University of Nova Gorica

Cutting-edge Slovenian achievements in optothermal spectroscopy

Achievements in photothermal science

The research in the field of photothermal science is performed in the Laboratory for Environmental Research of the University of Nova Gorica. The Laboratory, being an interdisciplinary research unit established in 1995, is tightly connected with the study programmes at the School of Environmental Sciences and those of the Graduate School, in oder to assure the continuous transfer of research outcomes and expert knowledge to students. The Laboratory hosts a growing number of national and international research projects and values collaborative initiatives and joint action on a number of environmental aspects. It hosts various thematic areas that together contribute to its interdisciplinary character. The Laboratory's international reputation is based on its quality achievements and its commitment in applying research skills to current environmental issues.

Research areas include:

- laser-based analytics,
- organic substances in the environment: monitoring, transformation and effects,
- materials for environmental applications (photocatalysis),
- sustainable natural resource utilization and protection.

Among the research achievements of great importance, the newly developed highly sensitive analytical methods based on laser photothermal techniques such as thermal lens spectrometry (TLS), which are combined with bioanalytical techniques (acetylcholinesterase, transglutaminase and immunological ELISA biosensors), flow injection analysis (FIA) and liquid chromatography, should be pointed out.

TLS detection for direct determination of free bilirubin in serum at sub-nanomolar levels

An ultra-highly sensitive thermal lens spectrometric (TLS) detection with prior chromatographic separation (TLS-HPLC) was established as a method that accomplished the first-ever direct determination of free bilirubin in blood serum (FIG.1).

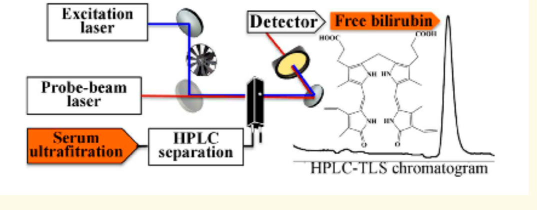

FIG. 1. HPLC-TLS experimental setup (Talanta 154, 92–98, 2016).

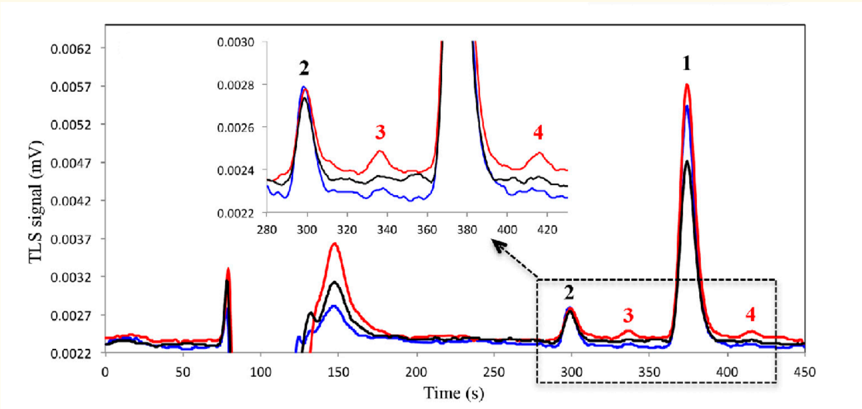

FIG. 2. HPLC-TLS chromatograms representing three replicates of human serum reused for the third time (frozen twice and re-warmed twice) (ANALYTICA CHIMICA ACTA, 809, 174-182, 2014).

By the application of the HPLC-TLS method the determination of free bilirubin is no longer allusive as shown in FIG. 2. This opens new frontiers in clinical and pre-clinical investigations of bilirubin. It must be pointed out that the lack of appropriate free bilirubin analysis has so far prevented the full understanding of its physiology.

The HPLC-T LS method is sensitive and sufficiently selective for precise and accurate free bilirubin determination 3A as well as to detect the degradation products derived from bilirubin.

The study revealed that free bilirubin concentrations of healthy adults are around 10 nM, which is in the range of previously reported values obtained either theoretically or experimentally. The intrinsic value of this study method is that it allows a direct detection of bilirubin degradation products even at trace levels, which can be used as an indication of the quality of sample preparation procedure, so its accuracy with respect to other approaches increases. The application of TLS detection instead of DAD has lowered the limits of both detection (LOD) and quantification (LOQ) by as much as 20-fold.

This method can be applied in clinical laboratories for research use and for blood analysis on daily basis.

Bilirubin is an Endogenous Antioxidant in Human Vascular Endothelial Cells

It was found that small changes in the extracellular bilirubin concentrations can be translated into substantially improved intracellular defence against oxidative stress. Biliverdin showed similarantioxidant properties as bilirubin, likely due to its conversion to bilirubin by biliverdin reductase (FIG. 3).

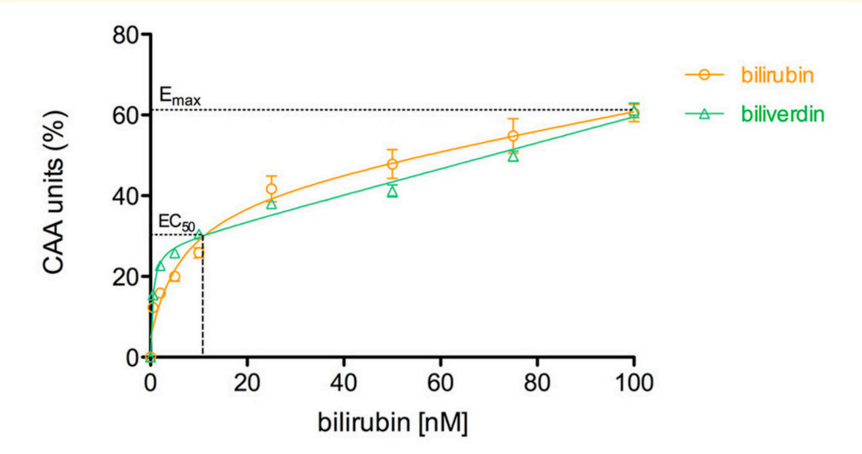

FIG. 3. Endothelial cellular antioxidant activity (CAA) of bilirubin, and its synthetic precursor biliverdin. Endothelial cells (Ea.hy926) were exposed to different concentrations of bilirubin or biliverdin (0.5, 2, 5, 10, 25, 50, 75 and 100 nM) in the albumin-free cell medium for a period of 30 min before the start of CAA the assay. The results are expressed as means ±SEM from hexaplicates of 3 independent experiments (Scientific Reports, DOI: 10.1038/srep29240).

TLM detection in microfluidic systems

The implementation of the thermal lens microscopy (TLM) in microfluidic systems for detection of chromate (Cr(VI)) was performed by the optimized TLM, that enables pump and probe beam displacements to account for the effects of microfluidic flow on the TLM signal, and to set the pump and probe beam radii for the highest sensitivity in a sample of a given thickness (FIG. 4-5).

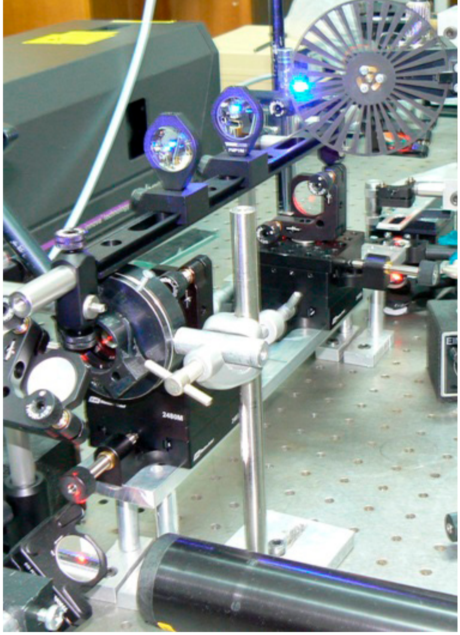

FIG. 4. Experimental setup for microfluidic-FIA-TLM for detection of Cr(VI)

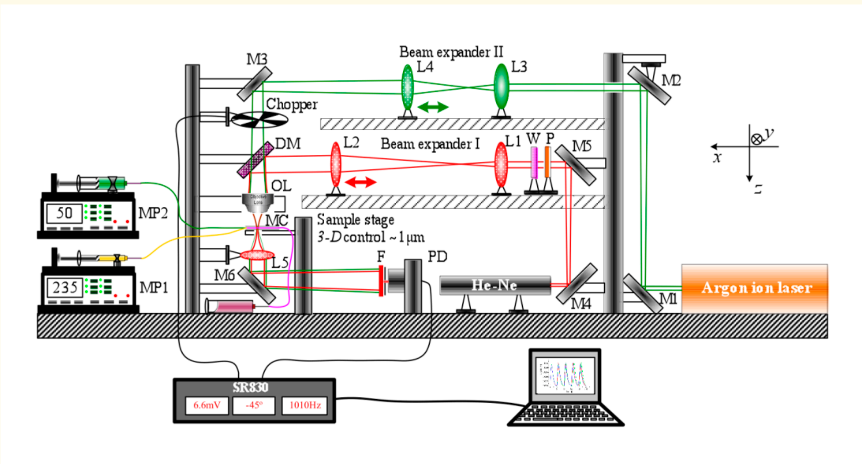

FIG. 5. Schematic diagram of a thermal-lens microscope with adjustable pump/probe beam radii and axis displacements (M1 – M6, mirrors; L1 – L5, lenses; CH, mechanical modulator; DM, dichroic mirror; S, microfluidic chip; W, half-wave plate; P, polarizer; F, interference filter (633 nm); and PD, photodiode (ANALYTICAL SCIENCES, 32, 23-30, 2016).

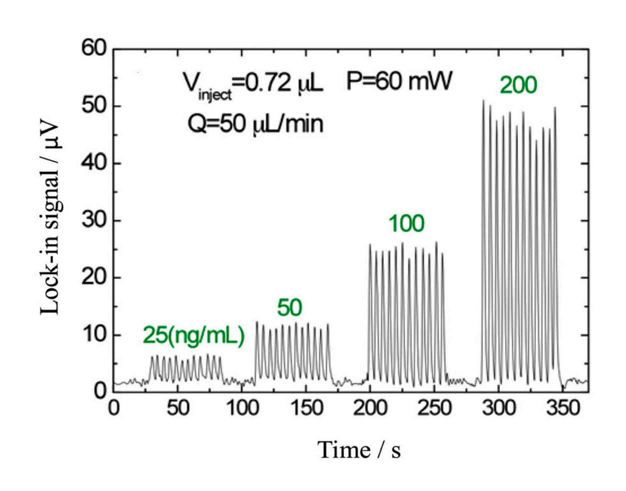

FIG. 6. µFIA-TLM signals from Cr(VI)-DPC of different Cr(VI) concentrations recorded at a carrier flow rate of 20 µL/min, a detection position 6 cm downstream from the junction, with a sample injection volume of 0.72 µL, and a 60-mW pump power in the sample (ANALYTICAL SCIENCES, 32, 23-30, 2016).

The measurements were performed with injections of 0.72 µL samples at a carrier flow rate of 20 µL/min. Under these conditions, analytical signals for twelve sample injections in 1 min could be recorded with good reproducibility (FIG. 6).

Using an excitation power of 60 mW, the LOD of 4 ng/mL of Cr(VI) was estimated. Reducing the flow rate from 20 to 5 µL/min, the LOD was decreased to the value of 1 ng/mL. A decrease in the LOD was achieved by sacrificing the speed of analysis, *i.e.* the number of µFIA-TLM signal peaks per time unit, which was reduced from ~12 peaks/min at 20 µL/min to only 4 peaks/min at 5 µL/min.

Using a higher excitation power (120 mW), the LOD was further decreased to about 0.6 ng/mL. Though this value is still 9-times higher than that which the LOD achieved in the conventional FIA-TLS (0.07 ng/mL), as well as an over 100-times lower sample/reagent consumption and a 4-times higher speed of analysis represent important and promising improvements in the direction of high-throughput vanguard analytical techniques.

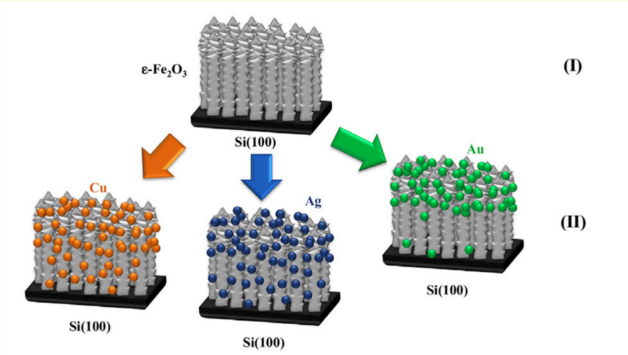

FIG. 7. Schematic representation of the adopted two-step preparation protocol for the fabrication of ε-Fe_2O_3 nanocomposites: (I) synthesis of ε-Fe_2O_3 matrices by thermal CVD; (II) functionalization with Cu, Ag or Au nanoaggregates by RF-sputtering (Optical Materials, 42, 370-375, 2015).

Determination of thermooptical and transport parameters of ε iron(III) oxide-based nanocomposites by beam deflection spectroscopy

The photothermal beam deflection (PBD) experiments have been used to characterize the thermooptical and transport properties of ε-Fe_2O_3-based nanocomposites. In particular, iron(III) nanostructures have been functionalized with Au, Ag and Cu nanoparticles (FIG. 7), tailoring both their nano-organization and their chemical state.

It was found that the optothermal (thermal diffusivity D_s and conductivity k_s) and transport parameters (energy band gap E_g and carrier life time τ) were influenced by the nature and oxidation state of the nanoparticles, which can serve as a key tool to master the material properties for their application in light-assisted processes.

The introduction of Cu, Ag and Au, characterized by different oxidation states, resulted in an efficient strategy for enhancing the lifetime of photogenerated charge carriers and decreasing the E_g values. Thanks to the achieved intimate contact between the single constituents, the role of Schottky and/or p-n junction in enhancing the final material properties of whole structure through an efficient separation of photoproduced holes and electrons and a higher light harvesting. The presented results demonstrate the existence not only of pure Schottky/p–n junction heterostructure but also of their combined presence, and provide a valuable

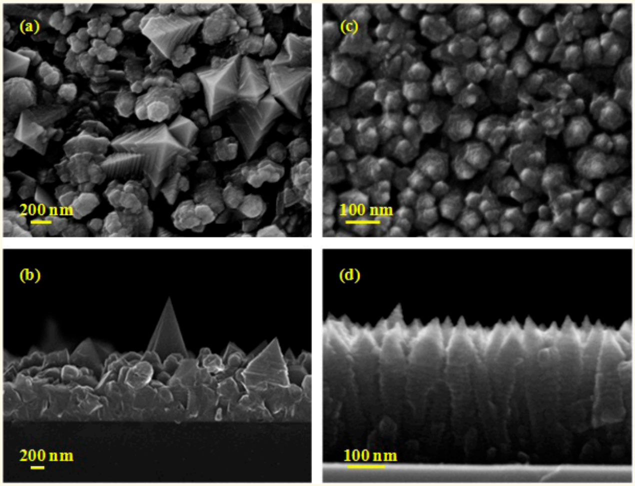

FIG. 8. Plane-view (top) and cross-sectional (bottom) FE-SEM micrographs for bare α-Fe_2O_3 (a, b) and ε-Fe_2O_3 (c, d) (ACS applied materials & interfaces, 5, 7130-7138, 2013).

experimental and scientific background towards the development of more efficient nanocomposite systems for light-activated applications, such as photoelectrochemical and solar cells, chemical/biological sensors and photocatalytic pollutants degradation. The material's thermal parameters are essential properties since the transfer of heat is involved in many industrial applications and processes, e.g. the determination of thermal conductivity is important for evaluation of thermal insulation performance of electronic devices whereas the determination of thermal diffusivity plays significant role for thermal stress calculations caused by fast temperature changes (thermal shock). Thus enhancement of the material's thermal properties is important for the thermal management of advanced electronic system, especially those of reduced sizes such as electronics chips that continue to be produced in smaller and smaller dimension.

Thermal and texture properties of surface modified α- and ε- Fe_2O_3 photocatalysts determined by beam deflection spectroscopy (BDS)

In case of α- and ε-Fe_2O_3 the difference in the determined values of their thermal parameters are attributed to the difference in structure and nano-organization between the two phases. α-phase shows mainly pyramidal and globular aggregates, whereas ε- Fe_2O_3 exhibits uniform nanorod-like structures perpendicular to the substrate surface (FIG. 8), along the direction of

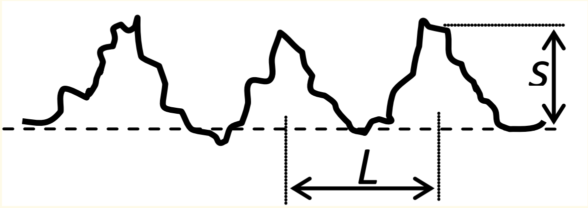

FIG. 9. Definition of the sample surface roughness (ACS applied materials & interfaces, 5, 7130-7138, 2013).

propagation of thermal waves. This makes the material more compact and with fewer interfaces compared to α- Fe_2O_3 and results in higher thermal conductivity and thermal diffusivity.

PBD analyses on the bare iron oxide samples provided values of their surface parameters (*s* and *L*) (FIG. 9).

Indeed, while the amplitude of surface roughness was comparable for the two specimens (s = 0.158 ± 0.006 μm and 0.164 ± 0.006 μm for α- and ε-Fe_2O_3, respectively), the roughness periodicity of α-Fe_2O_3 (L = 1.84 ± 0.04 μm) was one order of magnitude higher than the ε one (L = 0.172 ± 0.004 μm). These results are consistent with the globular and rod-like morphology of the α and ε polymorphs, respectively (FIG. 8), and suggest a higher surface area for the latter system.

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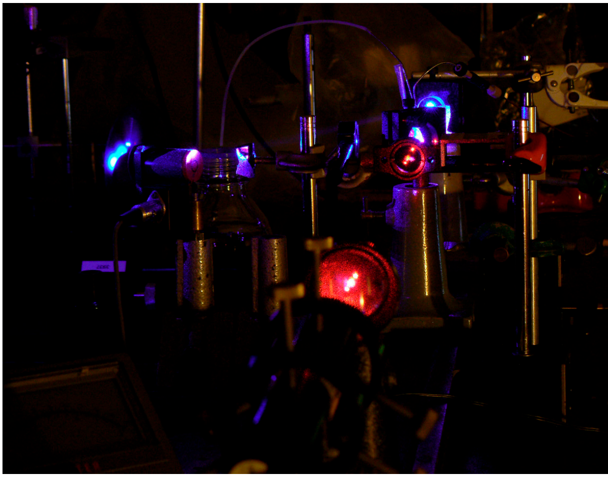


Other cutting-edge research achievements in the field of natural sciences

Research in the field of quantum optics

The Laboratory of Quantum Optics of the University of Nova Gorica bases its activity on the development and use of the CITIUS light source. The laser is a commercial titanium-sapphire system from Coherent Inc. and consists of:

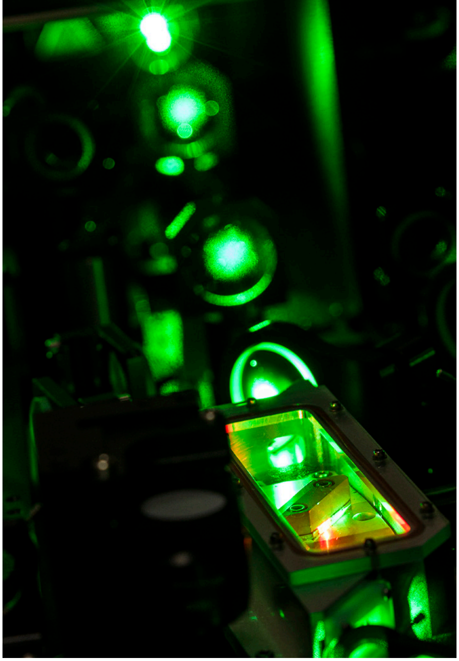
- Micra, master oscillator,
- Legend Elite Duo, multipass+single pass amplifier.

The system is equipped with an OPA (Optical Parametric Amplifier), OPerA from Coherent Inc., that generates light pulses in the spectral range (240 nm – 2600 nm) with more than 5 microJ/pulse.

The construction of CITIUS was funded by the program for Italy-Slovenia cross-border cooperation 2007-2013. The project relies on the collaboration between Italian and Slovenian public and private institutes and, in particular, on the tight collaboration between the University of Nova Gorica and Sincrotrone Trieste. The CITIUS source is based on the generation of high-order harmonics of a laser, which are generated when the latter is brought into interaction with a noble gas. The use of CITIUS allows the realization of a number of experiments, ranging from the chemical study of samples in solid or gas-phase state, to biology and medicine. The aim of the latter experiments is to characterize the behavior of samples containing Phthalocyanines, which are aromatic macrocyclic compound used for photo-dynamic cancer therapy.

So far, the group has contributed to the development of several technologically important materials, for example microporous catalysts, cathode materials for Li-ion batteries and other nanostructured materials, superconducting and ferroelectric ceramics, protective coatings, and macromolecules used in pharmacology. The group is actively involved in the development of new solutions for environmental protection in cases of pollution with heavy metals, and in a project for the preservation of ancient manuscripts. In parallel, the group performs the experimental study of multielectron photoexcitations in free and bound atoms to obtain information on the collective motion of electrons in the atomic system. The results obtained provided a significant experimental and theoretical contribution to the interpretation of the exact atomic absorption background in EXAFS spectra and thereby have helped improve the accuracy of the structural analysis with this method.

Theoretical studies are also foreseen in the framework of long-range interacting systems. The group activities also concentrate on the characterization of new materials with synchrotron radiation.



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Research in the field of electronic and environmental materials

Basic research in the field of electronic and environmental materials performed at the Materials Research Laboratory of the University of Nova Gorica focuses on:

- topological insulators,
- computational solid-state chemistry,
- photocatalysts for water splitting,
- topologically designed magnesium alloys for biomedical applications,
- polysilanes and polycarboslilanes.

In the area of topological insulators (TI), which are a special kind of materials that behave as insulators in their interior and have conductive surface because of present topological conductive states, the group studies crystallographic and functional properties of the interface between TI and metals.

In computational solid-state chemistry, simulations based on density functional theory (DFT) have become an extremely successful tool for describing the ground state properties of a wide range of bulk and more complex form of matter such as nanostructures and interfaces and also for calculation of activation energies of chemical reactions. For simulations of optical properties the group uses the most advanced and accurate approaches based on combination of GW method and Beth-Salpeter equation to solve problems like defects on atomic scale in amorphous silicon and oxidation of metal surfaces.

Within the research of photocatalysts for water splitting, the group develops new materials, studies structural, electronic and photocatalytic properties of catalysts and observes the influence of morphology, composition and particle size on photocatalytic activity, while the main objective of the project related to topologically designed magnesium alloys is to develop high performance magnesium (Mg) alloys readily adoptable in biomedicine as well as in lightweight mobility sectors. The alloys are to consist from abundant affordable components readily available from within the EU, which should facilitate the improvement of security, sustainability and socioeconomic prosperity of people in Slovenia, Europe and beyond.

Another area of research is that of polysilanes and polycarbosilanes, which are obtained with through thermal treatment of polysilanes. Further thermal treating at higher temperatures gives silicon carbide. In the laboratory, polysilanes are synthesised with the electrochemical reduction of chlorosilanes, which gives much more controlled conditions and safer polymerization than a widely used reduction with liquid sodium. In order to use polysilanes as precursors for polycarbosilanes and silicon carbide ceramics on nano scale, the group studies the size of macromolecules and their state in the solution (agglomeration/de-agglomeration), the effect of electrochemical conditions on the size and the structure of macromolecules, the thermal conversion and properties of obtained polycarbosilanes.

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Related study programmes at the Graduate School of the University of Nova Gorica

Are you interested in research work in natural sciences and in discovering new knowledge in this field? Join our international team of top researchers, professors, and experts in our doctoral study programmes in the field of natural sciences at the Graduate School of the University of Gova Gorica.

The programmes are accredited with 180 ECTS, of which 60 ECTS are allocated to obligatory and elective courses, while the remaining ECTS represent the students' individual research work. The latter can be carried out within the research units of the University of Nova Gorica or at other partner research institutions in Slovenia or abroad. All our programmes offer a high degree of electiveness in terms of study contents and are of interdisciplinary nature, enabling the tailoring of individual doctoral study programmes. Already during their studies, all our doctoral students publish the results of their research work in international scientific journals with a high impact factor.

All doctoral programmes are internationally oriented. The language of instruction is English. More than 50 % of doctoral students come from abroad, from various countries worldwide. Our graduates are capable of solving the most difficult tasks in their field of research in academic or entrepreneurial environment.

Admission requirements:

- a completed 2nd-cycle Master's study programme or a four-year academic undergraduate programme accredited with 240 ECTS credits in Slovenia or a completed equivalent programme abroad
- minimum level of English language skills required: B2 in accordance with CEFR

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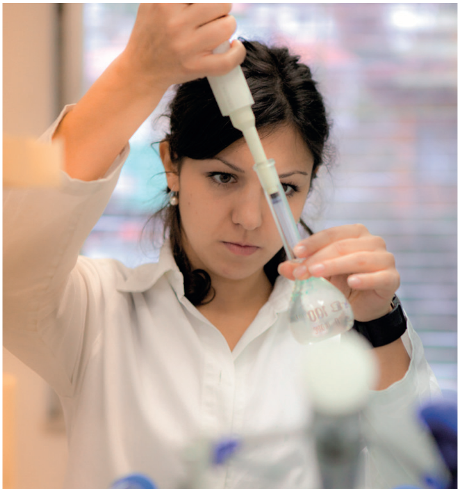

Environmental Sciences

The programme is interdisciplinary and research-oriented. The main objective of this study programme is to educate top experts possessing multidisciplinary knowledge in the field of environmental sciences. The students have the opportunity to explore the three segments of environment: water, soil and air. Within individual segments, the students can focus on different issues, such as waste management and the effects of waste disposal, advanced procedures and materials for treatment of wastewaters and air, chemical, measuring techniques for the detection and monitoring of pollutants in the environment, the physical, biological and health effects of pollution, and toxicology. After graduation they can work as experts in the areas of environmental research, technology, conservation, management and policy development.

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Physics

The programme is designed for students who wish to obtain excellent research skills and knowledge in the following fields:

- synthesis, characterization and modelling of novel materials;
- advanced numerical methods for multiphase systems and for aerodynamic surface;
- high-energy physics, which is linked to modern cosmology and astroparticle physics,
- physics of atmosphere, including LIDAR remote sensing of atmospheric properties and pollutants, and atmospheric impact on the performance of satellite navigation systems.

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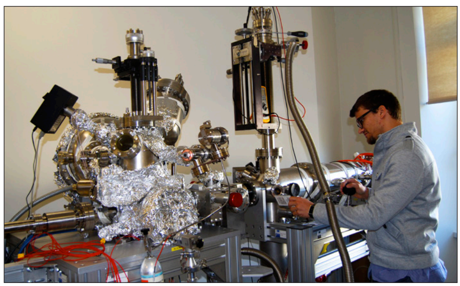

Molecular Genetics and Biotechnology

The doctoral programme offers education of young scientists in different fields of molecular genetics and biotechnology. The studies focus on several advanced topics such as control of gene expression, DNA replication, DNA repair and RNA processing; studies on human viruses, molecular immunology, molecular genetics, experimental haematology and human gene therapy, bacteriology and yeast genetics, plant virology, protein structure and bioinformatics. Graduates are able to work as molecular biologists in the fields of public health, nutrition and environmental protection and remediation, or as biotechnologists in the fields of industrial production of products useful to humans. The programme is carried out in close collaboration with The International Centre for Genetic Engineering and Biotechnology (ICGEB) from Trieste, Italy.

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