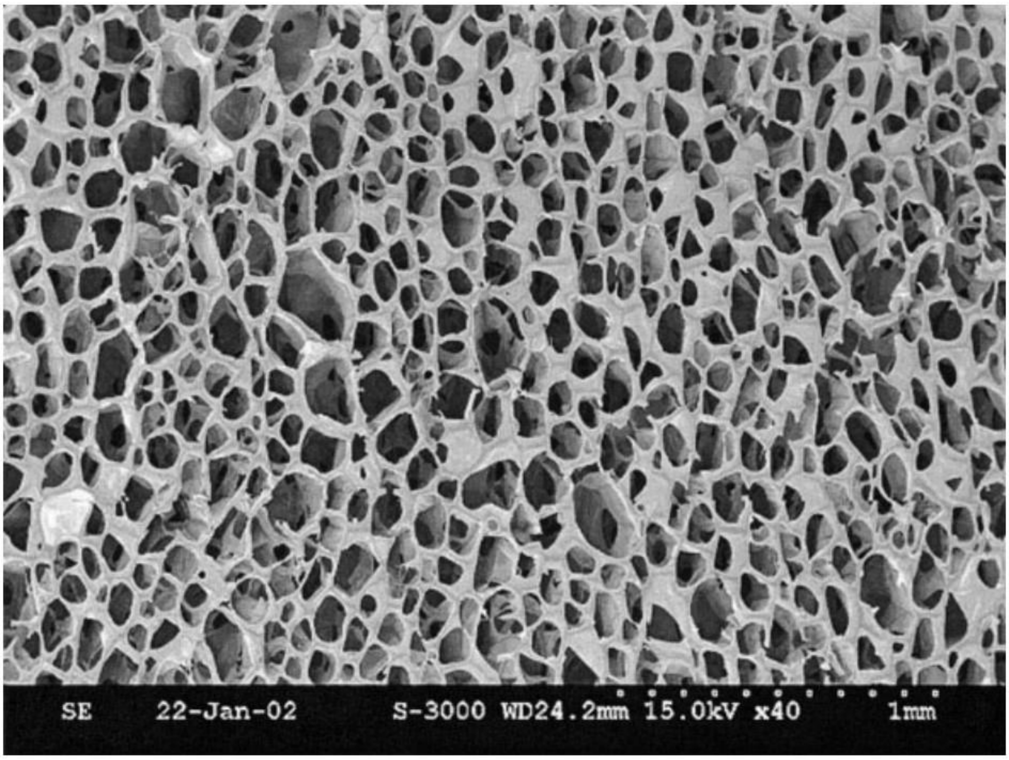

Figure 2. Typical top surface morphology of pure alginate scaffold (3% alginate, crosslinker: 0.03*M* $CaCl_2$, freezing temperature: – 40°C). Original magnification: x40.

Alginate in tissue engineering

The general objective of tissue engineering is to forge a structure that matches the physicochemical properties of the natural tissue (Gambotz and Wee, 1998), and eventually to fabricate living replacement parts for the body. Due to their mechanical properties and biocompatibility, ALG scaffolds are highly qualified candidates for the field. For example, the regeneration of bone after tissue loss is accomplished by using interconnected, highly porous ALG/hydroxyapatite composite scaffolds (Fig. 3), whose structure is similar to the bone tissue structure. Besides, ALG scaffolds are used as a space-filling agent because they provide bulking and prevent adhesions, or function as bioadhesives (Drury and Mooney, 2003; Lin and Yeh, 2004; Venkatesan et al., 2014). Therefore, ALG scaffolds are applicable in soft-tissue engineering, as well.

The advancement of nanotechnology has made possible to use ALG hydrogels in micro and/or nanodevices because gelation occurs even at such scale. As a result, artificial capillary blood vessels are built using the inkjet printing technique (Henmi et al., 2007), as well as *in situ* forming injectable hydrogel, a suitable delivery carrier for encapsulated stem cells for soft tissue regeneration (Deepthi and Jayakumar, 2017).

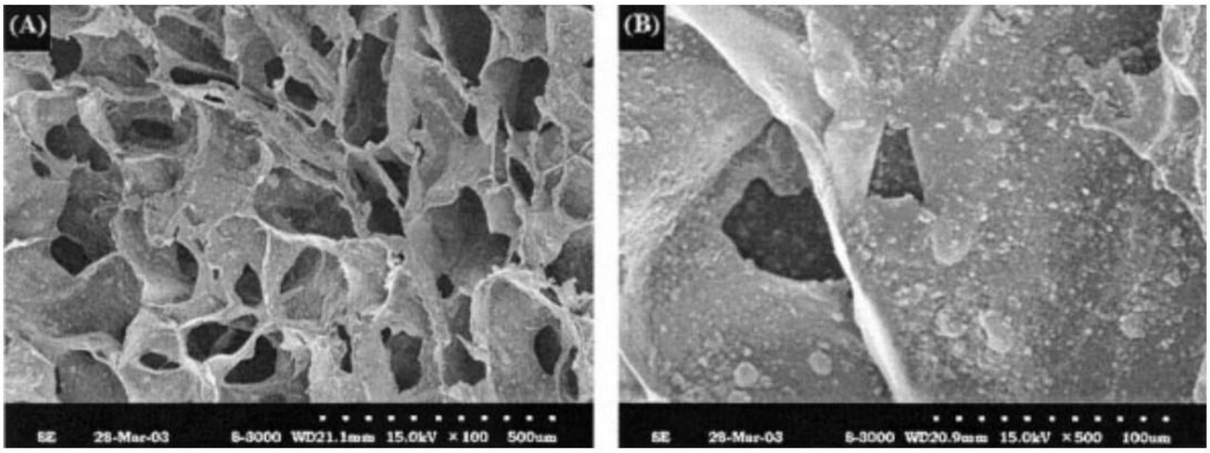

Figure 3. Surface morphology of 75/25 alginate/HAP composite scaffolds (3% alginate, crosslinker: 0.03*M* $CaCl_2$, freezing temperature: – 40°C). Original magnification: A = x100; B = x500.

Conclusion

This short review has a mission to point out the significance of alginates in the modern world, especially the numerous applications in the fields of biomedical science and bioengineering. Considering the favorable physicochemical properties and low price, this biopolymer remains a great candidate for further interdisciplinary studies.

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Alginati: primene u modernom svetu

Lazar N. Kulašević

Univerzitet u Nišu, Prirodno-matematički fakultet, Departman za hemiju, Višegradska 33, 18000 Niš, Srbija

SAŽETAK

Alginat je prirodni polisaharid koji se dobija ekstrakcijom iz ćelijskih zidova mrkih algi. Zahvaljujući njegovoj biokompatibilnosti, biodegradabilnosti, netoksičnosti i niske cene, ovaj biopolimer ima široki spektar primene u oblastima biomedicinskih nauka, kao i bioinženjeringa. Alginati služe kao gelirajući agenti u prehrambenoj industriji. Usled strukturalne sličnosti sa živim tkivima, hidrogel alginata se koristi u inženjeringu tkiva, a (mikro)kapsule za transport i doziranje lekova. Povrh toga, hidrogel alginata se koristi u nanotehnologiji za konstruisanje veštačkih krvnih sudova.

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Alginate : l'emploi dans le monde moderne

Lazar N. Kulasevic

Université de Nis, Faculté des sciences et mathématiques, Département de chimie, Visegradska 33, 18 000 Niš, Serbie

RÉSUMÉ

L'alginate est un polysaccharide naturel que l'on obtient par l'extraction des parois cellulaires provenant des algues brunes. Grâce à sa biocompatibilité, sa biodégradabilité, sa non-toxicité et à son bas prix, ce biopolymère possède un ample spectre de l'emploi au sein des sciences biomédicales et de génie biologique. Les alginates ont la fonction des agents de gel dans l'industrie alimentaire. En raison de sa similarité structurelle avec les tissus naturels, l'hydrogel de l'alginate s'utilise dans le génie de tissu, alors que ses (micro)capsules s'utilisent pour le transport et le dosage des médicaments. En outre, dans la nanotechnologie, l'hydrogel des alginates sert à construire les vaisseaux sanguins artificiels.

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Альгинат: применение в современном мире

Лазарь Н. Кулашевич

Университет Ниш, Факультет естественных наук и математики, Департамент химии, Вишеградская, 33, 18000 Ниш, Сербия

АННОТАЦИЯ

Альгинат представляет собой природный полисахарид, который получают путем экстракции из клеточных стенок бурых водорослей. Благодаря своей биосовместимости, биоразлагаемости, нетоксичности и низкой стоимости этот биополимер имеет широкий спектр применения в областях биомедицинских наук, а также биоинженерии. Альгинаты используются в качестве желирующих агентов в пищевой промышленности. Из-за структурного сходства с живыми тканями, гидрогель альгината используют в тканевой инженерии, и (микро) капсулы для транспортировки и дозирования лекарственных средств. Кроме этого, гидрогель альгината используется в нанотехнологиях для строительства искусственных кровеносных сосудов.

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Lithium-ion batteries

Miloš Nikolić

University of Niš, Faculty of Sciences and Mathematics, Department of Chemistry, Višegradska 33, 18000 Niš, Republic of Serbia, e-mail: milos.nikolic1@pmf.edu.rs

ABSTRACT

The demand for lithium-ion batteries is growing due to their characteristics (composition, size, charging time, capacity). There are various types that can be found on the market, which mostly depend on their purposes, which depend on their composition. They have different uses, starting with portable devices like mobile phones, cameras, and even smaller electric cars. They are being developed and improved (capacity, voltage, charging); additionally, their size is being reduced, which is particularly important in car industry where more rechargeable lithium-ion batteries are connected to get desired capacity. Similarly, to other types of batteries, these consist of cathodes, anodes and electrolytes, where gel or solid electrolyte is preferable to avoid the release of gas (hydrogen), and therefore their explosion or damage. From 2000 to 2010, the annual production of lithium-ion batteries in the world increased about 800%.

Keywords: *capacity, voltage, charging, electrolytes*

The cells that are the source of direct current have been found even in ancient Egypt: a pear-shaped copper cylinder wrapped around an iron rod (https://www.conopljanews.net/tajanstvene_stvari.html). However, the first modern battery was invented by Alessandro Volta around 1800, and consisted of two tiles of different metals in an electrolyte where they were connected to the upper part by an electrical connection and a one-way current (http://www.bibnum.education.fr/sites/default/files/volta-analysis-5.pdf). Batteries nowadays are based on the same principle. Rechargeable batteries are made of electrodes and electrolytes, which are usually made from mixtures of lithium-ion or nickel-metal hydride. As an unwanted effect of chemical reactions, heating of the batteries occurs during operation, which affects unfavourably electrolytes (http://inovatori.hr/wp-content/uploads/sites/225/2017/01/Punjenje_baterija-1.pdf; http://www.fer.unizg.hr/_download/forum/INEU_Seminar_Matija_Mikolcic.pdf). It is not recommended to empty the battery completely, as there is a degree after which they should not be discharged. Depending on the application, there are rechargeable lithium-ion and lithium polymer batteries. The greatest advantage of lithium batteries in comparison to others is easy and fast charging; however, their adverse environmental impact is not reduced due to the application or incorporation of various metals in their structure in order to improve certain properties (http://www.doiserbia.nb.rs/img/doi/0367-598X/2017/0367-598X1600031S.pdf). To reduce environmental pollution, it is, therefore, necessary to raise awareness of the recycling of batteries (Maschler et al., 2012; Xu et al., 2008).

Composition of lithium-ion batteries

Like other types of batteries, lithium ion batteries consist of a protective jacket, anode, cathode, and a separator with an electrolyte or gel separator. Cathodic material is applied to the aluminium collector, as a conductive additive; carbon and polyvinyl-difluoride (PVDF) are used as a binder. The ratio of these components is usually 85: 10: 5. The binder, which is usually PVDF, serves to cathode material to tightly bonds to the aluminium substrate, and carbon to increase the electrical conductivity of the material. The anode lithium ion battery makes a Cu collector, where an anode material made of graphite is applied using a small PVDF additive. Poly-tetrafluoroethylene (PTFE) is sometimes used as a binder. For the separator, polypropylene, which is soaked with electrolyte, is used. As an electrolyte, a solution of lithium salt ($LiPF_6$, $LiBF_4$, $LiAsF_6$ or $LiClO_4$, $LiCoO_2$, $LiNiO_2$,

$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$, $LiMn_2O_4$ and $LiFePO_4$) is used in some organic solvents, usually dimethyl carbonate (DMC), ethylene-carbonate (EC), or propylene carbonate (PC). In commercial batteries, $LiPF_6$ is often used as electrolyte which is dissolved in a mixture of ethylene carbonate and dimethyl carbonate (Espinosa et al., 2004).

During charging and discharging, the lithium ions move through the electrolyte to the electrode, while the electrons generated by the reaction $Li = Li^+ + e-$ go from one to the other current collector by an external electric circuit. During the discharge, the lithium ions are released from the structure of the negative electrode with the simultaneous oxidation of the host A and enter the structure of the positive electrode K, which is reduced. The reverse process occurs during charging (Zhang et al., 2014). The porous separator has the role of preventing contact between the cathode and the anode and the formation of a short circuit. Li-ion batteries contain inflammable and toxic organic electrolytes, so for this reason the organic electrolyte was replaced by aqueous electrolyte. The advantages of aqueous electrolytes are higher ionic conductivity that is about two orders of magnitude greater than for non-aqueous electrolytes; it cannot lead to ignition or battery explosion; it is more environmentally friendly, simplifies battery production and is cheaper. The biggest problem is to find an electrode pair in which lithium ions can be intercalated/deintercalated in the potential area where there is no water electrolysis, having good cyclic behaviour during a large number of charge/discharge cycles. For this reason, this type of battery cannot have a voltage greater than 2V (Li et al., 2014). Li-Polymer batteries differ from Li-ion by the type of electrolyte used. The first batteries using dry and solid polymer electrolytes were developed in the 1970s, and the first commercial Li-polymer batteries appeared relatively recently. They are using electrolytes on a plastic film that does not carry electricity within, but allows an uninterrupted exchange of ions (electrically charged by atoms or groups of atoms). Roughly speaking, the polymer electrolyte is replaced by the traditional porous separator, which is impregnated with liquid electrolyte. Dry polymer provides small cell thickness (up to 1 mm), relative simplicity of production and safety (lack of liquid or gel electrolyte eliminates the possibility of poisoning or burns). The disadvantages of the Li-polymer batteries in relation to Li-ion are that the use of high temperatures is required to achieve optimum performance from 60 to 100 ° C whereas Li-ion sometimes requires cooling, as the optimum temperature moves around 15° C. The main difference from Li-ion batteries is that Li-Pol have a porous separator, which causes a gradual degradation of the battery. The polymeric gel electrolyte is simply added here to expand the ionic conductivity (Basu, 1983; Mizushima et al., 1980).

Lithium as the basis for the production of batteries is used because it is very light metal; in addition, it has high electrochemical potential and provides the highest specific energy, so scientists come to the conclusion that it is suitable for making lithium-ion batteries. There is a problem because lithium batteries due to more charging and discharging become temperature-unstable and there may be an explosive reaction. Today's Li-ion rechargeable batteries are additionally protected (https://tanders.ru/bs/about-batteries-batteries-their-differences-and-features-types-of-modern-batteries-for-cars-and-prospects-for-development/).

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Litijum-jonske baterije

Miloš Nikolić

Univerzitet u Nišu, Prirodno-matematički fakultet, Departman za hemiju, Višegradska 33, 18000 Niš, Republika Srbija, e-mail: milos.nikolic1@pmf.edu.rs

SAŽETAK

Potražnja za litijum-jonskim baterijama raste zbog njihovih karakteristika (sastav, veličina, vreme punjenja, kapacitet). Na tržištu se mogu naći raznih vrste koje pretežno zavise od njihove namene, od koje će zavisiti njihov sastav. Imaju različite namene počevši od prenosivih uređaja poput mobilnih telefona, fotoaparata, pa sve do nekih manjih automobila. One se razvijaju i poboljšavaju (kapacitet, napon, punjenje); pored toga, njihova veličina se smanjuje, što je naročito bitno u industriji automobila gde se spajaju vise punjivih litijum-jonskih baterija kako bi se dobio željeni kapacitet. Kao i ostale vrste baterija i ove se sastoje iz katoda, anoda i elektrolita, gde je poželjnija upotreba gela ili čvrstih elektrolita kako ne bi došlo do izdvajanja gasa (vodonika), pa samim tim i do njihove eksplozije ili oštećenja. Od 2000. do 2010. godine godišnja proizvodnja litijum-jonskih baterija u svetu povećala se oko 800%.

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Les batteries au lithium-ion

Milos Nikolic

Université de Nis, Faculté des sciences et mathématiques, Département de chimie, Visegradska 33, 18 000 Nis, République de Serbie

RÉSUMÉ

La demande aux batteries au lithium-ion est en augmentation grâce à leurs caractéristiques (la composition, la taille, le temps du chargement, la capacité). Au marché, il existe plusieurs types des batteries au lithium-ion ; ils dépendent en général de leur usage qui définit leur composition. Elles ont des différents usages à partir des appareils mobiles, tels que les téléphones portables et les caméras, jusqu'à certains petites automobiles. Elles se développent et s'améliorent (leur capacité, leur voltage, leur chargement) ; en plus, leur taille diminue, ce qui se montre extrêmement important au sein de l'industrie des automobiles où plusieurs batteries au lithium-ion sont jointes afin d'obtenir l'effet voulu. Comme tout type de batteries, celles-ci sont aussi composées des cathodes, anodes et électrolytes où l'utilisation des gels ou des électrolytes solides est préférable pour éviter la séparation du gaz (hydrogène) et, en même temps, pour éviter leur explosion ou endommagement. De 2000 à 2010, la production annuelle des batteries au lithium-ion a augmenté d'environ 800%.

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Литий-ионные батареи

Милош Николич

Университета Ниш, Факультет наук и математики, Департамент химии, Вишеградская 33, 18000 Ниш, Республика Сербия, электронная почта: milos.nikolic1@pmf.edu.rs

АННОТАЦИЯ

Спрос на литий-ионные батареи увеличивается из-за их характеристик (состав, размер, время зарядки, ёмкость). На рынке можно найти различные виды, которые в основном зависят от их назначения, от которого будет зависеть от их состав. Они используются по-разному, начиная с портативных устройств, таких как мобильные телефоны, камеры и даже небольшие автомобили. Они развиваются и улучшаются (ёмкость, напряжение, заряд); Кроме того, их размер уменьшается, что особенно важно в автомобильной промышленности, где несколько перезаряжаемых литий-ионных аккумуляторов подключены для получения желаемой ёмкости. Как и другие типы батарей, они состоят из катодов, анодов и электролитов, где гель или твердый электролит предпочтительнее, чтобы избежать выделения газа (водорода) и, следовательно, их взрыва или повреждения. С 2000 по 2010 год ежегодное производство литий-ионных батарей в мире увеличилось примерно на 800%.

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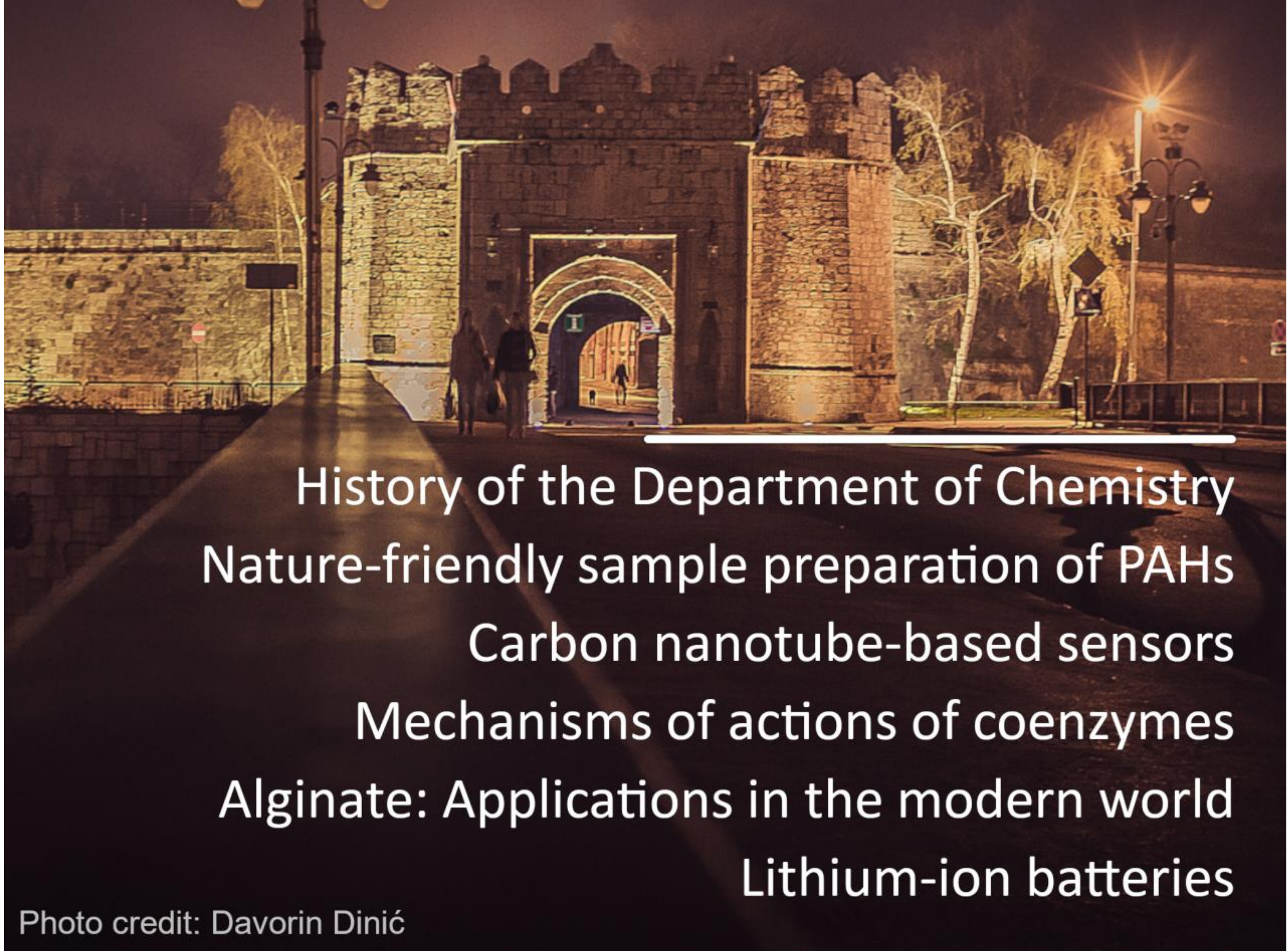

History of the Department of Chemistry

Nature-friendly sample preparation of PAHs

Carbon nanotube-based sensors

Mechanisms of actions of coenzymes

Alginate: Applications in the modern world

Lithium-ion batteries

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