OPTOELECTRONICS FOR R&R PROCESSES

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Book of Proceedings

Contents

INCDO-INOE2000 Research Institute for Analytical Instrumentation Subsidiary, ICIA

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The Center for Analytical, Control and Signaling Equipment, CAACS, Cluj-Napoca, established in 1986, having as main activity the research, design and manufacture of analytical laboratory equipment, as well as the development of analytical methods for a wide range of samples, became a subsidiary of INCDO-INOE2000 Bucharest and a national institute, the Research Institute for Analytical Instrumentation since 1996. Along with the development of the institute and in response to the demand for expertise in different fields, these concerns have expanded towards environmental programs, soil microbiodiversity, influence of climate change on the quality of the environment, food quality and safety, bioenergy, health, clean technologies, technological modernization. Also, the ICIA Subsidiary is authorized, in accordance with the provisions of Government Ordinance no. 129/2000 republished, to organize the Chemical Laboratory Specialization program, COR code: 311101, IF Series Authorization No. 416 of 24.10.2016/National Authority for Qualifications.

The activity directions of the ICIA Subsidiary are oriented towards industrial R&D and innovation, including technology transfer, by carrying out chemical analyzes and providing information, consultancy and representation services for the business environment.

1. Research & Development. The research activity addresses environmental and health programs (assessment of the quality of environmental factors such as soil, water, air, vegetation, food), the development of new types of systems, equipment, optoelectronic instrumentation for analytical investigation with applications in environmental protection, health, safety and food security, technology modernization, clean technologies, bioenergy-biomass, evaluation of soil microbiodiversity under the impact of climate change, through three research laboratories: ***(i)*** the Environment and Health Laboratory; ***(ii)*** the Bioenergy-Biomass Laboratory, and ***(iii)*** the Analytics and Instrumentation Laboratory.

2. Chemical Analyses, through the Environmental Analyses Laboratory, LAM, which is accredited by the Romanian Accreditation Association, RENAR, with the Accreditation Certificate No. 352-LI/22.07.2009, in agreement with the request of the SR EN ISO/CEI 17025 Standard, to perform analyses on soil, water, sediment, sludge, vegetation, food and certified by the ANSVSA (certificate no. 125/15.07.2016). LAM has all the necessary resources for the performance of high-quality analyses in optimal conditions, in order to provide reproducibility and accuracy of the results: climatized rooms, high-quality reagents/materials, modern analysis instruments and state-of-the-art equipment, some of them being unique in the country. The instruments are checked and metrologically calibrated and maintained according to the regulations. The personnel are highly qualified and experienced in the field of chemical analyses, achieved by constant improvement in prestigious laboratories, in Romania and abroad.

3. Technology transfer. The Technology Transfer Center CENTI Cluj-Napoca envisages the promotion and knowledge transfer of the R&D results, as well as the assistance of SMEs, Start-ups, NGOs and R&D institutions in order to grow and innovate on national and international level.

The INCDO-INOE 2000 ICIA Subsidiary is formed of a young team (chemists, physicists, analytical chemists, chemical engineers, electronic engineers, biotechnology engineers, environmental engineers, sub-engineers, technicians), highly qualified (more than 75% of the staff have master's degrees and doctoral degrees in various scientific fields of interest of the institute), with specializations in research laboratories achieved through experience exchanges and mobility programs at universities in Austria, Slovakia, Slovenia, Spain, Bulgaria, Moldova, France, Switzerland, Poland, Japan and China. The institute has concluded collaboration contracts with the universities of Cluj-Napoca (Babeş-Bolyai University, Technical University, University of Medicine and Pharmacy, University of Agricultural Sciences and Veterinary Medicine). In addition, within the institute, a large number of students from the universities of Cluj-Napoca carry out their research activity which is the basis of their bachelor's, master's or doctoral thesis.

The results of the research activity are materialized in: products, analytical methods and technologies, articles published in scientific journals with impact factor, books/book chapters, communications at national and international scientific events, patent proposals and granted patents, awards.

The results obtained by ICIA, the INCDO-INOE 2000's subsidiary, in the research activity enjoy national and international recognition: ICIA is a full member of the National Society of Environmental Science and Engineering, SNSIM, as well as a founding member of the clusters: Transylvania Energy Cluster-TREC, the "Advanced Materials, Micro and Nanotechnologies-ADMATECH" Innovation Cluster, the "Agro-Food Cluster-Ind Napoca" Association, the "Eco-innovative Cluster for a Sustainable Environment" Association-

CLEMS, the "Green Technology Innovative Cluster"-GREETINC and the Association "Transylvanian Furniture Cluster".

In the context of the knowledge-based economy, the ICIA Subsidiary, through all its activities, ensures the sustainable development of society, the promotion of a climate favorable to research and innovation, and the stimulation of cooperation between the business and research environments, in order to make a better use of research results and of the owned infrastructure, both human and material.

The Technology Transfer Center CENTI

S.C. BARSAN
National Institute for Research and Development of Optoelectronics Bucharest INOE 2000, Research Institute for Analytical Instrumentation, Department Technology Transfer Center, 67 Donath Street, 400293 Cluj-Napoca, Romania

The Technology Transfer Center CENTI is a department that has functioned in INCDO-INOE 2000 Bucharest, ICIA Cluj-Napoca subsidiary, since 2004.

The mission of CENTI is structured in 2 main directions: promotion and valorisation of the institute's R&D results, by facilitating the transfer of high-level scientific and tehnical knowledge towards the economic environment; provision of specialized services for SMEs, to enhance their competiveness and innovative capacities on national and international level.

CENTI has been working as an entity of the innovation and technology transfer infrastructure of the Romanian Ministry of Research, Innovation and Digitization, being accredited in the following activity fields: bioeconomy; energy, environment and climate change; health. The technology transfer activity of CENTI is ISO 9001:2018 certified, with well-established work procedures, as a guarantee for the quality of the services rendered to its clients.

CENTI offers SMEs advisory and partnering services to stimulate their sustainable growth, digitalization and resilience on their way regarding the Single Market access, internationalization and innovation. Therefore, the CENTI specialists provide advisory services on innovation and technology transfer, EU legislation and standards, EU policies and programmes, access to finance, access to new markets, resilience enhancement as well as support in the SMEs transition to more sustainable and digital business models.

The partnering services aim to help SMEs engage in establishing successful partnerships in business/ commercial collaboration, knowledge transfer as well as in collaboration fostering R&D activities of SMEs and leading to participation and funding of SMEs in national and European research programmes. For more than 14 years, CENTI has been partner of Enterprise Europe Network, the world's largest business and innovation support network for SMEs with international ambitions. In this capacity, CENTI has facilitated the access of dozens and dozens of companies with high ambition and potential to grow to the Single Market as well as to international markets.

The objectives of CENTI are aimed at enhancing the competitiveness and innovative capacities of the SMEs located in Macroregion 1 of Romania and, particularly, in the North-West part of Romania, to assist them to become more economically, environmentally and socially sustainable, by helping them to innovate, grow and scale in the Single Market and beyond.

The core objectives of CENTI are the following:

►To increase the performances of INCDO-INOE2000 activities, by promoting the R&D results in international data bases;

►To improve the INCDO-INOE 2000 innovation level, through the implementation, support and tracking of the processes specific for the Innovation Management System SR 13572:2016;

►To offer R&D services for SMEs, so as to be able to manufacture products and provide services with market demand and that lead to improved revenue;

►To provide support services on business and innovation for the companies located in North-West/ Macroregion 1 of Romania, especially for the innovative SMEs and clusters, to improve their economic competitivity and/ or innovation and retechnologisation/ advanced technology transfer;

►To provide entrepreneurial advisory services for start-ups;

►To support SMEs for identifying potential national and international business partners as well as investors by a) accessing international databases; b) stimulating their participation in international brokerage events and company missions.

►To increase the commercialization capacity of the SMEs innovation results, through stimulation and awareness of the intellectual property rights exploitation;

►To establish partnerships that facilitate contacts between research/ university teams and SMEs working in CENTI's activity fields, so as to submit project proposals in national, European and international calls;

►To support SMEs in preparing project proposals in national/ European funding calls;

►To provide information related to EU policies, programmes, legislation and business opportunities for SMEs located in the North-West region/ Macroregion 1 of Romania;

►To organise events (workshops, conferences) on issues related to access to finance, EU programme calls of interest, innovation, intellectual property, etc;

►To develop the competences of CENTI's advisors by their participation in workshops and trainings specific for their activity, so as to provide high-level and sucessful advisory and partnering services.

Some of the remarkable results obtained by CENTI are mentioned below:

- More than 18 years of continuous existence as entity of the innovation and technology transfer infrastructure, accredited by the Romanian Ministry of Research;
- Enterprise Europe Network active partner for almost 15 years;

- 13 finalized projects with national funding (out of which 3 as project manager and 10 as consortium partner);
- Finalization and/ or on-going as consortium partner of 6 projects EU funded (CIP, COSME, HORIZON 2020 and SMP COSME);
- Approx. 100 transnational partnerships in business, innovation, technology transfer and access to EU finance concluded by SME clients, as concretization of the advisory and partnering services received from CENTI;
- Documentation, implementation, certification and tracking of the Innovation Management System SR 13572:2016 processes in INCDO-INOE 2000.

ENVIRONMENTAL ANALYSES LABORATORY, LAM – analysis for third parties and future development in the framework of circular economy

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Abstract. Environmental pollution is one of most challenging problems that humanity is facing nowadays especially due to its high impact on human health. Air, water and soil pollution are most mentioned environmental factors which are subjected to pollution. Romania is facing multiple challenges in its attempt to comply to the European Union standards regarding environmental pollution. Waste is one of most common factors of environmental pollution. Circular Economy Action Plan present the new European strategy to deal with waste. Environmental Analyses Laboratory, specialized in studying environmental samples wants to be an integrated part of the transition process to a circular economy.

Keywords: Environmental analysis, Water, Soil, Air, Food, Materials, Analytical methods

1. Introduction

According to OECD Glossary of Statistical Terms, the term environment represents "*the totality of all the external conditions affecting the life, development and survival of an organism*" [1]. The environment (Fig. 1) has three major components: (1) physical – air, water and rocks; (2) biological – living mass, biomass and biota and (3) social – society, economics and politics [2, 3]. These components are severely compromised due to human activities and some natural events – *environmental pollution*. According to Britannica, the environmental pollution means *"the addition of any substance (solid, liquid, or gas) or any form of energy (such as heat, sound, or radioactivity) to the environment at a rate faster than it can be dispersed, diluted, decomposed, recycled, or stored in some harmless form"* [4].

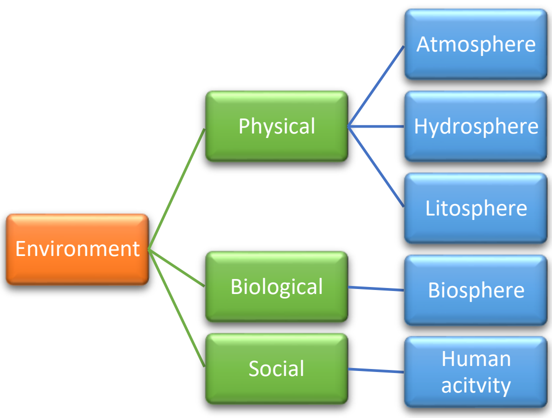


Fig. 1. Major environment components

Three components of the environment are mostly followed to establish the pollution degree: air, water and soil. The levels of pollution in Romania for these three parameters are presented below:

Air pollution

According to statistics, in 2019, 9 out of 10 people worldwide breathe polluted air and about 7 million people from low and middle developed countries die every year from air pollution [5]. The European Union (EU) air quality standards are regulated for 12 air pollutants: sulphur dioxide, nitrogen dioxide / nitrogen oxides, particulate matter (PM10, PM2.5), ozone, benzene, lead, carbon monoxide, arsenic, cadmium, nickel, and benzo(a)pyrene [6], where PM2.5 is considered to be a key factor for establishing the air pollution degree. PM2.5 are particles of 2.5 μm which inhaled can reach the respiratory tract and the lungs causing respiratory and cardiovascular diseases [7]. The most polluted countries reported to PM2.5 value are: Bangladesh – 76.9 μg/m³, Chad – 75.9 μg/m³ and Pakistan – 66.8 μg/m³ [8]. Romania is on 66th position with PM2.5 level of 13.7 μg/m³ [9]. According to EU standards, Romania do not exceed the maximum concentration level of PM2.5 in 2019 but according to U.S. Air Quality Index (AQI) Romania has a "moderate" air quality with risk for some people, particularly those who are unusually sensitive to air pollution [10].

Water pollution

An Organisation for Economic Co-operation and Development (OECD) Country's Report from 2019 discus the water situation and the pollution in Romania. Although it highlights the poor access to water and sanitation in rural areas, it affirms that over two-thirds of Romania's rivers have good ecological status, while the chemical status is good for around 98 %. It concluded that the quality of surface waters in Romania is good comparing with other EU countries [11]. The pollution of surface waters come from discharges not connected to sewer network (25% of surface water bodies), diffuse pollution from agricultural (12%) and urban wastewater (5%) [11]. According to The Statistical Yearbook of Romania from 2019, in 2016 in Romania there were 38346 million m^3/year of total water sources from which 33679 million m^3/year are surface waters and 4667 million m^3/year underground water [12]. The classification of these waters in function of their quality is presented in Fig. 2. The classes are defined as follows: Class I and II – very good and good; Class III – moderate; Class IV – poor and Class V – bad. These statistic data show that, in general, the Romanian waters are of very good, good and moderate quality.

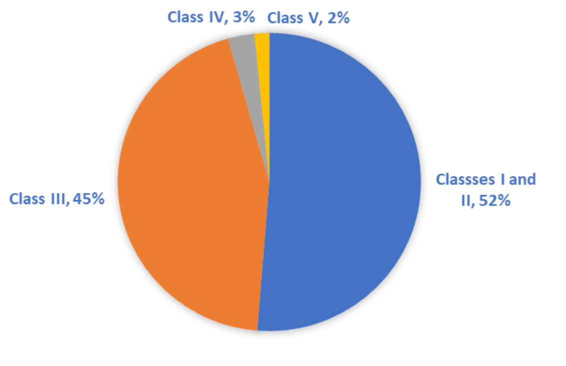


Fig. 2. Classification of Romania's waters in 2017

Soil pollution

Romania has a surface of 238.397 km² distributed according to Romanian Statistical Yearbook 2012 [13] as presented in Fig. 3.

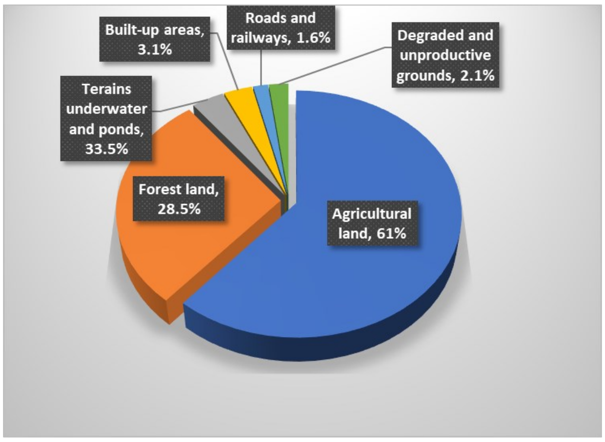


Fig. 3. Romania's soil use in 2012

Approximative 1,48% (3545.94 km²) from total Romania's surface is affected by pollution. The types of soil pollution and the surface [14] they occupied were identified by National Institute of Pedology and Agrochemistry (ICPA) and are presented in Table 1.

Table 1. Types of soil pollution and their surface distribution

No.	Types of soil pollution	Surface (ha)
1.	Soil pollution by mining and quarry activities	23017
2.	Pollution caused by ponds, mining dumps, non-complying landfills	6077
3.	Pollution produced by inorganic residues and waste (minerals, inorganic material, metals, salts, acids, alkalis)	4000
4.	Pollution caused by substances carried by the air (hydrocarbons, ammonia, sulphur dioxide, chlorides, fluorides, nitrogen oxides, lead compounds)	319000
5.	Pollution caused by salted waters from petroleum extraction, petroleum pollution	2500
	TOTAL	**354594**

The data regarding the quality of air, water and soil in Romania shows that a series of regulation must be implemented to reduce the pollution of environmental factors to reach the European Commission standards, especially because Romania is considered to be one of the most polluted countries in Europe.

In 2021 the European Commission sue Romania for following reasons:

1. Romania has not complied to Industrial Emissions Directive (Directive 2010/75 / EU) to prevent or reduce industrial pollution and didn't implement an air pollution control program
2. Illegal waste imports which are shipped through Romanian Port of Constanta [15]
3. Romania failed to comply with Landfill Directive (Directive 1999/31/EC) which sets standards and provides guidance to prevent or reduce as far as possible negative effects on human health and the environment from landfilling of waste. According to these regulations of the Directive, Romania should close and rehabilitate 68 landfills but succeed to rehabilitate only 26. This is the second time when Romania is sued by the European Commission for this problem [16].

One of the major contributors to the world-wide pollution is represented by wastes. They are produced in all human activities: Industrial, Commercial, Domestic, and Agricultural, their effects on the environment are translated in terms of air pollution, climate change, soil and water contamination, loss of biodiversity. In 2020 in Europe were produced 4808 kg/capita of waste while in Romania were produced 7338 kg/capita [17]. Within a Communication from European Commission to European Parliament it is estimated that annual waste generation will increase by 70% by 2050 (an estimation of regional waste generation is presented in Fig. 4). The Communication proposes an improved Circular Economy Action Plan (Fig. 5) which will ensure climate neutrality by 2050 and decoupling economic growth from resource use stating that "EU needs to accelerate the transition towards a regenerative growth model that gives back to the planet more than it takes" [20]. The implementation of Circular Economy Action Plan brings benefits to both business and citizens. The business will have new opportunities worldwide by creating the framework for sustainable products. The citizen will have high-quality, functional and safe products designed to be reused, repaired, and high-quality recycled [20].

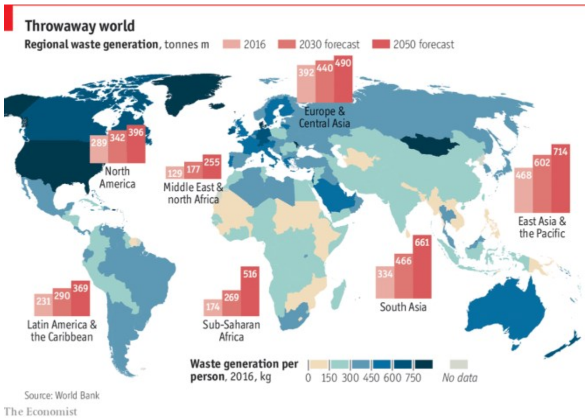


Fig. 4. Estimation of regional waste generation for 2050 [18]

So that Romania can implement all the European Directives regarding the environmental pollution and to comply the principles of the Circular Economy Action Plan it has to be supported.

Environmental Analyses Laboratory, LAM, specialized in studying environmental samples (air, water, soil, vegetation, sludge, and food), liquid fuels/biofuels, natural gas and materials offer technical support to which it may request it to ensure compliance with agreed environmental conditions and standards. The proposed technical solutions are based on standardize and in-house analytical methods obtained as result of the research projects conducted by the R&D department of INCDO-INOE2000, Subsidiary Research Institute for Analytical Instrumentation Cluj-Napoca.

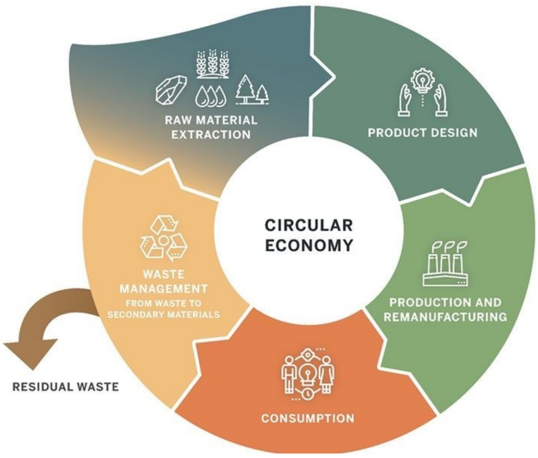


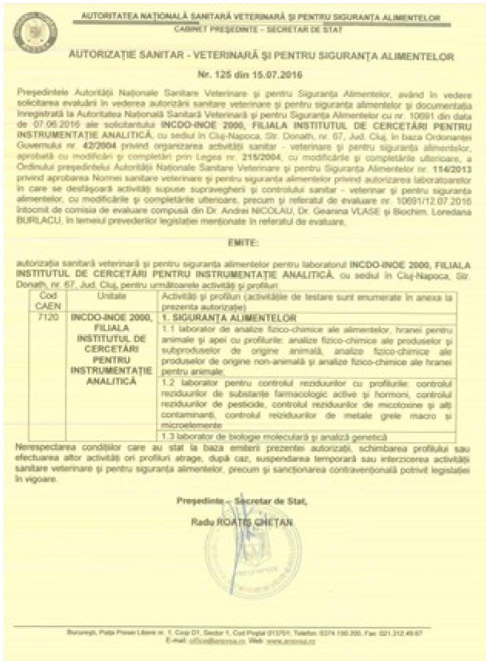
Fig. 5. Schematic of Circular Economy Action Plan [19]

2. History/Landmarks

Environmental Analyses Laboratory, LAM, is a department of INCDO-INOE2000, Subsidiary Research Institute for Analytical Instrumentation starting with the year 2000. Its history and current status are presented below.

History

- 2000 – ICIA adopted new research directions (environment, health, bioenergy and materials), which lead to the necessity of a testing laboratory, respectively LAM
- 2005 – LAM receives RENAR (Romanian Association of Certification) certification (certificate no. LI 352/13.07.2005) which states that LAM meets the requirements of SR EN ISO 17025:2005 – general requirements for the competence of test and calibration laboratories
- 2016 – LAM receives authorization from National Sanitary Veterinary and Food Safety Authority (ANSVSA) to perform food analysis, certificate no. 125/15.07.2016 (Fig. 6)
- 2018 – LAM receives RENAR (Romanian Association of Certification) certification (certificate no. LI 1778/25.05.2018) which states that LAM meets the requirements of SR EN ISO 17025:2018 – general requirements for the competence of test and calibration laboratories (Fig. 7)
- 2005-2022 – Continuous extension of offered services and developed analytical methods, due to a high number of ICIA's ongoing research projects in various fields.



AUTORITATEA NAȚIONALĂ SANITARĂ VETERINARĂ ȘI PENTRU SIGURANȚA ALIMENTELOR
CABINET PREȘEDINTE – SECRETAR DE STAT

AUTORIZAȚIE SANITAR - VETERINARĂ ȘI PENTRU SIGURANȚA ALIMENTELOR

Nr. 125 din 15.07.2016

Președintele Autorității Naționale Sanitare Veterinare și pentru Siguranța Alimentelor, având în vedere solicitarea evaluării în vederea autorizării sanitare veterinare și pentru siguranța alimentelor și documentația înregistrată la Autoritatea Națională Sanitară Veterinară și pentru Siguranța Alimentelor cu nr. 10691 din data de 07.06.2016 ale solicitantului **INCDO-INOE 2000, FILIALA INSTITUTUL DE CERCETĂRI PENTRU INSTRUMENTAȚIE ANALITICĂ**, cu sediul în Cluj-Napoca, Str. Donath, nr. 67, Jud. Cluj, în baza Ordonanței Guvernului nr. **42/2004** privind organizarea activității sanitar - veterinare și pentru siguranța alimentelor, aprobată cu modificări și completări prin Legea nr. **215/2004**, cu modificările și completările ulterioare, a Ordinului președintelui Autorității Naționale Sanitare Veterinare și pentru Siguranța Alimentelor nr. **114/2013** privind aprobarea Normei sanitare veterinare și pentru siguranța alimentelor privind autorizarea laboratoarelor în care se desfășoară activități supuse supravegherii și controlului sanitar - veterinar și pentru siguranța alimentelor, cu modificările și completările ulterioare, precum și referatul de evaluare nr. 10691/12.07.2016 întocmit de comisia de evaluare compusă din Dr. Andrei NICOLAU, Dr. Geanina VLASE și Biochim. Loredana BURLACU, în temeiul prevederilor legislației menționate în referatul de evaluare,

EMITE:

autorizația sanitară veterinară și pentru siguranța alimentelor pentru laboratorul **INCDO-INOE 2000, FILIALA INSTITUTUL DE CERCETĂRI PENTRU INSTRUMENTAȚIE ANALITICĂ**, cu sediul în Cluj-Napoca, Str. Donath, nr. 67, Jud. Cluj, pentru următoarele activități și profiluri:

Cod CAEN	Unitate	Activități și profiluri (activitățile de testare sunt enumerate în anexa la prezenta autorizație)
7120	**INCDO-INOE 2000, FILIALA INSTITUTUL DE CERCETĂRI PENTRU INSTRUMENTAȚIE ANALITICĂ**	**1. SIGURANȚA ALIMENTELOR**
		1.1 laborator de analize fizico-chimice ale alimentelor, hranei pentru animale și apei cu profilurile: analize fizico-chimice ale produselor și subproduselor de origine animală, analize fizico-chimice ale produselor de origine non-animală și analize fizico-chimice ale hranei pentru animale;
		1.2 laborator pentru controlul reziduurilor cu profilurile: controlul reziduurilor de substanțe farmacologic active și hormoni, controlul reziduurilor de pesticide, controlul reziduurilor de micotoxine și alți contaminanți, controlul reziduurilor de metale grele macro și microelemente
		1.3 laborator de biologie moleculară și analiză genetică

Nerespectarea condițiilor care au stat la baza emiterii prezentei autorizații, schimbarea profilului sau efectuarea altor activități ori profiluri atrage, după caz, suspendarea temporară sau interzicerea activității sanitare veterinare și pentru siguranța alimentelor, precum și sancționarea contravențională potrivit legislației în vigoare.

Președinte – Secretar de Stat,

Radu ROATIȘ CHEȚAN

București, Piața Presei Libere nr. 1, Corp D1, Sector 1, Cod Poștal 013701, Telefon: 0374.150.200, Fax: 021.312.49.67
E-mail: office@ansvsa.ro Web: www.ansvsa.ro

Fig. 6. ANSVSA authorization

Current status

The *main activities* which take place in LAM are:

- Applying the analytical methods developed by the ICIA's R&D Department (in the research projects carried out by the unit) to establish the analytical performances for implementation in the ICIA laboratories
- Performing analyzes from environmental samples (air, water, soil, vegetation, sludge, food), liquid fuels/biofuels, natural gas and materials for R&D Department
- Performing analyzes for third parties
- Developing, implementing and validating standardized and non-standardized analytical methods at request of R&D Department and/or of third parties
- Providing consulting services in environmental issues.

ASOCIAŢIA DE ACREDITARE DIN ROMÂNIA - RENAR
Bucureşti, Calea Vitan nr. 242, sector 3, cod 031301
CIF **RO 4311980**

RENAR este semnatar al EA-MLA pentru încercări.

CERTIFICAT DE ACREDITARE
Nr. LI 1178

Asociaţia de Acreditare din România – RENAR, fiind recunoscută ca Organism Naţional de Acreditare prin OG 23/2009, prin prezentul certificat atestă că organizaţia:

Institutul Naţional de Cercetare Dezvoltare pentru Optoelectronică INOE 2000
Filiala Institutul de Cercetări pentru Instrumentaţie Analitică Cluj-Napoca

Cluj-Napoca, Str. Donath nr. 67, judeţul Cluj
prin
Laborator analize de mediu

Îndeplineşte cerinţele **SR EN ISO/CEI 17025:2005** şi este competentă să efectueze activităţi de **ÎNCERCĂRI**, aşa cum se detaliază în Anexele la prezentul certificat de acreditare.

Această acreditare este menţinută cu condiţia îndeplinirii în mod continuu a criteriilor de acreditare stabilite de Asociaţia de Acreditare din România-RENAR.

Prezentul certificat este însoţit de Anexele nr. 1/12.02.2020 (4 pagini) şi nr. 2/12.02.2020 (1 pagină), părţi integrante ale acestuia.

Certificatul de acreditare este un document de acreditare esenţial, care poate fi revizuit şi emis periodic de către RENAR. Cea mai recentă versiune a certificatului de acreditare este disponibilă pe website-ul RENAR, www.renar.ro.

Data acreditării iniţiale: 25.05.2018
Data actualizării: 12.02.2020
Data expirării acreditării: 24.05.2022

DIRECTOR GENERAL AL STRUCTURII EXECUTIVE	**PREŞEDINTE AL CONSILIULUI DE ACREDITARE**
Alina Elena TAINĂ	**dr. ing. Dumitru DINU**

Certificatul de acreditare nu exonerează OEC de obligaţia de a obţine toate aprobările şi autorizaţiile necesare pentru funcţionarea sa conform legii.

Reproducerea parţială a prezentului certificat este interzisă.

Fig. 7. RENAR certificate of accreditation

The *LAM's range of basic analyses:*

- *Environmental samples* (mentioned in RENAR certificate of accreditation)
  - *Water:* Metals by Atomic Spectrometry; Ammonium content, phenol index, total cyanides, hexavalent chromium, anionic surfactants and dissolved sulfides by UV Spectrophotometry; Petroleum products by Infrared Spectrometry; pH and electrical conductivity by electrochemical analysis; Solvent extractible substances, suspended matters, CCO-Mn, CCO-Cr and (CBOn) for undiluted and diluted samples by volumetric methods; Total organic carbon (TOC) and dissolved organic carbon (DOC), the content of bounded nitrogen after oxidation to nitrogen oxides by N/C Analyzer; Fluorides, chlorides, nitrates, nitrites, orthophosphate and sulfates by Liquid Ion Chromatography; Polycyclic aromatic hydrocarbons (PAH) by High Performance Liquid Chromatography; Insecticides such as organoclorurates, polychlorinated biphenyls, chlorobenzenes, determination of volatile halogenated hydrocarbons, determination of BTEX content by Gas Chromatography
  - *Soil:* Metals by Atomic Spectrometry; Cyanides by UV Spectrophotometry; pH by electrochemical analysis; Water content and total hydrocarbons content by gravimetric methods; Petroleum hydrocarbons/ mineral oils by Gas Chromatography
  - *Air:* Sedimentable powders, suspended powders, PM10 and PM2.5 by gravimetric methods; Noise measurement; Physical parameters (speed, flow, temperature, humidity and pressure on sampling site), determination of gases concentrations (O2, CO_2, CO, SO_2, NO, NO_2) from gaseous effluents by on-site analysis, determination of mass concentration of total gaseous organic carbon in waste gases using an FID detector
- *Food*
  - *Food:* Polycyclic aromatic hydrocarbons using liquid chromatography with fluorescence detector (HPLC); Organochlorine pesticides using gas chromatography with electron capture detector (GC-ECD); Water content; Total crude protein; Metals by atomic absorption spectrometry with graphite furnace; Mercury by thermal desorption atomic absorption spectrometry; Aflatoxins B1, B2, G1 and G2 using liquid chromatography with fluorescence detector (HPLC); Antioxidant capacity; Water by Karl Fischer method; Density and viscosity; Total nitrogen content by combustion according to the Dumas principle; Lecithin by liquid chromatography coupled with mass spectrometry
  - *Feed:* Organochlorine pesticides using gas chromatography with electron capture detector; Water content; Total crude protein; Metals by atomic absorption spectrometry with graphite furnace; Mercury by thermal desorption atomic absorption spectrometry; Aflatoxins B1, B2, G1 and G2 using liquid chromatography with fluorescence detector (HPLC); GMO from soy, maize and derived products using TaqMan GMO Screening; Total nitrogen content by combustion according to the Dumas principle
  - *Food of non-animal origin:* GMO from soy, maize and derived products using TaqMan GMO Screening; Spectrophotometric dosage of total polyphenols using Folin -Ciocalteu method; Androsterone by liquid

chromatography coupled with mass spectrometry; Vitamins (B6, B9, C) by liquid chromatography coupled with mass spectrometry; Amino acids by liquid chromatography coupled with mass spectrometr.

- *Fuels/biofuels*: superior caloric power; density at 15°C; viscosity at 40°C; flash point; copper strip corrosion; sulphated ash; total contamination; sulphur content; water content; acid value; iodine value; ester, methyl ester and linoleic acid content; methanol content; monoglyceride, di- and triglyceride content, free glycerol and total glycerol; ignition quality for diesel engines. Cetan method
- *Natural gas* – gas composition and caloric power by Gas Chromatography
- *Materials:*
    - topography (texture, smoothness or roughness), morphology (shape and size) and composition (elements and compounds) data by Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis
    - elemental composition by X-Ray Fluorescence
    - crystalline phase identification by X-Ray Diffraction.

The activity in the laboratory (Fig. 8) is carried out by an interdisciplinary group of 27 members working part or full time in LAM. Their expertise in fields such as: chemistry, physics, environmental science and food industry was enriched with:

- training courses on specific topics of the LAM's activity (method and/or equipment);
- training courses regarding the requirements of SR EN ISO 17025:2018;
- internal audit courses for SR EN ISO 17025:2018;
- specialization at similar national / abroad laboratories.

The material resources which are available in LAM are:

- Modern equipment for sample preparation from top producers such as: Mettler Toledo, Retsch, Heildolph, Sartorius (Fig. 9)
- High performance analytical equipment: Gas (GC) and liquid chromatographs (LC) with various detectors (ECD, MS, UV, FLD); Inductively coupled plasma (ICP) with MS, AES or OES; X-Ray Diffraction (XRD), SEM-EDS (Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS)), infrared techniques (FT-IR, NIR), Raman and portable equipment for measuring imission and emission parameters from top producers such as: Agilent, Perkin Elmers, Thermo Fisher, Bruker, Tescan, Abi Sciex, Methrom, Rigaku, Analytic Jena (Fig. 10)

Fig. 8. Activity in LAM

Fig. 9. Sample preparation system

- High performance analytical equipment: Gas (GC) and liquid chromatographs (LC) with various detectors (ECD, MS, UV, FLD); Inductively coupled plasma (ICP) with MS, AES or OES; X-Ray Diffraction (XRD), SEM-EDS (Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS)), infrared techniques (FT-IR, NIR), Raman and portable equipment for measuring imission and emission parameters from top producers such as: Agilent, Perkin Elmers, Thermo Fisher, Bruker, Tescan, Abi Sciex, Methrom, Rigaku, Analytic Jena (Fig. 10)

- Standards and reagents of high purity degree from top producers such as: Merck, Supelco, LGC.

Fig. 10. Analytical equipment

SWOT (strengths, weaknesses, opportunities, and threats) analysis of LAM (Table 2) was performed to evaluate its performance, competition, risk and potential of a business.

Table 2. SWOT analysis

Strengths

Certifications: RENAR certificate of accreditation and ANSVSA authorization
Resources:
- Laboratory of appropriate dimensions to ensure traceability
- Modern equipment with service contracts that provide also periodic maintenance works
- Interdisciplinary staff with superior studies and additional training courses

Expertise: in the field of analytical chemistry proved by obtaining good results at international scheme of interlaboratory comparisons
Competitive analysis prices

Weaknesses

Lack of marketing strategy: potential partners and clients don't know about the existence of LAM
Lack of staff: lack of a laboratory analyst
Lack of equipment: due to the new legislation regarding the noise measurements it is necessary to acquire another sonometer in order to finish the measurements in time
Lack of infrastructure: lack of samples elevator

Opportunities

New analysis: for material characterization, fast, non-destructive, without requiring special sample preparation
Fast growth: the requests for standardized analysis and at analytical methods developed at request has been increasing
New segments: the request for testing the contamination and defects of own developed materials from industry and especially automotive industry has increased

Threats

Changes of regulations
Changes of working standards
Competition: the increase of environmental laboratory number, the diversification of competitor's analytical methods range
Price erosion: due to instability of the market
Delay of supplies: the inability of service providers to provide service, consumables and reagents in time
Staff departure

SWOT analysis is the foundation for effective strategic planning and was the base of defining the management policy and LAM's quality objectives.

The management policy regarding the quality within the testing laboratory is focused on carrying out the testing activities in accordance with SR EN ISO/CEI 17025:2018, the declared testing methods, satisfying the requirements of the clients and the regulations in force.

The organization of activities inside the laboratory in order to implement, maintain and improve the management system is the responsibility of the director and head of the laboratory and is carried out through the following measures:

- Ensuring the material and human resources corresponding to the good functioning of the laboratory activities, according to the requirements of the referential, of the clients and of the bodies that grant recognition;
- The organization considers the absence or minimization of conflicts of interest;
- Establishing and maintaining appropriate communication processes between all functions;
- Defining the responsibilities, authorities and mutual relations for the entire staff;
- Not subjecting the laboratory staff to any inappropriate internal or external pressure, of an economic, financial or other nature that could influence the quality of the activity;
- Ensuring the technical independence of the laboratory;
- Non-involvement of laboratory staff in any activity that could diminish confidence in the competence, impartiality, decision-making capacity or functional integrity of the organization;
- Treating clients in a non-discriminatory manner and under conditions of confidentiality;
- Ensuring the highest quality level of laboratory activities carried out;
- Ensuring compliance with good practices in the laboratory;
- Staff awareness regarding the role in the laboratory, as well as the importance of the activities for the achievement of the established objectives;
- Ensuring the integrity of the management system when changes to the management system are planned and operated;

- Identifying the risks associated with the processes and treating them in order to minimize them.

LAM's quality objectives are:

- Maintaining the laboratory's accreditation by carrying out the activity in accordance with the SR EN ISO / CEI 17025:2018 standard;
- Carrying out tests in accordance with the standardized test methods and regulatory requirements and the permanent updating of the requirements stipulated in the latest valid editions of the standards;
- Satisfying customer requirements at a level of excellence;
- Continuous improvement of the management system documents by revising them according to the latest recommendations of the policies, regulations;
- The continuous improvement of the staff regarding the quality management system according to the reference SR EN ISO / CEI 17025:2018 by participating in laboratory and external training, as appropriate;
- Improving the level of professional training of the laboratory staff by participating in doctorates, courses and scientific events;
- Maintaining at least the number of clients from 2021;
- Management's communication of the importance of meeting customer requirements and the annual evaluation of their degree of satisfaction;
- Permanent assurance of the validity of the results.

The Director and the head of the Environmental Analysis Laboratory assumes responsibility for fulfilling the policy in the field of quality and the established quality objectives.

In this sense, a quality management system was documented and implemented in accordance with the requirements of SR EN ISO/CEI 17025:2018.

Top management declaration

For the practical application of the quality policy and the fulfillment of the established objectives, we will permanently act for:

- satisfying the requirements expressed in SR EN ISO/CEI 17025:2018, of clients, regulatory and bodies that grant recognition;
- improving the professional competence of the staff and training in the field of quality through adequate training;
- ensuring the necessary resources for the good performance of the testing activity;
- establishing appropriate communication processes throughout the organization;
- knowledge, acquisition and application by the entire staff of the policies related to quality and the documentation of the laboratory's management system;
- ensuring the existence and maintenance of good professional practices in all laboratory activities;
- staff awareness of the importance of their activities;
- non-involvement of laboratory personnel in activities that could diminish confidence in their competence, impartiality, reasoning or functional integrity;
- lack of pressure of any kind on the laboratory staff, ensuring its technical independence;
- periodic analysis of the functioning of the management system to verify compliance with the documentation, identify and assess the risks associated with the processes within the laboratory and to improve the effectiveness of the management system.

3. Current developments and collaborations

Current developments in LAM are described in terms of:

- Methods developed in R&D Department and being implemented in LAM:
  - Determination of several vitamins (D3, K2) from food samples by High Pressure Liquid Chromatography developed in the project *"Innovative materials as dietary supplements for healthcare, IMA-HEALTH"*
  - Determination of several antibiotics (amoxicillin, doxycycline) from food samples by High Pressure Liquid Chromatography developed in the project *"Personalized intelligent matrices for tissue regeneration and meta-inflammation control" (PRIM_TISS)"*
  - Identification of crystalline phase from zeolites by X-Ray diffraction developed in the project "*Achieving the Transfer of Accumulated Knowledge and Technologies Developed by INCDO-INOE 2000, ICIA Branch in the Field of Materials for their Implementation in Romanian Enterprises (TREND)*"
  - Surface characterization and elemental composition identification of zeolites by Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis developed in the project "*Achieving the Transfer of Accumulated Knowledge and Technologies Developed by INCDO-INOE 2000, ICIA Branch in the Field of Materials for their Implementation in Romanian Enterprises (TREND)*"
  - Surface characterization and elemental composition identification of cements by Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis developed in the project "*Study on the properties of cement-based composite materials with the addition*

of lignocellulosic waste, using NMR technique"
- Method for testing the waste from electrical and electronic equipment (WEEE) by leaching test developed in the project *"Innovative Technologies for Advanced Materials Recovery from IT and Telecommunication Waste (TRADE-IT)"* – subproject "*Surveillance and control modern analytical methods for the technological flow used to obtain reusable materials from waste (MESUCO)"*
- Methods for determining the parameters of WEEE leaching test developed in the project *"Innovative Technologies for Advanced Materials Recovery from IT and Telecommunication Waste (TRADE-IT)"* – subproject "*Surveillance and control modern analytical methods for the technological flow used to obtain reusable materials from waste (MESUCO)"*
- Method for evaluating the elemental composition of the WEEE waste developed in the project *"Innovative Technologies for Advanced Materials Recovery from IT and Telecommunication Waste (TRADE-IT)"* – subproject "*Surveillance and control modern analytical methods for the technological flow used to obtain reusable materials from waste (MESUCO)"*
- Method for identifying the type of plastic mass in WEEE waste developed in the project *"Innovative Technologies for Advanced Materials Recovery from IT and Telecommunication Waste (TRADE-IT)"* – subproject "*Surveillance and control modern analytical methods for the technological flow used to obtain reusable materials from waste (MESUCO)"*
- Method for evaluating the degree of recovery of metals from waste developed in the project *"Innovative Technologies for Advanced Materials Recovery from IT and Telecommunication Waste (TRADE-IT)"* – subproject "*Surveillance and control modern analytical methods for the technological flow used to obtain reusable materials from waste (MESUCO)"*

- Methods which are being developed to offer a technical solution to new challenges related to environmental pollution:
  - Physico–chemical characterization of waste
  - Determination of dioxins from food and air samples by Gas Chromatography
  - Determination of new generation pesticides from food, water and soil samples
- Assuring good performance of current requests and economical contracts.

LAM has:
- Strong collaboration relationship with ICIA's R&D Department for implementing the analytical method obtain in research projects
- Interactive collaboration relationship with customers to meet their requests: physical – chemical analysis, data interpretation, consultancy in environmental issues and transfer of the results
- Collaboration with national and private laboratories with similar range of analysis
- Collaboration with several educational units by allowing their students to learn and practice analytical methods implemented in the laboratory (Figs. 11 and 12).

Fig. 11. Visit to Technical College Ana Aslan Cluj. Teaching high school students about air immissions: parameters, maximum admitted levels and determination methods

Fig. 12. Participation at Researchers Night 2022. Demonstrations for children, students and academia members

4. Recent results

The most important results of 2022 for LAM are:
- Large number of costumers, economic contracts and won auctions:
  - Costumers: ~ 350 (from household consumer to large manufacturing companies)
  - Won auctions: ~ 25 from 40
  - Economic contracts: ~100

- Important customers: Farmec, Carbochim, Plimob, Michelin, Astra Rail, CET Arad, Romgaz Ludus, Romgaz Medias, Primaria Valea lui Mihai, DRDP Brasov, DRPD Cluj-Napoca, CFR Marfa, CFR Calatori Cluj-Napoca, Transavia.

- Studies performed for several manufacturing companies which helped them plan their environmental strategy leading to less or none penalties
- Researches developed at costumers' requests which were completed successfully:
  - Monitoring the air parameters in big halls to test the efficacy of a modern air cleaning installation and to establish best working parameters
  - Developing and validating an analytical method to test several drugs from water in order to test the efficacy of a *water purification plant* and to establish best working parameters
  - Monitoring soil and plant parameters to establish their changes and the factors that lead to those changes that affected a *thuja culture*
  - Monitoring the migration of metals from enameled metal vessels
  - Monitoring the migration of metals from taps used in domestic water supply installations.

5. New directions of research

The new directions of research which will be promoted in LAM will follow to:

- To assure technical support for those who want to implement the principles of circular economy in their activity by performing analysis from the raw materials to the final product, analysis of resulted waste and analysis to reintroduce the waste in the production circuit, if it's applicable
- To assure environmental analysis in all production circuit to verify the compliance with national and European standards
- To verify food quality
- To test the biodegradability of packaging materials.

The analytical methods which will be developed to complete the range of existing analyses in order to achieve the proposed purpose are:

- Air
  - implementation and validation of quick in situ methods for determining air pollutants such as: COV, ozone, NO, NO_2, NO_x, CO, CO_2, SO_2 and NH_3 from immissions.

- Wastes:
  - implementation and validation of analytical methods for phisico-chemical characterization of waste
  - developing modern analytical methods to test the possibility to use wastes as raw material

- Food:
  - implementation and validation of quick in situ methods to identify the adulteration of vegetal oils
  - implementation and validation of quick in situ methods to identify the adulteration of nutritive supplements
  - implementation and validation of dioxins determination
  - implementation of new analytical methods for food quality analysis

- Materials
  - implementation and validation of analytical methods to test the biodegradable packaging

6. Perspectives

LAM follows, through its current activity and by achieving to implement the analytical methods proposed previously:

- to obtain superior knowledge in the fields of environmental, waste, materials and food
- to become more competitive in these fields
- to become known as an expert in the above-mentioned fields
- to develop strong working relationships with similar laboratories from Romania and abroad
- to develop strong relationships with decisional factors in implementing the directives of Circular Economy Action Plan
- to be an integrated part of the transition process to a circular economy
- to reach the degree of necessary maturity to become one of the national refence laboratory for environmental and food safety.

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Exploring innovative materials using advanced analytical techniques for prospective applications

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Abstract. One of the main concerns of INCDO-INOE 2000, subsidiary Research Institute for Analytical Instrumentation (ICIA) refers to the characterization and analysis of natural and synthetic materials designed for various applications. The most relevant results refer to: (*i*) characterization of natural, modified zeolites, (*iii*) recovery of precious metals from spent catalysts, (*iii*) scanning electron microscopy for materials characterization, (*iv*) simulated biological fluids and in vitro release testing, (*v*) nanoparticles in modern medicine and advanced materials for healthcare, (*vi*) non-destructive isotopic ratio method to establish the origin of Roman glazed ceramic, (*vii*) cement-based composite materials and (*viii*) meteorite identification and classification.

Keywords: Innovative materials, Characterization, Applications, ICIA Subsidiary

1. Introduction

With the up-to-date development of materials science, various cost-effective and high-quality materials have come into use in various fields of science and technology. Conventionally, this has been achieved by applying the developments in physics, chemistry and engineering that have permitted significant advances in the properties of materials such as metals, ceramics, polymers, composites, semiconductors, etc. Recently, materials science has extended into the field of nanotechnology and biomaterials. Many categories of materials with novel and interesting properties are complementary, rather than competitive, in our activities to achieve better quality of human life [1].

Currently, the materials converted multi-functional and require improvement and optimization in their characteristics. In this regard, the development of the material's structure, designed for each new application, requires understanding base matter characteristics, the changes in the microstructure and characteristics of the material during the obtaining process. The comprehensive characterization of materials is an important step to be taken before using the materials for any purpose. Physical and chemical characterization helps developers further understand of the material and final product, thus warranting quality control [2].

Depending on the envisioned application, the materials characterization can involve the measurement of a wide range of properties, such as mechanical, optical, thermal, electrical, chemical and other properties, in order to make sure that the material under consideration can function without failure for the life of the final product [2,3]. Consequently, it becomes imperative that choice of techniques, instruments, measurement parameters and analysis methods to be done in a judicious manner without losing sight of cost-effectiveness and performance requirements. Additionally, the non-destructive testing comprising various analysis techniques to monitor the properties of materials and components without producing damage to the original part, is preferred.

2. History

INCDO-INOE 2000, Research Institute for Analytical Instrumentation (ICIA) Subsidiary (*www.icia.ro*) is a national research institute focused on the fundamental and applied research, analytical methodologies elaboration for a wide range of samples, design and construction of laboratory analytical instruments, carrying out of chemical analyses and offering services of information, advice and representation for business.

Since 1996, ICIA became part of the INCDO-INOE 2000 national institute, being accredited in 2008 for research (ANCS Decision no. 9634/14.04.2008) and certified A+ in the process of evaluation and classification units and institutions of the national research-development system (ANCSI Decision no. 9008/01.07.2016), certifying the quality of both the methods used and the data obtained within the institute laboratories.

3. Current developments and collaborations

ICIA supports the sustainable development of society by endorsing a favorable climate for research and innovation, entrepreneurship and stimulating cooperation between business and research, to capitalize on research results. Working in collaboration with multiple national and international universities, research institutes, and private and public laboratories, ICIA offers an innovative and professional service to a diverse customer base.

In the field of the expansive and interdisciplinary field of materials science, the main interest of ICIA are focused on: - synthesis and physico-chemical characterization of (nano)materials with applications in conventional and modern technologies, - elaboration of analytical methodologies for a wide range of materials, - behavior of (nano)materials in simulated biological media; - evaluation of tissue biodistribution of silver and gold nanoparticles, - new tools and smart composites based on advanced nanotechnology for medical applications; - synthesis and characterization of biomaterials and endodontic cements with poly-functional properties; - synthesis and characterization of undoped and doped (nano)ferrites; - the fate and behavior of nanomaterials in surface and groundwaters; - testing of virgin and spent catalysts containing precious metals; -obtaining advance materials capitalizing local natural resources (natural zeolites), - non-destructive isotopic ratio method to establish the origin of Roman glazed ceramic, -obtaining and characterization of Cement-based composite materials with the addition of lignocellulosic waste and - meteorite identification and classification using a fast, non-destructive X-ray fluorescence analytical method, paired with machine learning techniques, - identification, for builders and economic agents, of the market requirements regarding the technologies, services and products in the fields of (nano)materials.

Since 2019, ICIA is a member of cluster *Advanced Materials, Micro and Nanotechnologies, ADMATECH* (*https://admatech.org/*).

ICIA has a large pool of modern instrumentation to attain a complex physico-chemical characterization of natural and innovative synthetic materials, such as spectrometric techniques (Inductively coupled plasma mass spectrometry, ICP-MS; Inductively coupled plasma - optical emission spectrometry, ICP-OES; scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDX); X-ray diffraction, XRD; X-ray fluorescence, XRF; high-performance liquid chromatography coupled with diode array detection (HPLC-DAD), Fourier-transform infrared spectroscopy, FT-IR; portable Rigaku Progeny Handheld Raman spectrometer; pH-meter; elemental analyzer; freeze-dryer; microwave digesters; ultrapure water systems; evaporator; shakers; ultrasonic bath; magnetic stirrers, cleanroom facilities; fume hoods (material infrastructure and offered services: *https://erris.gov.ro/ICIA-Cluj-Napoca*). The above-mentioned instrumentation plays important and complementary roles in materials characterization.

The relevant endowment in this field is Bruker D8 Advance X-ray Diffractometer (XRD), Tescan VEGA3 SBU-EasyProbe scanning electron microscope with energy dispersive X-ray spectroscopy Bruker Quantax 200 EDX detector, pXRF Brucker Tracer 5i, Thermo Scientific Flash 2000 CHNS/O analyzer, Perkin Elmer Elan DRC II inductively coupled plasma-mass spectrometer (ICP-MS), Thermo Scientific iCAP TQ inductively coupled plasma-mass spectrometer (ICP-MS), Perkin Elmer 5300DV inductively-coupled plasma optical emission spectrometer (ICP-OES), Perkin Elmer Spectrum BX II Fourier-transformed infrared spectrometer (FT-IR) and Perkin Elmer Lambda 25 UV/VIS spectrophotometer.

The most relevant recent research and development ICIA's projects in the field of materials are:

- *"Transfer of knowledge and technologies developed by INCDO-INOE 2000, ICIA subsidiary, in the field of materials for their implementation at enterprises in Romania"*, TREND, contr. no. 7/01.09.2016, 2016-2022 aiming at extending the transfer of knowledge and technology in the field of materials towards public and private enterprises, for the superior capitalization of the zeolitic volcanic tuff from Romania.
- *"Nanovaccinal approaches for colon cancer", NANOVACOL*, PED, contr. no. 323PED/2020, 2020-2022 pointing a new method of immunization through combined administration of functionalized gold nanoparticles.
- *"Personalized intelligent matrices for tissue regeneration and meta-inflammation control"*, PRIM-TISS, PED, contr. no. 348PED/2020, 2020-2022 focusing on a new matrix system based on polylactic acid (PLA) and nano-hydroxyapatite (nano-HAP) with embedded silver (Ag) and doxycycline (Doxy) and new method of treatment (personalized multimodal and sequential treatment targeted against periodontal pathogens) of periodontal disease.
- *"Innovative materials as dietary supplements for healthcare"*, IMA-HEALTH, PED, contr. no. 481PED/2020, 2020-2022 targeting a new preparation method and advanced materials based on sub-micron hydroxyapatite (HAP) as dietary supplements for healthcare.
- "*Complex analytical methods to study the Roman glazed ceramic from Dacian Kingdom for establishing the origin of archaeological artefacts, imports/local production, at the Eastern border of Roman Empire*", GLAZEX, 352PED/2020, 2020-2022 aiming the development a complex set of analytical spectrometric, modern, archaeometric methods (XRF, XRD, ICP-AES, ICP-MS (quantitative, multi-elemental, isotopic report method) for studying the Roman glazed ceramic from Dacia in order to determine the origin of the archaeologic artefacts, imports or local production of this subcategory of ceramic products manufactured by the Roman potters.
- *"Development of innovative nanomaterials based on advanced nanotechnology with applicability in prophylaxis of dental and periodontal diseases"*, INOVAMAT, PN II Program, contr. no. 241/2014, 2014-2016 focusing on the development and optimization of new dental biomaterials and endodontic cements with poly-functional properties, obtained by specific methods of molecular or colloidal self-assembly.
- *"Development of new tools and smart composites based on advanced nanotechnology for medical applications"*, DONTAS, PNII Program, contr. no. 171/2012, 2012-2014 pointing the development of new tools and smart composites based on advanced nanotechnology for medical applications.
- *"Recovery of precious metals from spent catalysts by supercritical CO_2 extraction assisted by polymers"*, SUPERMET, COFUND-ERANET-ERAMIN, contr. no. 48/2018, 2019-2021 aiming an eco-friendly disruptive technology for the recycling of precious metals, especially palladium (Pd) and platinum (Pt), from spent catalysts by extraction in supercritical CO_2

($scCO_2$) thanks to complexing polymers bringing the insoluble precious metals into the $scCO_2$ medium.

- *"Study on the properties of cement-based composite materials with the addition of lignocellulosic waste using NMR technique*", LIGNOCEM, PD, contr. no. PD79/2022, 2022-2023 targeting the production of a new composite cement-based material with the addition of lignocellulosic waste in order to increase specific properties and development/extension of NMR technique to characterize the construction materials made with lignocellulosic waste in order to obtain an optimal composition.

4. Spotlights on research activity. Recent results and transfers of results

4.1. Advanced analytical techniques for exploring innovative materials (ICIA)

4.1.1. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

ICIA has the necessary infrastructure to attain a complex exploring of innovative materials using advanced analytical techniques for prospective applications. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) is one of the most widely used and versatile methods of inorganic analysis. Compared with absorption spectrophotometers used for similar purposes, ICP-OES offers several advantages, such as multi-elemental analysis of multiple elements; wide linear calibration curve (up to 7 orders of magnitude), allowing the determination of elements in trace or as major constituents; few chemical interferences or ionization interference, offering the possibility to analyze high-matrix samples; low limit of detection for majority of elements (usually below ten ppb); the high number of elements that can be measured by this technique (including rare earth, P, B Zr, Ta, etc. that are very difficult to be analyzed by other technique). ICP-OES Perkin Elmer Optima 5300 DV is presented in Figure 1.

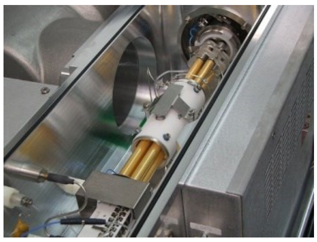
Fig. 1. ICP-OES Perkin Elmer Optima 5300 DV

One major application of ICP-OES is material analysis. Different materials can be analyzed: ceramics, cement, glass, natural zeolites, metallurgical samples, pharmaceuticals, cosmetics, and intermediate and finished products from the chemical industry. However, ICP-OES allows only the analysis of liquid samples. In this regard, the digestion of solid samples by microwave-assisted acid extraction procedures at high pressures and temperatures is often used. In this approach, the resulting liquid solution is homogeneous, allowing the determination of the concentration of metals. The preliminary step of sample preparation is significant in obtaining reliable results since the analyte's quantitative recovery, and the absence of contamination is essential. ICP-OES methodologies were validated in our laboratory both for the digestion step and for the instrumental determination.

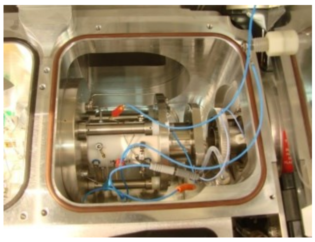
4.1.2. Inductively coupled plasma mass spectrometry (ICP-MS)

If innovative materials investigated require lower detection limit, inductively coupled plasma mass spectrometry (ICP-MS) can provide detection limit below 1 ppb, but ICP-MS analysis are destructive. However, an analysis usually doesn't require more than 5 ml of liquid sample and it can offer quantitative information about 60 to 80 elements or it can offer stable isotopic ratio data for some specific elements.

Both Perkin-Elmer Elan DRC II and ThermoScientific iCAP TQ inductively coupled plasma mass spectrometers (Figure 2 a and b) in our laboratory use a quadrupole as ion filter and while a quadrupole is a fast and versatile ion filter, due to its relatively low resolution, it can be a source of isobaric (different isotopes with approximatively the same mass, for example ^{204}Hg and ^{204}Pb) and polyatomic interferences (a group of ions with the same mass as the analyzed ion, for example $^{40}Ar^{16}O$ and ^{56}Fe).



(a)



(b)

Fig. 2. (a) Perkin Elmer Elan DRC II ICP-MS (single quad) and (b) ThermoScientific iCAP TQ ICP-MS (triple quad).

Isobaric and polyatomic interferences are the most common disadvantage to ICP-MS measurements, but various interference removing tools can be successfully used in modern spectrometers. Collision/reaction cells, placed before the main quadrupole, can be pressurized with either (*i*) a collision gas, like Helium, to remove most interferences based on kinetic energy discrimination (KED) technique, either (*ii*) a reaction gas (like ammonia, methane or oxygen) to either remove the interference agent by chemical reaction or to shift the mass of the analyzed ion to a higher value (by reaction with oxygen), where no interferences are present.

A more recent development consists in adding a third quadrupole (with the collision/reaction cell placed between the two main quadrupoles, on the ion travelling axis) and use that in conjunction with KED or mass shift approach to better tackle more persistent interferences.

The ICP-MS spectrometers can be used by themselves to deliver data, or coupled with a variety of modules, to extend their applications (HPLC, -High-performance liquid chromatography for elemental speciation analysis or a LA, -laser ablation system, for direct solid sample investigations).

4.1.3. Elemental CHNS/O analyzer

Carbon (C), nitrogen (N), hydrogen (H), sulfur (S) analysis by combustion analysis, and oxygen (O) determination by pyrolysis are commonly used for both the characterization and analysis of materials and for research and development purposes. Thermo Scientific Flash 2000 is a modern and compact analyzer intended for the determination of CHNS and O in any type of sample from solid to liquid. In the field of material characterization (glue/resin, papers, rubbers, cement, ceramics, carbon/ glass fibers, tires, pigments and dyes, refractory materials, building materials, inorganic materials, metals, textile fibers, wood powders) this analyzer allows the fast quantitative determination of these elements from few ppm to 100%.

4.1.4. Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Analysis (EDX)

Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Analysis (EDX) is used nowadays from research to industry, from the development of an application to testing the final product. It has applications in materials science, biology, food, environmental science, art and forensic science by providing important information about the sample surface such as: topography (texture, smoothness or roughness), morphology (shape and size) and composition (elements and compounds) [4].

EDX is a powerful tool to investigate the elemental composition of the samples (by point analysis), the changes of the phases' chemical composition along a selected cross-section (by line analysis) and the distribution of elements in a selected area (by mapping). It can also provide information about the number and the sizes of particles found on a selected area.

The sample preparation techniques can vary depending of the sample type. In case of dried solids, there are two simple ways to prepare the SEM stub, first by putting a carbon adhesive tape on the surface of the stub with the sample on top and second, by coating the sample with a gold thin layer (in case on non-conductive samples). In case of biological samples, the preparation is more complex, and it can last from several hours to several days depending on the particles which are to be investigated.

Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Analysis (EDX) analysis is carried out with a SEM TESCAN VEGA 3 SBU microscope with a Quantax EDS XFlash Detector (Figure 3). SEM TESCAN VEGA 3 SBU microscope is suitable for applications which requires low or high vacuum.

This technique has the following main features: (*i*) electron gun: tungsten heated cathode, (*ii*) magnification range: from 3× to 1,000,000×, (*iii*) electron beam energy: from 200 eV to 30 keV, (*iv*) sample chamber with an internal dimension of ø 160 mm, (*v*) detectors: Secondary electron detector (SE) and Retractable Back-scattered electrons detector (BSE). Moreover, the software permits real-time calculation of spot size of the sample, continuous shape adjustment and change of the size and position of the focusing window.

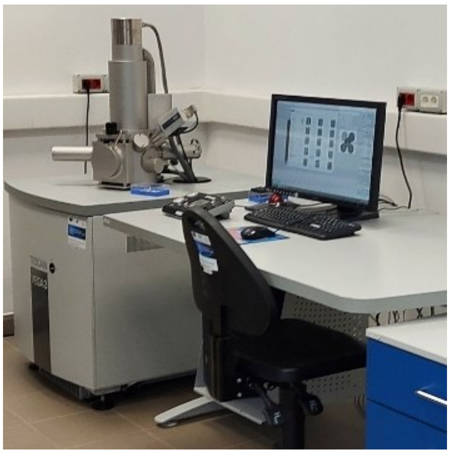


Fig. 3. SEM TESCAN VEGA 3 SBU microscope with a Quantax EDS XFlash detector

Quantax EDS XFlash detector allows energy resolution of 129 eV at Mn Kα, and active area 10 or 30 mm^2. EDX data are processed with Esprit software which provides the following main futures: spectra acquisition and qualitative analysis; spectrum preview and live spectrum display; interactive element identification tools; tools for standardless and standard-related quantitative spectra evaluation; qualitative and quantitative line scan options; surface mapping with tools for classical qualitative and quantitative mapping and HyperMap with a complete spectrum for each mapped point; external electron beam control, mode switching, and image acquisition; fast preview mode for scan area selection and beam adjustment; independent selection of acquisition time, image resolution and scan modes; pixel, line and frame averaging including power line synchronization (option); automatic and manual brightness, contrast and gamma correction; display of histogram; ESPRIT microanalysis package which allows to detect, measure and analyze any form of feature, and to provide its chemical classification [5].

4.1.5. Fourier transform infrared (FT-IR) spectrometry

FT-IR is a widely used method both for qualitative and quantitative analysis of materials (Figure 4). It allows the identification and characterization of unknown materials, detection of impurities or additives as well as the identification of different degradation processes. The identification of organic or inorganic compounds in a sample is based on the specific spectral bands that appear at different frequencies in the FT-IR spectrum. The quantitative analysis is possible based on the proportionality between the peak intensity and concentration of a compound. Generally, the FT-IR spectrum is recorded between 4000 and 400 cm^{-1} in transmittance or absorbance. A typical FT-IR spectrometer includes a source, sample compartment, detector, signal amplifier, and a computer.

Fig. 4. Perkin Elmer Spectrum BX II Fourier transform infrared spectrometer.

One interesting application of the FT-IR spectroscopy was the identification of minerals present in speleothems and sediments from caves (Figure 5). The peaks at 2512/1793/874/712 cm^{-1} and 1424 cm^{-1} specific for the C-O bond stretching vibration in carbonates confirmed the presence of calcite and dolomite in stalactite, stalagmite, and sediments. The signal intensity for C-O vibration bands was higher in stalactites and stalagmites compared to sediments. Instead, the vibration bands of the Si-O bond at 912/540 cm^{-1} and 1035/470 cm^{-1} associated to quartz and orthosilicate in kaolinite, were more prominent in the sediment sample compared to those in speleothems.

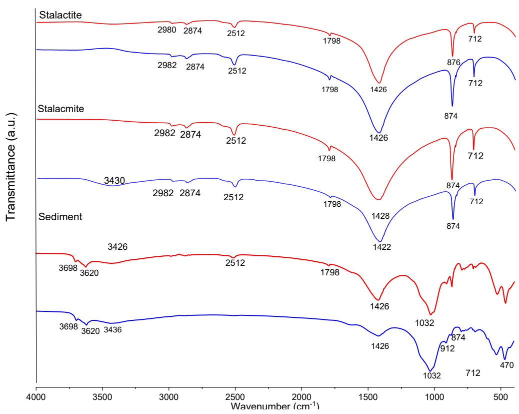


Fig. 5. FT-IR spectra of speleothems and sediments from Ursilor Cave.

4.1.6. X-ray fluorescence (XRF)

For innovative materials that require non-destructive analytical techniques, X-ray fluorescence (XRF) might provide the best approach for fast elemental analysis. Bruker Tracer 5i is a portable spectrometer that can be used both in the lab, but also in-situ, if sample can't be transported in a laboratory environment. Obtained XRF data can be used on their own, or the technique can be paired with other analytical tools, as a complementary investigation: inductively coupled plasma mass spectrometry (for lowering the detection limit) or X-ray diffraction (as a complementary tool). XRF data acquisition is relatively fast (usually no more than 60 seconds per sample, per reading) and for most cases there are no sample preparations steps (although sample homogeneity is essential for good analytical data).

Both qualitative and quantitative analyses are available, for a wide range of sample matrices: liquid, powder, solid (bulk) or alloys can be investigated in a completely non-destructive manner (samples are not affected during the measurement process). A variety of filters can be used (supplied by the manufacturer or custom made by the user) for better data acquisition and there's also the option to create a vacuum inside the sample tube, or to purge the device with helium, both approaches help with lowering the noise for elements with low atomic number Z.

4.1.7. X-ray diffraction (XRD)

XRD is a powerful nondestructive technique for extracting structural information from virtually any type of sample, regardless of shape, size and composition, under ambient or non-ambient conditions. Bruker D8 Advance (Figure 6) is a system that guarantees superior-quality results, the shortest possible measurement time, the highest analytical performance and offers information about phase composition, phase transition, amorphous content, percent crystallinity, crystallite size, lattice parameters, crystal structure, symmetry coordination and order/disorder. Bruker D8 Advance is equipped with an ultra-fast detector Lynxeye XE having high-speed data acquisition up to 450 times faster than a conventional point detector system and MTC-HIGHTEMP high temperature chamber for measurement between room temperature and +1600°C in air, inert atmosphere and vacuum.

Fig. 6. Bruker D8 Advance diffractometer.

The most relevant ICIA's results refer to the mineralogical composition of a wide range of materials, organic and inorganic, natural and synthetic, namely minerals, metals, ceramic, glass, plastic, drugs, paper, stalactites, and stalagmites, biomass pellets, etc.

The natural zeolites never exist in a unique form and usually comprise several minerals. In this regard, the XRD analysis of the natural zeolite sample from Chilioara quarry, Romania, raw and treated at different temperatures showed that the main minerals were clinoptilolite as major crystalline phase, accompanied by muscovite, quartz, montmorillonite, and albite. The non-crystalline components were not quantified by the XRD analysis, but the presence of amorphous volcanic glass in raw zeolite is indicated by the broad diffraction hump in the region 2θ=18-25 ° (Figure 7). The thermal treatment of raw zeolite up to 500 °C does not produce significant structural changes detectable by XRD, while further increase in the temperature produces a gradual collapse of the zeolite. The thermal stability up to 500 °C of the natural clinoptilolite rich zeolite from Chilioara, Romania can be explained by the reversible dehydration that takes place with little or no modification of the crystal structure. The total disappearance of the characteristic peaks of clinoptilolite indicating the complete amorphization did not take place up to 800 ºC.

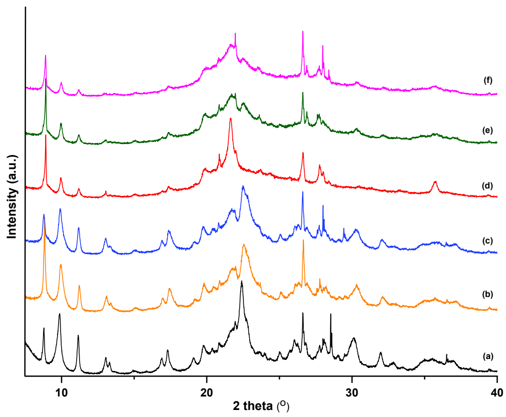


Fig. 7. XRD patterns of (a) raw zeolite and thermally treated zeolite at (b) 400, (c) 500, (d) 600, (e) 700 and (f) 800 ºC.

4.2. Natural, modified Romanian zeolites

Natural zeolites, which can be suitably used in different technological processes, are present in large sedimentary tuff deposits, often of volcanic origin, widespread all over the world. Natural zeolites are hydrated aluminosilicate materials with excellent physical and chemical properties, which include losing and receiving water in a reverse way, adsorbing molecules that act as molecular sieves, and replacing their constituent cations without structural change by ion-exchange and sorption properties.

Their effectiveness in diverse technological procedures depends on their physical-chemical properties that are closely linked to their geological deposits. The unique three-dimensional porous structure gives natural zeolites various potential applications. Due to the negative charge on the surface of zeolite, which results from the isomorphic replacement of silicon by aluminum in the primary structural units, natural zeolites fit the group of cationic exchangers.

Natural zeolites have many advantages compared with other cation exchange materials because they are inexpensive, show excellent selectivity for different cations, and release non-toxic exchangeable cations (K^+, Na^+, Ca^{2+}, and Mg^{2+}) to the environment.

In the frame of project TREND, 13 applications of Romanian natural zeolites were developed [6-22].

4.2.1. Adsorbent material based on zeolitic material for the retention of ammonium and hydrogen sulfide from contaminated environments

Natural zeolite from Racosu de Jos quarry, Brasov County, was grounded to obtain a grain size of 1.25-3 mm, then was thermally treated, and chemically activated (NaCl 2M) and characterized from a physical-chemical point of view. Its adsorption capacity for ammonium ion and sulfide was tested using contaminated solutions. It was found to be highly efficient in the removal of ammonium and hydrogen sulfide from contaminated water.

4.2.2. Adsorbent material based on zeolitic material for the absorption of hydrocarbons from contaminated environments

Natural zeolite from Racosu de Jos quarry, Brasov County, was grounded to obtain a grain size <10 µm, then was thermally treated (250-600°C). Its adsorption capacity for petroleum hydrocarbons was tested on diesel fuel. It can be successfully used for decontamination in fuel stations, oil refineries, car services, and industrial and naval platforms. The material soaked with petroleum hydrocarbons can be successfully used in cogeneration processes, and the resulting ash can be used in agricultural practices as a fertilizer, thus generating no waste.

4.2.3. Filtration media for retaining specific contaminants (Fe, Mn) for drinking water

Natural zeolite from Racosu de Jos quarry, Brasov County, with grain size 0.5-1.25 mm and thermally treated at 200°C, was used as filtering material in filters designed to retain Fe and Mn from underground contaminated water. The removal experiments were done at different flow rates in the range of 0.22-0.66 L/min and the removal efficiency for both elements was > 80%.

4.2.4. Slow-release fertilizer obtained by the absorption of nutrients and pesticides in the structure of the zeolitic volcanic tuff

Natural zeolite from Racosu de Jos quarry, Brasov County was used to produce a slow-release fertilizer obtained by the absorption of nutrients and pesticides in the structure of the zeolitic volcanic tuff. The usage of zeolites as soil fertilizers has several advantages: neutralization of the excessive acidity of some soils due to the alkaline character of zeolites; efficient retention of water in the zeolite structure (hydrophilic character) in rainy/wet periods and its gradual release in dry periods; storage of different active compounds (insecticides, pesticides, pheromones, etc.), which are later released into the soil in a controlled manner.

The retention in the zeolite structure of N and P nutrients was tested. Also, the retention in the zeolite structure of the fungicide fenhexamid and the insecticides cypermethrin and fenvalerate was verified. The experiments showed that the zeolite could retain these substances and release them in a controlled manner.

4.2.5. Filter material based on zeolitic material for removal of heavy metals and radioactive substances

Two grain sizes (<50 µm and 1.25 – 3 mm) of natural zeolite obtained from Racosu de Jos quarry, Brasov County, thermally treated, was used as filtering material for heavy metals (Cd, Pb, Ni, Cr, Cu) and radionuclides (Cs and Sr). The removal of heavy metal ions and radioactive elements from water by means of natural zeolites is carried out through a series of processes such as ion exchange, adsorption, and precipitation on the surface.

Ion exchange, using natural zeolites, can be considered one of the most attractive methods for pollutant retention. The ion exchange reaction takes place between the exchangeable cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}) located in the zeolite structure and the metal cations (M^{n+}). Depending on the initial concentration of contaminant, the removal efficiency can exceed 90 %. The lower grain size (<50 µm) was found much more efficient in heavy metals and radionuclides removal.

4.2.6. Material based on zeolitic volcanic tuff for the immobilization of heavy metals in contaminated soils

Natural zeolite from Macicas quarry, Cluj County was successfully used in the decontamination of soils by immobilizing metals with potential toxic (As, Cd, Cr, Co, Mn, Ni, Pb and Zn), having comparatively lower production costs with the materials currently used. The pot experiments showed that by adding a quantity of 5% material to the amount of soil (m/m) is effective in immobilizing metals and reducing the transfer of metals from soil to plants.

4.2.7. Zeolite filter material for the purification of some food products (beer filtration)

Zeolitic volcanic tuff from two quarries from Salaj County (Chilioara – containing 60-80% K-clinoptilolite and Valea Pomilor – having 35-40% Ca-clinoptilolite) was characterized and tested as potential filtering media for beer clarification. Two technologies were developed to produce filtering materials from the two deposits. Two different gain sizes materials (100 µm and 40 µm) were thermally treated at 600 °C) and used for beer clarification on a pilot scale installation. In Figure 8 is presented the filtering layers formed in filtration compartment.

Results obtained for the filtered product (within the filtration experiments carried out at the level of laboratory and pilot station levels have indicated that the filter material based on zeolite in the mixture with diatomite meets the strict requirements of the beer industry regarding purification and filtration at the same time and can successfully replace traditional filter materials.

Fig. 8. Filtering layers and the filtration compartment

4.2.8. Nutritional supplement and additive for animal feed, based on zeolitic material

Natural zeolite from Macicasu quarry, Cluj County was used to produce an additive for animal feed. Four amino acids (glycine, serine, asparagine, and phenylalanine) were combined with the zeolite. The tests showed that the nutritional supplement does not contain contaminants (Cd, Pb, As, polychlorinated biphenyls, pesticides) with concentrations exceeding the maximum value allowed by the norms in force for animal feed.

Other product for animal use was litter for animals produced in the form of pellets from wood waste combined with zeolitic material, presented in Figure 9.

Fig. 9. Pellets produced as litter for animals

4.2.9. Material based on natural zeolites to eliminate odors and reduce humidity

Natural zeolite was tested as material that eliminates odors and reduces humidity. They were obtained: a material for reducing humidity, a material for eliminating the smell of shoes and their storage spaces, and a product for eliminating the smell of tobacco from the rooms.

4.2.10. Automated filtration installation with zeolite-based filters for industrial water treatment plants

An automated installation with zeolite-based filters for purification of industrial water was developed. This installation is based on biological purification in which the zeolite works as a support for the activated sludge and as its adjuvant. The purification is based on two phases of nitrification, respectively denitrification, in the same enclosure, through discontinuous aeration of the elements containing zeolite.

4.2.1.11. Device with filter based on natural zeolitic material to retain radon from the air

The operating principle of the constructed device: the air in the room is passed, with the help of a fan, through the zeolite filter that retains/adsorbs on the filter material the radon from the ambient air. Due to its large pore volume natural zeolites have the capacity to retain Rn.

4.2.1.12. Natural zeolitic material for use in the cosmetic industry

A micronization and granulometric separation technology was developed to obtain materials applicable to cosmetics. Materials with two different grain sizes were obtained (63-100 µm, and < 20 µm). Micronized zeolite material was tested by preparing cosmetic formulations with the addition of 5% micronized zeolite material.

4.2.1.13. Installation with zeolite-based filters with devices for monitoring and controlling the filtration processes via the internet and mobile phone

An installation with zeolite-based filters was built and tested. The installation was designed to serve isolated households of 4-5 people, an installation for treating 2000 liters of water, presented in Figure 10. The tests and verifications of the prototype of the installation showed that it treats water and brings it within the parameters required by the norms in force.

Fig. 10. Prototype of the filtration installation

In the frame of TREND project, **four patent proposals** were published in the Patents – Official Industrial Bulletin (BOPI) Romania: (*i*) I.M. Vagner, I. Miu, O. Cadar, M. Senila, *Procedeu de obtinere a unui material pe baza de tuf zeolitic utilizabil ca adjuvant de limpezire a berii*, 135595, BOPI 3/2022, (*ii*) I. Aschilean, G. Chiorean, C. Roman, M. Senila, A.M. Hoaghia, *Material pe baza de zeoliti naturali pentru adsorbtia hidrocarburilor din medii contaminate*, 135642, BOPI 4/2022, (*iii*) I. Aschilean, G. Chiorean, L.C. Tanaselia, E.I. Neag, A.I. Torok, *Metoda de activare a unui material pe baza de tuf zeolitic pentru utilizarea sa ca material filtrant pentru fier si mangan din apa*, 134370, RO-BOPI 8/2020 and (*iv*) I. Aschilean, G. Chiorean, LD. Simedru, L.V. Babalau-Fuss, A.M. Moldovan, *Metoda de activare a unui material zeolitic pentru utilizarea ca material de retinere a amoniacului din ape statatoare*, 134371, RO-BOPI 8/2020.

4.3. Recovery of precious metals from spent catalysts by supercritical CO_2 extraction assisted by polymers

INOE 2000, ICIA subsidiary participated in a research project of which purposes was to develop an eco-friendly technology for the recycling of precious metals, especially palladium (Pd) and platinum (Pt), from spent catalysts, e.g. from automotive catalysts. The scarcity of these metals poses a risk for the European countries which do not have this primary resource. The technology consists of metal extraction in supercritical CO_2 ($scCO_2$) thanks to complexing polymers bringing the insoluble precious metals into the $scCO_2$ medium. The schematic presentation of the proposed recycling process of precious metal by supercritical CO_2 extraction assisted by polymers is shown in Figure 11.

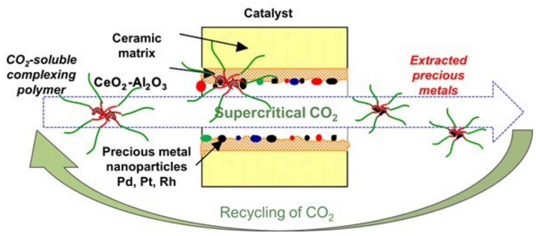


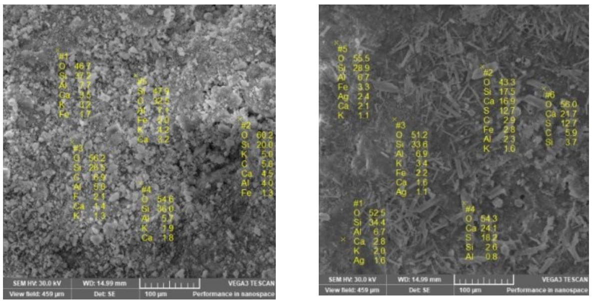
Fig. 11. Schematic presentation of the proposed recycling process of precious metal by supercritical CO_2 extraction assisted by polymers

Polymers synthesized in this study were soluble in supercritical CO_2 ($scCO_2$), a green solvent carrier for extraction of the metals from the catalysts. The synthesis of the complexing polymers has complexing groups able to interact with the precious metals and, in same time, are $scCO_2$-philic groups to ensure good solubility of the polymer in $scCO_2$.

INOE 2000, ICIA Subsidiary participated mainly to assure the control of processes by developing analytical methods for the determination of precious metals in initial catalysts, final products, and samples from different stages of technology. This is vital for getting to know the extraction rate of the metal from the catalyst and thus indispensable for the optimization and the scale up of the extraction process. ICIA developed methods based on microwave-assisted acid and measuring the amount or precious metals (Pt, Pd) by spectrometric techniques (ICP-OES, GF-AAS [23,24].

4.4. Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Analysis (EDX) – a useful tool for natural materials characterization

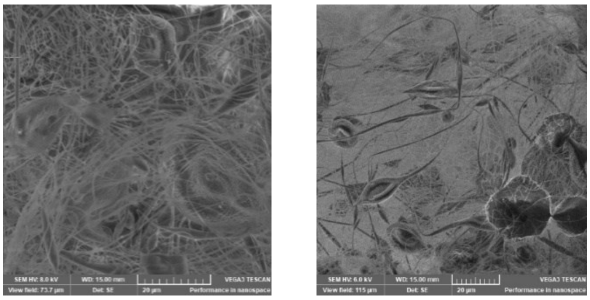
SEM-EDX technique was used successfully in research activities within ongoing ICIA's research projects and within economic contracts [25]. SEM-EDX was used to establish the topography, morphology, and composition of natural zeolites and to identify their structural changes appeared after their thermal and chemical treatments - TREND project. Examples of natural zeolite, before and after thermal and chemical treatment, are presented in Figure 12 (a and b).



(a) (b)

Fig. 12. SEM image of natural zeolite (a) raw and (b) after thermal and chemical treatments

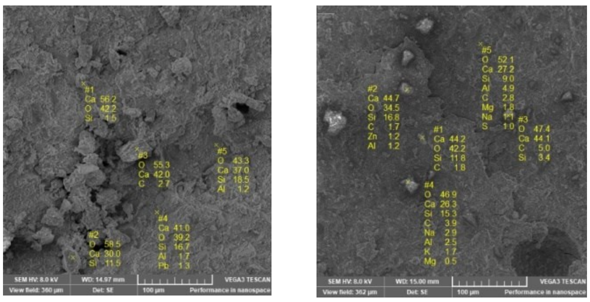
SEM-EDX was used to identify the changes of polylactic acid's shape during electrospinning process – PRIMTISS project (Figure 13 a and b).



(a) (b)

Fig. 13. SEM image of (a) nanofibers of polylactic acid Fibers of polylactic acid during electrospinning process

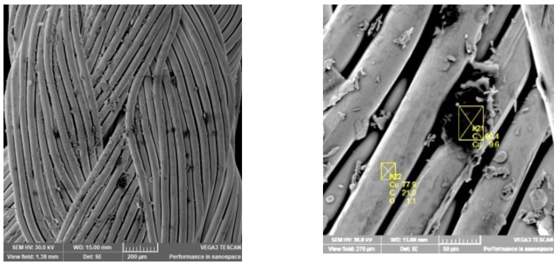
SEM-EDX was used to study the surface's futures of some new composite materials – LIGNOCEM project. The presence of cement traditional phases and their distribution on the surface's sample was established using EDX advanced futures. Pores size and the distance between them, main parameters in domain of cement-based materials, were also measured (Figure 14 a and b). The results allowed also drawing a conclusion regarding the hydration process of cement when lignocellulosic wastes are introduced.



(a) (b)

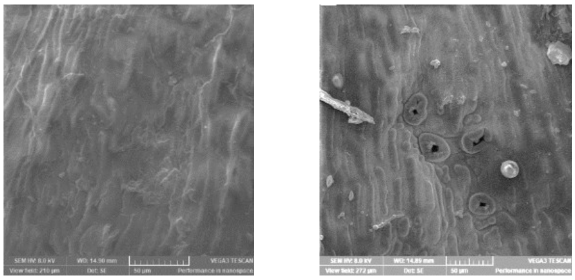
Fig. 14. Composite materials with the addition of lignocellulosic waste.

Additionally, some interesting studies focused on establishing the efficiency of manufacturing processes of Cu fibers, specifically the surface of some Cu fibers was investigated for defects (Figure 15) and establishing the factors which lead to the dead of a thuja culture namely the surface of a dead thuja tree bark was investigated comparatively with a healthy thuja tree bark (Figure 16).



(a) (b)

Fig. 15. Defects on the surface of Cu wires



(a) (b)

Fig. 16. SEM image of a healthy thuja tree. SEM image of a fungus attack on a thuja tree

4.5. Nanoparticles in modern medicine. Advanced materials for healthcare

Nanotechnology is an attractive and challenging science focused on the materials at nanoscale level and their employment in a wide variety of applications. Its applications in (nano)medicine are constrained due to the main concerns in understanding and predicting the behavior of nanoparticles (NPs) in complex biological fluids. The metal-based nanomaterials can be considered a fast-growing area due to their wide applications, including (nano)medicine, where nanotechnology has shown a lot of potential in therapeutics and diagnostics. Along with the increasing applications of nanomaterials in the medical fields, it is essential to know the systemic distribution of nanomaterials in the human body through a precise method for the biodistribution and biosafety assessment of nanomaterials.

Materials have become an integral part of modern medicine, used to target the delivery of drugs, expand and deliver cells in regenerative medicine to construct a wide variety of medical devices. Currently, the advanced materials are developed in the division to meet current medical challenges [1-3,26].

In the field of nanoparticles in modern medicine, the most relevant results refers to the development, optimization and validation of two methods for the determination of: *(i)* gold nanoparticles in simulated biological fluids and biological tissues, based on microwave digestion (MW) and graphite furnace atomic absorption spectrometry (GF-AAS) and (*ii*) silver in solid (nanopowders/ nanofibers) and liquid (simulated biological fluids) based on microwave digestion (MW) and graphite furnace atomic absorption spectrometry (GF-AAS) [27]. Among the optical spectrometric techniques, GF-AAS affords lower detection limits which represent an advantage for the determination of metallic nanoparticles where is expected to have low precious metal (Au, Ag) concentrations. The methods were characterized in terms of selectivity, limit of detection (LOD), limit of quantification (LOQ), accuracy, precision, linearity of calibration curve and uncertainty. The validation was performed considering the recommendations of the Cooperation for Analytical Chemistry in Europe (EURACHEM) guide [28].

In the field of advanced materials for healthcare, the following inexpensive, useful and simple methods were optimized and validated in respect of limit of detection, limit of quantification, specificity, linearity, working range, trueness, and precision was performed in correspondence with the European Pharmacopeia [29] for commercial tablets: (*i*) method for the simultaneous determination of vitamins D3 (calcitriol, cholecalciferol) and K2 (menaquinone-4 and menaquinone-7) in pharmaceutical formulations and simulated body fluids by ultra-high-pressure liquid chromatography (UHPLC), (*ii*) method for the simultaneous determination of amoxicillin and doxycycline in pharmaceutical formulations and artificial saliva by ultra-high-pressure liquid chromatography (UHPLC) multichannel DAD and (*iii*) HPLC multichannel DAD method for the simultaneous determination of metronidazole and ampicillin in pharmaceutical formulations and simulated biological fluids [30-32]. The validated methods are essential for the quality control analytical laboratories dealing with determining pharmaceutical formulations and simulated biological fluids using HPLC since it presents a simultaneous and fully validated method for this purpose. Moreover, they can easily and conveniently be implemented for the routine quality control analysis of the studied vitamins and antibiotics in pharmaceutical forms and simulated body fluids.

In the frame of DONTAS project, the following Romanian patent was published: M. Tomoaia-Cotisel, A. Mocanu, A. Pop, C.L. Garbo, M.G. Bud, G. Tomoaia, C. Roman, C. Roman, O. Cadar, C.P. Racz, *Nanomateriale pe baza de hidroxiapatita multisubstituita si procedeu de obtinere a acestora*, brevet de inventie nr. 133124/31.07.2017.

4.6. Simulated biological fluids with application for dissolution/ in vitro release testing

Controlled drug delivery systems have emerged as an alternative to the conventional sort to enhance the bioavailability, extent the drug release and preserve drug plasma levels within the therapeutic window with minimal side effects. Moreover, controlled drug delivery increases the drug solubility and stability and offers the selective delivery of drugs with a predictable rate and mechanism to specific organs/tissue/cells [33].

Dissolution testing is of utmost importance in following aspects: (*i*) as reliable predictor of in vivo dissolution performance of drug and (*ii)* a rate limiting factor in determining the physiological availability of drug, (*iii*) as quality control tool for monitoring the uniformity and reproducibility of production batches, (*iv*) as research tool in optimizing parameters and ingredients in new drug formulation, (*v*) it is widely accepted as animal experimentation has been restricted under the Act of Prevention of cruelty of animals [34,35]. In case of the routine quality control: simple dissolution media such as aqueous buffer solutions are preferred due to the low-cost, ease of preparation, recovery, and reproducibility, while in case of development: purposes more complex media simulating the composition of biological fluids of the site where the drug product will be administered and/ or absorbed [35].

The use of simulated biological fluids is up-and-coming in vitro method to better understand the release mechanisms and possible in vivo behavior of various materials, such as fibers, metal nanoparticles and nanomaterials. Furthermore, the use of simulated biological fluids in dissolution tests allows the determination of material biopersistence or, contrarily, bioaccessibility (release mechanisms) that can offer a valuable inference of a materials biodistribution, as well as its acute, short- and long-term potential toxicity [36].

The main administration routes and simulated biological fluids investigated in the framework of ICIA's research projects were: (*i*) parenteral: simulated body fluid (SBF) and simulated synovial fluid (SSF), (*ii*) oral: simulated gastric fluid (SGF), simulated intestinal fluid (SIF), simulated colonic fluid (SCF) and (*iii*) buccal and sublingual: simulated saliva (SS). The main applications in term of short-term and long-term release, focused on nanomaterials, natural and synthetic materials, pharmaceutical formulations, dietary supplements. We developed controlled release systems: adsorbed/ encapsulated systems, reservoir/ matrix diffusion systems for different elements (Ca, Mg, Sr, Ba, P) and organic compounds (soluble and liposoluble vitamins, antibiotics) [14,37,38]. The purpose of the controlled release drug delivery systems is to maintain drug concentration in the blood or in target tissues at the effective level [39].

The mathematical modelling in drug delivery has high potential to enable the product development and evaluations of the same and supports understanding the complex pharmaceutical dosage forms. There are large variety of formulations devoted to the oral controlled drug release, and the various physical properties that impact the drug release from these formulations. The use of in vitro drug dissolution data to predict in vivo bio-performance can be considered as the rational development of controlled release formulations [39,40].

We used five dependent models such as Zero-order, first-order, Higuchi, Korsmeyer-Peppas, Hixson-Crowell to predict drug release mechanisms of: (*i*) liposoluble vitamins, namely vitamins D3 (calcitriol, cholecalciferol) and K2 (menaquinone-4 and menaquinone-7) from innovative composite materials based on poorly crystallized hydroxyapatite (HAP) and highly crystallized hydroxyapatite, (*ii*) antibiotics (amoxicillin, doxycycline, metronidazole and ampicillin) from matrix systems based on polylactic acid (PLA) and nano-hydroxyapatite (nano-HAP) with embedded antibiotics in various simulated biological fluids (SBF, SSF, SIF, SGF, SCF and SS), at 37 ºC and different time intervals. The obtained results indicated that the developed materials are promising candidates as slow of prolonged drug delivery systems.

4.7. Non-destructive isotopic ratio method for establishing the origin of Roman glazed ceramic

One of the key advantages of ICP-MS over other related analytical techniques based on optical phenomena (ICP-OES or flame atomic absorption spectrometry - FAAS) is the possibility of measuring isotopic ratios. This expands the ICP-MS capabilities into other areas beyond determining a sample elemental concentration, like sample origin and authenticity analysis or geochronological age determination analysis. But, the performance of isotopic ratio analysis is restricted by the design of mass filter.

The best approach, which offers the best sensitivity for isotopic ratio analysis, would be the use of a thermal ionization mass spectrometer (TIMS) or a multi-collector, sector field (high-resolution) mass spectrometer (MC-HR-ICP-MS). Such systems are generally installed for clearly defined purpose and repurposing them would be costly in terms of financial and human resource levels. Moreover, the acquisition cost of a MC-HR-ICP-MS is usually an order of magnitude higher than the acquisition cost of a quadrupole ICP-MS.

A quadrupole ICP-MS is a more versatile analytical technique that can easily be repurposed to serve a large variety of sample matrices. Its main drawback is the relatively low operating resolution due to quadrupole design, which might lead to more isobaric and polyatomic interferences. However, recent developments tend to overcome this disadvantage, by offering innovative ways of dealing with unwanted interferences, either by employing a pressurized cell (reaction and/or collision cell) before the main mass filter that would deal the interferences before the ion reach the quadrupole, by having an extra mass filter, used usually in conjunction with a collision/ reaction pressurized cell. Concerning the isotopic ratio analysis, a fundamental limitation is built into the design of the spectrometer: plasma variation during measurements process. Since there are no multi-collectors available, each isotope is measured sequentially and plasma variation between each measurement affects the precision of the isotopic ratio analysis. This results in an obtainable precision above 0.1% RSD [41]. Depending on the study area, the error might be acceptable, which makes a single collector, quadrupole ICP-MS a suitable tool for origin investigations.

Glazed ceramics are artifacts used in the ancient world probably starting with Mesopotamia region, more than 4000 years ago. Only much later, around 1st century BC it found its way into Roman Empire and Mediterranean basin, trough regions like Syria and Asia Minor, also spreading to Dacian kingdom, due do its unique properties and long-time storage advantages offered by glazed ceramic artifacts (Figure 17) [42,43]. The extensive use of lead (Pb) oxide in the technology of glazed ceramics artifacts marks an important milestone in the development of this technique. Moreso, the high content of lead can be used for tracking its origin.

Fig. 17. Glazed ceramics

Pb has four, naturally occurring, stable isotopes [44]: ^{204}Pb (1.4% abundance), ^{206}Pb (24.1% abundance), ^{207}Pb (22.1% abundance), ^{208}Pb (52.1% abundance), with ^{204}Pb being the only one that is not radiogenic. ^{206}Pb is the result of the ^{238}U decay chain, ^{207}Pb is the result of the ^{235}U decay chain, while ^{208}Pb is the last element in the decay chain of ^{232}Th.

To optimize the Pb signal on the ICP-MS detector, usually a longer dwell time is set during analysis set-up for the lowest abundance isotope (e.g., in the case of ^{204}Pb/^{208}Pb, the detector would spend significantly more time collecting ^{204}Pb ions than ^{208}Pb ions). Another method for improving data acquisition would be by pressuring the collision/reaction cell with an inert, non-reactive gas (He, Ne etc.) to dampen the short-time variation of the ion beam.

ICP-MS is generally considered a destructive analytical technique, since the liquid sample is completely consumed in the plasma (or sent to waste, thus lost). This approach is not desirable when dealing with rare archaeological artifacts. Due to high Pb content in the upper layers of glazed ceramic samples, it’s possible to extract enough Pb ions, through a leaching process, to gather relevant isotopic data about sample origin and the leaching can be performed without damaging the samples.

^{204}Pb determination can be affected by the isobaric interference with ^{204}Hg and the resolution requirement to discriminate between the two isotopes is at least one order of magnitude higher than the performance of current HR-ICP-MS instruments. Thus, an alternative procedure most be applied to the measurement process in order to eliminate this interference, since increasing the resolution is not feasible for quadrupole instruments.

By pressurizing the collision/reaction cell with ammonia, Hg ions are neutralized while reacting with the gas, while Pb ions will pass through the cell without any chemical interaction with the ammonia gas. If the Hg ions are neutralized, the quadrupole will no longer guide them through the cell’s exit spot, meaning only Pb ions will get through the cell, while Hg ions will be eliminated from the ion beam. This approach is possible only in a triple-quad system, where the pressurized collision/reaction cell is placed between the two main quadrupole that act as mass filters: the first quadrupole will only filter mass 204, meaning both lead and mercury, the cell will filter out mercury, and the remaining lead isotopes on mass 204 will be guided by the final quadrupole to the detector.

During the GLAZEX project, a patent application was submitted for developing a non-destructive method for lead isotopic ratio measurements on glazed ceramic. The precision obtained is sufficient to be able to distinguish between different artifacts from different regions, while the analyzed samples were not altered and if the method is calibrated with artifacts of known origin, quadrupole ICP-MS isotopic ratio measurements can be used for sample origin analysis.

5. New directions of research

5.1. Cement-based composite materials with the addition of lignocellulosic waste using NMR technique

One of the main environmental concerns is the large amount of lignocellulosic waste generated annually by various sectors, such as agriculture, forestry, and furniture manufacturing. Agriculture produces several waste categories, such as waste from plant cultivation and viticulture. In Romania, one of the most spread agricultural activities is viticulture. Vine shoot waste represents a substantial source of lignocellulosic biomass, which can be used in different industry branches. Lignocellulosic biomass is used for energy production, *i.e.* in producing pellets, briquettes and bioethanol [45,46].

Cement-based materials are another field in which the vine shoot waste can be used as an additional component. The cement-based materials are widely used in construction. The active part (water, cement) and the rigid skeleton (different size aggregate) are the components of the cement-based materials. The rigid skeleton is inert compared to the active part, which hardens by hydration and hydrolysis. Most of the hydration and hydrolysis reactions occur during the first 28 days, and the cement-based material hardens in this period. In the last years, researchers have been looking to enhance the characteristics of cement-based materials and minimize the amount of cement used. Currently, different additives (superplasticizers) or admixtures (silicon nanoparticles fibers, polymers, waste, etc.) are used in cement-based materials to improve their characteristics [47-49].

A non-disruptive, non-invasive technique that can be used in the investigation of cement-based materials is the Nuclear Magnetic Resonance (NMR). This technique does not require any prior processing of the test sample and may be used during the hardening process as well [50,51]. LIGNOCEM project proposes applying the NMR technique to study the properties of cement-based composite materials with the addition of lignocellulosic waste. This project is characterized especially by the cement paste's active part in the cement-based materials. The manufacturing process of the cement paste using vine shoot waste is presented in Figure 18.

The LIGNOCEM project has two major objectives: to produce a new composite cement-based material with lignocellulosic waste with high specific properties, and to extend the NMR techniques in the characterization of the new composite cement-based material with addition of lignocellulosic waste. Starting from these major objectives, the specific perspectives are obtained. The specific perspectives include: the recovery of the lignocellulosic waste, the use of the lignocellulosic biomass in cement-based materials and the use of the NMR techniques in the construction field to obtain materials with improved characteristics.

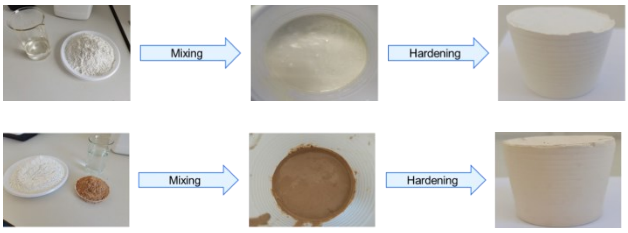


Fig. 18. The manufacturing process of the cement paste (a) and cement paste with vine shoot waste (b)

5.2. Meteorite identification and classification using a fast, non-destructive X-ray fluorescence analytical method, paired with machine learning techniques

Currently, there are over 70000 classified and catalogued meteorites. Since most meteorites are relatively small (most common mass for a stony meteorite, the most common type of meteorites, is less than 500 grams), it means they are considered rare and valuable artifacts (even if over 40 tons of extraterrestrial material falls through Earth's atmosphere each day, most of it never reaches the ground, due to interaction with upper layer of atmosphere).

(a) *(b)*

Fig. 19. (a) Mocs Meteorite, Cluj, Romania (ordinary chondrite) and (b) Holsinger Meteorite, Arizona, SUA (iron meteorite)

Thus, it's essential to have non-destructive analytical techniques available for initial meteorite identification and further scientific studies, if the initial extraterrestrial origin of the sample is confirmed. Moreso, a non-destructive method could be useful for museum that host meteorite collections, to fulfill UNESCO recommendation stating that within museums primary functions should also be activities related to scientifical studies of their own collections.

Meteorites can be classified into two major categories, based on their bulk compositions and textures: *chondrites* and *achondrites* and each category have further subgroups (for instance, achondrites contain *iron* and *stony iron* meteorites, along with planetary ones, like *Martian* and *Lunar* meteorites). Over 80% of currently identified meteorites belong to chondrite group (which also contains subgroups like *carbonaceous*, *ordinary* and *enstatite*).

X-ray fluorescence (XRF) is considered a reliable analytical technique for the chemical characterization of geological samples; thus, methods developed for terrestrial rocks can be extended to meteorite samples. XRF can offer good results for elements that are essential for meteorite characterization (Cr, Mn, Fe, Ni or, with modern instruments, even Ca, Mg and Si) [52].

Better knowledge of meteorites and their parent bodies can be used in future planetary defense mission, helping us better understand asteroid structure and composition, thus better plan a strategy for altering their trajectory, in case an impact with Earth would be statistically significant in the near future. Meteorites also contain information about the origins of our Solar System and could offer clues regarding Earth's future. Since we still lack direct access to Mars soil and rocks samples (a Mars sample return mission is currently scheduled for 2033), Martian meteorites are the only samples that can offer insights regarding the Red Planet geological past, when it better resembled Earth. Considering all this, having a non-destructive analytical method for differentiating real meteorites from fake ones (called "meteowrongs") could be beneficial to multiple institutions (museums, universities, research institutions) and serve multiple purposes.

Best results are obtained for more homogeneous, allow samples, thus iron meteorites analysis data will probably have the best precision. Usually, XRF will have different parameters for light elements (lower Z, Mg to Zn) and heavy elements (higher Z, Ti to U). In order to have good excitation for elements like Fe, Co, Ni and Cu, the Ti/Al filter (25 μm Ti, 300 μm Al) would remove some background; Tube voltage should be set to 40 keV, while count rate will be adjusted starting from 5 μA current intensity. Good conditions for light elements (up to Zn, Z=30) in alloy analysis would require no filter and a 15 keV tube voltage, paired with at least 10 μA current intensity. Even Al and Si have a good enough signal so that no controlled atmosphere is required during measurements. For geological samples that are different than metallic allows, using He would significantly improve detection of very light elements, like Na, Mg and Al, keeping the tube voltage at 15 keV, but increasing the current to at least 15 μA. Increasing the voltage to 45 keV would provide better excitation conditions for heavy elements, from Ti to U if current is increased to 50 μA (no need to use He or vacuum for high Z element detection).

Machine learning (ML) algorithms can be used to differentiate between meteorites and meteowrongs, by initially training the algorithms using a collection of known meteorites, preferably spanning across all classes and subgroups, with various settings for the XRF instrument (direct analysis, filters, voltage, beam intensity) and analyzing the meteorite fragment on multiple spots (crust, bulk etc.), since it's known that their composition is non-homogeneous at millimeter scale. The ML algorithm will perform better if the initial training set is large (N>100). Data can be acquired in raw format or calibrated, against certified reference materials or known meteorite material that could be used as a reference material.

Once trained, the ML algorithm can be continuously improved by feeding data from known meteorite and simultaneously used to investigate new meteorites, classify them and separate them from terrestrial samples.

6. Perspectives

Materials science is an interdisciplinary field concerning the properties of matter and its applications to many areas of science and engineering. The implementation of new materials is essential to meet the societal requirements related to energy, health, transport and climate change. In this field, ICIA focus lies on research and characterization of both natural materials, and innovative materials or improving existing ones.

Thus, ICIA's perspectives in the field of natural and synthetic materials refers to the: - synthesis and characterization of (nano)materials with applications in conventional and modern technologies, - new tools and smart (nano)composites based on advanced nanotechnology for medical applications, - behavior of (nano)materials in various simulated biological media considering the parenteral, oral, buccal and sublingual, and ophthalmic routes, - evaluation of tissue biodistribution of metallic nanoparticles, - fate and behavior of nanomaterials in surface and groundwaters, - fate of cosmetics ingredients in surface and groundwaters, - occurrence of microplastics in the aquatic environment.

ICIA intends to increase the complexity and growing scale of national and international (Horizon programme) research projects in the field of nanotechnologies, advanced materials, advanced manufacturing and processing, aiming better excellence capacity and resources, more interdisciplinary research, improved research skills, increased visibility at national and European level, new approaches in research collaboration, improved mobility of qualified scientists, etc.

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Food safety and innovation in the complex context of global trading, climate change and economic hardship

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In the complex context of current economic and environmental situation food safety and food security are not guaranteed. New solution must be found and implemented to ensure the integrity of the food sector. INCDO-INOE ICIA Cluj-Napoca Subsidiary through its research aims to help find solution and applications that will ensure food safety and security.

Keywords: Food safety, food adulteration, digitalization in food technology, alternative proteins

1. Introduction

Food is the center of our living style. It has the ability to bring together people, express cultural heritage, it can make us feel better but it can also be the source of negative outcomes when the food is not safe for consumption, it gives low nutritional value or is scarce. [1-2]

Different factors put extra pressure on the food chain like climate change, global trade and economic hardship. (fig. 1)

Fig. 1 Relationship between food chain and exterior factors

The purpose of research is to enhance society by advancing knowledge. It must offer solutions to problems society is facing. [1, 4]

Factors that help maintain the food chain are:

- Technology progress:
- Complex control systems;
- Added value solutions.

All these barriers that help protect the food chain are based on advance knowledge from different fields like agriculture, biotechnologies, material science, industrial processes to data science and AI solutions. Complex solutions must be created taking into account not only direct problem but all the factors and look at the situations as a connected ecosystem not just like a standalone problem. [2, 4]

That way is important for data to be shared and for scientists from different fields to collaborate across borders. [5]

Purpose of INCDO-INOE ICIA Cluj-Napoca Subsidiary in the food sector is to:

- develop advance analytical solutions for food safety and nutrition;
- offer technical solutions for enterprises in the agri-food sector;
- offer efficient solutions to ensure food security.

2. History/Landmarks

Research activities in the field of quality control of food products of animal and plant origin have led to the development of a series of new procedures.

The research activity within the laboratory in the field of quality control of food products of animal and vegetable origin is focused on the development of advanced, innovative analytical methods, intended for the analysis of the entire food chain, in order to increase the safety and security of agricultural and food production, in order to: determine metals and persistent organic pollutants (POPs); determining the presence of GMOs in food products; evaluation of the presence of mycotoxins in products of plant origin and in feed and their metabolites in products of animal origin; evaluation of the presence of allergens in foods of vegetable and animal origin; determining the functional character of food and quantifying some compounds with functional characteristics in food. The analysis of chemical compounds naturally present in food is also desired: vitamins (B6, B9 and C), amino acids (DL Alanine, DL Tyrosine, DL Histidine, Glutamic Acid, DL Phenylalanine, Aspartic Acid and Glycine), lecithin, testosterone and total polyphenols; of compounds from the environment: polycyclic aromatic hydrocarbons, pesticides, industrial dyes and pharmaceutical products (hormones, antibiotics and opioids).

The research activity in the field of quality control of food products of animal and vegetable origin within the laboratory was realized by carrying out within the unit specific research projects such as those presented below.

In 2007, within the project "*Development of the Laboratory for the control of chemical residues in food products, with a view to integration into the European network" - REZALIM* - (Contract 138/CPI/19.09.2007) a new endowment of the laboratory and the arrangement of new spaces were performed. The funding was obtained from the State Budget - Ministry of Education and Research through the PNCDII Program.

As a result of the research project entitled "*Improvement of methods and techniques for the identification and determination at the nanoscale of steroid structures contaminated in food products of animal origin*" (Acronym: CONTALIM, Contracting Authority: ANCS, Program: PNCDII, Year of completion: 2009) modern methods that use high-performance analytical techniques, were developed such as: high-performance liquid chromatography coupled with mass spectrometry (LC-MS) or LC-MS/MS, gas chromatography coupled with mass spectrometry (GC-MS) for the purpose of determining contaminants with steroid structures from different complex matrices, at the nanoscale level; identification and determination of metabolites that can form as a result of the interactions of compounds with steroid structures with the animal or human body; as well as the use of SP(M)E solid phase (micro)extraction techniques.

The project "*Advanced techniques for the determination of chemical residues in food of animal origin*" (Acronym: TECHIM, Contracting Authority: CEEX 62/2006 Agrar, Year of completion: 2008) pursued the development of methods for the quantitative determination of chemical residues of veterinary origin.

Another project in which advanced methods of determination using the gas chromatographic technique were developed was the project "*Research on the realization of an advanced methodology for determining recipes for blending Romanian wines, assisted by an expert system*" (Acronym: CUPEXVIN, Contracting Authority: CNMP, Program: PNII, Year of completion: 2010). The main objective of the project was the analytical evaluation of the blending recipes, achieved through the mathematical and statistical interpretation and comparison of the results obtained from the gas chromatographic analysis of the wines (controls and blends). Within the framework of the project, analytical methods were developed that use the gas chromatographic (GC) technique coupled with the flame ionization detector (FID), for the determination of volatile compounds, characteristics of the aroma of wines.

Also in the field of wine quality analysis, another project was carried out "*New, modern method of fingerprinting and quality control of wines, by MRI and RES*" (Acronym: VINMES, Contracting Authority: CNMP, Program: CEEX-CALIST, Year of completion: 2006) which pursued the creation of a model for the analysis and identification of wines, of secondary products appearing in winemaking products, as well as of various substances appearing over time due to different processing and/or storage conditions through modern cutting-edge methods: the coupling of chromatographic methods with various RES and NMR spectral techniques.

In 2015, another modernization/equipment of the laboratory was carried out through the project entitled "*Multisite Infrastructure for Increasing Research and Innovation Capacity in the field of optoelectronics and Analytical Instrumentation*" (Acronym INOVA-OPTIMA, Sectoral Operational Program Increasing Economic Competitiveness Priority Axis 2 - CDI: Operation 2.2.1, Year of completion: 2015) which aimed to increase the competitiveness of the INOE 2000 institute, through the more efficient use of the existing expertise thanks to the new infrastructure and by strengthening the approach base for some researches focused on the development of innovative processes, oriented towards the transfer technologically, with an impact on the economic environment. One of the directions addressed by the INOVA-OPTIMA project, relevant at national but also European level, is food security, with the aim of obtaining products and services with high added value and qualitatively competitive on the integrated EU market.

Within the project "*Modern, advanced optospectral methods for the evaluation of the contamination of agricultural crops and its propagation in final products*" (Contract no.: PN 09 27/2009/OPTRONICA III, PN 09-27.01.06, Year of completion: 2015) methods for the determination of mycotoxins and pesticides in agricultural products and along the food chain were realized.

The modern methods addressed in the laboratory involve the use of:

• high-performance liquid chromatography (HPLC and LC-MS), for the analysis of aromatic polycyclic hydrocarbons, mycotoxins, pesticides, androsterone, etc.

• atomic absorption spectrometry (AAS), for the analysis of minerals and heavy metals in food samples,

• gas chromatography (GC-ECD, GC-MS MS, GC-FID), for the analysis of pesticides, wine aroma, etc.

• photo-chemiluminescence for determining the antioxidant capacity of water-soluble products (expressed in vitamin C equivalents) and fat-soluble products (expressed in Trolox equivalents),

• polymerization chain reaction (PCR), for the determination of genetically modified organisms present in food and some allergens.

• molecular absorption spectrophotometry in VIS, for the determination of total polyphenols.

The laboratory's qualified staff includes specialist engineers, physicists, chemists and biologists, including doctoral and master's students.

In addition to the analyzes carried out on a contract or direct order basis, the laboratory offers the infrastructure and specialized personnel for the development of research contracts, doctoral theses and bachelor's theses in the field of food quality control.

The laboratory spaces are specially designed and built to comply with the rules imposed regarding the analysis flow, the optimal analysis conditions according to each technique approached and the safety of the personnel.

The laboratory carries out interlaboratory comparison activities within the profile research networks in Europe (eg: QFCS – Quality in Food Chemistry PT Scheme).

In the year 2016, INCDO INOE 2000 ICIA Cluj-Napoca received the authorization from the National Sanitary Veterinary and Food Safety Authority (A.N.S.V.S.A.) Romania Certificate number Nr. 125/15.07.2016.

Other projects have done that focuse not only on the contaminants but also on the nutritional value, biotechnologies, life cycle, technology and so one.

One of these projects is: *Development of analytical methods for the evaluation of Spirulina changes under oxidative stress conditions* (REGESPI). Financing program/Sub-program: PNIII Program 3 – European and International Cooperation Sub-programme 3.1 Bilateral/ multilateral/ RO-MD No. contract: 19BM/2016, Duration: 16.09.2016-31.12.2017. The main objective was to assess change and redox status of stress gene expression related Spirulina (Arthrospia) under conditions of oxidative stress.

A hands-on approach was the results of the project *Modernizarea liniei de sortare la Centrul Agro Transilvania Cluj, prin extinderea capacitatii de sortare a legumelor si fructelor (CALIPSO*) Program 2- Cresterea competitivitatii economice romanesti prin cercetare, dezvoltare si inovare, Subprogramul 2.1. Competitivitate prin cercetare, dezvoltare si inovare – competitia „ Transfer de cunoastere la agentul economic- Bridge Grant" 2016 Contract nr 9BG/2016, Durata: 19.10.2016-30.09.2018, where a washing machine was developed for carrots, potatoes and other root vegetables.

Another project is: *The development of a modern, advanced ecological (thermal) weeding system for wine culture*, (ECOERBVITIS), within the framework of the project "*Complex, integrated system for technological optimization and superior valorization of viticultural by-products*" (VINIVITIS) Program 1 - Development of the national research-development system, Subprogramme 1.2. Institutional performance Institutional development projects - Complex Projects carried out in CDI consortia competition 2017 Contract no. 4PCCDI ⁄ 2018 Duration: 01.03.2018-31.03.2021. The main objective was to develop a prototype for the treatment of weeds using steam.

Materials base on natural zeolites with application in food storage were developed in the project: "*Material based on zeolites for eliminating odors and reducing humidity*" (ECO-ODOR) Financing program/Sub-programme: Competitiveness Operational Program 2014-2020, Priority Axis 1 – research, technological development and innovation (CDI) in support of economic competitiveness and business development, Action 1.2.3, Project type: Partnerships for Knowledge Transfer, No. contract: 7/01/09/2016, SMIS 105654, Subcontract S4.

An import aspect of food safety which is food adulteration is the focus of the project: *Development of methods for determining food adulteration*, (NUCLEU). Funding program/Sub-programme: NUCLEU Program, No. contract: 18N/08.02.2019, PN19-18.01.01, Duration: 08.02.2019-31.12.2022,

EURALIM - *European research infrastructure for food safety* - determining authenticity and detecting food fraud is an *open access* concept that was borne out of the needed to have excellence centers in the food filed.

The scientific field in which EURALIM will carry out its activity is Health and Food, a field that can be found in the ESFRI Roadmap and in the CRIC report, and is correlated with the intelligent specialization field Bioeconomy, from SNCDI. Ensuring food safety is an important component of solving some societal challenges related to the quality of life and ensuring a sustainable development, and EURALIM has the ability to contribute to the achievement of the basic objectives of the Regional Strategies and national ones such as: the Regional Innovation Strategy of the North-West Development Region; RIS 3 NV Region, Priority I.1 – AGRI-FOOD; The National CDI Plan; National Strategy for Employment; National Competitiveness Strategy 2021-2027.

EURALIM wants to become the initiator of a large national research infrastructure that will become a regional development pole for ensuring food safety by detecting food fraud (the problem that Europe is facing more and more acutely in recent years) and, through the analysis of soil microbiodiversity, to provide relevant, scientifically based data for the achievement of a sustainable agricultural management, all of which are put at the service of the development of a sustainable agriculture.

2.1 Main infrastructure

- Liquid chromatograph 1200 Series from Agilent coupled with mass spectrometer Applied Biosystem 3200 QTrap - Patented hybrid triple quadrupole/linear ion trap technology takes you far beyond the capabilities of any conventional ion trap, enabling you to screen, identify, and quantify proteins or small molecules in a single analysis. By combining true triple quadrupole scanning functionality with sensitive linear ion trap scans, you can reduce analysis time and get more information from every experiment. It is used for the determination of new age pesticides, vitamins, amino acids, mycotoxins from food and environmental samples. (fig. 2)

Fig. 2 LC MSMS Applied Biosystem 3200 QTrap

- Dioxin analysis system - is formed of a Dionex AS 350 Accelerated Solvent Extractor, a Sample clean-up system (DEXTech 16) and a Gas Chromatograph coupled with mass spectrometer GC Tracer 1300 series +TSQ 9000 TermoFisher. It is used for the analysis of dioxin from food and environmental samples. Which are a group of chemically-related compounds that are persistent environmental pollutants. They are mainly by-products of industrial processes but can also result from natural processes, such as volcanic eruptions and forest fires. Dioxins are of concern because of their highly toxic potential. (fig. 3, 4, 5)

Fig. 3 GC Tracer 1300 series +TSQ 9000 TermoFisher

Fig. 4 Dionex AS 350 Accelerated Solvent Extractor

Fig. 5 Sample clean-up system (DEXTech 16)

- D8 ADVANCE Bruker X-ray diffractometer: X-ray diffraction is the method of choice for extracting structural information from virtually any type of sample, regardless of shape, size or composition, under ambient or non-ambient conditions. Bruker D8 Advance is a system that guarantees superior-quality results, the shortest possible measurement time, the highest analytical performance and offers information about phase composition, phase transition, amorphous content, percent crystallinity, crystallite size, lattice parameters, crystal structure, symmetry coordination and order/disorder. (fig. 6)

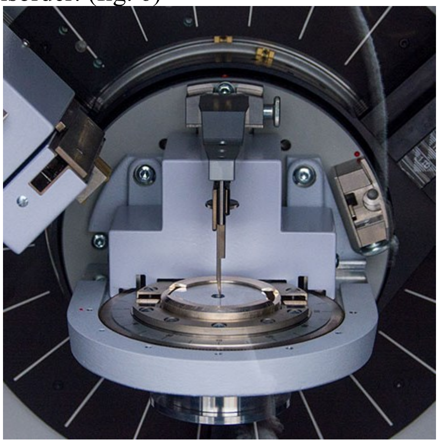

Fig. 6 D8 ADVANCE Bruker X-ray diffractometer

- Absorption Spectrometer Perkin Elmer model PinAAcle900T is an atomic absorption spectrometer which includes in a single instrument flame and furnace atomization system with a high flexibility to switch between flame and furnace in seconds. Thus, it provides capabilities for measuring metals with very good specificity (characteristic atomic absorption spectrometry), on a wide range of concentrations (ppb level using furnace atomization and ppm level using flame atomization system). Hollow cathode lamps or electrodeless discharge lamps are used specifically for quantitative analysis of metals in environmental and food samples. (fig. 7)

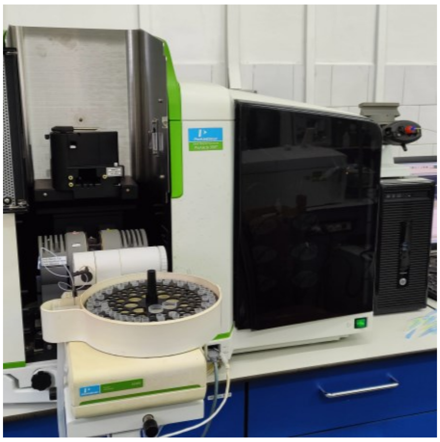

Fig. 7 Absorption Spectrometer Perkin Elmer model PinAAcle900T

More about our services and infrastructure can be found at:

- Virtual tour of ICIA Cluj-Napoca laboratories:
    - https://www.youtube.com/watch?v=dYQYAY2Wwm8&t=262s
- EERIS: https://eeris.eu/ERIF-2000-000L-1019

3. Current development and collaborations

INCDO-INOE 2000 ICIA Cluj-Napoca tries to stay connected with the SME's in the region and with the latest research direction set at EU level and at global level. The available infrastructure and research done allow the development in different directions. Building strong relationships with national and international, academic or private partners is a purpose in its self because research must serve society.

Some of these developments are:

- Superior valorification of byproducts from the agri-food industry:
    - enhancing products through fermentation processes;
    - extraction of high value components.
- Diversification of food products line for food industry companies, thought the development of new products with enhance nutritional value.
- Digitalization solutions for the food safety agri-food industry.
- New sources of nutrients and proteins for animal feed.
- New substrates for natural supplements that ensure better adsorptions of active compounds - Case study vitamin D and K.;
- New food product with high antioxidant capacity (water and honey based).

3.1 International collaborations

- University of Bologna, Italy;
- University of Leon, Spain;
- Uzhhorod National University, Ukraine;
- BYS GRUP, Turkey;
- ASINCAR, Spain;
- EUROPEAN FOOD INFORMATION RESSOURCE AISBL, Belgium;
- Norwegian Research Centre AS, Norway;
- Incontext Technology, Germany;
- NETO Innovation, France.

3.2 National collaborations

- AgroTransilvania Cluster;
- University of Agricultural Sciences and Veterinary Medicine, Cluj-Napoca;
- University of Life Sciences (IULS), "Ion Ionescu de la Brad“, Iasi;
- Ştefan cel Mare University of Suceava;
- National Research and Development Institute for Food Bioresources, IBA Bucharest;
- Academy of Agricultural and Forestry Sciences "Gheorghe Ionescu-Sisesti" (A.S.A.S.)
- Technical University of Cluj-Napoca.
- Viticulture Research-Development Station, Murfatlar.

3.3 Private sector collaborations

- Moldovan Carmangerie, Cluj;
- Bonas, Cluj-Napoca;
- PhenAlex, Oradea;
- BEIA International, Romania;
- Enviro Naturals Agro, Bucharest;
- Rom Honey Group, Iasi;
- Transilvania Nuts, Alba-Iulia;
- Romserg Exim, Cluj;
- Taf Presoil, Cluj;
- Suc de Catina, Botosani.

4. Recent results and transfer of results

In the context of research projects and collaboration with other entities analytical methods for the assessment of food safety, nutritional value as well as new products and processes were developed.

4.1 Obtaining and characterizing extracts of *Prunus spinosa* for use as a food additive

In the PhD thesis of Vanda Babalau-Fuss with the title “Research on obtaining and characterizing extracts of Prunus spinosa for use as a food additive” the characterization of the raw material used to obtain *Prunus spinosa* extracts was performed by comparative evaluation of the characteristics of the biological material.

The determination of the essential minerals in blackthorn fruit showed the impressive amount of potassium and calcium in these fruits. Comparison of the obtained concentrations of the essential minerals with the concentration of the recommended daily dose revealed that the fruits contain a significantly increased amount of these essential minerals. By analyzing the concentrations of polyphenols and antioxidant capacity, a directly proportional increase of these two parameters was noticed. The determination of the content of polycyclic aromatic hydrocarbons in fruit showed that phenanthrene, fluorene, naphthalene, pyrene and fluoranthene are the most present contaminants in the samples.

The assessment of the impact of environmental factors on the raw material (*Prunus spinosa* fruit) was performed by calculating transfer factors of metals from soil to fruit and polycyclic aromatic hydrocarbons from soil to fruit. In the case of calculating the transfer factors of essential metals from soil to fruit, the highest ratio was recorded for potassium at Borhanci (2.6459). The transfer of polycyclic aromatic hydrocarbons from soil to fruit indicated significantly increased values for most of the indicators analyzed in Floresti location. Pollution of this area due to heavy traffic is also found in the vegetation of the area.

The results obtained, in their entirety, showed that *Prunus spinosa fruits* are a valuable source of vitamins and minerals, being recommended in the treatment of certain diseases, but their location is a particularly important factor in choosing fruits, because soil pollution and of air can influence the quality of their healing properties.

Prunus spinosa extracts were made by two techniques: the solvent-accelerated extraction technique and the supercritical fluid extraction method, using carbon dioxide and a small amount of solvent, ethanol. The extracts obtained by accelerated solvent extraction were analyzed in terms of total polyphenol concentration and antioxidant capacity to demonstrate the effectiveness of the extraction. The results obtained were not satisfactory, the extracts showing significant concentrations of polyphenols (154 mg / ml), and the antioxidant capacity showed extremely low values. The correlation matrix of the two parameters indicated a correlation of only 0.42, which is why these extracts were not used in future analyzes, and implicitly this extraction technique was discarded.

The second extraction technique, that of supercritical fluids, was developed using carbon dioxide as a supercritical fluid and a small amount of solvent. The extracts were analyzed in order to determine the characteristics of interest for this paper. Total polyphenol concentrations (1212 mg / ml) and antioxidant capacity (2407 µg / ml) were determined and it was observed that these parameters show maximum values in the last sampling campaign, November 2019. Significance of these values increased after the first frost, confirms that these fruits reach full maturity only after contact with low temperatures. The results obtained with this type of extraction were significantly positive, which is why the concentrations of essential and toxic heavy metals were determined.

Considering the data obtained regarding characterization of the extracts, it can be stated that the favorable extraction of this type of fruit is the extraction with carbon dioxide used as supercritical fluid. The parameters of the extraction made with carbon dioxide used as supercritical liquid help to transfer minerals and beneficial properties of fruits in extracts, making them a valuable product for human consumption, and due to antioxidant properties, the extract obtained by research underlying this thesis can be consumed as such or can be introduced into food.

The concentration of total polyphenols was determined from all the fruits and extracts obtained; the results being interpreted comparatively in order to demonstrate the transfer of these compounds in the new product obtained. For the Chinteni location, the values of polyphenol concentrations in fruits and extracts increase in direct proportion, the highest value being recorded in the last sampling campaign (fruit - 628 mg / kg, extract - 909 mg / ml). The same ascending slope is observed in the case of samples from the Pata sampling area (fruit - 782 mg / kg, extract - 1071 mg / ml). Borhanci location shows low concentrations of polyphenol concentrations in the sampling campaign October 2018. The same phenomenon is encountered at the Floresti sampling location in October 2018. For all sampling locations, the concentration of polyphenols in fruits and implicitly, extracts are increased in the last month of sampling, November 2019. The comparative situation of the averages of polyphenol concentrations, shows that the Borhanci location is the location with the highest values of both fruit concentrations and extracts. The correlation matrix of the two parameters indicates a positive correlation 0.81.

The antioxidant capacity of the extracts was determined compared to that of the fruits, in the case of Chinteni location the situation being similar to that of the concentration of total polyphenols. The increase of the antioxidant capacity is progressive, the maximum value being registered in the last month of sampling. The Pata location shows a decrease in the antioxidant capacity of the extracts compared to that of the fruits, in the last month of sampling (October 2018 fruit - 645 µg/mg AAE, extract - 594 µg/ml AAE) the situation being totally opposite in the last sampling campaign (November 2019 fruit - 1125 µg/mg AAE, extract - 2098 µg/ml AAE). In the case of Borhanci location, a significant decrease of the antioxidant capacity is observed in the second sampling campaign, the maximum value being reached in the last sampling campaign (extract 2407 µg/ml AAE). The case of the Făget location is similar to the case of the Pata location, the recorded values being close. The values obtained for the Floresti location show a continuous and linear increase of the antioxidant capacity for both matrices. As with other locations, the maximum value is obtained in the last sampling campaign. The comparative situation of the averages of the antioxidant capacity of fruits and extracts grouped by location shows that after extraction, the antioxidant capacity of the extracts is higher than that determined in fruits, except for Făget location, where the values are approximately equal (fruit - 1509 µg / mg AAE, extract - 1947 µg/ml AAE). The Borhanci location presents the highest values for the antioxidant capacity of fruits and extracts.

The analysis performed on the fruit matrix of *Prunus spinosa* resulted in a valuable extract in terms of composition and properties. This extract contains a number of essential minerals for the human body (Ca–187mg/kg K–11458 mg/kg, Mg–753 mg/kg,) and significant concentrations of polyphenols (872 mg / kg). The antioxidant capacity of this extract (1947 µg/ml AAE) makes its use multiple and beneficial to several industry sectors.

Extracts obtained by the extraction technique using carbon dioxide as a supercritical fluid were introduced into vegetable and animal products. The ability of the extract to stop the oxidation produced by polyphenoxidase enzymes has been demonstrated in samples of vegetable origin. This product stopped the oxidation of the apple samples throughout the experiment. The part of the untreated apple samples completely oxidized after 6 hours, whereas the complete oxidation of the potato samples was performed after 24 hours. As far as animal products are concerned, the extract has completely stopped the formation of hydrogen sulphide and ammonia compounds, these two substances being responsible for the putrefaction process of meat products. By determining these parameters, it can be stated that the addition of extract to products of plant or animal origin leads to the extension of the shelf life of the products, so this new product can be used as a food additive.

The analysis of *Prunus spinosa* fruits revealed the special character of the fruits and the wide range of possible fields of their use Both fruit and fruit extracts possess an impressive amount of essential mineral elements, present in concentrations well above the recommended daily dose.

4.2 Applications of natural zeolites fertilizers for carrot varieties

Marius-Lucian Dordai PhD thesis "*Improvement of some carrot varieties as functional food products by using synergetic irrigation and fertilization with natural zeolites*" aimed to identify ecological and technological solutions to improve the functional food characteristics of three carrots: Royal Chantenay, Atomic Red, and Purple Haze F1, by the synergistic use of irrigation and fertilization with natural zeolites. The behavior of the three varieties of carrots in terms of quality indices in irrigation / non-irrigation conditions and fertilization followed the behavior of the three varieties of carrots in terms of quality indices in irrigation / non-irrigation conditions and fertilization. The experiments were performed in the hilly area of Transylvania, Aiton locality (46 ° 31 'and 46 ° 31' northern latitude; 23 ° 40 'and 23 ° 48' east longitude), containing three repetitions, 18 variants, and 54 experimental plots. The comparative cultures were ordered in a multifactorial system, completely randomized, with subdivided actions. The production quality was analyzed regarding the content of antioxidants, minerals, and heavy metals. Analyzed the production quality regarding the content of antioxidants, minerals, and heavy metals.

Over the whole period of 2016-2018, irrigation, independent of fertilization and biological material, had a very significant effect on the antioxidant content of plants (difference of 41.50 µg / mg).

Chemical fertilization and zeolite produced significant effects in all experimental variants, regardless of the biological material used or the irrigation variant (difference of 7.54 µg / mg and 44.88 µg / mg).

The antioxidant content of Purple Haze F1 was very statistically significantly higher compared to the control sample (difference of 694.38 µg / mg). Atomic Red had a statistically significant positive effect compared to the control with a difference of 0.98 µg / mg.

Regarding the technological factors in both fertilization and basic fertilization variants, irrigation, in combination with the biological material factor, determined a very significant effect on the antioxidant content for the Purple Haze F1 variety. In contrast, the Royal Chantenay variety had an impact. Statistically positive only in the irrigated-chemically fertilized variant. The Red Atomic variety had a distinctly significant effect compared to the control in the irrigation-fertilization combination with zeolite, the rest of the variants not having a significantly distinct effect compared to the rule in terms of antioxidant content.

Chemical fertilization and zeolite fertilization produced significant effects in all experimental variants, regardless of the biological material used or the irrigation variant (difference of 472.91 ug/mg and 1629.07 ug/mg, respectively. Over the whole period of 2016-2018, independent fertilizer and biological material irrigation significantly affected plant mineral elements' content (difference of 1225.49 mg/kg). Carrots on the range of mineral features, Atomic Red and Purple Haze F1 had a very significant negative effect compared to the control variant (Royal Chantenay) with differences of (-1056.30 mg/kg respectively -2103.52 mg/kg). The combination of factors in all variants has very significant effects compared to the control variant.

4.3 Methods/advanced materials based on sub-micron HAP as dietary supplements for healthcare

Innovative materials as dietary supplements for healthcare, IMA-HEALTH (Executive Unit for Financing Higher Education, Research, Development and Innovation (UEFISCDI), Contract number:481 PED /2020,) project aims to validate at laboratory scale, preparation methods/advanced materials based on nanoHAP with controlled size and shape of particles and crystallinity, as dietary supplements for healthcare. These supplements are expected to have a high effect on osteoblasts and endothelial cells related to the production of alkaline phosphatase, which is essential in regeneration of healthy new bone with impact on prevention and treatment of osteoporosis, and cardiovascular and arterial health.

The main objective was the validation at laboratory scale of preparation methods/advanced materials based on sub-micron HAP as dietary supplements for healthcare.

The specific objectives are:

- increasing the capacity of research organizations to develop innovative solutions validated in laboratory;
- development of sub-micron size HAP and hydroxyapatite/vitamins complexes;
- optimization of IMA-HEALTH advanced materials;
- demonstrating the utility and functionality of IMA-HEALTH; • dissemination of project results in articles and scientific communications.

Within this project a UHPLC method was developed, validated and implemented for the determination of Vitamins D3 (Calcitriol, Cholecalciferol) and K2 (Menaquinone-4 and Menaquinone-7) in dietary supplements and biological fluids.

4.4 Analytical methods for food safety

The Project "*Development of methods for determining food adulteration*" had a total duration of 4 years and was funded by Romanian Ministry of Research and Innovation. The research activities were dedicated to the development of analytical methods that are bought robust and rapid for determining food adulteration, in different matrices: vegetable oil, dairy products, animal products (meat + fish) and alcoholic products. In each year of the project, methods for a new matrix will be developed. The working protocols and the new analytical methods developed will support the control institutions at national and international level, responsible for verifying food safety and security, in order to overcome the technology limitations presented by the current methods of food fraud determining.

The methods developed within these projects are:

1. Raman method for the detection of food adulteration from: pumpkin seed oils, walnut oil, *in situ*; (fig.8)

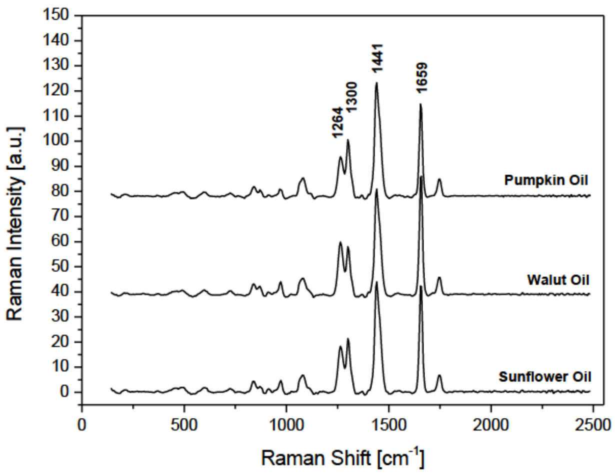

Fig.8 Raman spectra of investigated pumpkin, walnut and sunflower oils

- Better correlation coefficients were obtained for the prediction model used for pumpkin oil (99.26%) than for the prediction model for walnut oil (98.43%);
- The multiple regression analysis demonstrated that the maximum from 1263 has the greatest impact on the variation of the degree of pumpkin oil adulteration;
- The multiple regression analysis demonstrated that the maxima from 1263 and 1300 have the greatest impact on the variation of the degree of adulteration of walnut oil.

2. HPLC method for the determination of Vitamin E form different food samples.
3. HPLC method based on tocopherol profile for the quantification of food adulteration from: pumpkin seed oils, walnut oil (fig.9)
   - The degree of prediction was higher for walnut oil (98.66%) compared to pumpkin oil (98.31%);
   - α-Tocopherol and β-Tocopherol + γ-Tocopherol have the greatest impact on the variation of the degree of adulteration for walnut oil;
   - For pumpkin oil, when applying the multivariable regression, all 3 X variables (α-Tocopherol, β-Tocopherol + γ-Tocopherol and δ-Tocopherol) were chosen, which are used for the prediction model;
   - By the PLS technique, only 2 α-Tocopherol and β-Tocopherol + γ-Tocopherol were chosen as components for establishing the prediction equation of the degree of adulteration.

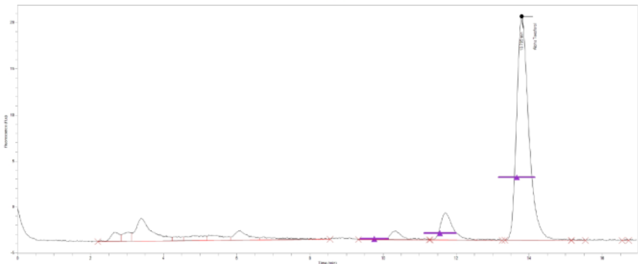

Fig. 9 Chromatogram of tocopherols for sunflower oil

4. Raman method for the detection of food adulteration from: milk samples.
   - The selected correlation coefficients led to obtaining a 99.8% goat milk prediction model;
   - The multiple regression analysis demonstrated that the maximum at 818 cm-1 has the greatest impact on the variation in the adulteration degree of goat's milk;
   - The multiple regression analysis demonstrated that the maxima from 818 and 1441 cm-1 have the greatest impact on the variation in the adulteration degree of goat's milk.
   - The relationships between the answer and the variables in the model are significant from a statistical point of view (p value <0.05).
   - The variation of the answer Y can be explained in a very large percentage by the chosen variables.
   - The model fits the data well, they demonstrate that the equation can be used to predict the degree of adulteration of goat's milk with cow's milk.

5. FT-NIR method for the determination of food adulteration of cheese and other milk products (yogurt, fermented cream, curds);
    - Selected correlation coefficients led to obtaining a 99.46% prediction model for goat milk yogurt.
    - The relationships between the answer and the variable in the model are significant from a statistical point of view (p value <0.05).
    - The variation of the answer Y can be explained in a very large percentage by the chosen variable.
    - The model fits the data well, they demonstrate that the equation can be used to predict the degree of adulteration of goat's milk yogurt with cow's milk yogurt.
6. HPLC method for the detection of beta-carotene from milk samples;
7. HPLC method for the determination of Vitamins B1, B2, B6, B9 and B12 in non-animal origin products.
8. HPLC method for simultaneous determination of vitamins D3 (Calcitriol, Cholecalciferol) and K2 (Menaquinone-4 and Menaquinone-7) in dietary supplements (fig. 10)

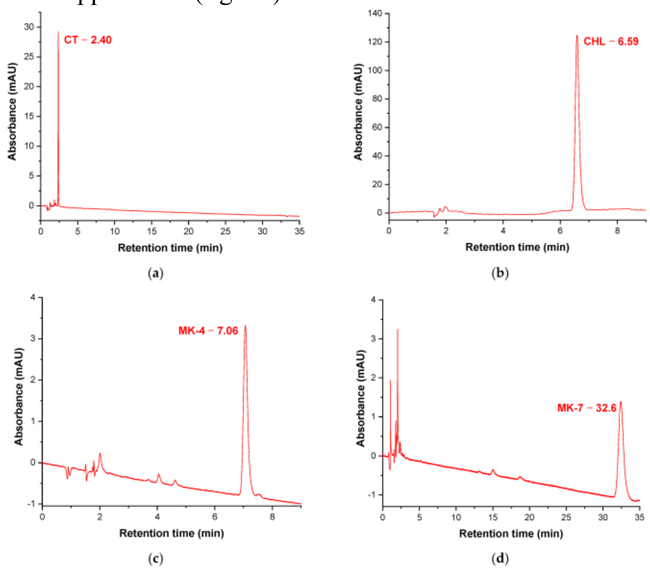

Fig. 10 HPLC chromatograms of the analyzed D3 and K2 vitamins: (a) calcitriol, CT; (b) cholecalciferol, CHL; (c) menaquinone-4, MK-4; (d) menaquinone-7, MK-7.

9. HPLC method for the detection of some antibiotics from meat products.

4.5 Materials base on natural zeolites

Within the ECO-ODOR project two prototypes materials have been developed:

1. Zeolite base products for the adsorption of humidity and smell from refrigerators, ECO-ODOR.(fig. 11)
2. Natural filter with zeolites for the retention of PAHs from smoke with applications in the food industry (fig 12)

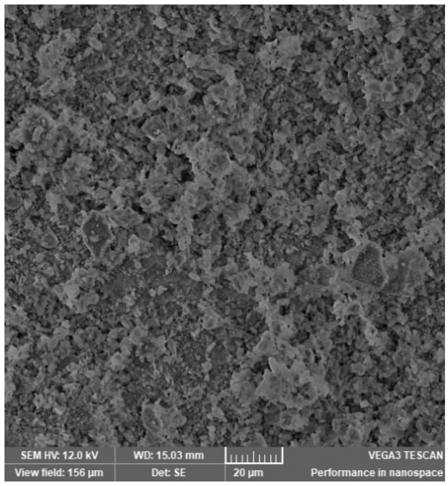

Fig. 11. The SEM analysis of the zeolite sample for humidity control

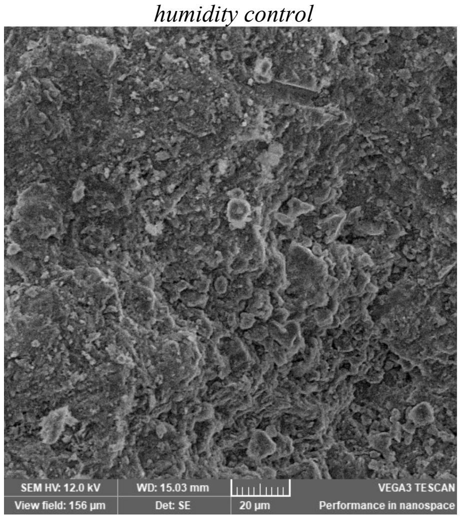

Fig. 12 The SEM analysis of the zeolite sample for HAP filtration

Two types of treatment methods for zeolite activation were applied: chemical (acid, basic) and thermal. The acid treatment was done using HCl. The thermal treatment was performed at 400 °C. These products have been tested to probe their efficiency in different conditions. The zeolite with particle sizes of 3–5 mm activated by acid treatment adsorbed twice as much PAHs (89.56 ng/g) from air as the zeolite that was thermally treated (38.92 ng/g). While the thermally-activated zeolite had a significantly better performance regarding humidity control, the acid treated zeolite had the best results in adsorbing the PAHs

The knowledge was transferred to Enviro Naturals Agro, Bucharest.

4.6 Industrial processes

Within the VINIVITIS project, an optimize process for high-pressure extraction of antioxidant compounds from Feteasca regala leaves was developed.

Collaboration with „Ștefan cel Mare” University from Suceava resulted in an optimize industrial process for capitalization of sea buckthorn waste by fermentation and obtaining a novel refreshing drink.

4.7. List of most significant publications

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2. Becze, Anca, Vanda Liliana Babalau Fuss, Daniela Alexandra Scurtu, Maria Tomoaia-Cotisel, Aurora Mocanu, and Oana Cadar. 2021. "Simultaneous Determination of Vitamins D3 (Calcitriol, Cholecalciferol) and K2 (Menaquinone-4 and Menaquinone-7) in Dietary Supplements by UHPLC" Molecules 26, no. 22: 6982. https://doi.org/10.3390/molecules26226982
3. András Hoffer, Beatrix Jancsek-Turóczi, Ádám Tóth, Gyula Kiss, Anca Naghiu, Erika Andrea Levei, Luminita Marmureanu, Attila Machon, András Gelencsér, Emission factors for PM10 and PAHs from illegal burning of different types of municipal waste in households, Journal Atmospheric Chemistry and Physics Discussions, pp. 1-18
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5. Lacrimioara Senila, Emilia Neag, Oana Cadar Melinda Haydee Kovacs, Anca Becze, Marin Senila Chemical, Nutritional and Antioxidant Characteristics of Different Food Seeds, Appl. Sci. 2020, 10(5), 1589; https://doi.org/10.3390/app10051589
6. Lacrimioara Senila, Eniko Kovacs, Daniela Alexandra Scurtu, Oana Cadar, Anca Becze, Marin Senila, Erika Andrea Levei, Diana Elena Dumitras, Ioan Tenu, Cecilia Roman Bioethanol Production from Vineyard Waste by Autohydrolysis Pretreatment and Chlorite Delignification via Simultaneous Saccharification and Fermentation Molecules 2020, 25(11), 2606; https://doi.org/10.3390/molecules25112606
7. Anca Becze, Dorina Simedru, Rapid detection of walnut and pumpkin oil adulteration using Raman spectroscopy and partial least square methodology, Notulae Botanicae Horti Agrobotanici Cluj-Napoca, acceptat spre publicare
8. Eniko Covaci, Marin Senila, Loredana Florina Leopold, Neli-Kinga Olah, Codruta Cobzac, Violeta Ivanova-Petropulos, Biljana Balabanova, Oana Cadar, Anca Becze, Michaela Ponta, Augustin Catalin Mot, Tiberiu Frentiu, Characterization of Lycium barbarum L. berry cultivated in North Macedonia: A chemometric approach, Journal of Berry Research, vol 10, 2020 : 223 – 241.
9. Laura Budiu, Emil Luca, Andreea Ona, Leon Muntean, Anca Becze, Dorina Simedru, Melinda Kovacs, Dalma Kovacs, Response Of Antioxidant Potential And Essential Oil Components To Irrigation And Fertilization On Three Mint Species (Mentha Spp. L.) ROMANIAN AGRICULTURAL RESEARCH, NO. 36, 2019 Print ISSN 1222–4227; Online ISSN 2067–5720
10. Alexandra Tăbăran, Ionuţ Vlad Cordiş, Anca Becze, Sorin Daniel Dana, Oana Reget, Gheorghe Ilea, Dana Liana Pusta, Ioan Pasca, Mihai Borzan, Marian Mihaiu, Evaluation Of Polycyclic Aromatic Hydrocarbons In Pork Meat Products Obtained In Traditional Systems In Romania, 2STUDIA UBB CHEMIA, LXIII, 1, 2018 (p. 189-198) DOI:10.24193/subbchem.2018.1.14
11. Coroian Aurelia, Vioara Mireşan, Cristian Ovidiu Coroian Camelia Răducu, Daniel Cocan, Luisa Andronie, Anca Naghiu, Adina Lia Longodor, Zamfir Marchiş, The level of polycyclic aromatic hydrocarbons (PAHs) from pork meat depending on the heat treatment applied, Romanian Biotechnological Letters, 2018

5. New directions of research

5.1 Alternative proteins

In the current context of climate change, economic hardship and rising food allergies, finding new sources of proteins that can simultaneous contribute to reduction of carbon foot print of the food industry, provide high nutritional value at a low cost is essential. Proteins are essential nutrients not just for the people but for animals too.

At INCDO-INOE ICIA Cluj-Napoca Subsidiary we want to develop more knowledge, application and products in this field of alternative protein by:

- Identifying new sources of proteins;
- Optimizing processes for obtaining high value proteins;
- Developing, testing and prototyping new feed and food formulations.

5.2 Digitalization

Our world is becoming more and more digital, which has impact on every aspect from economy to industry and healthcare. Although the ethic concern regarding AI is complex its uses and benefits are undeniable.

The hole food industry chain has a lot of benefits from applying AI solution to different aspects. From block chain data basses to ensure food sources can be verified in a click of a button no matter from where they come to intelligent solution for control of crops and food processes.

- Implementation of solutions for Agriculture 4.0 and Industry 4.0
- Open access science solutions;
- Integrative systems for the food chain.

5.3 Food for everyone

One of the problems that society faces today in terms of nutrition is the restricted diets due to underlining illnesses which lead to the lack of essential elements in the deists. Very often products designed for people with dietary restrictions is very expensive and can contain other harmful ingredients like preservatives, dyes and heavy metals.

That is way INCDO-INOE 2000 ICIA Cluj-Napoca wants to develop new formulation for peoples with different dietary restrictions by looking different at the protentional sources of nutrients.

Another society problem is facing due to many factors but mostly because of climate change is lack of yield for the usual crops and the need for new crops adapted to extreme climate conditions.

INCDO-INOE 2000 ICIA Cluj-Napoca wants to test different crop available in harsh conditions to study the their adaptability but also the potential for exploitations of new crops better adapted to extreme conditions.

6. Perspectives

Base on the available know-how and infrastructure, INCDO-INOE 2000 ICIA Cluj-Napoca aims to apply to different HORIZON-CL6 programs like:

- HORIZON-CL6-2022-FARM2FORK-02-01-two-stage: Agroecological approaches for sustainable weed management which aims support the farm to fork's strategy objective of a transition to a fair, healthy and resilient European agriculture, notably its objective to promote agroecology, and the target to reduce the overall use and risk of chemical pesticides 185 , by unfolding the potential of agroecology to provide alternative weeding strategies that reduce or eliminate the use of pesticides used as herbicides
- HORIZON-CL6-2022-FARM2FORK-01-04: Innovative solutions to prevent adulteration of food bearing quality labels: focus on organic food and geographical indications which aims to accelerate the transition to sustainable farming and food systems by, inter alia, promoting the growth of organic farming with a view to achieve the target of at least 25% of the EU's agricultural land under organic farming by 2030.
- HORIZON-CL6-2022-CIRCBIO-01-04: Maximising economic, environmental and social synergies in the provision of feedstock for bio-based sectors through diversification and increased sustainability of agricultural production systems whih is in line with the European Green Deal and the EU bioeconomy strategy, successful proposals will demonstrate the potential of diversification strategies in the primary production sector for providing feedstock in bio-based value chains.

INCDO-INOE 2000 ICIA Cluj-Napoca is also focused on the development of the EURALIM RI network by developing further the available infrastructure and by adding new members to the network.

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BIOMASS and BIOENERGY - new perspectives and future challenges

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Abstract. The work presents the results obtained by the ICIA in the field of "Biomass-Bioenergy". Energy is a crucial factor affecting current life style and social-economic development. Biomass is an abundant resource, and specific technologies can be used to produce biofuel and value-added products. ICIA has a significant number of results, nationally and internationally acknowledged, regarding biofuels such as biodiesel, bioethanol, biogas, technologies, installations and scientific publications. This chapter describes the technologies developed in research projects regarding biofuel production from various biomass types and highlights the significance of biomass wastes for the production of clean and renewable biofuels.

Keywords: biomass, bioenergy, biofuels, bioplastics

1. Introduction

The subsidiary of INCDO-INOE 2000, the Research Institute for Analytical Instrumentation (ICIA) Cluj-Napoca (http://www.icia.ro) is a national research institute dedicated to applied analytical chemistry in three main directions: Environment and Health, Bioenergy-Biomass, and Analytics and Instrumentation.

The institute performed numerous projects in the Energy Research direction. The alternative for the production of biofuel from biomass contributes to the reduction of CO_2 emissions. In these circumstances, one alternative is to replace fossil fuels with biofuels. The importance of energy issues and efficient utilization of energy reserves in the actual context of human development are problems that cannot be ignored. The relevance of the energy topic must be considered from two essential points of view: (i) security of primary energy supplies, in terms of quantity and competitive prices, and (ii) necessity of environmental protection and climate change mitigation, by reduction of greenhouse gas emissions [1].

Over the past hundred years, biomass has been intensively exploited, particularly in its fossil form of coal, oil and natural gas, which has led to a significant contribution of carbon dioxide into the atmosphere.

As a result, scientists in the field are increasingly recommending the use of renewable fuels derived from fresh biomass. Renewable energy technologies use biomass and have a lower impact on the environment compared with conventional technologies. It is estimated that Europe's oil resources will be depleted in about 40 years, natural gas in 60 years, which means that Europe will have to import most of its energy over the next 20 years. Romania has a considerable biomass energy potential with an agricultural surface of 14590,9 thou hectares, of which arable land is 9352,3 thou hectares (with one of the highest qualities in Europe), 6362,5 thou hectares of forests.

Bioethanol production increased sixfold in the first 18 years of this century, reaching 122 billion liters in 2018. Biodiesel is the second most produced biofuel in the world. USA and Brazil are the main producers, whereas EU covers only 41% of the world production. The raw material used for biodiesel production was mainly rapeseed oil. In addition to biodiesel and bioethanol, biogas is an important biofuel. [2].

Depending on the process, various types of biomasses can be converted into bioenergy. Based on the biomass used, biofuels are divided into: first (1G), second (2G), third (3G), and fourth generation biofuels (4G). The raw materials used for the first-generation bioethanol production are: carbohydrate materials (sugar cane, sugar beet, sorghum, corn, some fruit, etc.); starch biomass (corn, wheat, potato, cassava) [3].

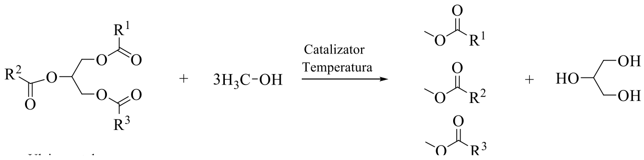
Biodiesel is obtained from oils and fats by:

- catalytic transesterification of the oil with alcohol;
- esterification of acidified oil with methanol;
- converting the oil to fatty acids and then to alkyl ester using an acid catalyst.

(a) Acid-catalyzed transesterification reaction of free fatty acids (equation 1)

$$RCOOH + CH_3OH \underset{}{\overset{H_2SO_4}{\rightleftharpoons}} RCOOCH_3 + H_2O$$

(b) Base-catalyzed transesterification reaction of triglycerides [4] (equation 2).



The second-generation biofuels include: bioethanol produced from lignocellulosic biomass and biowaste by advanced hydrolysis and fermentation, biodiesel produced from vegetable oils and animal fats by hydrotreated, synthetic natural gas from lignocellulosic biomass and residues by gasification and synthesis and biohydrogen by gasification, synthesis or biological process.

The most important benefits of bioethanol:

- renewable resources;
- reduced impact on air quality, due to clean combustion;
- reduction of carbon dioxide emissions (greenhouse gases);
- energy security: less dependent on oil;
- development of the market opportunity in the agricultural sector.

The third generation (3G) biofuels include algae and wastewater, while the fourth-generation biofuels use genetically modified algae to enhance biofuel production [5, 6].

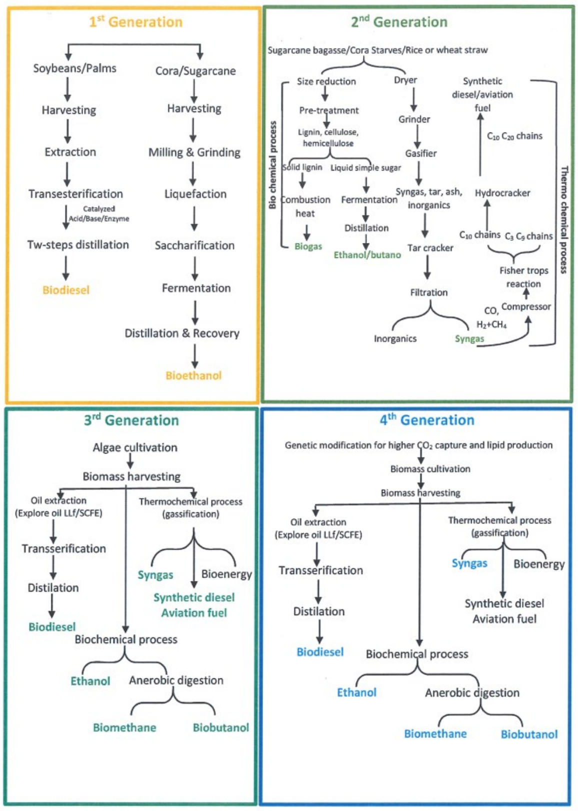


Fig 1. Biofuel production technologies [adapted after [5]

The ICIA institute contributes to science with several technologies used for the production of first, second, and third generation of biofuels.

One of the significant challenges for second-generation bioethanol was overcoming the obstacles in the pretreatment process for separating carbohydrates from the biomass source. The introduction of environmentally friendly pretreatments, such as autohydrolysis and supercritical pretreatment was an important contribution of the institute to the energy science.

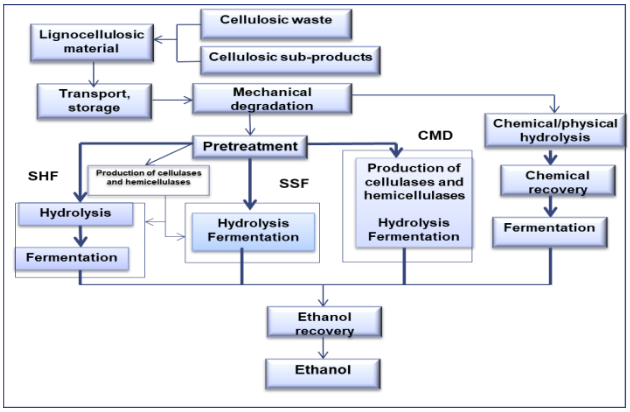


Fig. 2. Schematic overview of producing bioethanol from cellulosic waste

2. History/landmarks

ICIA has a significant number of results, nationally and internationally acknowledged, regarding biofuel such as biodiesel, bioethanol, and biogas embodied in projects, technologies, installations and scientific publications.

The „Bioenergy-Biomass" Laboratory is focused on obtaining renewable fuels (biodiesel, bioethanol, and biogas) from biomass and by-products; developing technologies and installations for renewable fuels (biodiesel, bioethanol, and biogas) production, and implementing advanced processes for the conversion of biomass to electricity and heat. It is composed of:

(1) **"Renewable Energy" Laboratory**, LER, for the elaboration and development of innovative processes for new, modern and cost-effective technologies intended for the superior capitalization of renewable resources and biofuels production, for their large-scale implementation on the market and

(2) **"Biofuel Quality Certification" Laboratory**, CABIO, for elaborating and developing innovative processes dedicated to biofuels quality determination and performing analyses in order to certify the biofuels quality, according to European standards for biodiesel and bioethanol (SR EN 14214 and SR EN 15376).

- ✓ *Bioethanol analyses according to SR EN 15376*: alcoholic strength, saturated higher alcohols content (C3-C5), methanol content, water content, inorganic chloride content, copper content, total acidity, appearance, phosphorus content, total dry extract, sulfur content.
- ✓ *Biodiesel analyses according to SR EN 14214*: ester content, density at 15°C, viscosity at 40°C, flash point, sulphur content, cetane number, octanic number, water content, total contamination, copper strip corrosion, oxidation stability at 110ºC, acid value, iodine value, linoleic acid methylester (C18:3), methanol content, monoglyceride content, di- and triglyceride content, free glycerol, alkaline metals, phosphorus content, calorific value, cloud point, cold filter plugging point (CFPP), total biodiesel content in diesel fuel.

The first investigations in obtaining biodiesel were carried out through the developed technologies for biodiesel production from crude oil (rapeseed oil).

➢ *Biodiesel production from oil (rapeseed oil)*

The technology for obtaining second generation biodiesel from crude and used oil was developed in the CARENZI project ("*Technology based on enzymatic transesterification process in order to obtain 2nd generation biofuels*"). The aim of the project was:

❖ the development of an innovative, cost-efficient and safe technology for the production of green alternative fuel from waste vegetable oils whose application leads to the reduction of greenhouse emissions [7];
❖ the construction of a pilot plant for the use of this technology.

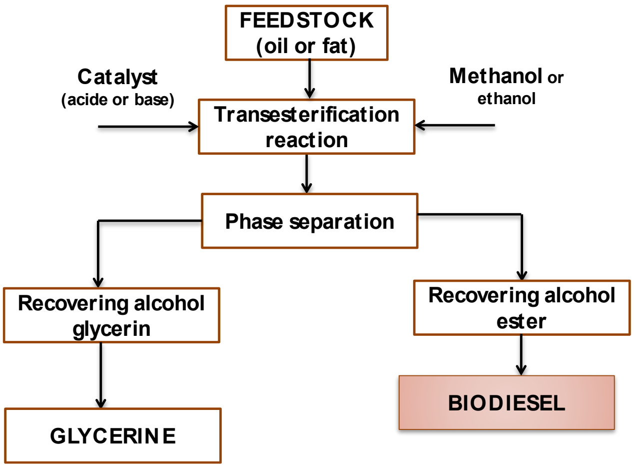


Fig. 3. Biodiesel production from oil and fat [7]

Fig 4. Pilot plant installation used for biodiesel production from rapeseed oil

➢ *Bioethanol and secondary by-products production from lignocelluloses*

Starting with 2009, during the NUCLEU project entitled „*Elaboration of modern technologies with optimum efficiency for the superior valorization of biomass (lignocellulosic waste and algae) for 2nd and 3ed biofuel obtaining*", NUCLEU PN 09 27 03 02 (2009 - 2011) the production of bioethanol from lignocellulosic biomass and biodiesel from algal biomasses was initiated.

Lignocellulosic biomass is a versatile energy resource for biofuel due to its chemical composition. Cellulose, hemicellulose and lignin are the major constituents of lignocelluloses. Celluloses and hemicelluloses can be converted into bioethanol by using enzymatic and fermentation processes [8, 9, 10].

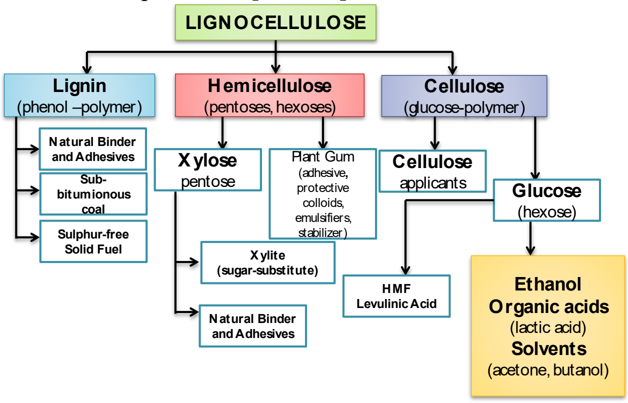


Fig. 5. Bioethanol and secondary by-products production from lignocelluloses

➢ *Biogas production*

In the BIOGEF project "*Highly efficient technology for biogas production from biomass, in an integrate system generating electric power and heat, in the case of Romanian agricultural farms*" a technology for biogas production under small medium farms conditions was developed. Anaerobic digestion provides possibilities to produce renewable energy from organic wastes in decentralized sites, producing a methane rich biogas from manure (human and animal) and crop residues. A part from supplying renewable energy, biogas plants have other positive effects including the strengthening of closed loop recycling management systems, reducing emissions from manure storage and producing a valuable organic fertilizer.

The raw materials used for biogas production are:

❖ landfill,
❖ communal waste and industrial sewage water,
❖ organic waste from households and market,
❖ organic waste from industry,
❖ excrements,
❖ byproducts of agriculture and food production,
❖ material from landscape conservation,
❖ wood,
❖ urine and
❖ nutrition in sewage water.

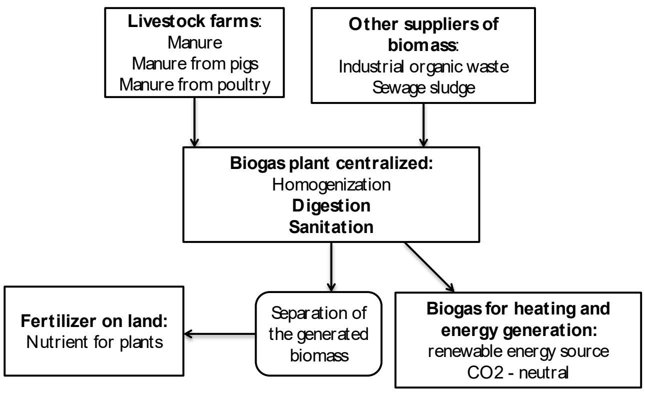


Fig. 6. Plant for biogas production

The anaerobic digestion is carried out in four stages:

1►**hydrolysis** of biomass with water, in which insoluble complex molecules such as carbohydrates and fats are broken down into sugars, fatty acids and amino acids,

2►**fermentation** and acidification, in which fermentative bacteria transform sugars into organic acids, alcohols, carbon dioxide, hydrogen and ammonia,

3►**acetogenesis**, where the products from fermentation are converted into hydrogen, carbon dioxide and acetic acid,

4►**methanogenesis**, where methanogenic bacteria transform acetic acid, carbon dioxide and hydrogen into biogas.

3. Current development and collaboration

ICIA collaborates with the National Institute of Agronomic Research, Laboratoire de Biotechnologie de l'Environnement (INRA-LBE), Narbonne, France in the frame of the project entitled "***Improving lignocellulosic biomass pretreatment to increase biogas yields-LIGNOBIOGAS***", Contract no. 16BM/2019, PN-III-P3-3.1-PM-RO-FR-2019-2020, Bilateral Brancusi Romania-France project (2019 -2021). The project aimed to **(1)** develop ecological methods for the pretreatment of lignocellulosic biomass before anaerobic digestion and **(2)** develop biogas technologies. ICIA has laboratories, equipment and reactors designed for anaerobic digestion of different types of lignocellulosic biomass, the pretreatment of biomass, and chemical analysis of compounds.

Fig. 7. The Automatic methane potential Test System (AMPTS II) (Bioprocess Control) used for biogas production and analysis

The technology for biogas production from lignocellulosic biomass contains the following stages: (1) pretreatment, (2) anaerobic digestion and (3) analysis and purification of biogas.

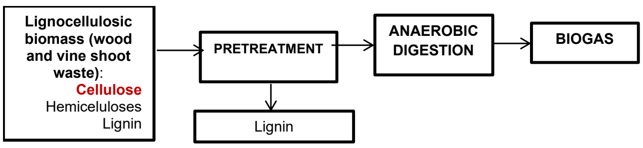


Fig. 8. Biogas production from lignocellulosic biomass

The experiments for biogas production were carried out in the Automatic Methane Potential Test System (AMPTS II) which offers:

- ❖ precise and accurate data;
- ❖ significant reduction in time, labour and skill demands;
- ❖ standardizing measurement procedures, data interpretation and reports;
- ❖ remote access and user-friendly operations.

AMPTS II was equipped with a gas endeavor detector used as an analytical platform for biodegradability, digestibility and respirometry analysis. The Gas Endeavor was used for measuring low gas volume and flow for any type of gas production or consumption from biological respiration or fermentation processes. Fully integrated and automatic, Gas Endeavour saves time and labour in performing analysis, leading to more efficient research and more profitable production. It is the perfect analytical instrument for research and industrial applications, including animal nutrition, wastewater, ethanol fermentation, hydrogen production, biodegradability analysis, greenhouse gas emissions, evaluating microbial communities and more.

The project entitled "***A complex integrated system for technology optimization and superior valorization of the winemaking and viticulture by-products (VINIVITIS)***" Contract no. 4PCCSI/2018 was formed of seven partners (UTCN, USAMV Cluj-Napoca, ASAS, SCV Murfatlar, USAMV Iasi, UMF Cluj-Napoca) and five projects. Project P1 – VALOVITIS was part of the VINIVITIS project, where ICIA was the project manager. This project aimed to recover energy from biomass as an energy source: biofuel production (bioethanol) and solid biofuel for cogeneration (heat and/or electricity).

Fig. 9. Bioreactor Lambda 25 used for fermentation processes

VINIVITIS project results:

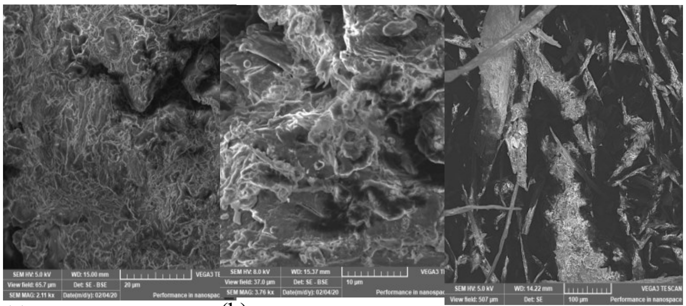
i. *second-generation bioethanol from vineyard waste by simultaneous saccharification and fermentation (SSF) process*;

The technology for bioethanol production from vineyard wastes (SSF) consists of the following stages: (1) pretreatment of vineyard wastes; (2) delignification of pretreated biomass; (3) enzymatic hydrolysis and fermentation of sugars to bioethanol.

Bioethanol can be produced also from residues such as vine-shoots with a comparable structure to that of conventional wood and contain lignocellulosic materials with cellulose, lignin and hemicellulose as main components. Autohydrolysis is an environmentally friendly pretreatment method using only water as reaction medium, at high temperature (170–230°C) and pressure (up to 5 MPa). Autohydrolysis pretreatments have been applied to vine shoot waste varieties in order to obtain hemicellulosic sugars-containing liquors and spent solids as substrates for bioethanol production [11].

Fig. 10. Parr reactor used for the pretreatment process

Due to their high cellulose content, the vineyard cutting wastes were used for the bioethanol production.



(a) (b) (c)

Fig. 11. *Scanning electron microscopy images of the samples (vine-shoot waste): (a) untreated, (b) autohydrolysed, (c) delignified*

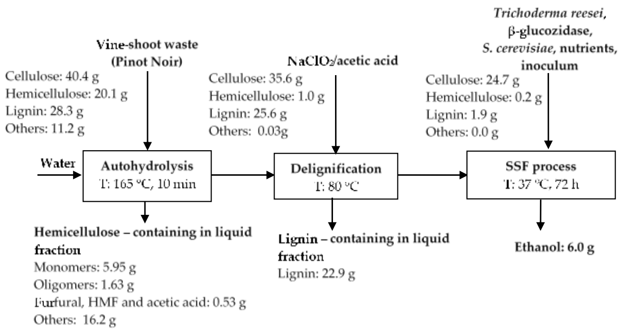


Fig. 12. Mass balance for bioethanol production from vineyard waste [11]

ii. *bioethanol, by using separate hydrolysis and fermentation processes*

The technology for bioethanol production from vineyard wastes (SHF) consists of the following stages: (1) pretreatment of vineyard wastes; (2) delignification of pretreated biomass; (3) enzymatic hydrolysis of pretreated and delignified biomass and (4) fermentation of sugars to bioethanol.

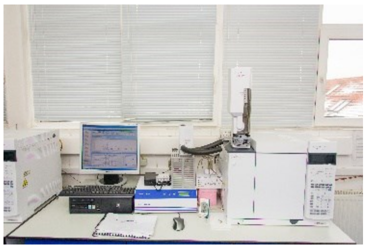


Fig. 13. GC-FID used for analysis of superior alcohols

Fig. 14. Refractometer Mettler Toledo used for analysis of ethanol

iii. *pellets obtained from vineyard waste by densification without additives, for domestic boilers and cogeneration plants;*

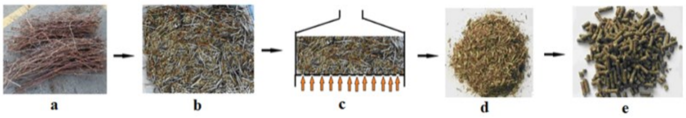


Fig. 15. Simplified scheme of the pellets production process from vineyard wastes: (a) vineyard wastes; (b) course grinding;(c) drying;(d) fine grinding; and (e) pelletization.

The densification technology of vineyard wastes into pellets includes the following stages: (1) course grinding, (2) drying under controlled temperature; (3) fine grinding (with particles smaller than 4 mm); and (4) pelletization.

The samples were purchased from the vineyard plantation located at the "Vasile Adamachi" farm, belonging to the University for Life Sciences Iaşi; the plantation is part of the Copou Vineyards, located near the city of Iaşi (the partner of the VINIVITIS project).

Table 16. Chemical characterization of pellets, according to ISO 17225-6:2014 [12]

Nr. crt.	Savignon Blanc	Pinot Noir	Feteasca Regala	Busuioaca de Bohotin	Muscat Ottonel	Cabernet Sauvignon	Feteasca Neagra	Feteasca Alba	Standard ISO 17225-6
Moisture (%)	10.2	10.5	9.8	10.9	9.6	10.3	11.2	10.04	M ≤ 10
Length (mm)	23.1	18.3	21.8	23.4	16.9	20.9	18.8	23.1	3.15 < L ≤ 40
Diameter (mm)	10	10	10	10	10	10	10	10.0	D06 -D25
NCV (MJ/kg)	17.49	17.18	17.60	17.00	17.18	17.34	17.20	17.19	Q≥14.5
Ash (%)	3.57	4.42	4.47	3.67	4.29	3.5	4.02	4.79	A < 4
N (%)	1.0	1.0	0.90	1.6	0.90	0.85	0.84	0.87	N ≤ 0.5
Fine particles (%)	1.25	1.23	1.24	1.25	1.27	1.25	1.20	1.25	F 2.0 ≤ 2.0
S total (%)	0.020	0.0024	0.024	0.024	0.017	0.018	0.021	0.023	S ≤ 0.05
Cl (%)	0.07	0.06	0.06	0.07	0.04	0.06	0.07	0.05	Cl ≤ 0.08
As (mg/kg)	0.17	0.18	0.08	0.09	0.21	0.09	0.16	0.56	≤ 1
Cd (mg/kg)	0.02	0.04	0.04	0.02	0.03	0.44	0.08	0.06	≤ 0.5
Cr (mg/kg)	8.58	26.8	2.13	67.3	2.48	4.57	3.32	12.2	≤ 50
Cu (mg/kg)	36.1	15.18	14.47	11.22	15.32	9.87	15.36	17.1	≤ 20
Pb (mg/kg)	1.36	1.41	5.8	2.2	2.46	2.83	2.76	3.56	≤ 10
Hg (mg/kg)	-	-	-	-	-	-	-	-	≤ 0.1
Ni (mg/kg)	2.93	3.76	1.68	1.54	2.4	1.62	2.55	8.38	≤ 10
Zn (mg/kg)	25.3	30.2	22.2	24.9	37.3	18.7	29.8	33.9	≤ 100

The obtained pellets were characterized according to existing EU standards for non-woody pellets.
The obtained results suggest that these biomass wastes can be used successfully for the production of pellets, aiming to enhance the research for the manufacturing of these sustainable biofuels with some remarks regarding risk of corrosion and slag formation during prolonged use [13].

iv. *briquettes obtained from vineyard waste by densification without additives, for domestic boilers and cogeneration plants*

Fig. 17. Briquettes obtained from vineyard wastes

The production of briquettes is based on a set of mechanical technologies (screw-type press, rollers type press, piston press—mechanically or hydraulically driven—or manually operated press) in order to convert the vegetable biomass (from different crops) into a uniform and compacted fuel, with a higher density and energy content and a lower moisture content compared with the raw material. Different studies recommend a moisture content between 5% and 12%, depending on the nature of biomass.

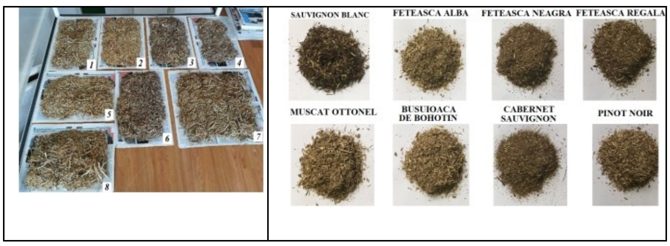


*Fig. 18. Sieving of the ground tendrils: (**a**) grinded tendrils, before sieving; (**b**)—grinded tendrils, ready for briquetting.*

The technology steps for briquettes production from vineyard wastes are presented below:

Dormant pruning of vine

⇩

Tendrils prelevation and transport

⇩

Storage of tendrils

⇩

Natural drying of tendrils

⇩

Coarse and fine chopping of the tendrils

⇩

Sieving and separation of the particles bigger than 8 mm or smaller than 3.15 mm

⇩

Briquetting

⇩

Conditioning and cooling of the briquettes

⇩

Packing of the briquettes

Fig. 19. The technological process for briquettes production from vine tendrils [14]

The obtained briquettes are analyzed according to the ISO 17225-3 (2014) standard and the results of the experimental tests show that the briquettes from vine shoots satisfy the requirements of the quality class A1.

v. *gaseous emissions evaluations from the combustion of pellets and briquettes obtained from vineyard waste*

The obtained pellets and briquettes were carried out as solid biofuel and the flue gases and particulate matters were measured.

Fig. 20. The flue gases measured in cogeneration plant

The flue gases obtained by vineyard pellets burning in a pellet stove compared with the limit values enforced in Romania and those reported in other studies. The fuel gases were evaluated by the combustion of pellets in a domestic boiler. The emissions of pollutants, such as CO, NO_X, and SO_2 were determined and they were below the limit value, except for carbon monoxide which exceeded the limit due to incomplete combustion.

Table 1. The flue gases identified after the combustion of solid biofuels

Gases (mg N^{-1} m^{-3})	CO	NO	NOx	SO_2
Pellets	1973	131	203	32
Briquettes	2165	207	141.3	33
Romanian Legislative Decree D. Law 462/1993	250	-	500	2000

Briquettes produced from vineyard waste were subjected to combustion in a cogeneration plant. The burning time was 2-4 times longer than that of pellets. The results of combustion were combustion gases, ash, slag and heat. The combustion process depends on the volume of oxygen required for combustion.

The high quantity of CO produced was due to the incomplete burning or decomposition of carbon dioxide. In the present study, the average NO_x (expressed as NO_2) was 140 mg $N^{-1}m^{-3}$ and the SO_2 content was 32 mg $N^{-1}m^{-3}$. The values for both parameters were below the maximum levels set by the Romanian legislation. The NO_x and SO_x emissions obtained are in accordance with the fuel indices calculated [14].

The project results suggested that high-quality pellets from vineyard wastes significantly influence the environment and the economy.

Fig. 21. UHPLC with DAD, RI and ELSD detectors used for sugar analysis

vi. *Life cycle assessment (LCA) of bioethanol production from vineyard wastes.*

Life cycle assessment (LCA) is a standardized method used to evaluate how a production system performs from a broad environmental point of view during the entire life time, starting from raw material extraction and processing, via production and use, to the final disposal. The LCA framework is comprised of four phases, namely (1) goal and scope definition; (2) inventory analysis; (3) impact assessment and (4) interpretation.

The potential environmental impact of bioethanol production was assessed based on ISO 14040 and ISO 14044 standards using the SimaPro software.

The goal of the study was to evaluate various environmental effects generated by the production of bioethanol based on vine shoot waste. An attributional LCA was performed taking into account the activities from the vineyard to the laboratory, covering biomass transport, biomass conversion and bioethanol production. The functional unit was set to 1 kg of bioethanol. The system boundary was defined for a “cradle to grave” analysis, including all process entries and associated emissions (*Fig. 22*).

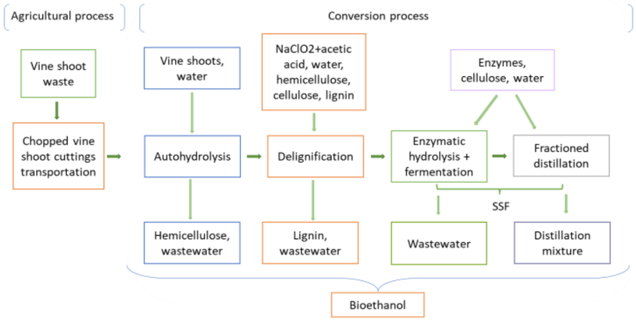


Fig. 22. System boundary of the bioethanol production [15]

The life cycle inventory (LCI) phase consisted of data gathering. Primary data was collected in the period October 2018-November 2019 and it resulted from the three main stages of the bioethanol production process, namely: the pretreatment (autohydrolysis), delignification, and simultaneous saccharification and fermentation (SSF).

The life cycle impact assessment (LCIA) phase used the global ReCiPe Midpoint H method with the help of the SimaPro software.

The results showed that global warming, freshwater eutrophication and ecotoxicity, terrestrial ecotoxicity, fine particulate matter formation, fossil resource scarcity, water consumption and human toxicity (*Fig. 23*) are the main impact categories affected by the biofuel production process from vine shoot waste.

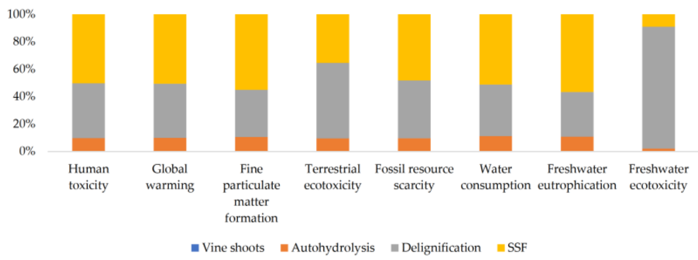


Fig. 23. Bioethanol production impact categories

Within the stages of bioethanol production, delignification has the greatest impact, causing freshwater and terrestrial ecotoxicity, followed by SSF, mainly responsible for fine particulate matter formation, freshwater eutrophication, global warming, water consumption, and by autohydrolysis.

The life cycle assessment showed that due to the consumption of chemical reagents, to the high consumption of electricity and water, the bioethanol production process has significant contributions to water consumption, ionizing radiation and freshwater ecotoxicity impact categories. The delignification stage contributes with a percentage of over 50% to the non-carcinogenic toxicity and deficit of mineral resources impact categories. The SSF stage contributes to the fine particle formation, freshwater eutrophication and ionizing radiation impact categories (*Figure 24*).

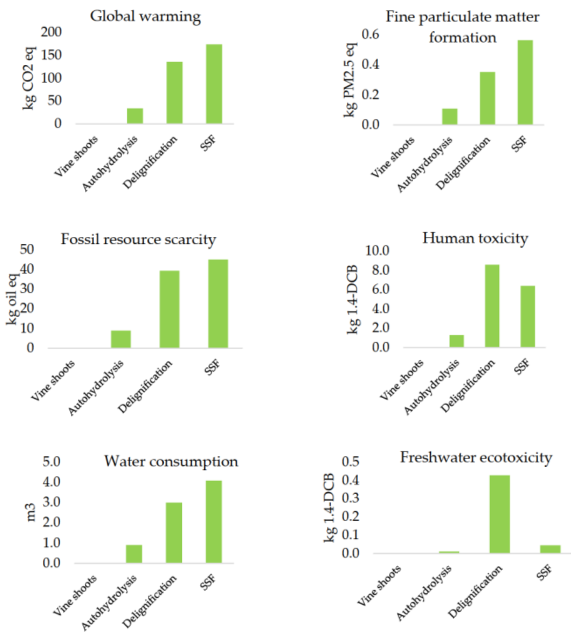


Fig. 24. Characterization of the impact categories of bioethanol production

When compared to pellets/briquettes production, bioethanol production resulted in a greater contribution to several environmental impact categories.

The project entitled "*Hydrogen production from hydroxylic compounds resulted as biomass processing wastes (HYCAT)"*, project number: PN-II-PT-PCCA-2011-3.2-0452, had the following goals: **(i)** developing methods for bioethanol production from wood wastes; **(ii)** testing fermentation medium produced from wood waste as raw material for catalytic hydrogen reforming and correlation between the methods used for bioethanol production and content of produced hydrogen [16, 17].

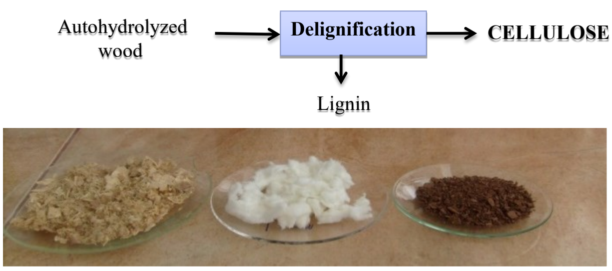


Fig. 25. Cellulose production from wood waste [16]

The project - „*Elaboration of modern technologies with optimum efficiency for the superior valorization of biomass (lignocellulosic waste and algae) for 2nd and 3ed biofuel obtaining,* NUCLEU PN 09 27 03 02 (2009 -2011). ***Project results***: **(i)** development of technologies for 2nd generation biofuels obtained from cellulosic waste by steam explosion pretreatment in the presence of catalysts, acid hydrolysis, and fermentation of sugars obtained with *S. cerevisiae* yeast.

Bioethanol obtained from wood has great potential to replace the existing fuels and can reduce greenhouse gas emissions. Autohydrolysis pretreatment is a process that uses water as a reaction medium, being a simple, low-cost, and environmentally friendly pretreatment. Delignification method using sodium chlorite eliminates almost in totality lignin. Enzymatic hydrolysis was performed in all cases with Accellerase 1500 complex enzymes, cellulose enzymes having the capacity to hydrolyze both cellulose and hemicellulose. The optimal conditions for sugar obtained from silver fir wood in this work were defined by temperature (190°C), pressure (60 bar), residence time (10 minutes), solids loading (2%), and hydrolysis time (72 hours). These conditions led to obtaining 33 g glucose/100 g of wood. Overall, the processing of 100 g wood would result in the recovery of 74 g of products. The sugars formed after enzymatic hydrolysis can be further fermented for bioethanol production [18, 19, 20, 21, 22].

(ii) technology for biodiesel production from algae oil

The raw materials for 3rd generation biodiesel - microalgae - have emerged as one of the most promising alternative sources of lipids that can be used in biodiesel production due to their high photosynthetic efficiency in biomass production, growth rates and productivity large compared to conventional cultures.

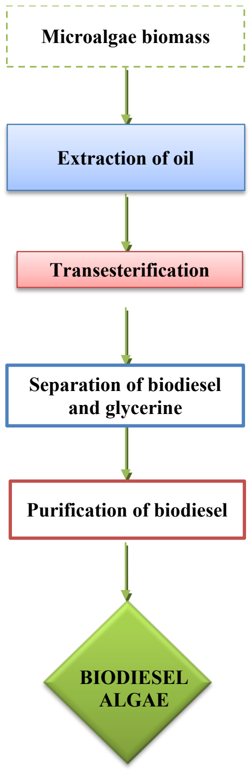


Fig. 26. Technology for biodiesel production from algae biomass

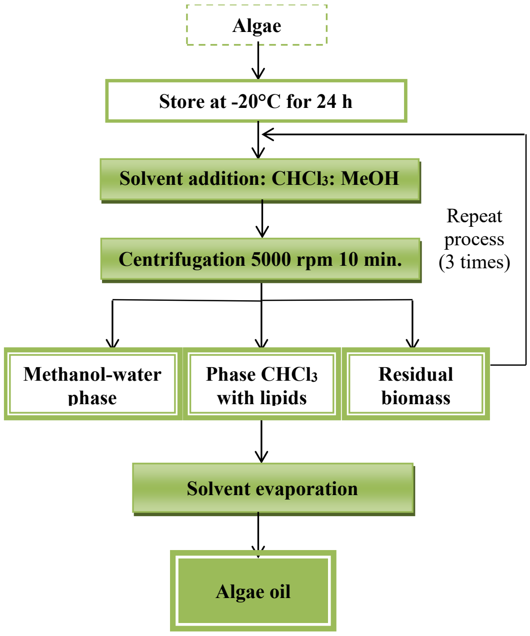


Fig. 27. Algal oil extraction with solvent

Transesterification in basic catalysis has been the most intensively used to date for obtaining biodiesel from vegetable oils. This is done by mixing the basic catalyst with methanol to form the methoxide (of sodium or potassium) and it is introduced over the oil.

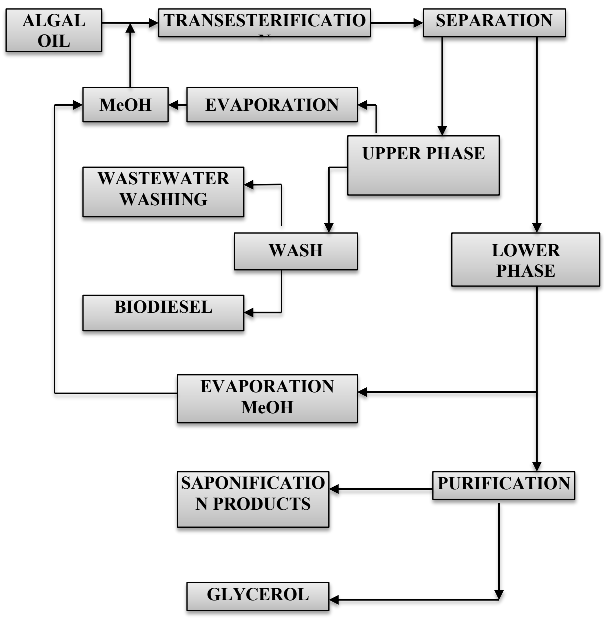


Fig.28. Technology for biodiesel production from algae oil by basic catalyst

4. Recent results and transfer of results

Project in progress

The preliminary results regarding bioplastic production from lignocellulosic biomass was obtained in the frame of the project "*Innovative technologies for valorizing lignocellulosic waste to bioplastics, LIGNOBIOPLAST*" contract no. TE 37/2022. The major objectives of the LIGNOBIOPLAST project are (i) the development of innovative technologies for obtaining bioplastics (PLA and PHA) from lignocellulosic waste, (ii) the characterization of bioplastics for establishing physical-chemical qualities.

The present project aims to develop new environmentally friendly technologies regarding the lignocellulosic waste utilization in order to obtain bioplastics (PLA and PHA) by using a supercritical CO_2 pretreatment method for carbohydrate separation, fermentation with microbial strains, physical-chemical characterization of the bioplastic obtained and quality determination.

Pretreatment is the most important step in the separation process of important components from lignocellulosic biomass. Bioplastics can be produced biologically and are a potential alternative to petroleum-derived plastics. The obtained sugars from lignocellulosic biomass are used as substrate for fermentation to produce polylactic acid (PLA) or polyhydroxyalkanoates (PHAs). PLA can be produced from renewable sources by simultaneous saccharification and fermentation (SSF) of cellulose and hemicellulose by using specific microbial strains, followed by purification and polymerization stages. Currently, some technologies for the production of bioplastics from lignocellulosic biomass were proposed, based on the use of different pretreatment methods. Supercritical carbon dioxide is widely used due to its moderate critical conditions (31.1°C and 74 bar). The mechanism involves the formation of hydrogen-bond and it acts as a Lewis acid and base. In order to increase its polarity, it is recommended to use a co-solvent. The presence of moisture content together with CO_2 can generate carbonic acid, which enhances the hydrolysis of hemicellulose in the liquid phase.

In this project, the production of PLA from lignocellulosic biomass was investigated after supercritical CO_2 pretreatment, hydrolysis and fermentation with specific strains.

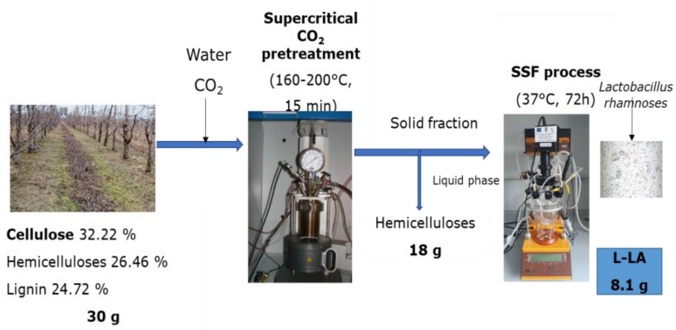


Fig. 29. Mass balance for L-LA production from lignocellulosic biomass

In this study, the influence of supercritical CO_2 pretreatment on apple orchard waste was investigated for separating sugars into cellulosic and hemicellulosic fractions. The resulted sugars were used as raw material for obtaining bioplastics. For 30 g of raw material, approx. 20.0 g of solid phase could be obtained after pretreatment and, after the SSF, 8.1 g of L-lactic acid (L-LA) was obtained.

ICIA holds numerous technologies obtained during the development of various research projects:

Technologies:

(1) Technology for biogas obtained from lignocellulosic biomass (LIGBOBIOGAS);
(2) Technology for obtaining bioethanol from vine shoot waste (SHF and SSF) (VINIVITIS);
(3) Technology for pellets production from vineyard wastes (VINIVITIS);
(4) Technology for briquettes production from vineyard wastes (VINIVITIS);
(5) Laboratory technology to obtain 2nd generation biofuels by acid hydrolysis of wood waste (NUCLEU, HYCAT project);
(6) Laboratory technology to obtain 2nd generation biofuels by enzymatic hydrolysis of cellulosic waste (NUCLEU project);
(7) Technologies for 2nd generation biofuels obtained from waste vegetable oil by transesterification (CARENZI);
(8) Technologies for obtaining biodiesel from algae (NUCLEU);
(9) Technologies for obtaining biogas from biogenic waste (BIOGEF);
(10) Technology for the purification of glycerin resulted as a byproduct in the process of biodiesel production;
(11) Technology for biodiesel/additive production from renewable sources, through a carbonatation reaction of glycerol acetals (on lab-scale);
(12) Technology for obtaining biopetrols from white beet biomass (BIOBENZ);
(13) Biodiesel obtained by treating fatty acids, their esters, and glycerides with hydrogen-enriched gas (BIOHID).

Others: ♦small capacity installation (200 l/charge) for biodiesel production from vegetable oil (homologated and transferred to the beneficiary);

Patents:

(1) Senila L., Chintoanu M., Gog A., Roman M., Pitl G., Roman, C. ”Technology for preparing bioethanol from lignocellulose biomass (wood waste)” RO126407-B1, 2012;
(2) Senila L., Gog A., Roman M., Roman C. ”Technology for preparing bioethanol by converting cellulosic wastes during a simultaneous saccharification and fermentation process” RO127297-B1 2014;
(3) Roman C., Gog A., Senila L., Roman M. ”Technology for preparing diesel bio-fuel from algae oil” RO128691-B1, 2014;
(4) Senila L., Varaticeanu C., Kovacs E.M., Scurtu D., Cecilia R. Preparing bioethanol from grapevine cordons by subjecting dried and ground grapevine cordons to self-hydrolysis with water, performing delignification, carrying out enzymatic hydrolysis and simultaneous fermentation, Patent no. RO135656-A2.
(5) Senila L., Varaticeanu C., Kovacs E.M., Scurtu D., Cecilia R. Preparing bioethanol by treating grapevine cordons by drying and grinding, then subjecting to microwave pretreatment in the presence of water, performing delignification with sodium chlorite and carrying out enzymatic hydrolysis in sodium citrate solution, Patent no. RO135657-A2.

The results can be transferred to: universities, research centers, institutes, laboratories, SMEs, etc.

5. Future challenges and perspectives

Biofuels have certain benefits over fossil fuels. Important factors to take into account include sustainability, greenhouse gas emissions, air pollution, soil and water resources, biodiversity and land use. Consequently, the development of advanced technologies and new strains through genetic engineering must be refined and developed to facilitate and resolve these problems. Certainly, biofuels produced from energy crops and micro-algae appear to be the most efficient and attractive solution. It needs to be further researched or developed to enhance the production of biofuels using genetic engineering on a larger commercial scale. There are a number of environmental advantages to biofuels compared to fossil fuels. Biodiesel blends in low-sulphur diesel fuel (ULSD) have the potential to significantly reduce transportation-related CO_2 and GHG emissions and air pollution. However, land use, water and biodiversity issues should be taken into account in the development of guidelines for assessing the impacts of the biofuel sector.

This chapter highlights the importance of technological aspects of biofuels. Biofuels production and utilization offer opportunities and find a sustainable solution to contribute to local and national energy security, economic growth, diversification of the rural economy and employment, import substitution with direct and indirect effects on the trade balance, energy supply and diversification through the creation of new industries [14].

Residual biomass resulting after the fermentation of lignocellulosic biomass can be recovered and transformed into valuable compounds. As a result of SSF fermentation, the recovered wastes can be used for the production of various bio-products, including enzymes, organic acids, bio-fertilizer, bio-pesticides, surfactants, pigments, vitamins and antibiotics.

Biomass is an energy-rich raw material for biofuel production, but its conversion process is constrained by a number of operational conditions, the type of conversion process chosen and the cost of benefits.

The main technological challenges for biofuel production include:

- ✓ inedible raw materials such as lignocellulosic biomass and the use of other organic waste,
- ✓ logistical aspects of production,
- ✓ energy-efficient pre-treatment, enzymatic hydrolysis and fermentation technologies;
- ✓ efficient use of co-products,
- ✓ establishing standards for biofuels;
- ✓ distribution logistics,
- ✓ social and economic advantages and acceptance thereof,
- ✓ reduce its effects on the environment to a minimum [23].

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BIODIVERSA: microbiota, response at global change and solution towards raised challenges

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Globally, soil biodiversity is under constant pressure from major threats, such as climate change, land use change and intensification, properties decline, and increased levels of pollution. Global and constant monitoring initiatives that target soil biodiversity and ecosystem functions across space and time are required for comprehensive acknowledge of potential pressures impact on further supplying of goods. BIODIVERSA laboratory recognize that such initiatives are necessary to fully understand the consequences of ongoing global environmental change on the multiple ecosystem processes and services supported by soil organisms, and not finally to find solutions throughout to cope these current challenges.

Keywords: biodiversity, soil microbiota, ecosystem services

1. Introduction

Biodiversity is defined as the "sum of all living things from the Earth (microorganisms, fungi, plants, animals, etc.), their genotypic and phenotypic variation, and the communities and ecosystems of which they are a part" [1]. Simply, this means the Earth. Now, the global biodiversity change as consequence of global change induced pressures. These changes are one of the most pressing environmental issues of our days. This is because biodiversity provides the foundation for ecosystem services as those of provisioning (food, fiber, biomass, fuel, freshwater, natural medicines, etc.), supporting (nutrient cycling, water cycling, soil formation, etc.), regulating (air quality, climate, water runoff, erosion, natural hazards, pollination, etc.) and cultural ones (ethical values, existence values, recreation, ecotourism, etc.) [2]. All these are intimately linked with human well-being. This foundation is now becoming endangered as the global changes that sums climate change and anthropogenic activities related modifications increases and are positively correlated with biodiversity declines. The decline of biodiversity is not only meaning the biodiversity loss, but also it refers to alterations of biodiversity distribution, composition, and abundance [3]. Such changes could modify organisms – environment interrelations as a result of fitness alteration which leads into availability decline for resources and functions, those altering the ecosystem balance as a whole.

Soil is one of the most important and complex ecosystems. According to Convention on Biological Diversity (CBD) soil biodiversity was defined as "the variation in soil life, from genes to communities, and the ecological complexes of which they are part, that is from soil micro-habitats to landscapes" [4]. In other words, soil biodiversity sums up the total variety of life belowground and encompass the number of distinct species (richness), their proportional abundance present in a system (evenness), and the phenotypic (expressed), functional, structural and trophic diversity. Usually, the total biomass from the soil belowground exceeds that of the aboveground, whilst the biodiversity from the soil always exceeds that from the corresponding surface by orders of magnitude, especially at the microbial extent – see Fig. 1.

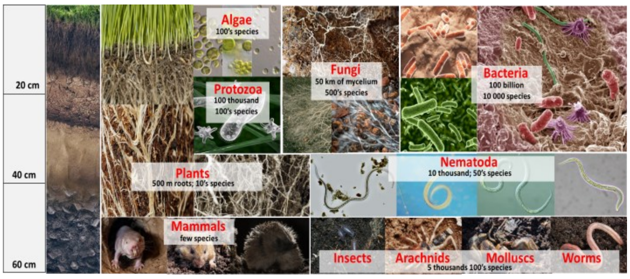


Fig. 1. Soil biodiversity expressed in numbers

As a unique medium, interest in soils as reservoirs of biodiversity has increased in the last several years, especially referring to soil microbiodiversity. This is because soil microbiodiversity encompasses a wide range of functional attributes in ecosystems (see Table 1) in addition to being concerned with the numbers of species present in ecosystem.

Table. 1. Soil microbiota involvement in soil functions and processes that assure diverse support, provision and regulation services provision by soil ecosystem (adapted after Aislabie and Deslippe, [5])

Service	Ecosystem services	Soil function
Support	*Primary production*	Support for terrestrial vegetation
	Role of soil microbiota: Net and gross primary productivity is assured by soil microbiota through reactions in that transform organic and inorganic compounds into usable form for other organisms. Also, microbiota mobilize nutrients	

	from insoluble minerals to support plant growth	
	Soil formation and renewal	Soil formation processes
	Role of soil microbiota: Microbiota speed up and modify soil physicochemical processes	
	Nutrient cycling	Storage, cycling, processing of nutrients and delivery to plants
	Role of soil microbiota: Nutrient cycling among organic and inorganic pool is driven by soil bacteria, archaea and fungi turnover	
	Platform	Supporting structure for human activities
	Role of soil microbiota: Microbes contribute to soil formation through elements cycling, and compounds and organic matter production. They are involved in minerals weathering. Microbial products are critical to soil aggregation. Improved soil structure makes it more habitable for living organisms	
Provision	*Refuge*	Habitat for resident and transient populations (terrestrial habitat)
	Role of soil microbiota: Soil bacteria, archaea and fungi contribute to soil formation and are the foundation of soil food webs thereby underpinning the diversity of higher trophic levels	
	Water storage	Water retention and supply in the landscape
	Role of soil microbiota: Soil microbiota are food and nutrient resources contribute for higher trophic level organisms as plant roots, earthworms and other. These at macropores formation, which are related with hydrological processes (infiltration, drainage)	
	Supply of food, fibers, biofuels and wood (biomaterials)	Provision of plant growth and production
	Role of soil microbiota: Soil microbes produce antimicrobial agents and enzymes useful for several biotechnological purposes. Microbiota species produce plant growth hormones, symbioses (mycorrhizal fungi and N2 fixing bacteria), pathogen control, degradation of stress ethylene (ACC deaminase - gram positive bacteria)	
	Supply of raw materials of mineral origin	Provision of source materials
	Role of soil microbiota: Soil microbes are involved in minerals weathering processes	
	Biodiversity and genetic resources	Source of unique biological materials and products (soil biota)
	Role of soil microbiota: Soil bacteria, archaea and fungi comprise a vast majority of the biological diversity on earth. Further they are the foundation of soil food webs thereby underpinning the diversity of higher trophic levels. Interactions among soil microbes and plants often determine plant diversity	
Regulating	*Control of potential pests and pathogens*	Population regulation (soil biota) to control pests, pathogens and diseases
	Role of soil microbiota: Soil bacteria, archaea, and fungi support plant growth through increasing nutrients availability, and by outcompeting invading pathogens through inter- and intra-specific interactions (symbiosis, competition, host- prey association).	
	Recycling and remediation action	Disposal and decomposition of residues and pollutants
	Role of soil microbiota: Soils absorbs and retain solutes and pollutants, avoiding their release into water. Microbiota contribute to both the hydrophobicity and wettability of soils, impacting the ability of soil to filter contaminants	
	Water quality regulation	Filtration and buffering of water
	Role of soil microbiota: Soil macropores are formed by plant roots, earthworms and other soil biota, which may depend on soil microbes as food or for nutrients. Also, microbiota is involved in pollutants degradation	
	Water regulation, and flood and drought control	Regulation of hydrological flows buffering and moderation of hydrological cycle
	Role of soil microbiota: Soil pores through its capacity to retain and store quantities of water can mitigate and lessen the impacts of extreme climatic events. Soil microbiota are involved in soil pores characteristics definition as macropores formation and soil aggregate formation	
	Regulation of atmospheric GHG and climate regulation	Carbon sequestration and accumulation, regulation of the atmospheric chemical composition and climate processes
	Role of soil microbiota: Soil microbiota is involved in litter fragmentation and decomposition, physical and chemical stabilization of residue carbon. By mineralizing soil carbon and nutrients, microbes are major determinants of the carbon, storage capacity of soils. Denitrifying bacteria, fungi, and methane producing and consuming bacteria regulate N_2O and CH_4 emissions from soil. Methane production is done by methanogens, while methane oxidation by methanotrophs. Chemoautotrophic nitrification, heterotrophic nitrification, denitrification, and codenitrification is assured by nitrifying and denitrifying bacteria and fungi	
	Erosion control	Sediment retention
	Role of soil microbiota: Soil microbiota promote plant growth through nutrients cycling and transformation in available form for plants, as well through soil - root exchange enhancement, thus alleviating soil surface enhancement. Microbiota produce biological glues, and facilitate physical entanglement by roots and fungal hyphae	

Also, within the terrestrial ecosystems, soils may contain some of the last great “unknowns” of many of the biota. One of such unknowns refer at soil microbiota. At moment only one percent of microorganism are known from the soil. Moreover, there are several knowledge gaps related to their functions and response under challenges of global change pressures.

2. History and landmarks

BIODIVERSA laboratory was established in 2018 at Research Institute for Analytical Instrumentation (ICIA), subsidiary of INCDO INOE 2000 as a response of the identified global challenges – see Fig.2.

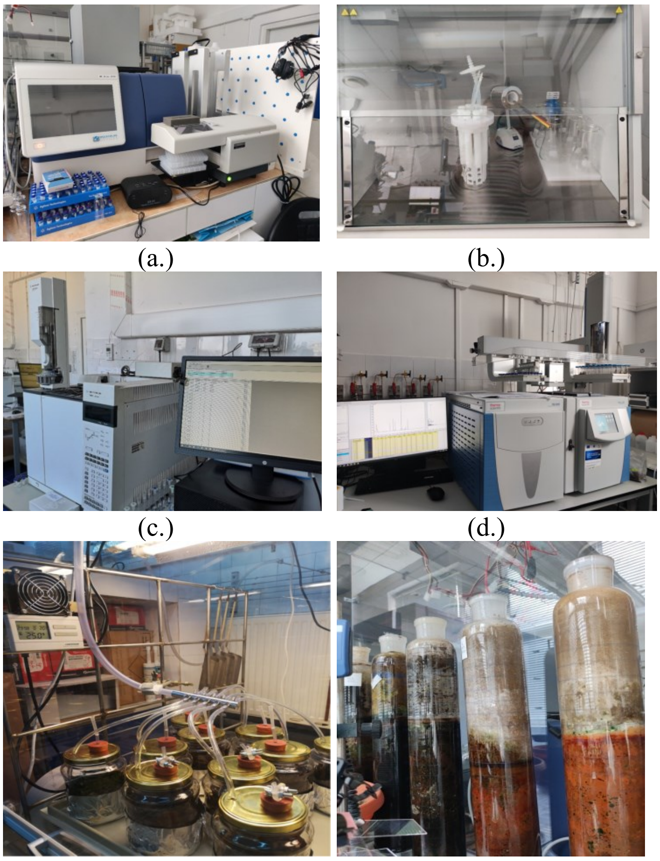


Fig. 2. Representative infrastructure of BIODIVERSA laboratory, a.) *microplate reader;* b.) *clean chamber;* c.) *gas chromatograph with flame ionization detector;* d.) *gas chromatograph with triple quadrupole mass spectrometer;* e.) *climate chamber with forest litter biome experiment*; f.) *microorganism colonization on artificial support*

Therefore, in the frame of Global Soil Biodiversity Initiative and of 2030 Agenda for Sustainable Development, the laboratory has as main goal to contribute at overcoming knowledge gaps related to soil biodiversity under pressures of global change those to ensure the protection of soil.

BIODIVERSA researches focus on soil microbiota phenotypic structure abundance assessment, direct observation and counting species, and functional assays of microbiota functional activities, especially for those that are involved in mediation of soil ecosystem services.

2.1. Microbiota quantitative assessment

Starting with these knowledge gaps, and because soil microbiota are key elements in mediation of numerous biogeochemical cycles and reactions in soil, through NUCLEU PN18-28 02 01 Project, 33N/16.03.2018 contract, an improved analytical approach was used to quantitatively assess the soil microbiota.

The analytical approach was built on lipidomic approach where phospholipids derived fatty acids (PLFA) were used for quantitative assessment of soil microbiota phenotypic structure and abundance; neutral lipids derived fatty acids were used for assessment of shifts in different phenotypic groups; while glycolipids derived fatty acids for assessment of development level of major bacterial and fungal groups. These were done with the reason to understand changes on soil microbiota (community structure, abundance, cell membranes fatty acids, etc.) due to pressures of global change drivers. Importance to fill these gaps of knowledge are given by that potential changes in soil microbiota could modify soil functioning and provision with ecosystem services. Further, using of these soil microbiome indicators could contribute in establishment of an early warning system of potential losses of these soil services and goods.

2.1.1. Lipids derived fatty acids GC analysis

Within microorganism cell membranes, lipids present a large structural diversity. Generally, when soil microbiota cell analysis is targeted analytical approaches for fatty acids derived from phospholipids, glycolipids or neutral lipids could be applied.

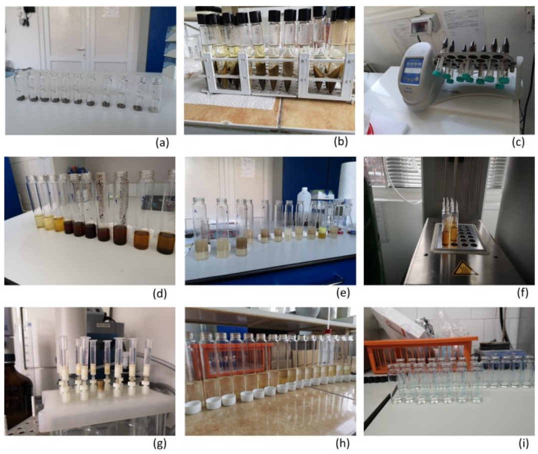


Fig.2. Sample preparation for lipid derived fatty acids extraction. (a) homogenized soil samples; (b) Blight and Dyer reagent addition; (c) sample – reagent homogenization; (d) lipid extract; I phased separation; (f) supernatant evaporation; (g) lipid fractionation; (h) lipid derived fatty acids conversion into fatty acid methyl esters; (i) finalized extract

Their gas chromatographic analysis (GC) involves multiple steps as: sample preparation; lipid extraction;

lipid fractionation; fatty acids derivatization; and, gas chromatographic separation and quantification followed by phenotypic identification of analyzed soil microbiota structure using MIDI Microbial Identification Software. In Fig. 2 are presented images from extraction process.

Analysis of fatty acid methyl esters were performed using an Agilent 7890A gas chromatograph with flame ionization detector GC – FID (Agilent Technologies, Santa Clara, CA). Polyethylene glycol stationary phase DB – WAX column (Agilent J&W) with 30 m x 0.25 mm I.D., 0.25 μm characteristics was used for fatty acid methyl esters separation. Chromatograms as signature of phospholipids derived fatty acids biomarkers of a soil samples are presented in Fig. 3.

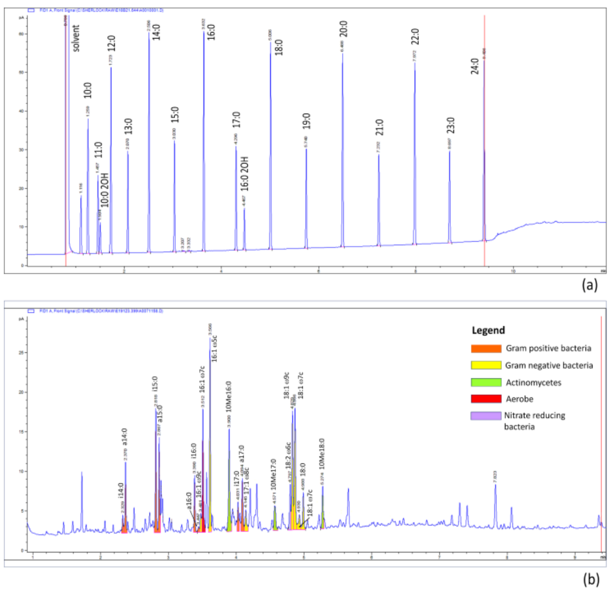


Fig.3. Chromatograms of phospholipids derived fatty acids obtained (a) after analysis of used signature phospholipids derived fatty acids biomarkers standard; and (b) a soil samples (agricultural land with winter wheat cultivars)

With this gas chromatographic method, the recovery of fatty acids methyl esters varied within 96 – 105 %.

2.1.2. Fatty acids binding assessment

Fatty acids binding assessment was based on an extended separation and analysis of derived fatty acids fraction. The drawbacks of simple silicic separation of phospholipid fractions by total lipids is given by the fact that although alkaline saponification preserve acid sensitive component as cyclopropane fatty acids, it not releases amide linked fatty acids as hydroxylated fatty acids. On the other hand, use of acid catalyzed hydrolysis which has the ability to release amide hydroxylated compounds it could cause in the same time the degradation of cyclopropane fatty acids. Therefore, the obtained phospholipids after lipids fractionation were continued for chemical separation thus to allow amide-linked components release (hydroxylated fatty acids) without the alteration of cyclopropane fatty acid's structure. This involved in further a double steps separation based on aminopropyl and benzosulphonic acid separation step, respectively, as presented in Fig. 4.

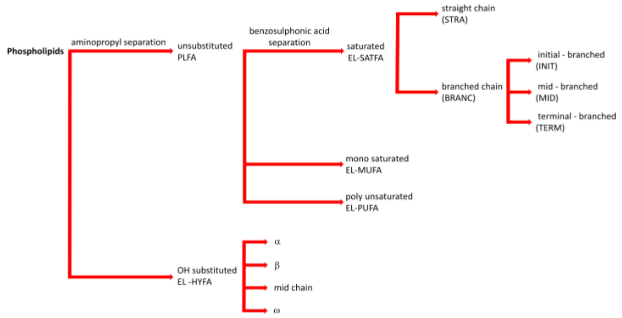


Fig.4. Chromatograms of phospholipids derived fatty acids obtained (a) after analysis of used signature phospholipids derived fatty acids biomarkers standard; and (b) a soil samples (agricultural land with winter wheat cultivars)

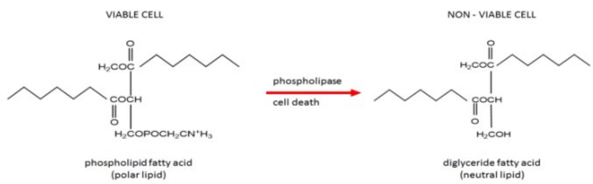
Gas chromatographic analysis was performed on the extracts obtained after aminopropyl - benzosulphonic acid double step separation, according with method described by Zelles, [6].

This allowed both the extraction of the total phospholipids derived fatty acids in a larger amount even if some fatty acids were presented in a lower amount, as well it allowed the preservation of OH substitutions in phospholipids derived fatty acids during esterification process. With this extraction procedure, after gas chromatographic analysis, it was established also the positions of unsaturation in monounsaturated fatty acids and of the multiple double bonds in polyunsaturated fatty acids.

Through separation of phospholipid derived ester linked saturated fatty acids by phospholipid derived ester linked monounsaturated fatty acids, cyclopropane fatty acids were easily analyzed through gas chromatography.

2.1.3. Soil microbiota growth status and non-vitality assessment

In nature, phospholipids are rapidly degraded to diglycerides after cell death or lysis. This is the reason why phospholipid derived fatty acids are considered as suitable biomarkers for quantifying vital soil microbiota structure and abundance from moment of sampling.



Reaction 1. Phospholipid derived fatty acid conversion to diglyceride fatty acid after cell death or lysis [7]

Besides that, PLFA approach give an insight on both changes in structure and abundance of microbiota, as well on physiological response of microbiota cells to shifts, as consequences of induced pressures by global change drivers. After cell non-viability, cellular phospholipase hydrolyzes the phospholipids from membranes, releasing their polar head group. The remained moiety from phospholipids, after enzymatic hydrolyzation are diglycerides which contains the same fatty acids as the phospholipid, see reaction of (see Reaction 1).

These are neutral lipids. Their analyses were done in order to could receive information about the life cycle of microbial biomass from soil. For microbiota structure life cycle assessments, the obtained neutral lipid fraction was subjected for aminopropyl separation in double step (see Fig. 5) which allowed also the separation of neutral lipids ester linked unsaturated fatty acids by those of neutral lipids ester linked OH substituted fatty acids. Therefore, lose in specific phenotypic structure was determined.

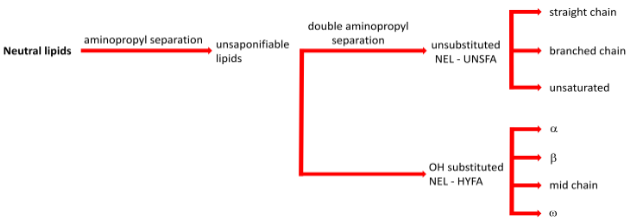


Fig.5. Neutral lipids multiple fractionations with aminopropyl

Glycolipids profile was also analyzed with aim to get information about the growth status of microbiota components.

Applying these optimized methods, obtained through NUCLEU PN18-28 02 01 Project, 33N/16.03.2018 contract, both the soil microbiota phenotypic structure abundance as well their growth status and non-vitality has become possible to be quantified by BIODIVERSA laboratory.

2.2. Soil microbiota functional and physiological profile assessment

Whereas effects of global change drivers on soil physicochemical properties are observed in time, soil microbiota respond to any environmental changes in a much shorter period. Phenotypic measurement of soil community structure and abundance offers numerical information about the dominant members of soil microbiodiversity. Thus, functional assessment of soil microbiota community under challenges of global change driver are required to could better understand their functioning under external pressures, and to predict soil functions and ecosystem services provision in that they are involved.

To achieve these objectives, BIODIVERSA laboratory through NUCLEU PN 19-18.01.01 Project, 18N/08.02.2019 contract, continued to extend its capability to assess soil microbiota functioning and physiological profile.

These purposes were acquired based on: average metabolic response and community metabolic diversity analysis through sole carbon (C), nitrogen (N) and phosphorous (P) source consumption (CLPP, community level physiological profiling); and on basal (BR) and substrate induced respiration (SIR) rate analysis.

2.2.1. Soil microbial community metabolic diversity assessment

In that project, the potential changes in soil microbiota community structure and their functional diversity were identified through microbiota catabolic fingerprinting assessment which was estimated based on C, C with N, and C with P consumption from sole nutrient sources.

Previously, it was reported by Ge et al., [8] and Zabaloy et al., [9] that identification of changes in nutrient utilization pattern by soil microbiota could indicate also differences in soil microbiota community composition as well. According with that, different nutrient sources consumption rate by heterotrophic microorganisms were analyzed using either commercially available well plates or in laboratory prepared well plates.

Totally 31 nutrient sources were tested of that 19 are sole C source, 10 are C and N source, and 2 are C and P source. The chemicals selected as nutrient source were carbohydrates, carboxylic acids, amino acids, amines, polymers and phenolic compounds. These sources correspond with those that are prevalent in nature under normal conditions. List of tested nutrient sources is presented in Fig. 6.

Category	Carbon substrate	Nutrient		
		Carbon	Nitrogen	Phosphor
Carbohydrates	d - cellobiose	■		
	α - d - lactose	■		
	β - methyl - d - glucoside	■		
	d - xylose	■		
	i - erythriol	■		
	d - manitol	■		
	n - acetyl - D - glucosamine	■	■	
	glucose - 1 - phosphate	■		■
	d, l - α - glycerol phosphate	■		■
	d - galactonic acid γ - lactone	■		
Carboxylic acids	pyruvic acid methyl ester	■		
	d - glucosaminic acid	■	■	
	d - galacturonic acid	■		
	γ - hydroxybutyric acid	■		
	icatonic acid	■		
	α - ketobutyric acid	■		
	d - malic acid	■		
Amino acids	l - arginine	■	■	
	l - asparagine	■	■	
	l - phenylalanine	■	■	
	l - serine	■	■	
	l - threonine	■	■	
	glycyl - l - glutamic acid	■	■	
Amines	phenylethylamine	■	■	
	putrescine	■	■	
Phenolic compounds	2 - hydroxy benzoic acid	■		
	4 - hydroxy benzoic acid	■		
Polymers	tween 40	■		
	tween 80	■		
	α - cyclodextrin	■		
	glycogen	■		

Fig.6. List of used nutrients sources during performed assessments and experiments

In order to could assess soil microbiota metabolic diversity, isolation of microbial cells from soil was performed. From homogenized and sieved soil samples, 1 g of soil was used for bacterial cells isolation. Solutions efficiency was tested based on inoculum grown and abundancy principles – see Fig. 7.

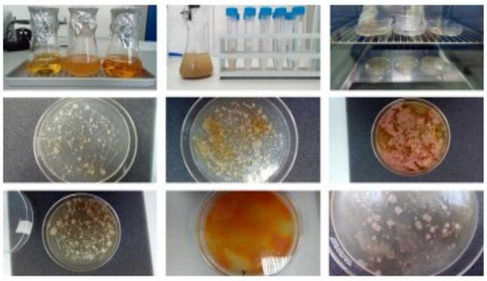
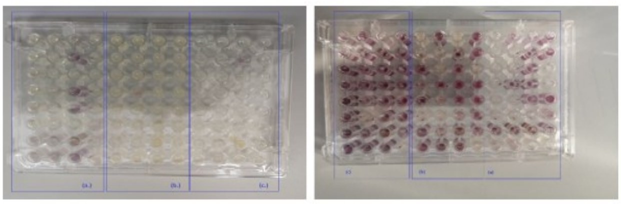
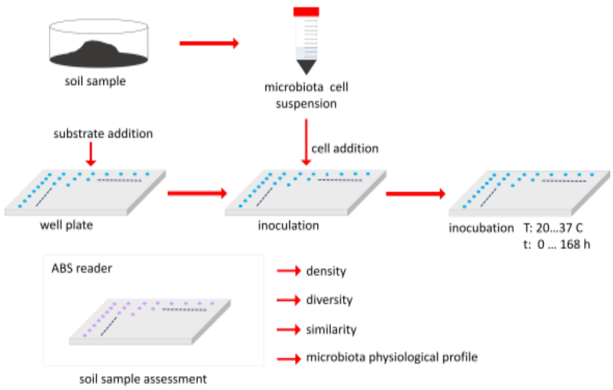


Fig.7. Cell isolation selection based on petri dish test

The optimal microbial cells suspension solution was transferred into microplate wells which contained sole nutrient sources. These sources, though an optimal incubation condition (time, temperature) allowed microbial colonies development (see Fig.8.).



(a.)



(b.)

Fig.8. Microbiota metabolic diversity assessment. a.) Microbiota development after 24h (left) and 7 days (right) of incubation when the three cell extracting solutions were tested; b.) Sample preparation for soil microbial community metabolic diversity assessment

Microbial community response at nutrients source - community - level carbon utilization pattern (often named as catabolic fingerprinting) was determined based on the optical densities (OD) of bacterial suspensions using the average well color development principles (AWCD). With this method, BIODIVERSA laboratory gained the capacity to determine: microbial growth rate (see Fig.9.) and functional diversity indexes as catabolic richness (S), catabolic diversity index (H), Shannon-Evenness index (E), Simpson index and Simpson evenness (E_D).

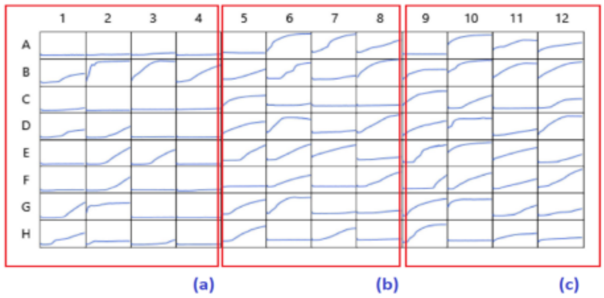


Fig.9. Microbiota population growth S - curve. Microorganisms cell were extracted with (a) physiological water; (b) phosphate buffer; (c) low-enriched phosphate buffer;

2.2.2. Soil microbiota respiration assessment

Anthropogenic or climate change related drivers could seriously hamper the ability of soil microbiota to perform functions in soil. Through NUCLEU project, soil basal respiration allowed the assessment of the continuous rate of heterotrophic microorganism respiration in soils. Generally, this originates from soil organic matter mineralization. Therefore, soil heterotrophic microorganism biomass basal respiration is considered as a first view indicator of soil quality and is often attributed as indicator to soil fertility also [10].

Substrate induced respiration is considered a common method used for soil heterotrophic microbiota physiology assessment, specifically the soil active heterotrophic microorganism growth rate. Briefly it triggers soil heterotrophic microorganism metabolic activity when are exposed at excess of readily available nutrient sources (see Fig. 10).

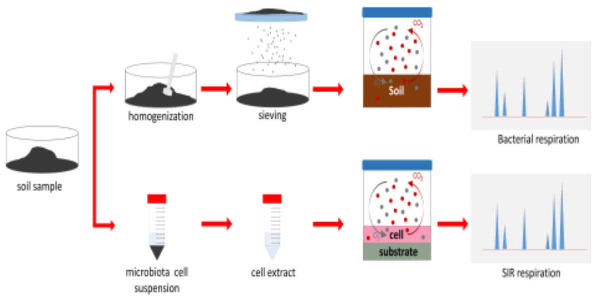


Fig.10. Soil respiration assessment schematic diagram, include basal soil respiration and substrate induced respiration

Therefore, affinity of soil heterotrophic microorganisms at specific nutritive substrate was established. Substances as d - glucose, d - galactose, l - malic acid, citric acid, α - ketoglutaric acid and γ - aminobutyric acid were used as grown and development facilitating substrates. When selective inhibitors were used, as nystatin or streptomycin for fungi or bacteria inhibition, respectively, contribution of major phenotypic groups at total respiratory response was established. Influence of above - mentioned substrate concentration on bacterial or fungal groups of soil was also monitored.

Both respiration type assessment was performed applying headspace technique to a closed chambers where headspace gases were sampled each day twice with a gas tight syringe through chamber septum and analyzed with thermal conductivity detector (TCD) of a 7890 Agilent gas chromatograph (GC - FID - TCD - TCD 7890, Agilent Technologies). In case of this gas chromatographic method, the limit of detection for oxygen and carbon dioxide was established at 0.0002 % mol.

3. Current developments and collaborations

With described methods for soil microbiota, as they are considered an essential element of soil ecosystem, BIODIVERSA laboratory performed complex assessment of soil microbiota abundance from different biomes. Studied biomes are presented in Fig.11.

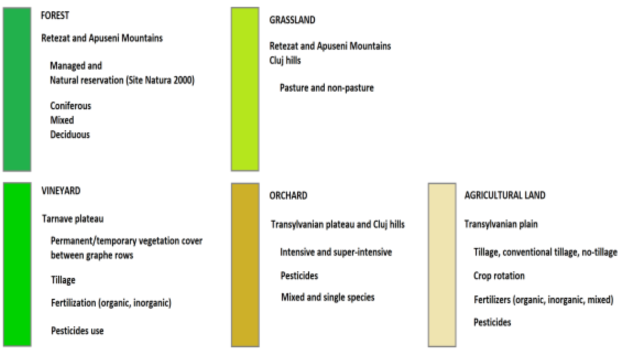


Fig.11. Biomes selection according with land use gradient

Variations both in structure as well abundance of microbiota phenotypic structure were observed for studied biomes.

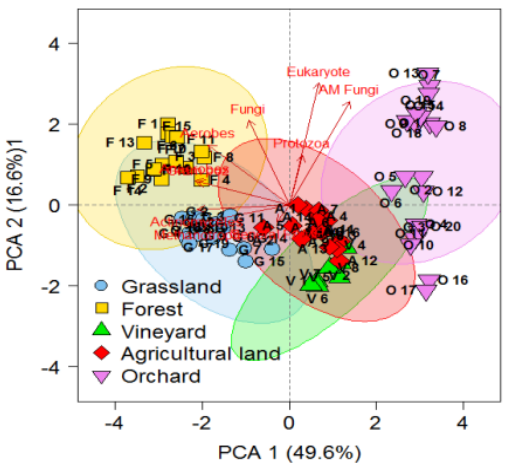


Fig.12. Principal component analysis of soil microbiota community abundance related with different land use

Principal component analysis (Fig.12.) explained the total variance of 66.2 % ($p = 0.001$) between microbiota abundance of different biomes, of that PC1 explain 49.9 % and PC2 16.6 %. The differences were relevant especially in case of bacteria where large squared cosine was obtained for samples collected from forest (0.909) followed by those collected from orchard (0.855), agricultural (0.731), grassland (0.728) and vineyard (0.716) lands, respectively.

At microbiota community structure level, the average value of total bacteria followed the following pattern within biomes: forest (342.1 nmol·g^{-1}dw) > grassland (240.2 nmol·g^{-1}dw) > orchard (141.1 nmol·g^{-1}dw) > vineyard (137.8 nmol·g^{-1}dw) > agricultural land (106.3 nmol·g^{-1}dw). In the five studied biomes, the average value of fungal abundance, expressed as sum of arbuscular mycorrhizal fungi, saprotrophic fungi, ectomycorrhizal fungi and other general fungi, vary between 3.2 and 6.3 nmol·g^{-1}dw. Higher values were detected in soil samples collected from forest and orchard – see Fig.13.

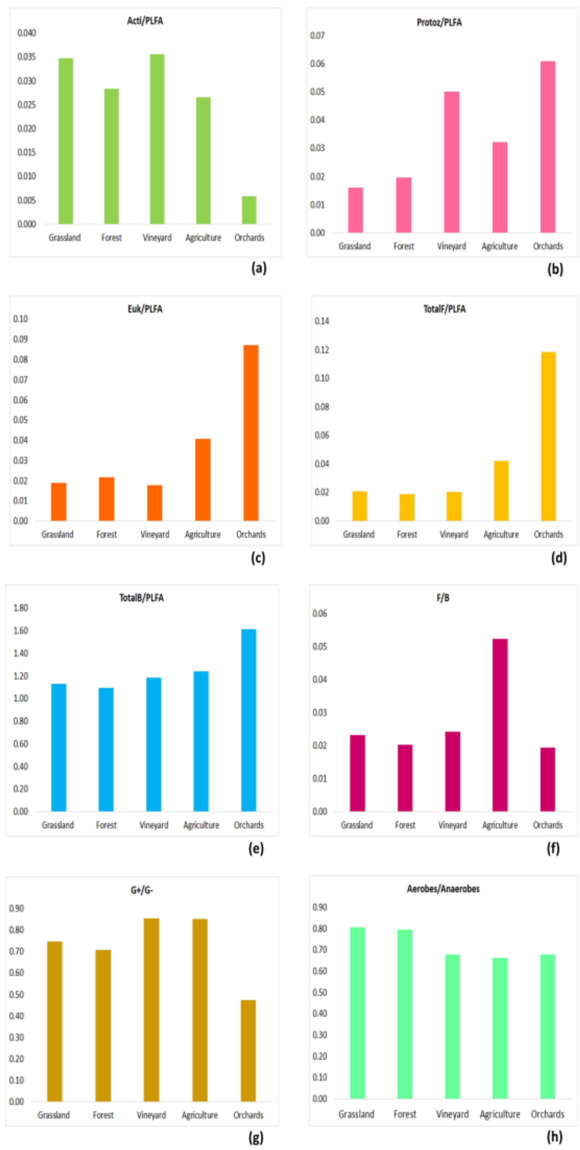


Fig.13. PLFA of studied biomes

For proper interpretation of obtained data about soil properties different geostatistical models are applied by BIODIVERSA team.

These models quantified soil property parameters spatial distribution and variability in accordance with spatial scale of the monitored area, and with distance between sampling points. Also, modeling semi variograms of spatial pattern are applied.

Generally, the tested geostatistical models are kriging interpolation, inverse distance to a power, modified Shepard's method, minimum curvature method, and radial basis function. Therefore, spatial variability of the measured variations both between soil microbiota abundance as well community structure pattern within studied biomes sampling points is performed. In Fig.14 – 16 are presented the case studies of a forest soil from Retezat Mountains, Romania.

Transforming all experimental data regarding components of microbiota structure, the summary statistics parameters related to interpolation performance are obtained after cross validation of studied interpolating tools. Commonly, these refer at mean error (ME), root mean squared error (RMSE), root mean squared prediction error (RMSP), and mean standardized prediction error (MSPE).

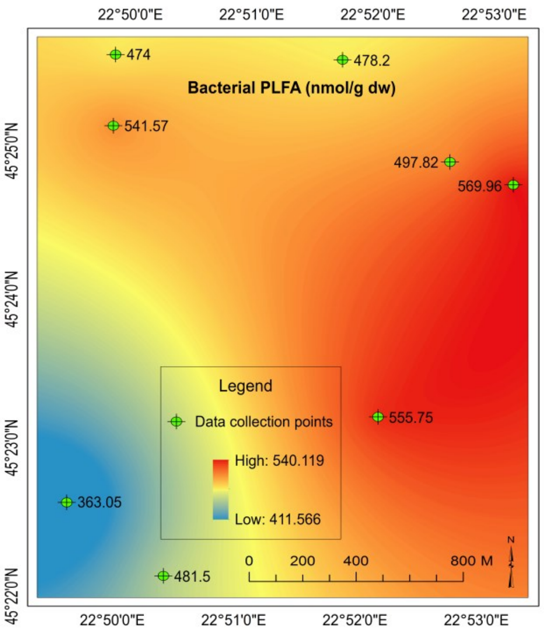


Fig.14. Geospatial distribution of Retezat Mountains forest soils bacterial PLFA (samples collected in May, 2018)

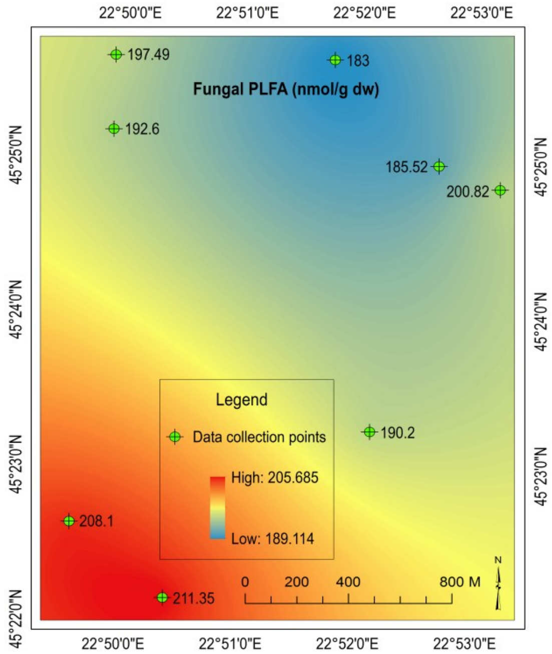


Fig.15. Geospatial distribution of Retezat Mountains forest soils fungal PLFA (samples collected in May, 2018)

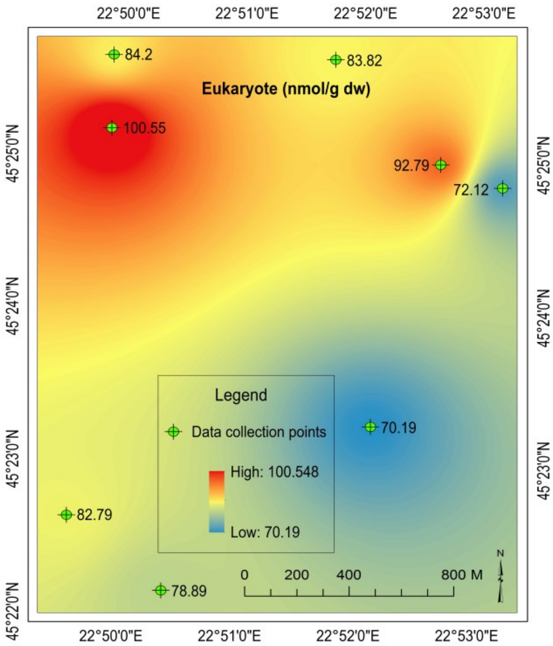


Fig.16. Geospatial distribution of Retezat Mountains forest soils eukaryote PLFA (samples collected in May, 2018)

BIODIVERSA laboratory established collaboration with foreign research centers involved in soil biodiversity study through two bilateral cooperation projects and two collaborative projects destinated for young researchers. These are Sun-yat Sen University, Guangzhou, China (BM54, 2016), Capital Normal University, Beijing, China (26BM/2018), Nagoya University, Nagoya, Japan (PN III-P1-1.1.MC-2018-2826, Contract no. 741/22.10.2018), Polish Academy of Sciences, Institute for Agricultural and Forest Environment, Poznan, Poland (PN III-P1-1.1.MC-2017-2334, Contract no. 651/18.12.2017) – see Fig.16 and Fig.17.

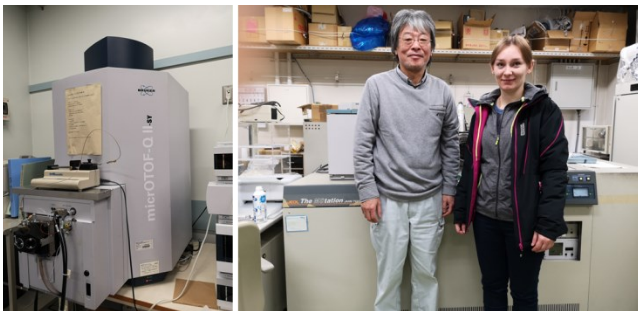


Fig.16. BIODIVERSA laboratory member at Nagoya University, Nagoya, Japan

Fig.17. BIODIVERSA laboratory members at Capital Normal University, Beijing, China

4. Recent results and transfers of results

Performed research studies through BIODIVERSA laboratory materialize through numerous publications (articles, book chapters) and patent request.

A representative article published by BIODIVERSA team describes soil rhizobiota changes as abundance, structure and function under a common global change drivers' pressure [11].

In that paper [11], the effect of common non-steroidal anti-inflammatory drugs on *Lycopersicon esculentum* rhizosphere microbiota is described. Team members performed experiments using artificially contaminated soil with ibuprofen (0.5 $mg \cdot kg^{-1}$), ketoprofen (0.2 $mg \cdot kg^{-1}$) and diclofenac (0.7 $mg \cdot kg^{-1}$) [12].

Obtained results evidenced that the rhizosphere microbiota abundance decreased especially under exposure to diclofenac (187–201 $nmol \cdot g^{-1}$ dry weight soil) and ibuprofen (166–183 $nmol \cdot g^{-1}$ dry weight soil) if compared with control (185–240 $nmol \cdot g^{-1}$ dry weight soil), while the fungal/bacteria ratio changed significantly with exposure to diclofenac (<27%) and ketoprofen (<18%) [13]. Compared with control samples, the average amount of the ratio of Gram-negative/Gram-positive bacteria was higher in rhizosphere soil contaminated with ibuprofen (>25%) and lower in the case of diclofenac (<46%) contamination. Carbon source consumption increased with the time of assay in case of the control samples (23%) and those contaminated with diclofenac (8%) [14].

This suggests that rhizosphere microbiota under contamination with diclofenac consume a higher amount of carbon, but they do not consume a larger variety of its sources [15]. In the case of contamination with ibuprofen and ketoprofen, the consumption of carbon source presents a decreasing tendency after day 30 of the assay. Rhizosphere microbiota emitting volatile organic compounds were also monitored. Volatile compounds belonging to alcohol, aromatic compounds, ketone, terpene, organic acids, aldehyde, sulphur compounds, esters, alkane, nitrogen compounds, alkene and furans were detected in rhizosphere soil samples [11]. Among these, terpene, ketone, alcohol, aromatic compounds, organic acids and alkane were the most abundant compound classes (>75%), but their percentage changed with exposure to diclofenac, ketoprofen and ibuprofen [16].

Such changes in abundance, structure and the metabolic activity of *Lycopersicon esculentum* rhizosphere microbiota under exposure to common non-steroidal anti-inflammatory drugs suggest that there is a probability to also change the ecosystem services provided by rhizosphere microbiota [17].

Further, recent findings regarding soil microbiota emitted volatiles changes in the context of global change pressures were published in "*Gas Chromatographic: Mass Spectrometric Mining the Volatilomes Associated to Rhizobiota Exposed to Commonly Used Pharmaceuticals*" [18].

It was acknowledged that rhizobiota are involved in plant protection through plant development facilitation and plant defense against stress factors [15, 19-22]. Therefore, pressures of global change either as abiotic or biotic stress factor could modify rhizobiota abundance, community structure, or functioning [23]. Such change could result in anomalies of plant development [18].

Human and veterinary medicines are widely used pharmaceuticals. Their active ingredients are not fully adsorbed and metabolized by living organisms and are therefore excreted unmodified [24]. As current technologies of wastewater treatment plants are not designed to remove these contaminants, pharmaceuticals may be discharged into the environment and reach the soil in multiple ways [24, 25]. At present, there are no standard procedures or methodologies that could be easily applied and cover pharmaceuticals impact on soil microbiota. Besides that, available molecular and genetic approach through which soil microdiversity abundance, structure, and functions are evaluated involves high and expensive technology, which is not easily available to laboratories widespread [18].

In this chapter, the proposal of an effortless way to address this issue by using gas chromatography–mass spectrometry (GC–MS) approaches was presented. With this GC–MS analytical approach the main emitted volatile organic compounds measured as emitted by rhizosphere of the three aromatic plants were terpenes, alcohols, aromatic compounds, ketones, and organic acids [18, 21].

Patents requested by BIODIVERSA team refer at microbiota phenotypic structure and abundance assessment, as well to their functionality assessment when are exposed to pressures of global change drivers.

5. New directions of research

Considering the vitality for a safe and healthy microbiota, the central aims of BIODIVERSA laboratory remain to find tools for protecting the soil biological key drivers and the functioning of soil ecosystems.

Protecting soil key drivers and the ecosystem services they support requires insight into soil biodiversity, its role in the functioning of ecosystems, and the way it responds to stress. Also required are tools and methodologies for properly assessing biodiversity. Therefore, BIODIVERSA laboratory will continue to provide information on soil biodiversity and soil functions (both targets of protection goal options) as well as on the effects of various global change related stressors (including their respective regulations) on soil biodiversity. The ambitious aims of the BIODIVERSA team, are to:

- Determine and harmonize tools and approaches for identification and recovery of declined microbiodiversity of a threatened ecosystem
- Fulfill existing knowledge gaps related to microbiota response at challenges of global change drivers and pressures
- Develop, and optimize novel management approaches and strategies using precision sampling and analysis as well modelling tools, which are capable of ensuring: soil ecosystem services supplying; soil life and functionality balance; and responsible exploitation strategies of microbiota ability to mediate specific ecosystem services

6. Perspectives

Is well established that biodiversity is essential for numerous ecosystem services. Biodiversity offers sustainability for humanity and other living organisms, as they obtain goods and services from the functioning of ecosystems.

Assuming that all changes in biodiversity can influence the supply of ecosystem services, the preservation of biodiversity through fulfilling current knowledge gaps and improving current attitude on how we handle and manage the biodiversity is recognized as crucial for further development of humanity.

Through comprehensive identification of biodiversity decline or threaten under pressures of global change drivers, as well through identification of potential solutions which will continue to ensure soil ecosystem services supplying and soil life and functionality balance will increase the access at biodiversity resources (either direct: species, genetic resources; or indirect ones: provided resources and functions).

Moreover, such knowledge will contribute at improvement of exploitation of biodiversity components and functions in the pharmaceutical industry through new biotechnological solutions, agricultural and industrial procedures through new biotechnologies, and environmental remediation through optimized bioremediation solutions.

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Environment & Health- Environment quality, risk assessment and remediation

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The Environment and Health Laboratory develop research focused on the assessment of the waters, soil and air quality, development of new, sensitive methods for identification of legacy and emerging pollutants, identification of pollution sources, as well as on the identification of health risk posed by these pollutants. New research direction in the field of environmental biomonitoring and pollution remediation will be developed in the near future.

Keywords: Water quality, Soil pollution, Pollution indices, Health risk assessment

1. Introduction

Environmental pollution is the global challenge of the 21st century. Urbanization and industrialization pose high pressure on the surrounding environment, often altering its quality. Thus, the assessment of the presence and concentration of pollutants in different compartments of the environment is of great importance. Living in a polluted environment as well as using polluted waters and soils for domestic purposes and food production may led to important risks for the human health.

This chapter presents the main research activities carried out by the Environment and Health Laboratory in the frame of various research projects, as well as the future perspectives and research topics.

2. History

Research Institute for Analytical Instrumentation (ICIA) was founded in 1986, having as primary objective the design and development of analytical laboratory equipment and the development of analytical methods for a wide range of samples. Since 1996 ICIA has become part of the National Institute for Optoelectronics INOE 2000. The Environment and Health Laboratory (LFM) was founded in 2000 to conduct research and development activities related to environment and health. The research is focused on method development for assessment and monitoring of the environment, design of methods and technologies for pollution prevention and environment decontamination, preservation and sustainable management of natural resources. Beside the research activities, the LFM is actively involved in the dissemination of the research results to the society, as well as in raising the awareness on the environmental pollution, and promotion of sustainable environment.

In 2004 the acquisition of key equipment, started with an inductively coupled plasma mass spectrometer (ICP-MS), for determination of the trace metals from environmental matrices. The ICP-MS along the existing inductively coupled plasma optical emission spectrometer (ICP-OES) and flame atomic absorption spectrometer (FAAS) allowed the determination of metals in a wide range of concentrations from different matrices. In the following years, the acquisition of gas chromatographs, liquid chromatographs, ion chromatograph, inductively coupled plasma optical emission spectrometer, inductively coupled plasma mass spectrometer and atomic absorption spectrometer with flame and graphite furnace atomization sources, as well as elemental analyser, carbon analyser, mercury analyser, UV-VIS spectrophotometer, Fourier-transform infrared spectrometer, X-ray diffractometer allowed the determination of a wide range of parameters from environmental samples.

3. Current developments and collaborations

The Environment and Health Laboratory participated in several research projects that allowed tackling a broad range of topics on environmental pollution.

The project "*Environmental quality changes in the Aries River basin under the influence of anthropic pressures*" (2004-2006), carried out in collaboration with the Institute of Geography of the Romanian Academy (IGAR) and Babes-Bolyai University, allowed the identification the several pollution sources present in the Aries River basin, and the changes in the water and sediment quality driven by the pressures posed by these pollution sources.

The project: "*An integrated assessment of environmental impacts of mining activities in two selected catchments (upper Crisul Alb and Certej) in the Apuseni Mountains, Romania, and transboundary river pollution*" (2005-2007), carried out in partnership with the Swiss Federal Institute of Aquatic Sciences and Technology, (EAWAG) and the Institute of Geography of the Romanian Academy (IGAR), allowed to obtain comprehensive data on the impact of mining activities on river catchments.

The project "*Ecological, complex assessment method for the monitoring of Somes River basin*" (2005-2008), carried out in cooperation with the Babes-Bolyai University and Institute of Geography of the Romanian

Academy (IGAR), proposed an integrated biomonitoring method applicable to river basins.

The project "*Cancer risk assessment for heavy metals chronically exposed population"* (2005-2008), carried out in cooperation with Iuliu Haţieganu University of Medicine and Pharmacy, Babes-Bolyai University, Oncology Institute Prof. Dr. Ion Chiricuţă Cluj-Napoca and Institute of Public Health Cluj-Napoca, produced new data on the cancer risk assessment associated with chronic exposure to low dose of heavy metals, single or in mixtures.

The project "*Modeling of the heavy metals impact on aquifers by complex study of groundwater fauna and monitoring in GRID, MODEL-ACVASUB system*." (2007-2010) carried out in cooperation with Romanian Academy, Cluj-Napoca branch, Emil Racovita Institute of Speleology and Babes-Bolyai University allowed the integration in a unitary evaluation system of multi-proxy, geological, hydrological, water chemistry (heavy metals, organic pollutants and micropollutants) and faunistic studies.

The project "*Bioremediation of soils contaminated with products from the petroleum industry for their restoration in the socio-economic circuit*" (2007-2010), carried out in cooperation with the University of Agricultural Sciences and Veterinary Medicine of Cluj-Napoca, CRAIM and Norwest Ploiesti, developed a lab-scale remediation method based on the inoculation of soils with a microbial consortium adapted to high levels of pollutants.

The project "*Comparison of metal pollution patterns in soils from industrial areas of France and Romania*" (2015-2016) carried out in collaboration with Geosciences Environment Toulouse, France studied the multielemental and isotopic fingerprint of several pollution sources.

The project "*Innovative technology for ex-situ bioremediation of polluted soils with hydrocarbons*" (2014-2016), carried out in cooperation with the Technical University of Cluj-Napoca, National Research and Development Institute for Soil Science, Agrochemistry and Environment – ICPA Bucharest, University of Agricultural Sciences and Veterinary Medicine of Cluj-Napoca and MINESA Cluj-Napoca, developed a pilot-scale remediation technology based on microbial removal of petroleum hydrocarbons by "biopile" technique.

The project *"Assessment of the impact of anthropogenic activities (mine, traffic, urban, land use changes) on river contamination in France and Romania*" (2017-2018) carried out in cooperation with University Paris Sud studied the surface water and sediments in rivers under the influence of anthropogenic activities and identified the impact of different types of anthropogenic activities on river quality.

The project "*Food chains in the dark: diversity and evolutionary processes in caves*" (2018-2022), carried out in cooperation with Romanian Institute of Science and Technology, Babes-Bolyai University and Iuliu Hatieganu University of Medicine and Pharmacy, studied the diversity patterns of the cave microbiome on different substrates and in different microclimatic conditions and identified the possible commonalities with surface microbiomes. Also, the gut microbiome diversity in oligotrophic and chemoautotrophic cave representatives at different food levels, the parallelisms and convergences between cave invertebrates and their gut symbionts as an adaptation to low food, and new cave bacteria with natural antibiotic resistance were studied.

The project "*Monitoring and risk assessment for groundwater sources in rural communities of Romania*" (2019-2023), carried out in cooperation with the Romanian Academy - Emil Racovita Institute of Speleology in Cluj-Napoca, University of Bergen and Babes Bolyai University, will develop the best method for groundwater microbiological monitoring to ensure water quality for human use and to better protect against possible outbreaks of pathogen bacteria in the drinking water.

4. Recent results and transfers of results

4.1. Water quality

Access to good quality water is crucial for human health as well as for economic and social development. Water quality is one of the most important elements in water resource management and is highly influenced by natural and anthropogenic factors. It can be assessed based on the physical, chemical and biological parameters [1]. Generally, groundwater is less exposed to chemical and microbial contamination and more stable than surface waters, making it more suitable for drinking. Nevertheless, groundwater is highly vulnerable to both depletion and degradation, and its composition is influenced by the rock type that hosts the water, the residence time, the original composition of the groundwater, the water flow path as well as by the type of land use and land use practices in its vicinity [2].

The quality of surface water is influenced by both natural and anthropogenic processes and reflects the influence of basin lithology, climatic conditions, and pollution sources. Anthropogenic discharges pose constant pressure to rivers, whereas the natural processes can vary with the season and climate. Metal pollution endangers the environment quality due to its high persistence and toxicity.

In the Environment and Health Laboratory, the water quality in rivers, groundwaters and springs was assessed, and the anthropogenic sources of pollution were studied.

The main pollution sources in Aries River are the dissolution of river bed minerals, acid mine drainage and domestic activities. The river water is mostly polluted with Cu, Mn and Fe [3].

The quality and typology of groundwater in Romania using various physical and chemical parameters were also studied. With the exception of nitrates in some springs from Dobrogea region, the physico-chemical parameters met the quality guidelines for drinking waters set by the international drinking guidelines and directives [4-6].

4.2. Soil pollution

Urbanization and industrial development led to an increase in soil pollution. Metals are a major environmental problem due to their high toxicity, low biodegradability, and cumulative nature and they represent a serious threat to human health by entering into the food chain or by leaching into groundwater [7]. Metals in soil are associated with different components that define their mobility and bioavailability. To assess the impact of contaminated soils on the environment, it is not sufficient to know the total concentration of a particular metal without considering its speciation [7, 8]. Generally, the determination of bioavailable metal fractions is based on single or sequential extraction procedures. For plants, soil is the main source of metals that can act as nutrients or contaminants, in function of the metal species and concentrations.

Mining is one of the drivers of economic growth, but it also has a significant negative impact on the environment. As most mining activities are presently closed or in conservation, tailings disposal and storage are most important pollution sources [9].

The impact of legacy pollution on the total and bioavailable metal content in soil in Baia Mare area was assessed by Levei et al. [7], while the relationship between the total and mobile metal fractions in polluted and unpolluted soils was studied by Senila et al. [8]. The contamination and ecological risk caused by As, Cd, Cr, Cu, Pb and Zn in urban soils situated near a metallurgical complex, based on several indices was assessed by Hoaghia et al. [10].

4.3. Air pollution with PM10

Air pollution is another critical environmental concern all over the world. Particulate matter (PM) is a complex mixture of solid particles and liquid droplets suspended in the atmosphere. These particles may have different concentration, size, shape, chemical composition, surface area, acidity, solubility, reactivity, and origin [11].

The major sources of air pollution with particulate matter with a diameter below 10 µm (PM10), are road transport, domestic heating, energy production, agriculture, industry, and waste burning [12].

Exposure to high PM concentrations pose an important health risk for humans, as inhaled particulates may penetrate the lungs causing severe lung pathologies [11].

The daily PM10 concentrations measured in Cluj-Napoca for the period 2009–2019 ranged between 20-30 $\mu g/m^3$. They were below the annual limit value of 40 $\mu g/m^3$ set by EU legislation, but above the annual air quality guideline of 20 $\mu g/m^3$ set by WHO [12, 13]. In the winter, the monthly average PM10 concentrations were higher than in the rest of the year. The decrease of the difference between the average and median annual PM10 concentration from 2009 to 2019 indicated the reduction of the days with high PM10.

The air quality index showed good to moderate quality of the air during the whole decade. However, the daily PM10 concentration showed that in each year, there were a certain number of days, with unhealth air quality, especially for sensitive population groups [12, 14].

4.4. Metal bioavailability

Metals are among the most ubiquitous environmental pollutants since they are widely distributed and often in concentrations above the natural background [15]. Moreover, metals persist in the environment for a long time and can be transferred into the food chain; thus, the assessment of their content in soil and the estimation of their transfer rates to vegetation are of great interest. The soil quality guidelines are usually based on total metal content, although it is generally accepted that total metal content includes both bioavailable and non-bioavailable fractions. The estimation of bioavailable metal fractions is typically based on single or sequential extraction procedures, but these provide only a classification of metal fractions in the soil compartments. Additionally, in the pre-treatment stage of these procedures, the soil's physical-chemical equilibrium may be affected.

Diffusive gradients in thin films technique (DGT) is based on relatively simple device that accumulates dissolved substances in a controlled way (DGT Research) [16]. It can be used for measuring:

- trace metals, phosphate, sulphide, and radionuclides
- average concentrations (hours to weeks) in waters
- fluxes and concentrations in soils and sediments
- effective solution concentrations (bioavailable fraction).

DGT device consists of a plastic base (2.5 cm diameter) loaded with a resin gel, a diffusive gel, and a filter. DGT in water measures species that are in labile equilibrium and can bind to the binding agent. When deployed in soils, the concentrations of metal ions in the soil adjacent to the device are lowered. This can induce a supply of metal ions from the solid phase to the solution in the soil layers near the device. The total metal accumulated during the deployment is measured. To date, a universally accepted procedure for metals bioavailability prediction does not exist, and the development and validation of such methods that allow the estimation of the risks posed by toxic metals in soils is necessary.

DGT technique is a good surrogate for plant uptake mechanism because both plants and DGT perturb the soil system on the same scale. While DGT responds only to the chemical and physical processes in the soil, thus these processes are of primary importance in controlling plant uptake [17-19].

The contributions of our laboratory to this field of research were achieved in several research projects focused on developing experimental designs based on unconventional techniques (DGT combined with spectrometric methods) for studying the changes in metals mobility and speciation under the influences of the plant-soil system. Significant correlations between concentrations measured by DGT and plant uptake were found. Thus, the DGT technique was used for the assessment of metals (Cu, Zn, and Cd) bioavailability to vegetables grown in garden soils from rural areas affected by mining activities in NW Romania. Multivariate statistical approaches were used to reveal the relationships between soil properties, metal concentrations in soil, and their bioaccumulation in vegetables [20]. The results obtained showed that the concentration of metals measured by DGT was the most effective in predicting their accumulation in edible plants. Thus, is a good option for the general evaluation of the risks associated with toxic metals in soil. In another study DGT was used to simulate the Pb bioavailability in contaminated and uncontaminated soils [21]. That study demonstrates the utility of the DGT technique for the assessment of Pb bioavailability because it provided a better evaluation than the results obtained by chemical extractions when these were correlated with metals accumulated in vegetables.

4.5. Pollution indices

The water and soil quality can both be affected by human activities, such as effluents from local sewage treatment plants, untreated wastewater, industrial or mining activities, leachate from agricultural activities, atmospheric deposition, and natural processes [22]. For the assessment of contaminants enrichment many computational tools have been applied [23]. Pollution indices are useful tools for assessing the natural enrichment of water and soils with various contaminants [24].

4.5.1. Water

In recent years, the quality of rivers, lakes, and groundwater had progressively decline, becoming a global issue of concern [25]. The water bodies pollution is a threat to human health. Therefore, many indices for assessing water quality (water quality index- WQI) and heavy metal pollution (heavy metal pollution index – HPI; heavy metal evaluation index - HEI) based on water quality parameters have been designed [26].

The most useful tool in assessing and classifying water quality according to possible usages is represented by Water Quality Index (WQI). WQI is based on various physico-chemical parameters and gives a measure of the water quality [27]. Using WQI, Senila et al. evaluated the quality of a waste water before and after purification process with natural zeolite, in order to confirm and quantify the removal efficiency for 13 physico-chemical parameters [28].

The Heavy Metal Pollution Index (HPI) is a useful tool, which gives the comprehensive influence of several heavy metals on the overall quality of water. The Heavy Metal Evaluation Index (HEI) indicates the overall quality of water sources with respect to the heavy metals content [29].

The surface water from Aries River basin's quality status and vulnerability was assessed through various heavy metal pollution indexes. Due to high concentrations of As, Fe, Mn, and Pb, HPI indicated a relatively high degree of heavy metals pollution in some samples. In contrast, HEI indicated low to high levels of heavy metal pollution of the studied water samples [30] (Fig. 1).

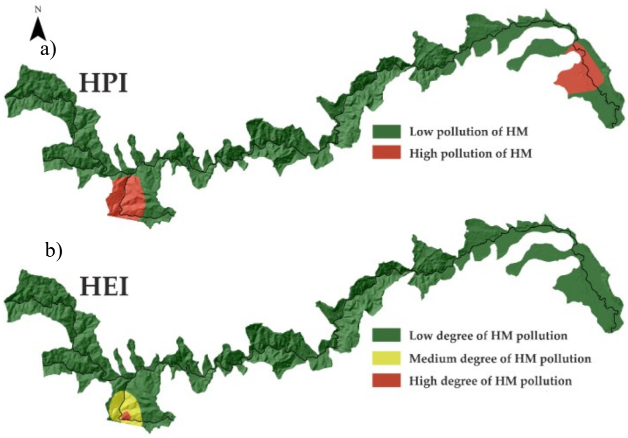

Fig. 1. Spatial variation of the heavy metal pollution index (HPI) (a) and of the heavy metal evaluation index (HEI) (b) in the Aries River basin [35].

In the case of some drinking water from Medias Town (Romania), the pollution indices showed low contamination degree, all values being lower than the critical ones [31].

4.5.2. Soil

In the case of soils, there are two types of pollution indices: individual and complex indices. The individual indices are tools used for the unitary assessment of soil pollution with a particular contaminant. While, the complex indices establish, in a more holistic way, the degree of soil pollution with various contaminants [32].

Among individual indices, the most frequently used are the contamination factor (C_f), and geo-accumulation index (I_{geo}), while, contamination degree (Cd), pollution load index (PLI) and potential ecological risk index (PERI) are the most commonly applied complex indices [32].

Calculation of soil pollution indices requires the assessment of the geochemical background, referring to the average content of the element in the earth's crust [33]. Even so, a regional background is recommended to be used as geochemical background due to significant differences of the soil chemical composition [34].

The level of soil and sediment contamination in a former mine area located in the Aries River basin was assessed [35, 36]. Both, PLI and PERI, showed that surface soil and sediments from Roșia Montană and Roșia Rivulet were highly polluted (PLI = 1.58, 1.95) by hazardous metals, the average potential ecological risk index values for soil and sediments decreasing in the order of Cu>Cd >As >Cr >Hg >Mn >Zn (Fig. 2).

The study of Hoaghia et al. [37] assessed the contamination and ecological risk caused by As, Cd, Cr, Cu, Pb, and Zn in urban soils situated near a metallurgical complex in NW of Romania. The results showed concentrations above the geochemical background in more than 80 % of samples for heavy metals and all the indices showed a level of contamination in the studied area.

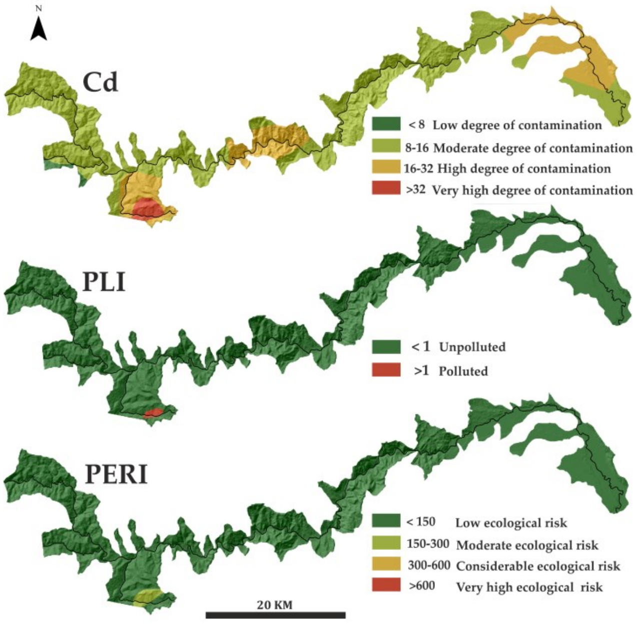

Fig. 2. Spatial distribution of contamination degree (Cd), pollution load index (PLI) and potential ecological risk index (PERI) of soil samples in Aries River basin [35]

4.6. Human health risk assessment

Water quality is associated with human health. Water rich in toxic substances (heavy metals, pesticides, nitrogen compounds, salts, also toxins produced by bacteria) can induce health risks if ingested or after dermal contact. Direct exposure to toxic substances which exceed the maximum allowable concentrations (established by national or international regulations and guidelines for the protection of drinking water quality), and water sources used for the drinking purpose can influence and negatively affect human health. Generally, the human health risk related to different chemicals and components through water ingestion or after dermal contact is assessed with the help of five major indices: the Chronic Daily Intake (CDI)), the Hazard Quotient (HQ), the Total Hazard Index (THI) and the Incremental Life Cancer Risk (ILCR). The Chronic Daily Intake, the Hazard Quotient, and the Total Hazard Index are included in the non-carcinogenic category, while the Incremental Life Cancer Risk is part of the cancer risk category [38-41].

The Total Hazard Index measures the potential risk to human health caused by exposure to multiple heavy metals, assuming the cumulative effect of metals. On the other hand, the Hazard Quotient determines the risk of one particular heavy metal. Chronic Daily Intake refers to the daily intake of a particular toxic element in the human body and is expressed as mg/kg/day. The cancer risk represents the hazard from a lifetime average dose exposure to 1.0 mg/kg body weight/day of a chemical element or component [41, 42]. This risk expresses the probability of cancer occurring over a lifetime (70 years), due to daily exposure to carcinogens. This probability is expressed as the Incremental Lifetime Cancer Rick (ILCR) [42].

These five indices are calculated based on the concentrations of studied pollutants, reference dose, and cancer slope factor. The reference dose and cancer slope are specific to each chemical or compound and were established by the United States Environmental Protection Agency (US EPA) and mentioned in the Integrated Risk Information System (IRIS) substance list [42]. After calculation, the obtained score is associated to a risk status. Each index has a defined equation, as it follows, according to Eq. [1-4]:

$$HQ = \frac{CDI}{RfD} \quad (1)$$

$$THI = \sum_{i=1}^{n} HQ \quad (2)$$

$$CDI = \frac{C * DI}{BW} \quad (3)$$

$$ILCR = CDI * CSF \quad (4)$$

Where, HQ represents the hazard quotient, RfD is the oral toxicity reference dose, C is the concentration of the specific contaminant (μg/L), DI is the daily intake (2L/day), BW represents the body weight (72 kg) and CSF as the cancer slope factor. If the source of risk is represented by water ingestion, the values for the RfD are the following: RfD_{As}= 3x10^{-4} mg/kg/day; RfD_{Cd}= 5x10^{-4} mg/kg/day; RfD_{Cu}= 4.0x10^{-2} mg/kg/day; RfD_{Hg}= 3.0x10^{-4}; RfD_{Pb}= 3.5x10^{3-} mg/kg/day; RfD_{Ni}= 2.0x10^{-2} mg/kg/day; RfD_{Zn}= 0.3 mg/kg/day; RfD_{NO2}= 0.10 mg/kg/day; RfD_{NO2}= 1.60 mg/kg/day [41, 42].

According to US EPA IRIS [42], the cancer slope factor was established only for As (CSF_{As}= 1.5 per mg/kg-day). In the case of HQ, there are two risk categories, namely possible chronic risk generated by water ingestion of dermal contact, which could appear if the HQ score is higher than one (HQ>1.0). The second category includes the scores below one (HQ<1.0), indicating that no chronic risks occur if the water is ingested [39, 42]. Similarly, if THI scores are lower than one (THI<1.0), they indicate an acceptable level of risk. In contrast, THI higher than one (THI>1.0) indicates an unacceptable risk of non-carcinogenic effects on human health [43]. The minimum acceptable cancer risk is considered to be within the range of 1x10^{-6} – 1x10^{-4} [41].

The potential risk of different heavy metals, chloride, and nitrogen compounds (nitrate and nitrite) caused by the ingestion of water from different sources was studied for groundwater collected from water wells, karstic springs, and bottled waters. The studied groundwater sources were collected from Medias town, Romania, near a former non-ferrous ore smelter. The applied risk indices were related to the content of nitrate, nitrite, Cd, Cr, Cu, Mn, Ni, Pb, and Zn determined in the studied groundwater used as drinking water sources. The results indicated a high risk of nitrate for more than 72% of the studied samples and no risks for nitrite and the studied heavy metals [44]. The sources of the high nitrate content were related to agricultural practices and household activities [44].

The study of karstic springs suggested that the studied water samples, collected from rural areas in the south-eastern part of Romania (Dobrogea Region), were vulnerable to noncarcinogenic nitrate risks. On the other hand, heavy metals (Cd, Cr, Cu, Fe, Ni, Pb, Zn) in water did not pose noncarcinogenic risks [45].

The health risk assessment for the bottled water indicated potential risks at chloride, nitrate and aluminium. Sources of the contaminants were represented by the water-rock interactions [46].

Based on the results of these studies the possible risks posed by water pollutants may be prevented by water treatment or use of alternative water sources for domestic uses.

4.7. Microbial risk assessment

Risks of microbiological contamination are a serious issue for human health. Many microorganisms such as bacteria, viruses, fungi, protozoa and helminths can contaminate food or drinking water and cause a variety of illnesses. Securing the microbial safety of food and drinking water should aim to prevent contamination and reduce contamination to levels not injurious to human health [47]. Several risk assessment methods have been developed to understand and predict the effect of human exposure to microbial contamination.

Microbial risk assessment (MRA) is a valuable tool for understanding, reducing, and preventing risks when a population is exposed to hazardous microorganisms [48]. The microbial risk can be estimated as qualitative or quantitative based on the scientific data and used methods. Risk assessment should lead to risk management implementation and decision-making to minimizing their impact on human health.

Quantitative Microbial Risk Assessment (QMRA) integrates scientific data on human exposures to pathogens and the probability that the exposures can determine infection or illness [49]. QMRA is a four-step risk assessment process including:

- Hazard identification - focusing on the identification of pathogens and the adverse health effects that microorganisms cause;
- Exposure assessment - measuring the dose of microorganisms to which individuals are exposed;
- Dose-response assessment - calculating infectious rates due to that specific pathogen;
- Risk characterization - evaluating how likely a person is to get infected from exposure to a pathogen. The results estimate whether the water supply system is capable to meet an established acceptable benchmark [50].

In the *Monitoring and risk assessment for groundwater sources in rural communities of Romania* project (GROUNDWATERISK), our research group assessed the microbiological quality of karst springs water from rural communities in Apuseni Mountains, estimated the health risk for the consumers and implemented educational actions to raise awareness of the risk of illness.

Standardized and alternative rapid, low-cost microbiological methods were tested and validated, and the most feasible methods for groundwater microbiological monitoring were selected for future monitoring actions.

Thus, the microbial water contamination was analyzed by the determination of *E. coli*, total coliforms, intestinal enterococci, *Pseudomonas aeruginosa*, and heterotrophic plate count at 37 and 22°C with the membrane filtration method and by the pour plate method. In addition, some microbial indicators, such as *Staphyloccocus aureus*, *Salmonella spp*., *Listeria monocytogenes*, *Bacillus cereus*, were determined by an alternative method RIDA-COUNT (R-Biopharm AG, Germany).

Microbial contamination data were inputted into a QMRA model. QMRA was applied to estimate the risk of gastrointestinal illness for adults and children due to enteropathogenic *E. coli* contamination [51]. The dose-response assessment was established on the Beta-Poisson model. The probability of infection/day (P_{inf}), the probability of infection/year ($P_{inf\ annual}$) and the probability of illness (P_{ill}) were calculated with equations 5-7, respectively.

$$P_{inf} = 1 - (1 + D / \beta)^{-\alpha} \quad (5)$$

$$P_{inf\ annual} = 1 - (1 - P_{inf})^{n} \quad (6)$$

$$P_{ill} = P_{inf\ annual} \times P_{ill/in} \quad (7)$$

where, D – is the average dose ingested (volume of water consumed/day × average value of *E. coli*), α and β are dose-response parameters, with values of 0.050, 1.001 for adults, and 0.084, 1.44 for children, n – is the number of days of exposure/year due to the pathogen dose.

Based on the presence of *E. coli*, a QMRA model for estimating other pathogens such as *Campylobacter* and *Rotavirus* was formulated [52]. Our findings revealed microbiological contamination of springs water and a high risk of infection and illness even if the ingestion dose of pathogens was low [52]. As a general remark, the probability of illness increases as the number of cells ingested increases. Comparing the obtained results with the benchmark, QMRA values exceeded the WHO recommended limit of 10^{-4}. These QMRA results showed that rural communities consuming the contaminated water are exposed to immediate and long-term health threats.

Future QMRA approaches must take into consideration some limitations referring to: the representativeness of the collected samples for the data set, the representativeness of the data set for the system, the feasibility and precision of the methods, the accuracy of the data on water consumption (who consumes and how consumes water). In the QMRA, some uncertainties and variabilities which are related to each particular scenario of microbial contamination should also be considered. Infection may or may not result in illness and these are conditioned by three biological entities with a high degree of variability: pathogen, consuming host, and water. Moreover, the distribution of contamination is non-random and non-homogenous and the level of the pathogen can change drastically in a short amount of time, consequently, the risk estimation model could generate different data set.

4.8. Soil remediation

Soil is a complex system that has essential functions contributing to the sustainability of terrestrial ecosystems and support of life. Contaminated soils can harmfully affect other environmental factors such as water and air, vegetation and food quality, and finally human health. Soils can be exposed to many contaminants, including heavy metals or trace elements, petroleum hydrocarbons, and persistent organic pollutants.

Although many research efforts have been dedicated to the remediation of soil functionality through the application of a variety of soil reclamation techniques, additional work in this important area there are still required. In-situ or ex-situ bioremediation, involving bacteria and/or fungi, is a recognized as an approach to clean up contaminated soils.

Our laboratory participated in research projects focused on the biodegradation of organic contaminants, with particular attention to petroleum hydrocarbons. Our main contribution in these projects was to monitor the content of petroleum hydrocarbons in soils during the biodegradation experiments. The biopile method was used for decontamination of soil polluted mineral oils. It was found that the soil can be efficiently depolluted by adding micro-organisms *Pseudomonas* and *Bacillus*. We developed an analytical method for petroleum hydrocarbon determination in soil by Fourier transform-infrared spectroscopy. The method was validated in terms of selectivity, limit of detection and limit of quantification, working range, trueness, precision, and recovery. The obtained method limit of quantification was 30 mg/kg, the working range was 30-2500 mg/kg, and a recovery of 105%, which represents satisfactory results [53].

The developed biopile technology was applied in a pilot scale experiment in which soil polluted with petroleum hydrocarbons was decontaminated using microorganisms (*Pseudomonas* and *Bacillus*) for 12 weeks. Starting from an initial petroleum hydrocarbons concentration in soil of 4280 ± 400 mg/kg, after 12 weeks the content of petroleum hydrocarbons decreases below 1000 mg/kg, which is two times below the intervention threshold for less sensitive soil uses (2000 mg/kg) established by Romanian legislation (Order no. 756/1997).

For remediation of soils polluted by heavy metals, our laboratory was involved in a research project designed to develop a decontamination technology based on a bioleaching approach. The bioleaching process depends on the ability of micro-organisms to transform solid compounds into soluble and extractable elements that can be recovered.

4.9. Phytoremediation

Bioremediation is an alternative method for removing pollutants that involves the management and use of different types of biomaterials and living cells [54-55]. Phytoremediation is part of the bioremediation process and it is based on the plants' natural potential to scavenge certain contaminants from the polluted environment and to maintain the balance of the ecosystem [56]. Plants phytoremediation capacity in aquatic ecosystems is affected by inorganic and organic compounds concentrations, contaminant's mobility, solubility in water, ionic charge of the pollutant, temperature, and pH of the ecosystem [56]. Therefore, phytoremediation studies are important for a better understanding of the organic pollutant's remediation mechanism and the effect of contaminants on living organisms. The equilibrium isotherm models (Langmuir, Freundlich, and Dubinin-Radushkevisch) are often used to understand and predict the metal behavior in living organisms and offer quantitative estimations of the contaminant's adsorption by plants or algal biomass. Photosynthetic pigments (carotenoids, chlorophyll *a* and *b*) and antioxidants capacity are used to assess the effect of the abiotic stress induced by pollutants on plants [57].

Various algal and plant species were tested in our laboratories to identify the most effective hyperaccumulator, abiotic stress resistant species for phytoremediation processes. *Nannochloropsis oculata* microalgae and *Spirulina* cyanobacteria capacity to remove dyes, Rhodamine B and Methylene blue from aqueous solutions was studied. The experimental data were analyzed using Langmuir, Freundlich, and Dubinin-Radushkevisch isotherm models. The results showed that the studied algal species are highly functional for dye removal. Therefore, the removal of Rhodamine B from aqueous solutions using *Nannochloropsis oculata* and *Spirulina* occurs via physical interactions. The Methylene blue removal by *Spirulina* is a chemical process, while by *Nannochloropsis oculata* is a physical adsorption process.

Lemna minor, an aquatic plant, was collected from a local pond from Floresti area, Cluj County, and was left for vegetative multiplication under laboratory conditions (ICIA). The *Lemna minor* species was used for phytoremediation experiments, to investigate its ability to reduce pollutants from wastewaters. The obtained results showed a high potential to reduce the total oxidizable organic pollutants from the wastewater by 65%. Moreover, high removal efficiencies were obtained in the case of As, Cd, Cr, Co, Mn, and Pb (ranging from 96.9 to 99.4%). Additionally, *Lemna minor* has a remarkable ability to accumulate high concentrations of Na, Al, Hg and Fe from wastewater [58].

4.10. Lithium- an emerging pollutant

Lithium (Li) is the 30th most abundant element, which covers about 0.006 wt% of the earth's crust [59]. It is the most critical element in next-generation technologies. The application areas for Li are about 35% for batteries, 32% for glasses and ceramics, and below 10% in the case of polymers production, sanitization, pharmaceutical, organic synthesis, or constructions [60]. On the commercial scale, Li consumption increased between 2000 and 2015 by approximately 20% [60].

Lithium-ion batteries are among the most promising rechargeable batteries due to their low cost and efficient energy storage [61]. Therefore, it was estimated that in 2025 the consumption of Li for lithium-ion batteries would increase by 66% [62]. According to the Benchmark Lithium index, the global weighted average price has increased by more than threefold from 2016 to 2021 and the price is still increasing "as the cars go green" (ednHUB). The primary Li element resources are brines and lakes (20 to 1500 mg/L Li content), shale rocks, and minerals (*e.g.,* spodumene, pegmatites, petalite, lepidolite, zinnwaldite, and amblygonite), as well hectorite, and authigenic clays [59, 62-64]. The top leading producers and exporters are known to be Australia (39%), Chile (33%), Argentina (16%), and China (5.5%) [62]. In the case of Romania, there is a lack of data on the occurrence of Li in the environment and in particular in the natural waters.

The biochemical role of Li in the lifecycle of living organisms is still unclear. Various studies present Li as an essential element with many beneficial roles at specific concentrations in human health and in the plant's development. However, there are no recommendations or regulatory thresholds for Li consumption in human health.

Different plant species can absorb a noticeably high amount of Li, which can positively affect growth and development [64]. However, plant species have various Li uptake capacities with specific toxicity symptoms. Therefore, several studies investigate Li uptake, role and toxicity signalling in the living organism exposed to various Li concentrations [64].

According to the Li importance in various industrial fields, our research interest is focused on the (*i*) identification and assessment of Li resources in Romania; (*ii*) study of Li bioavailability, uptake, and accumulation rate in plants for a better understanding and determination of the Li uptake mechanism, and biochemical role in the lifecycle of living organisms. The Li content was assessed by Török et al. [65], to study the divergence in the samples and to find a connection between the Li concentration in plants, compared to soil, and water, in two important karst areas in Romania. The studied groundwater, soil, and plants (ryegrass-*Lolium sp*., nettles-*Urtica sp*., and mint-*Mentha sp*.) were collected in September 2020 from six sampling points located in rural areas of the Dobrogea and Banat regions, Romania. Analysis of Li was performed using ELAN DRC II (Perkin–Elmer, Waltham, MA, USA) inductively coupled plasma mass spectrometer (ICP-MS). The macro- (Na, Mg, K, Ca, and Fe) and microelements content (Li, Al, V, Cr, Mn, Co, Ni, Cu, Zn, As, Sr, Cd, Ba, and Pb) of water samples were also determined, to characterize the studied areas elements content of the studied areas and to assess the chemical behaviour of Li. The soil and plant samples were mineralized by a wet-digestion method prior to the macro- and microelement determinations. The quantitative ICP-MS method for Li determination was optimized for three different matrices (water, soil, and plants). The obtained results revealed higher Li concentrations in the case of the water and soil samples in Dobrogea region than in those from the Banat region. The Li concentrations in the water samples were between 1.40 and 12.2 μg/L, while in the soil samples they ranged from 6.50 to 11.3 mg/kg. The accumulation of Li in plant species is highly influenced by the growth medium. Among the plant's samples, the highest Li concentrations were measured in the case of the *Lolium sp*. (8.8-11.1 mg/kg Li) from the Dobrogea region, while the species from the Banat region had a low content of Li (lower than 0.5 mg/kg) [65]. Further studies need to be performed in order to map the Li content occurrence in different regions of Romania. Studies conducted by our research team on the Li uptake are in progress with free-floating aquatic macrophytes (*Salvinia natanas* and *Lemna minor*) as test plants.

4.11 Mercury as legacy pollutant

Mercury is a natural element in the earth's crust, but due to human activity, terrestrial and aquatic ecosystems are contaminated with mercury. The main environmental sources of mercury are mining activities, the use of amalgamation to extract precious metals such as gold, the burning of coal in power plants, electronic waste and industrial activities where Hg is used as a catalyst [66].

Because of the negative effects of mercury on human health the monitoring of mercury levels present in the environment are important. In 2013 the Minamata Convention was adopted and it was ratified by 140 countries between 2013 and 2018 [67]. Based on the adopted convention, the European Council and the European Parliament adopted regulation 2017/852 for mercury. The regulation showed that between 40 and 80% of the total deposition of mercury comes from outside the EU because of cross-border pollution. As a result, the regulation established that each EU member must take measures to reduce its anthropogenic mercury emissions in the environment by 2020 [68].

Out of the three forms the mercury present in the environment (elemental, organic and inorganic), the organic mercury species, especially methylmercury, is the most abundant and the most toxic. It possesses a high potential of bioaccumulation in the marine food chain; therefore, fish are the highest source of exposure to mercury from food to human health [69].

Several sediment samples were collected from the Arieș river near the former alkali chemical plant in Turda and were analysed for the determination of total mercury and methylmercury [70]. Arieș River is located in north-western Romania, it flows through Turda and it discharges into the Mureș River [71]. It is one of the polluted rivers in Romania due to the mining exploitation and chemical industry present in the area. The results showed that the majority of mercury species detected in sediments were of inorganic nature, with values between 1.2 and 4.6 mg/kg total mercury content. The organic species present was in minority, with values between 0.045-0.209 mg/kg. Although inorganic mercury is not as dangerous to human health as the organic species, the presence of mercury in these sediment samples raises a sign of alarm and authorities need to be involved in decontamination actions to prevent exposure of the local population to any form of mercury [72].

4. New directions of research

The broadening of the existing research topics as well as the existing infrastructure in Environment and Health Laboratory is a constant preoccupation. The following research topics are proposed as new avenues to explore: (i) assessment of the various pollutant fate in the environment, (ii) identification of the pollution patterns and trends in various ecosystem's; (iii) pollution biomonitoring using natural or transgenic plants and tree species, (iv) phytoextraction and phytomining of critical elements using various hyperaccumulator plants, (v) development of water and soil remediation methods, (vi) development of new analytical methods for the analysis of emerging pollutants such are personal care products, different drugs and microplastics.

5. Perspectives

Environmental degradation and climate change are important issues all over the world. The growing interest in environmental pollution assessment as well as the development of new, low-cost, ecological remediation methods will be the future drivers of the environment protection policies in the EU.

To respond to public concerns about environmental issues and related health risk, all EU countries committed to European Green Deal that proposes to put the economy and society on a sustainable path.

In this sense, the assessment of the environment quality, identification of polluted sites as well development of new remediation methods are just few of the topics to which our team could contribute by developing research needed to fundament future polices and mitigation measures. Another topic that could respond to the new environmental challenges is the mapping of critical elements distribution in different region and the development of new phytomining methods that could be used for the sustainable recovery of critical and toxic elements from different environmental media.

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CIRCULAR ECONOMY: New technologies and analytical methods for the implementation of the circular economy principles

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Abstract. This paper describes the Bioenergy-Biomass Laboratory of INCDO-INOE 2000, Research Institute for Analytical Instrumentation Subsidiary (ICIA) Cluj-Napoca, involved in activities focused on obtaining renewable fuels, such as biodiesel, bioethanol, and biogas from biomass and by-products. The major achievements of INCDO-INOE 2000 ICIA and the recent results obtained toward a circular economy are presented. The main findings obtained by INCDO-INOE 2000 ICIA related to lipid extraction from microalgae, the technologies for bioethanol and biogas production from lignocellulosic biomass, and the analytical methods for material recovery from IT and telecommunication wastes are discussed.

Keywords: biofuels, ICP-MS, microalgae, XRF, biomass

1. Introduction

The circular economy concept has gained attention since the 1970's, as a means of transitioning from the current linear model of the economy to a circular one in which resources are kept in use for as long as possible [1]. The circular economy concept implies using natural resources or wastes to produce valuable products in order to minimize waste discharged into ecosystems, maximize values, and reduce greenhouse gas emissions [1,2].

Human activities generate large volumes of wastewater on a daily basis, significantly affecting water quality [3]. Thus, wastewater treatment has the potential to contribute to a circular economy by recovering the resources contained in wastewater that have a secondary use [4]. Currently, microalgae gained attention due to their potential to recover nutrients from wastewater and produce valuable products such as proteins, polysaccharides, lipids, and pigments. Thus, microalgae integrate into a circular economy through simultaneous wastewater treatment and highly valuable biomass production that can be used as a renewable resource for biofuel production. Moreover, algae-based wastewater treatment represents an environmentally friendly alternative with reduced operating costs compared to traditional industrial wastewater treatment methods [3,5,6]. During the growth process, algae will remove contaminants from wastewater. Afterward, the algal biomass will be used for biofuel production [7]. Microalgae can effectively remove heavy metals due to their cell wall's high binding affinity. The heavy metal removal process occurs in two phases: the first phase implies the adsorption of metals into extracellular materials and in the cell wall, and the second phase implies the absorption and accumulation of the metals inside the cell. These phases can be affected by pH, temperature, and algae type. Consequently, considerable research efforts have been dedicated to investigating the effect of parameters such as algae type, pH, heavy metal concentration, and algal cell size for heavy metal removal [7]. Moreover, the selection of suitable algae species compatible with the properties of the wastewater to be treated is mandatory [8].

Microalgae species represent a promising biodiesel and bioethanol production feedstock due to their high lipids and carbohydrate contents [9,10]. The steps involved in converting microalgae to biodiesel are cultivation, harvesting, drying, lipid extraction, and transesterification in the presence of catalysts [11]. The main challenges related to microalgal biodiesel production include process optimization for wastewater treatment in order to sustain microalgae populations over long periods of time with high productivity and lipid yield, the efficiency of the transesterification reaction, and biodiesel quality [9,10,12]. Microalgae-based carbohydrates can be converted into bioethanol through fermentation and residual biomass into biogas through anaerobic digestion and methane fermentation [9,13,14].

Lignocellulosic biomass, an abundant raw material to produce energy effectively, is one of the best alternatives to fossil resources. Lignocellulosic biomass has a great potential to produce high-value bio-based products. Lignocellulosic biomass comprises 40 – 50 % cellulose, 25 – 35 % hemicellulose, and 16 – 33 % lignin [15]. The structure of the cellulosic chain from lignocellulosic biomass is presented in Figure 1.

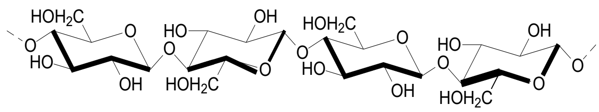


Fig. 1. The structure of the cellulosic chain from lignocellulosic biomass

Lignocellulosic feedstocks can be used to produce a wide variety of organic matter, high value-added products, and relatively green fuels. While there are many environmental benefits to these materials, there are many challenges to entirely replace petroleum products with lignocellulosic sources. The solution to these problems is to use lignocellulosic biomass in a sustainable economic cycle to produce materials with high added value and lower environmental impacts. Bioenergy derived from renewable resources plays a central role in the transition toward net-zero carbon dioxide emissions and a low-energy circular economy. The European Commission (2018) defines bio-economy as the development of diverse renewable biological sources and their conversion into high-value bio-based goods. The circular economy uses biomass to produce bioenergy, biochemicals, and bio-products in a biorefinery concept (Figure 2) [15].

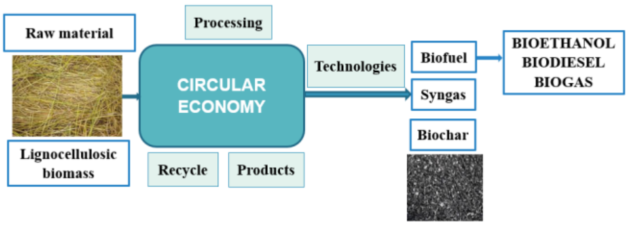


Fig. 2. Modern circular economy for bioenergy and bio-products sustainability (adapted after[15])

Biofuels hold a unique position in the bioeconomy. The circular bioeconomy emphasizes the efficient and sustainable use of biomass in biorefineries, as well as the cascading use of tailings and waste. The bio-waste used for bio-products and energy production includes biowaste digestate, lignocellulosic biomass, sugar beet pulp waste, biowaste digestate, food waste, coconut residues, etc. Some of the methods used for producing bioproducts are: solid state fermentation, thermochemical process, biological pretreatment, anaerobic digestion, chemical pretreatment, combustion, gasification, fermentation, enzyme hydrolysis, etc. Numerous bioproducts can be obtained from biowaste, like bioethanol, biogas, pure sugar, hydrolytic enzymes, biosurfactants, biopesticides, etc. [16].

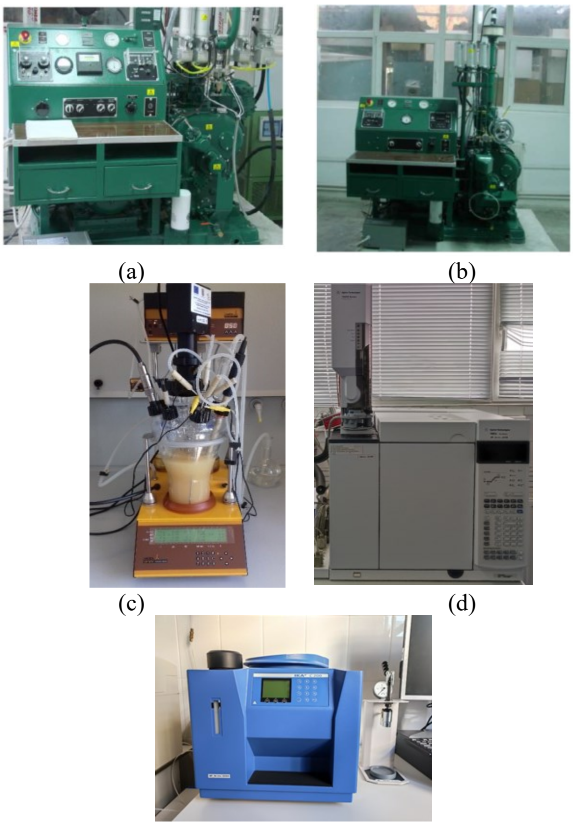
The recent technological development of modern society requires new communication and information transmission technologies and the automation of various technological processes. The equipment is changing at an alert pace, leading to an accelerated increase in waste from the electrical and electronic field due to the ever-increasing demands and offers regarding the application of these technologies. This waste also contains precious metals that can be recycled and reused (it's estimated that 1 million mobile phones contain 16 tons of copper, over 300 kg of silver, over 30 kg of gold, and about 15 kg of palladium). The problem of continuously accumulating waste is taken very seriously at international and national levels. Internationally, there are programs that oblige the manufacturer to limit the level of toxic substances in the electronic boards they produce, to use as much recyclable material as possible, and to collect a fee from buyers to cover part of the collectors' fees. Nationally, the problem has been tackled relatively recently. According to EUROSTAT [17], significant differences were observed between EU member states regarding waste recycling. While countries such as Slovenia, Italy, Belgium, Poland, and Germany recorded very high proportions of recovery, in countries such as Bulgaria, Romania, Greece and Malta, wastes were disposed of instead of being recycled. One of the main means of disposal is incineration, which raises the problem of air pollution due to the various toxic compounds released during the process. In Romania, there are programs that deal with the collection of electrical and electronic waste [18], but there are no adequate means of recovery in terms of costs, energy consumption, and environmental pollution.

The main objectives of the European Union's environmental policy are the preservation, protection, and improvement of the quality of the environment, the protection of human health, and the prudent and rational use of natural resources. In this context, Directive 2012/19/EU of the European Parliament and of the European Council from 4th of July 2012 on waste electrical and electronic equipment (WEEE) mentions the rapid increase in waste electrical and electronic equipment due to the market growth and the shortening of innovation cycles. These wastes contain hazardous substances such as mercury, cadmium, lead, hexavalent chromium, polychlorinated biphenyls (PCBs), and substances that deplete the ozone layer. Currently, WEEE recycling is not sufficiently carried out, leading to the loss of valuable resources. This situation requires taking measures to reduce the hazardous substances used in the construction of WEEE, while also encouraging an increase in the lifetime of these products, their recycling, and reuse [19].

2. History/Landmarks

The research and development activity of INCDO-INOE 2000, Research Institute for Analytical Instrumentation Subsidiary (ICIA) Cluj-Napoca is focusing on three main directions: Bioenergy and Biomass, Instrumental Analytical Chemistry and Environment and Health.

The Bioenergy-Biomass Laboratory is involved in activities focused on obtaining renewable fuels, such as biodiesel, bioethanol, and biogas from biomass and by-products, the realization of technologies and installations for renewable fuel production, and developing advanced processes for biomass conversion to electricity and heat through the valorization of agro-forestry waste by implementing the circular economy principles. It comprises the Renewable Energy Laboratory (LER) and the Biofuel Quality Certification Laboratory (CABIO). LER is involved in elaborating and developing innovative and cost-efficient technologies for the superior capitalization of renewable resources for obtaining biofuels and their large-scale implementation on the market. CABIO is involved in elaborating and developing innovative processes for the quality determination of biofuels and performing analyses to certify the biofuels quality according to European standards for biodiesel and bioethanol. Both laboratories were modernized by the acquisition of key equipment, such as devices for determining cetane (Figure 3a) and octane number (Figure 3b), fermenter - bioreactor (Figure 3c) to measure and control the parameters of the culture, gas chromatographs for the determination of ester, methyl ester and linoleic acid content (Figure 3d), methanol content, monoglyceride, di- and triglyceride content, free glycerol and total glycerol, calorimeter for determining gross calorific values of liquid and solid samples (Figure 3e), rotational viscometer for the determination of viscosity at 40 °C, flash point tester and copper stip corrosion tester, automatic methane potential test system, bioreactor simulator and gas endeavor for biogas production, UHPLC with DAD, RI and ELSD detectors, GC-MS, FID and ECD detectors for analysis of carbohydrates and by-products obtaining from biomass.



(a) (b) (c) (d) (e)

Fig. 3. INCDO-INOE 2000 ICIA equipment

3. Current developments and collaborations

INCDO-INOE 2000 ICIA has made significant scientific contributions to the development of advanced technologies for biofuels production (biodiesel, bioethanol) from wood and algae, the validation of new analytical methods for biofuels production, biofuels quality certification (biodiesel and bioethanol), and to the elaboration of the national strategy for biofuels and the BIOMASS Action Plan. Also, INCDO-INOE 2000 ICIA organized public information campaigns regarding the advantages of biofuels and other renewable fuels usage and the benefits of their implementation on a large scale.

The significant achievements of INCDO-INOE 2000 ICIA are the following: ♦technologies for bioethanol production from lignocellulosic biomass by acid hydrolysis and enzymatic hydrolysis using environmentally friendly methods (lab scale) (Patent no. 127297/30.04.2014, Patent no. 126407/28.02.2012) [20,21]; ♦technologies for the production of second-generation biofuels from crude and used oil by transesterification (Patent no. 127018/30.08.2013) [22]; ♦technologies for biodiesel production from algae (lab scale) (Patent no. 128691/30.05.2014) [23]; ♦technologies for biogas production from biogenic wastes; ♦technology for glycerin purification resulted as a byproduct in the process of biodiesel production; ♦small capacity installation (200 l/charge) for biodiesel production from vegetable oil (homologated and transferred to the beneficiary); ♦technology for biodiesel/additive produced from renewable sources, through a carbonation reaction of glycerol acetals (on lab scale); ♦biodiesel obtained by treating fatty acids, their esters, and glycerides with hydrogen-enriched gas; ♦traffic testing of the biodiesel produced from vegetable oils (in Cluj-Napoca); ♦solutions to elaborate modern, non-pollutant, cost-efficient technologies for biofuel production (biodiesel, bioethanol, biogas) from renewable resources.

INCDO-INOE 2000 ICIA submitted multiple projects proposal in national and international competitions. The projects carried out by INCDO-INOE 2000 ICIA related to biofuels production are: ♦BIOHID (pilot plant for the production of enriched biodiesel by catalytic treatment of fatty acids contained in vegetable oils and animal fats), ♦BIOBENZ (pilot plant for the production of sugar beet bioethanol); ♦BIOGEF (up-flow pilot plant for biogas production from biogenic wastes); ♦BIOVALP (pilot plant for the production of biodiesel from soybean oil and protein derivatives); ♦PN 09 27 03 02, NUCLEU project entitled "*Elaboration of modern technologies with optimum efficiency for the superior valorization of biomass (lignocellulosic waste and algae) for 2nd and 3rd generation of biofuels*". In the PN 09 27 03 02 project, a laboratory scale technology was developed for biodiesel production from algae. The technology implies the oil extraction from *Nannochloropsis oculata* algae with hexane using a Soxhlet extractor system followed by the algae oil transesterification by alkaline catalysis for the conversion of triglycerides into methyl ester. The analysis of the obtained biodiesel with the newly developed technology showed that the quality requirements of the SR EN 14214+A2:2019 standard [24] were obeyed, except for the iodine index, which reflects the degree of unsaturation of the feedstock. The obtained biodiesel should be subjected to a hydrogenation step in order to increase the oxidation stability of biodiesel in time.

The NUCLEU project (contract no. 18N/08.02.2019) proposes applying the principles of circular economy through the superior valorization of microalgae biomass used in wastewater treatment to obtain pigments, lipids, biodiesel, and bioethanol. The project objectives are: ♦the development and optimization of algae growth methods (at laboratory level) for wastewater treatment; ♦development and optimization of methods for pigment, lipid, and reduced sugars extraction from microalgae; ♦development and optimization of microalgae-based technology for biodiesel production; ♦development and optimization of microalgae-based technology for bioethanol production. Within the frame of the project, a photobioreactor for continuous monitoring of microalgal growth parameters (Figure 4) was designed by ELECTRONIC APRIL SRL. The photobioreactor consists of: ♦a gas mixing system; ♦a growth chamber with a stirrer; ♦a gas disperser and heater; ♦an RGB lighting source with a remote controller; ♦an additional water tank equipped with a micropump to keep the water level constant; ♦a robot arm to introduce the sensors in the growth chamber and ♦a human computer interaction unit to set up and control the experiments.

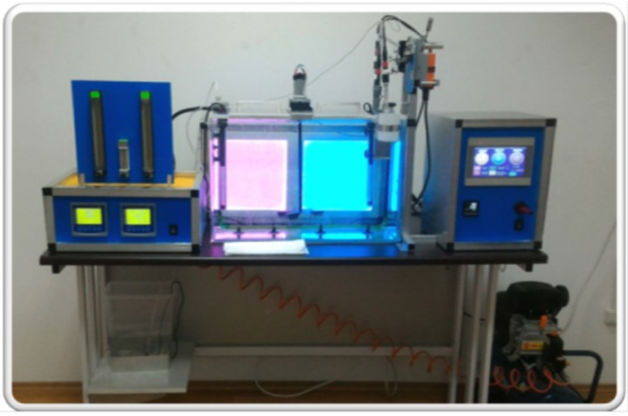


Fig. 4. Photobioreactor for continuous monitoring of microalgal growth parameters

The project entitled "*Surveillance and control modern analytical methods for the technological flow used to obtain reusable materials from waste*" (MESUCO/TRADE-IT PN-III-P1-1.2-PCCDI-2017-0652) aims to quantify the transformations occurring in the chemical composition of some e-waste (from electrical and electronic equipment) during the transformation process from waste in reusable materials as a result of chemical and electrochemical processes to which they can be subjected in the preliminary stage. In order to achieve the proposed goal, the development, validation, and implementation in the INCDO-INOE 2000 ICIA laboratories of a set of modern analytical methods for the characterization of waste during the transformation process from waste into reusable materials is pursued. Thus, several modern analytical methods were developed, validated, and implemented, such as: ♦a method of testing the waste during leaching; ♦a method for determining the parameters to be leached; ♦a method for the evaluation of the waste from an elemental point of view, following precisely the metals of interest to be recovered; ♦a method for identifying the type of plastic mass from waste and ♦a method for evaluating the degree of recovery of metals from waste.

Establishing the efficiency of metal recovery methods from e-waste requires the development of complex eco-friendly analytical testing methods. In this context, multiple analytical methods were developed and used to determine the metal content of e-waste: X-ray fluorescence spectroscopy, atomic absorption spectrometry, ion exchange chromatography, and mass spectrometry with inductively coupled plasma. The following techniques were used to develop the analytical methods and to identify the type of plastics present in e-waste: energy dispersive X-ray spectroscopy (EDXS), ion chromatography (IC), ion-selective electrode technique, and headspace gas chromatography (GC-MS). By developing and deploying the analytical methods in the laboratory, INCDO-INOE 2000 ICIA has now the required tools to analytically investigate e-waste and thus be a part of the decision process that brings the IT and telecommunication waste back into the circular economy cycle.

4. Recent results and their transfer

INCDO-INOE 2000 ICIA research directions towards a circular economy include analytical methods for lipid and total reducing sugar extraction from microalgae, technologies for bioethanol and biogas production from lignocellulosic biomass, and analytical methods for advanced material recovery from IT and telecommunication wastes.

4.1. Analytical methods for lipid and total reducing sugar extraction from microalgae

Lipid productivity is essential for selecting the most appropriate algal species for biodiesel production. Findings reveal that: some microalgae species with high lipid content cannot adapt and grow in wastewater, microalgae isolated from industrial wastewater and grown in a cultivation media supplemented with different organic carbon substrates exhibited higher biomass and lipid productivity than freshwater medium, most microalgae showed a high lipid yield under stress conditions, the cultivation parameters affect lipid production, and the fatty acids composition affects the characteristics of the produced biofuel [7]. Roman et al., 2011 [25] stated that algae-based biofuel has the potential to revolutionize the energy industry playing a leading role in the fight against greenhouse gas emissions and climate change.

In this context, the INCDO-INOE 2000 ICIA research team studied the extraction of lipids from *Nannochloropsis oculata* microalgae using hexane and determined the composition of fatty acids for biodiesel production. The findings showed that *Nannochloropsis oculata* microalgae exhibited high lipid content and could be a potential feedstock for biodiesel production [26]. Further, the effect of sodium nitrate concentration on biomass and lipid production of cyanobacterium *Synechocystis* PCC 6803 was studied by the research group. The results revealed that the nitrate limitation increased the volumetric biomass productivity and lipid accumulation in cyanobacterium *Synechocystis* PCC 6803 [27]. In the INCDO-INOE 2000 ICIA laboratories, species of microalgae, such as *Porphyridium* spp., *Nannochloropsis* spp., and *Chlorella vulgaris,* were cultured successfully. The sub-culturing and maintenance of the *Porphyridium* spp., *Nannochloropsis* spp. microalgae in the INCDO-INOE 2000 ICIA laboratory is presented in Figure 5.

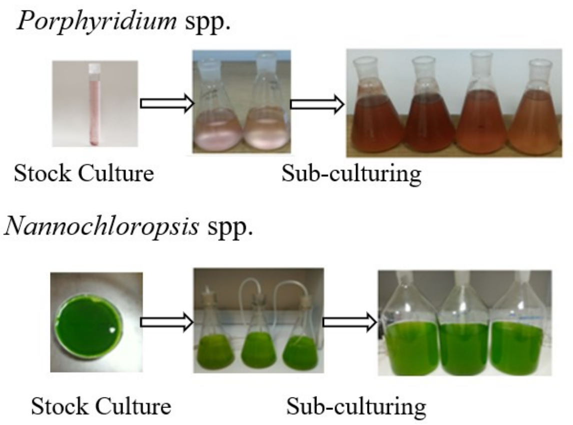


Fig. 5. Maintenance of the microalgae cultures in laboratory conditions by sub-culturing

Chlorella spp. grown in the INCDO-INOE 2000 ICIA laboratory can be observed in Figure 6. Recently, the use of chicken manure leachate as a nutrient source for cultivating *Chlorella* spp. at a laboratory scale was investigated. The results showed that the biochemical oxygen demand and the total organic carbon reduction were 96.4 % and 86.1 %, respectively, after 15 days of cultivation in chicken manure leachate. Also, the findings suggest that *Chlorella* spp. biomass cultured in this medium had higher protein content than the biomass grown in the control medium [28].

Fig. 6. Chlorella vulgaris grown in the INCDO-INOE 2000 ICIA laboratory

Within the frame of the NUCLEU project, an analytical method for lipid extraction from microalgae biomass was developed. The Taguchi experimental design method was used to optimize various parameters for lipid extraction from *Spirulina* spp. by ultrasound application and mechanical stirring. The optimum conditions were found to be: methanol: chloroform ratio of 1:1; biomass: solvent ratio of 1:60, and extraction time of 30 min, out of which the biomass: solvent ratio had the highest contribution (92.3 %) for the lipid extraction process [29]. Also, the Taguchi experimental design method was used to optimize the total reducing sugar extraction from microalgae biomass using dilute sulfuric acid for bioethanol production. The results showed that the total reducing sugar content from *Spirulina* spp. biomass after the lipid extraction was 11 %.

4.2. Technologies for bioethanol production from lignocellulosic biomass

The main components of cellulosic biomass, namely cellulose and hemicellulose, can be transformed into bioethanol. The vine shoot waste resulting from vine pruning is a lignocellulosic waste that can be used as a renewable source of biomass. Vine shoot waste has a chemical structure similar to lignocellulosic waste. It contains cellulose, hemicelluloses, lignin, and extractable substances. Bioethanol production from the by-products resulting from vineyards involves the separation of cellulosic components [30]. The possibilities to valorize the vineyard waste are presented in Figure 7.

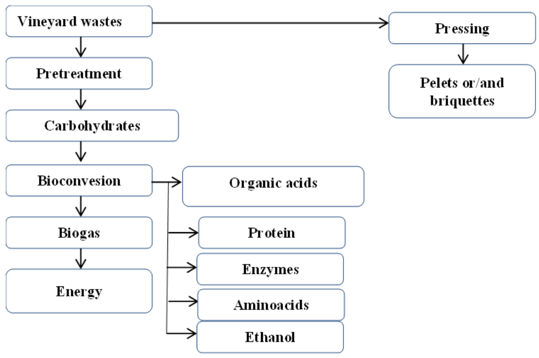


Fig. 7. Valorization of vineyard wastes (adapted after [30]).

Within the VINIVITIS project entitled "*A complex integrated system for technology optimization and superior valorization of the winemaking and viticulture by-products*", contract no. 4PCCSI/2018, technologies for bioethanol production from vineyard wastes were developed by simultaneous saccharification and fermentation (SSF) process, and separate hydrolysis and fermentation (SHF) process. The obtained technology by the SSF process is presented in Figure 8.

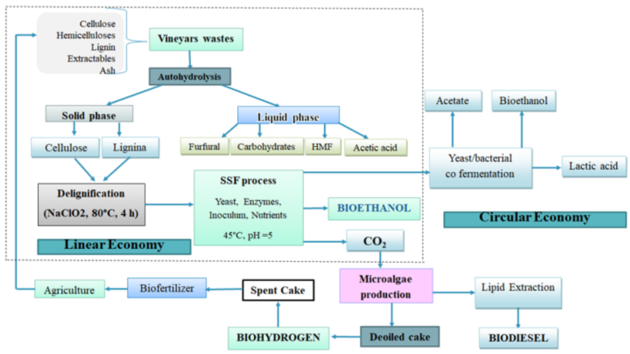


Fig. 8. Technology for bioethanol production obtained from vineyard wastes by the SSF process

The developed technology for bioethanol production from vineyard wastes by the SSF process consists of the following stages: pretreatment of vineyard wastes, delignification of pretreated biomass, and enzymatic hydrolysis and fermentation of sugars to bioethanol [31-35]. The Parr reactor, presented in Figure 9, was used for the pretreatment of vineyard wastes.

Fig. 9. Parr reactor used for the pretreatment of vineyard wastes

The conversion of polymers (cellulose and hemicelluloses) into monomers requires thermochemical and biochemical processes. Microbial fermentation transforms sugars generated from vineyard wastes into bioethanol. The developed technology for bioethanol production from vineyard wastes by the SHF process is presented in Figure 10.

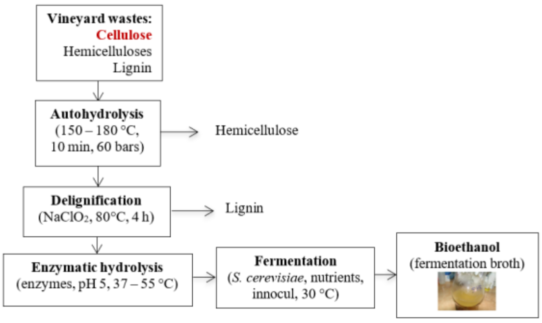


Fig. 10. Technology for bioethanol production obtained from vine shoot waste by the SHF process

Within the project entitled "*Improving lignocellulosic biomass pretreatment to increase biogas yields*", LIGNOBIOGAS, contract no. 16BM/2019, PN-III-P3-3.1-PM-RO-FR-2019-2020, a technology for biogas production from lignocellulosic waste was developed (Figure 11).

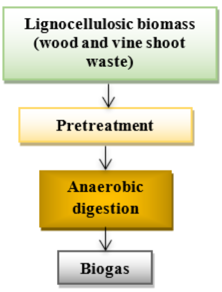


Fig. 11 Technology for biogas production obtained from lignocellulosic biomass

The reactor used for biogas production from lignocellulosic biomass is presented in Figure 12.

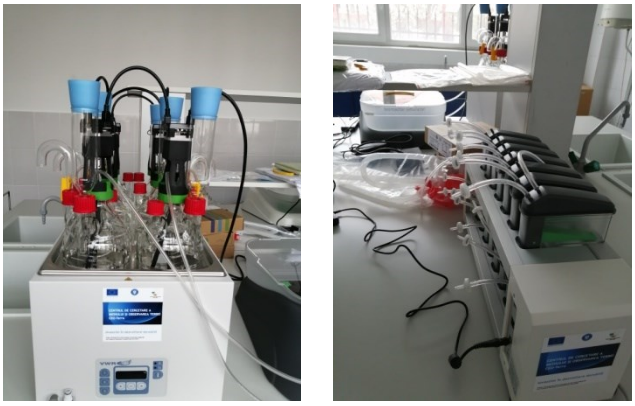


Fig. 12. Reactor used for biogas production (AMPTS II from Bioprocess CONTROL)

According to literature studies, lignocellulosic biomass can be degraded to biogas, but the major impediment is the presence of lignin. Consequently, a pretreatment step must be introduced before anaerobic digestion to remove lignin [36]. The schematic representation of the processes that take place during the anaerobic digestion of lignocellulosic biomass is given in Figure 13 [37].

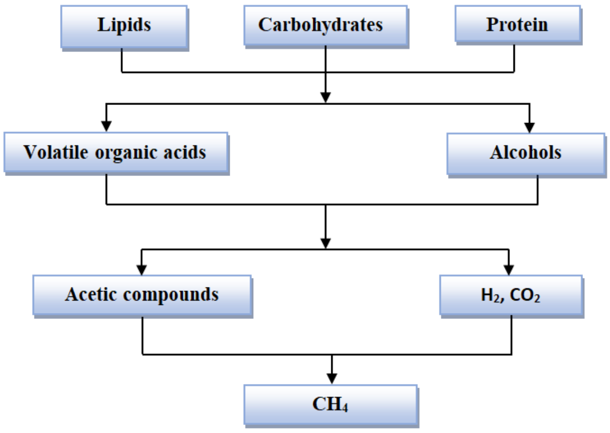


Fig. 13. Schematic representation of the processes that take place during the anaerobic digestion of lignocellulosic biomass (adapted after [37])

The combination of autohydrolysis and delignification gives a suitable substrate for the anaerobic digestion process [38].

The analysis of carbohydrates, bio-products (furfural, HMF, levulinic acid, etc.) was carried out by ultra-high performance liquid chromatography. The equipment offers the highest functionality and operates at pressures up to 1300 bars (Figure 14). The equipment contains: ♦1290 Infinity II flexible pump – quaternary pump; ♦1260 Infinity II Diode array detector for UV spectral detection from 190 to 950 nm; ♦1260 Infinity II Refractive index detector for analysis of non-UV absorbing analytes and ♦1260 Infinity II Evaporative Light Scattering Detector.

Fig. 14. UHPLC liquid chromatograph used for carbohydrates and bio-products analysis obtained from lignocellulosic biomass (Agilent 1290 Infinity II Prime LC)

4.3. Analytical methods for advanced materials recovery from IT and telecommunication wastes

Within the project "*Surveillance and control modern analytical methods for the technological flow used to obtain reusable materials from waste* (MESUCO/TRADE-IT PN-III-P1-1.2-PCCDI-2017-0652), the following analytical methods for advanced material recovery from IT and telecommunication boards were developed within INCDO-INOE 2000 ICIA to TRL 6 (technology demonstrated in relevant environment): leaching waste test method, establishing parameters for the leaching waste method, elemental evaluation of waste composition, a method for identifying the plastic compounds from waste and a method for evaluating the degree of metals recovery from waste.

The purpose of the *leaching waste test method* is to correctly identify the optimal way to carry out the leaching process so that the soluble constituents of e-waste can be accurately identified and quantified after coming into contact with water. For this, only one parameter was considered, the turbidity of the leachate. The tests were performed at room temperature and normal pressure. Distilled water was used for all trials. The electronic boards used for the measurements were initially washed with distilled water (for removing any dust) and then subjected to the leaching test for 24 hours while being immersed into a leaching agent. After 24 hours, the turbidity of the leaching solution is measured. The increase in water turbidity indicates an increase in the number of e-waste constituents in the water, which in real conditions (depositing e-waste in warehouses where they can come into contact with water) does not occur. Values below 5 NTU (nephelometric turbidity units) are considered safe for the environment. The method is based on the EN 12457-2:2002 [39] standard. The following analytical equipment were used: LS 500 Laboshake horizontal shaker, XT 220A SCS, Precisa analytical balance, and WTW Turb 555 IR turbidimeter were used.

The analytical method *establishing parameters for the leaching waste* was developed based on the SR EN ISO 10304-1:2009 [40] and SR EN 1484:2001 [41] standards. This method allows for the determination of chlorine and fluorine ions in the first phase, followed by the determination of total organic carbon and dissolved organic compounds in the second phase. The sample is pretreated to remove solids, sulfite, and metal ions, if necessary, for fluorine and chlorine ions concentration measurements. The anions of interest are separated by liquid chromatography using an anion exchange resin, and the detection is carried out using a conductivity detector (CD). It is essential that the eluents present a sufficiently low conductivity, due to the detector used. For this reason, CDs are usually combined with a suppressor (cation exchange) device that will reduce the conductivity of the eluent and convert the species in the sample to their respective acids. Methrom IC 761 Compact Ion Chromatograph is the analytical equipment used for this phase of the method.

For total organic carbon and dissolved organic compound determination, the oxidation by thermocatalytic combustion of organic carbon from water to carbon dioxide in the presence of Pt/Al_2O_3 catalyst is used. A non-dispersive infrared detection system determines carbon dioxide formed by oxidation. In the direct determination of TOC, the inorganic carbon is removed by acidulation and purging and in the case of indirect determination, TOC can be determined by subtracting the total inorganic carbon (TIC) from the total carbon (TC). The method is applied for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC) in drinking water, underground water, surface water, seawater, wastewater, and it allows the determination of the organic carbon content between 0.3-1000 mg/L concentration interval. Lower values can be determined with this method for drinking water, and higher concentrations can be determined after appropriate dilution. TOC measures the carbon content of dissolved or undissolved organic substances in water. It does not provide information about the nature of organic substances. TOC can be determined directly after the removal of inorganic carbon by purging the acidified sample with a gas that does not contain CO_2 and organic compounds. Alternatively, TOC can be determined indirectly by subtracting the TIC from the TC. This method is particularly suitable for samples where TIC is lower than TOC. The stripping process can partially remove purgeable organic substances, such as benzene, toluene, cyclohexane, and chloroform. In the presence of these substances, the TOC concentration is determined separately, or the differential method can be applied. The TOC value should be greater than the TIC or at least of similar magnitude using the differential method. Cyan, cyanate, and elementary carbon particles present in the sample will be determined together with organic carbon. Multi N/C 2100S Analytic Jena analytical equipment was used to develop and validate this method.

Elemental evaluation of waste composition method derives from ISO 17294-2:2016 [42] standard. The Elan DRC II SCIEX Perkin Elmer Inductively Coupled Plasma Mass Spectrometer (ICP-MS) was used for all the measurements during the method development and validation (Figure 15). The equipment includes a two-channel dynamic reaction cell (DRC) to reduce or eliminate isobaric and polyatomic interferences.

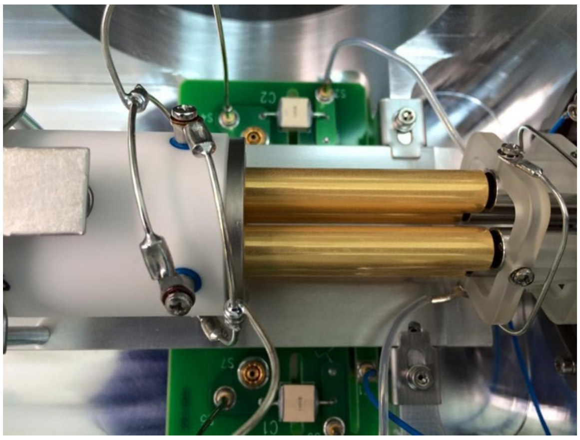


Fig. 15: Quadrupole section (mass filter) used in the Elan DRC II SCIEX Perkin-Elmer inductively coupled plasma mass spectrometer (ICP-MS) for the evaluation of waste composition

Multielement determination by inductively coupled plasma mass spectrometry includes the following steps [43]: ♦the introduction of a solution to be analyzed in a plasma induced by high frequency (the sample introduction system is performed by pneumatic nebulization) followed by energy transfer procedures generated by the plasma that cause the desolvation, atomization and ionization of the elements; ♦the extraction of ions from the plasma through a vacuum interface, using differential pumps and a system of cones and ion lenses, with integrated ion optics, and their separation according to the mass/charge ratio in the mass spectrometer (quadrupole); ♦the introduction of ions into the mass separation unit (a quadrupole) and the detection, carried out by an electron multiplier and the treatment of the ion information by a related system; and ♦the quantitative determination after calibration with suitable calibration solutions, using a calibration curve or a semiquantitative analysis (for As, Ba, Cd, total Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se and Zn). A dynamic reaction cell is used for interference control (*e.g.*, for As analysis, the mass-shift approach is used by pressuring the DRC with oxygen and shifting the determined mass from mass 75 to mass 91, since mass 75 is affected by $^{40}Ar^{35}Cl$ dimer interference).

The leachate sample from the e-waste is filtered and then transferred to a mineralization vial (using a membrane filter). In the mineralization vial, equal amounts of nitric and perchloric acids are added. Further, the sample is submitted to a microwave treatment until the mineralization process is complete. The resulting solution is fed to the ICP-MS equipment for analysis.

A method for identifying the plastic compounds from waste was developed in order to identify the following plastic compounds: acrylonitrile butadiene styrene (ABS), acrylonitrile styrene acrylate (ASA), acrylonitrile styrene (SAN), polystyrene and polypropylene from e-waste by gas-chromatography. An Agilent 6890N-5975B gas chromatograph (GC-MS) coupled with a mass spectrometer was used to develop and validate the method.

The samples (Figure 16) are introduced into a specific HP-GC vial tubes and heated to 90 °C in a water bath, then introduced into the HP-GC-MS system using a specific syringe heated to 90 °C. A specific silica chromatographic column will be used to separate the above-mentioned compounds. The furnace, injector and detector will be heated to 300 °C. A complete description of the method is presented in Kovacs et al. [44].

Fig. 16: Intermediary treatment of e-waste samples for identifying the plastic compounds using gas-chromatography and mass spectrometry

The method for evaluating the degree of metals recovery from waste was used to assess the degree of recovery of metals from leaching solutions resulting from the dissolution of exposed metals from e-waste. For this purpose, a combination of both ICP-MS (Figure 17) and X-ray fluorescence (XRF) was used.

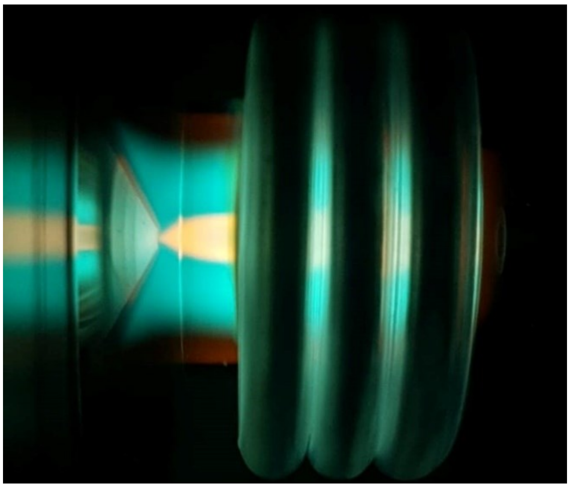


Fig. 17: Inductively coupled plasma used in a mass spectrometer for evaluating the degree of metals recovery from e-waste

The first step consists of quickly evaluating the sample metal content of solid samples by XRF analysis (before mineralization), which offers a good overview of the elemental composition, but has a relatively high detection limit (around 100 mg/kg for most elements). For concentrations below this value, further ICP-MS investigations are necessary to determine the concentration levels for As, Ba, Cd, Cr total, Cu, Hg, Mo, Ni, Pb, Sb, Se, and Zn. XRF data is also useful in determining the concentration range for an optimal interval of the calibration curve used in the ICP-MS analysis.

5. New directions of research and perspectives

The research carried out in the NUCLEU project (contract no. 18N/08.02.2019) will be extended to identify the optimum conditions for biodiesel and bioethanol production from the obtained microalgal oil and microalgal hydrolysate, respectively. The main challenges related to microalgal biodiesel production are biodiesel quality and the efficiency of the transesterification reaction. Thus, the optimum parameters for microalgal oil conversion into biodiesel (optimum catalyst dosage, temperature, agitation speed, reaction time) will be identified in order to obtain a biodiesel that meets the requirements of the European standard SR EN 14214+A2:2019 [24]. Microalgal biodiesel characteristics (including ester content, density at 15 °C, viscosity at 40 °C, flash point, sulphur content, cetane number, octanic number, water content, copper strip corrosion, oxidation stability at 110 °C, acid value, iodine value, linoleic acid methylester content, methanol content, monoglyceride, diglycerides and triglyceride content, free glycerol, alkaline metals, phosphorus content, calorific value and cloud point) will be determined to meet the requirements stated in the SR EN 14214+A2:2019 standard [24]. The microalgal hydrolysate obtained using the Taguchi methodology will be subjected to a fermentation process. Afterward, the bioethanol yield and the fermentation efficiency will be determined.

The preliminary research regarding bioplastic production from lignocellulosic biomass was obtained in the frame of the project entitled "*Innovative technologies for valorizing lignocellulosic waste to bioplastics*", LIGNOBIOPLAST contract no. TE 37/2022 (2022 -2024). The biodegradable bioplastics (PLA and PHA) will be produced from lignocellulosic biomass after applying a modern technology for the conversion of monomeric sugar into bioplastics. The technology based on supercritical conditions consists of an ecological method which disrupts the structure of cellulose and hemicelluloses.

The methods developed within the project "*Surveillance and control modern analytical methods for the technological flow used to obtain reusable materials from waste*" (MESUCO/TRADE-IT PN-III-P1-1.2-PCCDI-2017-0652) can be further extended to include other parameters for better e-waste characterization. One direction would be to extend the ICP-MS spectrometer-based methods to include other metals, particularly precious metals (Au, Ag, and Pd), since ICP-MS analytical technique excels in trace and ultra-trace concentration levels. This allows for a more thorough evaluation of e-waste before being processed and introduced into the economic cycle. The gas-chromatographic methods can also be extended to detect other organic compounds of interest. However, separation methods will have to be developed since new chromatographic columns will be needed for this new task.

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Sensors and Optoelectronic Devices for Tackling Societal Challenges

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The Department of Technological and Constructive Engineering has been one of the peer innovators in the field of optoelectronic devices in Romania. Throughout its existence, it was involved in 12 international projects and over 39 national projects, received 32 awards for its patents and over 80 prizes at international exhibitions. The innovative equipment developed by the department members and their collaborators have aided in ensuring a better and safer life for many people. Its involvement in a wide range of applications and its ever-extending field of research and development bring the department to the forefront of international research.

Keywords: optoelectronics, lasers, sensors, fibre optics, health, plasmonic, environment.

1. Introduction

Novel engineering systems, sensors and intelligent systems are increasingly used in society and in the living environment. Cutting-edge technology is an essential tool in improving the quality of life, promoting sustainability and progressing towards smart infrastructure, homes or hospitals [1,2]. Sensors and optoelectronic devices evolved, in the past decades, due to digitization and miniaturization trends, providing clear benefits for applications such as, food safety, hazards detection, health monitoring and treatment, environmental monitoring, communication, aerospace, smart vehicles, improved road traffic, smart phones etc. [2–5]. Scientists are continuously trying to optimize the sensitivity, accuracy and longevity of sensors and optoelectronic devices [6] and to incorporate these technologies into intelligent systems towards the benefit of society. This is also the aim of the team from the *Department of Technological and Constructive Engineering – lasers, laser devices and fibre optics*.

The main objective of the department is to develop fundamental and applied research in the field of optoelectronics: solid state lasers, image acquisition and processing and interaction of electromagnetic radiation with matter. The team also optimizes and incorporates lasers, optical devices and optical amplifiers in intelligent systems with various applications. In addition, the department is involved in researching sensors and fibre optic communications, oriented towards the development of intelligent devices for industry, medicine, environment and energy. The activities of the department are in line with the European Union Missions on *Conquering Cancer*, developing a *Climate Resilient Europe* and helping to *Restore our Ocean and Waters*. The activities also contribute towards the achievement of the United Nation's Sustainable Development Goals. The department's objectives address mainly SDG3 *Ensure healthy lives and promote well-being for all at all ages* by developing optoelectronic systems for cancer detection, surgery, blood sampling, wearable health monitors, narcotic drug detection, microbial contamination in food and water. The team also addresses SDG6 *Ensure availability and sustainable management of water and sanitation for all* by involving in research regarding protection and restoration of aquatic ecosystems. It also contributes to SDG 9 *Build resilient infrastructure, promote inclusive and sustainable industrialization and foster innovation* by providing novel solutions to information and communications technology. Finally, it responds to SDG 11 (*Make cities and human settlements inclusive, safe, resilient and sustainable*), SDG 13 (*Take urgent action to combat climate change and its impacts*) and SDG 15 (*Protect, restore and promote sustainable use of terrestrial ecosystems, sustainably manage forests, combat desertification, and halt and reverse land degradation and halt biodiversity loss*) by involving in research related to anthropogenic impact on aquatic ecosystems health and the increase of natural hazards in urban and peri-urban environments.

This chapter describes the main activities and results of the Department of Technological and Constructive Engineering [7], reflected through the numerous projects and collaborations developed in over 25 years since its foundation (Fig. 1). The history of the department and the landmarks that defined the diversified nature of the main topics and applications will be presented. The main results of the department will be discussed in relation to fundamental societal challenges: ensuring effective and accessible health instruments, providing solutions to environment protection and response to natural hazards, developing fast information and communication devices, ensuring road safety. Also, the main infrastructures, and their objectives and services, will be introduced. Finally, the perspectives and recent directions of research will be discussed.

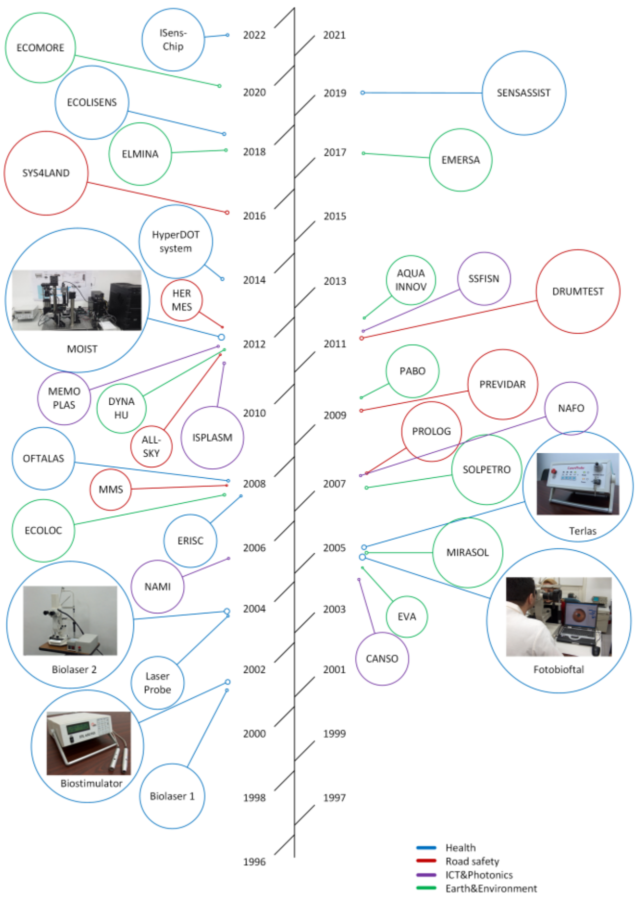

Fig. 1. The constellation of projects and results of the Department of Technological and Constructive Engineering.

2. History and landmarks

The Department of Technological and Constructive Engineering was established in 1996, when the National Institute of Research and Development for Optoelectronics, INOE 2000, was founded. Since its establishment, the department has been led by Dr. Eng. Dan Savastru and gathered a team of engineers, theoretical physicists, biophysicists and medical physicists. Great emphasis was given to the influx of young graduates, who have undertaken their master and doctorate studies in the department's laboratories and have continued their research under the same affiliation.

The department started its activity with applied research under contracts with SMEs. Thus, between 1996 and 2000, the team developed several optical devices, such as a system for the detection of underground metal objects or binoculars with laser telemeter (Fig. 1). Considering its successful collaboration with SMEs, in 2001, the department enlarged its research sphere by constructing medical devices. The first such system was a laser microscope used for surgical and post-surgical treatment of eye disorders, BIOLASER 1 (Fig. 2). Specifically, the system was designed for eye surgeries, such as posterior capsulotomy and pupillary membranectomy. The laser pulse energy could be varied in 11 steps, allowing its use in diverse surgical circumstances. After performing several tests at the Eye Emergency Hospital Bucharest, the system was medically graded and put into production by S.C. IOR S.A. Bucharest. The laser microscope was awarded the AGIR 2003 grand prize. This system was the foundation for technologically improved models, such as FOTOBIOFTAL, BIOLASER 2 and OFTALAS.

Fig. 2. The BIOLASER 1 system.

FOTOBIOFTAL contained a biomicroscope and a module for image acquisition, processing and storage, used in eye surgery, iridology etc (Fig. 3). The image module included a digital camera and was made of two sub-assemblies: a divisor and an adaptor tube. The divisor was specifically designed with the following characteristics: to ensure image transmission towards the eye and reflection at a 90° angle towards the digital camera, 50% / 50% division ratio, size fitted to collect the entire beam on both ways. The images were processed with a specific software, which also stored main data about the patient, such as date, diagnosis, treatment and eye image.

Fig. 3. The FOTOBIOFTAL biomicroscope with image acquisition, processing and storage, used in eye surgery or iridology.

BIOLASER 2 system (Fig. 4) was an improved version of BIOLASER 1. This biomicroscope allowed a greater variation of laser pulse energy, compared to its predecessor. This version could be used for new microsurgery procedures of the anterior and posterior eye chambers. The system was patented and was awarded gold medals at the ARCA Exhibition, in Zagreb, Croatia in

2008, and at the EUREKA International Competition, in Brussels, Belgium, also in 2008. In addition, it received a silver medal at the Geneva International Exhibition of Inventions, in 2009.

Fig. 4. The BIOLASER 2 system.

OFTALAS was the last system developed for eye disorders. Its design started in 2008, during a collaboration with S.C. Apel Laser S.R.L. The device used a solid state YAG:Nd laser, which emitted very short pulses in the infrared wavelength region (Fig. 5). It was also equipped with an optoelectrical modulator to continuously attenuate the laser radiation. The system allowed the stereoscopic examination of the transparent media of the cornea and the execution of microsurgery procedures of the anterior and posterior eye chambers. OFTALAS modules were also patented and received gold medals at the ARCA Exhibition, in Zagreb, Croatia and at the EUREKA International Competition, in Brussels, Belgium, in 2008.

Fig. 5. The OFTALAS system.

Starting with 2002, other medically graded systems were developed: the BIOSTIMULATOR and the LASERPROBE. The BIOSTIMULATOR (Fig. 6) was used for low level laser therapy and it included a low power laser diode that emitted in continuous or pulsed waves. It could be used for specific procedures of irradiation in dental health care, dermatology, rheumatology, traumatology, sports medicine, gynaecology, otorhinolaryngology, gastroenterology, plastic surgery or acupuncture.

Fig. 6. The BIOSTIMULATOR system for low level laser therapy.

The LASERPROBE was constructed in 2004 (Fig. 7) in collaboration with the National Institute for Laser, Plasma and Radiation Physics. This was a solid state Er:YAG surgical laser instrument for in vivo blood sampling. LASERPROBE sent focussed laser mono-pulses to easily puncture the skin for contactless and painless collection of blood droplets, needed to monitor diabetes or hepatitis. This solution offered maximum protection from contamination of the sample. The system was transferred to S.C. PRO OPTICA S.A. for commercial production.

Fig. 7. The LASERPROBE system for blood sampling.

The department contributed to cancer research by designing and constructing several devices based on optical coherence tomography and laser technologies. The first such device was developed in 2006, in collaboration with the National Institute for Laser, Plasma and Radiation Physics. The BIOT system, which included an infrared optical tomograph, offered accurate detection of breast cancerous lesions (Fig. 8). The system contained two laser diodes emitting at 780 nm and 835 nm.

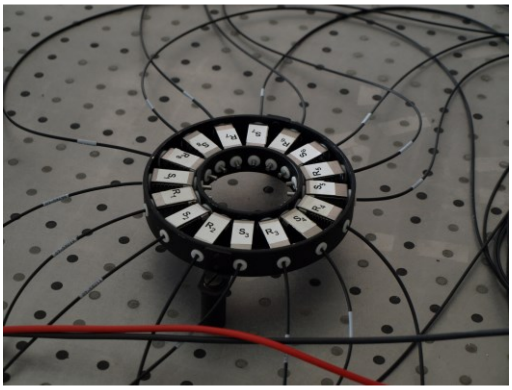

Fig. 8. BIOT system, the first device for breast cancer detection developed within the Department of Technological and Constructive Engineering .

Research and development on medical devices for cancer detection continued in 2012 with the MOIST system for breast cancer surgery (Fig. 9). This was a benchtop real-time multimodality imaging system for guiding breast tumour resection by intraoperatively evaluating the status of surgical margins on the excised specimen. The multimodal imaging instrument combined two systems: an SD-OCT system (Spectral-Domain Optical Coherence Tomography) and a reflectance/fluorescence imaging system. The instrument had the following parameters: 1310 nm, spectral resolution 1.2 mm, and image field of 2.5 mm in air and 1.75 in tissue. It successfully identified all types of tissue near the tumour, it could generate a map of all tissue types and it could evaluate the relative surface of each identified tissue type. The MOIST system led to the development of an improved version named HyperDOT. This system was based on a novel and accurate imaging technique combining diffuse optical tomography (DOT) and hyperspectral fluorescence (HF). It was able to provide a valuable adjacent method to current clinical mammographic investigation modalities. This clinical use functional model was capable to detect in real time the nature of the lesion, by reconstructing tissue images, with a probability of over 92 %. At the time of its construction, HyperDOT system exceeded the characteristics of marketed systems.

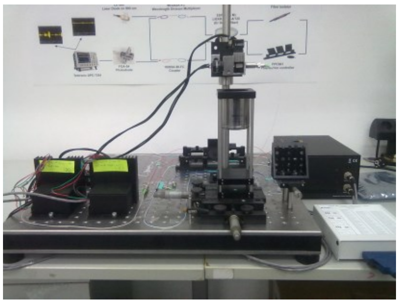

Fig. 9. MOIST system, the multimodal imaging instrument based on (Spectral-Domain Optical Coherence Tomography)

In parallel to the medical devices research, the department established a long term collaboration, since 2001, with the Joint Institute for Nuclear Research from Dubna, Russia. The collaboration started with the reconstruction of the local network of the Nuclotron automated control unit using fibre optics technology. Later, the department participated in the digitalization of the Nuclotron physics experiments and the modernization of the main control unit. In 2005, it contributed to the development of the upgraded control system for the Nuclotron. In 2008, the department participated at the upgrade of the data acquisition system and associated software, needed for the Nuclotron control unit. In the following two years, the team developed and equipped the local network of the Nuclotron with devices and software. In 2011, the department engineered a fibre optic system to monitor the profile of the Nuclotron beam.

One main topic of research involved plasmonics used for the development of optoelectronic devices. These studies were also the foundation of another fruitful collaboration with the National Institute for Laser, Plasma and Radiation Physics and the University Politehnica Bucharest. The first project, NAMI, funded starting with 2005, led to the development of amorphous nanostructures for intelligent memory devices, based on multicomponent chalcogenide materials. Further projects, such as MEMOPLAS [8] led to the development of all-optical memory using photo-induced – optical dichroism that occur in films of semiconductor chalcogenide glasses after the irradiation with polarized light (Fig. 10). This innovative method allowed processing speeds 1,000 times higher than conventional memory devices. Similar materials were used for the construction of optoelectronics sensors, chemical sensors development of photonic crystals or micro lens networks. These solutions were patented and received gold medals at the Geneva International Exhibition of Inventions, ARCA Exhibition, in Zagreb, Croatia and at the EUREKA International Competition, in Brussels, Belgium, PROINVENT Cluj Napoca or the European Exhibition of Creativity and Innovation, starting with 2007.

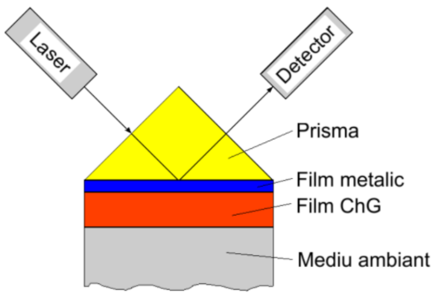

Fig. 10. Surface plasmon resonance structure with amorphous chalcogenide film which involve foto-induced dichroism.

Another key research topic of the department was represented by safety and security with several projects and activities, starting with 2007. The first project, PROLOG, developed a method as well as an equipment for dynamic testing of road and highway pavement uniformity on longitudinal direction. The system could also be used for airstrips. In order to achieve these profiles, a laboratory vehicle (Fig. 11) was equipped on its side with laser sensors that measured the longitudinal road profile and the vertical movement of the vehicle, without the use of inertial references, which have been generally used in commercial technologies.

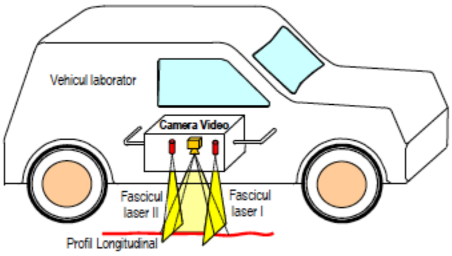

Fig. 11. The design of the PROLOG system mounted on a laboratory vehicle.

The research made under PROLOG project allowed the development of a complex robotic system for video data collection of road surfaces, PREVIDAR (Fig. 12). The equipment integrated the data regarding road cross profiles and GPS data, with GIS data. Specifically, it simultaneously marked two cross sections of the road using two continuous laser beams and collected images of the section with a high resolution camera. The digital images were further processed to extract numerical data that allowed the detection of pavement defects, such as grooves, fissures and cracks.

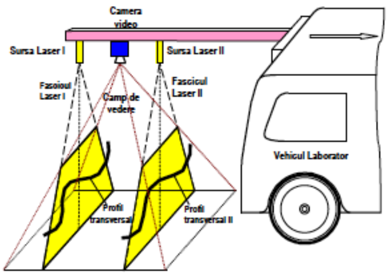

Fig. 12. The design of the PREVIDAR system.

The system was further upgraded during the DRUMTEST project, funded under the Sectoral Operational Program. The system was completed, in 2014, within the FP7 HERMES project in collaboration with research institutions and SMEs, experts in technologies development and product marketing. The final system allowed more effective measurements of road profiles, compared to previous prototypes, by fast integration of GPS data and powerful processing of the immense database generated by the HERMES vehicles. It provided quick information on the locations that required urgent repairs, improving the road safety and reducing the costs of monitoring pavement profiles. In 2016, the prototype was awarded gold medals at the at the EUREKA International Competition, in Brussels, Belgium, and at the Geneva International Exhibition of Inventions.

The department also contributed to the safety and security domain with two main projects, ISPLASM and ALLSKY, funded in 2012 by the Executive Unit for Funding of Higher Education, Research, Development and Innovation (UEFISCDI). Within the ISPLASM project, the team developed, in collaboration with the National Institute for Laser, Plasma and Radiation Physics, an original designed system interface coupled to mass spectrometer. Specifically, the system was an ultra-fast, easy to use and low cost solution dedicated to the surface analysis (nanometre (nm) depth resolution) of soft materials (skin, clothes, paper, etc) contaminated with drug traces. Not only that this system provided an analysis in a few seconds, but it also allowed direct simultaneous elemental and molecular measurement with an increased detection sensitivity of the mass spectrometer of 1 ppm [9]. The invention received a special prize from the State Office for Inventions and Trademark, Romania. It was also awarded a gold medal at the Geneva International Exhibition of Inventions, in 2016.

The ALLSKY project led to the development of a station radio / video assisted GPS / Galileo for meteor detection. The system provided an integrated solution of detection and filtration of false positive data for radio detection of meteorites. It used a national network of stations, connected to a central server. The system's software corroborated the video information with radio data and normalized the final result with the ultraprecise time offered by GPS/Galileo network. This would allow the construction of a national networks with such stations to automatically monitor the Romanian air space, at altitudes between 20 and 70 Km, and to trace the meteor trajectories.

In the past two decades, the department also focussed on generating solutions for reducing the impact of natural hazards. One such project was SyS4LAND, where together with SMEs, the team constructed a system for detection, monitoring and real-time analysis of landslides [10]. The system was based on the 4G technology and used the triangularization method integrated with wireless sensors to detect, in real time, events in risk areas (Fig. 13). This proved highly efficient in natural hazards management and increased the ability of authorities to act in emergency cases.

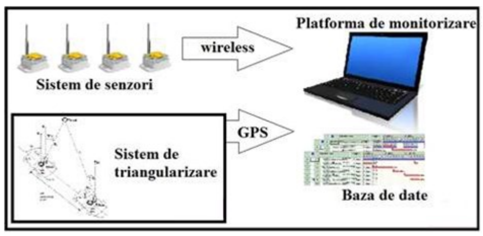

Fig. 13. The design of the Sys4LAND system.

Great importance has been given to continuous monitoring, surveillance and assessment of seismic hazard in Romania due to Vrancea source. Through analysis and applied mathematical models for time-series data of in-situ and geospatial seismic pre-signals, the research team forecasted and located future moderate earthquakes, and developed proper solutions for preventing and minimizing possible damages. Several projects were undertaken over the years focussing mainly on the Vrancea region [11,12], which is a tectonically active region, associated with strong and moderate depth earthquakes (Fig. 14), posing a significant seismic hazard/risk in South-East Europe [13,14]. The team integrated available satellite, GPS and *in situ* geophysical data to characterize seismic hazards and determined the earthquake precursors. Specifically, the team used multispectral and multiresolution time-series satellite data from MODIS Terra/Aqua, Landsat TM/ETM/OLI, IKONOS, together with ESA software tools, such as EnviView, ESOV and NEST. Services for seismic hazard assessment, surveillance and mapping were extracted from each project.

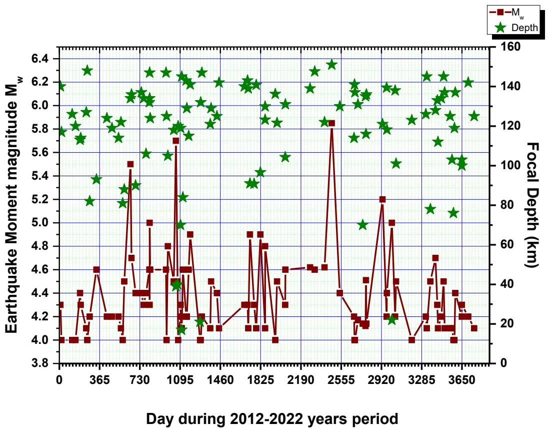

Fig. 14. Seismic activity in Vrancea region during 2012-2022

Satellite data were also used to assess the anthropogenic impact on the urban environment. One such project, BUGREEN, provided an advanced geospatial monitoring system of urban vegetation dynamics, spatial and temporal evaluation framework of anthropogenic and climatic stressors impacts on different urban/peri-urban test sites of Bucharest metropolitan area [15]. The team combined in-situ monitoring of biogeophysical/climate parameters with information derived from long time-series satellite remote sensing data (NOAA/AVHRR, MODIS, ENVISAT MERIS, SPOT, Landsat TM/ETM, IKONOS, Qickbird, METEOSAT MSG 2-3 and Sentinel missions). Based on this dataset, it was able to develop spectral climatic/ecological models at different scales and validate them as analytic methods needed for locating urban vegetation "hot spots" areas. Another project, GEOLASDATA, used satellite and georeferenced data to provide a novel solution for integrated assessment of industrial and mine landfills. It applied the Trimble technology with a field controller, equipped with GPS to test landfill areas.

A final topic of research within the department was related to finding solutions for the evaluation of aquatic ecosystems. The first project, EVA, funded in 2005, focussed on the ecological reconstruction of the lower Arges Basin, which was severely affected, in the past decades, with pollution from urban and rural sources. The team was able to identify a method based on fluorescence spectroscopy to quickly identify microbiological pollution in water (Fig. 15). This technique was improved along the years, and in 2014 it was patented and awarded a gold medal at the Geneva International Exhibition of Inventions, in 2016. The method was further integrated in studies and projects aiming to assist in environmental management in urban residential areas, or to investigate soil pollution with aromatic hydrocarbons. Furthermore, based on its expertise, the team was involved in a large collaborative project to study the environmental, ecogeomorphological, social and economic specificities of the urban fringe zones [16]. The collaboration led to the development of an innovative service for the analysis and prediction of land use (SINOLand), useful for land planning and environmental impact studies.

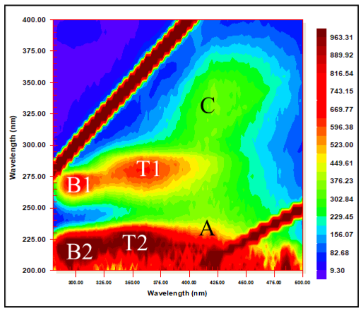

Fig. 15. Fluorescence excitation-emission matrix of sewage sample.

In 25 years, the Department of Technological and Constructive Engineering has coordinated or participated in 12 international projects and over 39 national projects. These led to 32 awarded patents for systems and methods, and received over 80 prizes at international exhibitions. In addition, the number of publications in ISI indexed journals has increased over the years, reaching over 250 papers (Fig. 16).

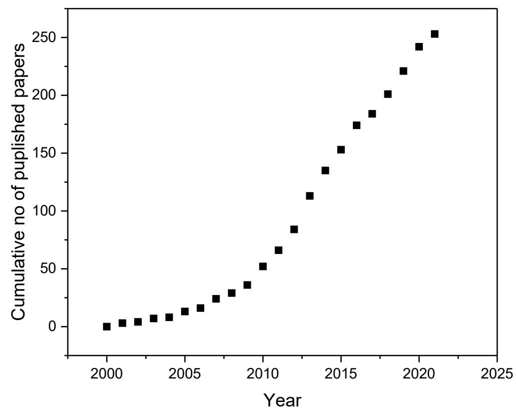

Fig. 16. The progress of ISI indexed publications in the period of 2000 and 2021.

3. Current developments and collaborations

Access to infrastructure funds allowed the establishment and upgrade of the main department facilities, where most of the studies and projects were undertaken. The evolution of the main facilities increased the portfolio of collaborations with world leading institutions. The Infrastructure of characterization and diagnosis by optical and complementary methods (INDICO) was established in 2007 and certified for standard measurements in Romania and the European Union [17]. The Laboratory for optospectral methods for water quality assessment (MOCA) was developed starting with 2006 [18]. Both facilities were upgraded with state of the art equipment, between 2017 and 2020, under the CEO-Terra project, co-funded by the European Fund for Regional Development, through the Competitiveness Operational Program 2014-2020.

3.1. INDICO

The main aim of INDICO is to characterize materials, components and systems with applications in optoelectronics, by optical and complementary methods, according to the requirements of the European Union regarding assessment of compliance with technical regulations. Specifically, the methods offered by INDICO relate to the measurement of specific optical parameters for optoelectronic applications (identification and characterization of the composition of some materials used in optoelectronics, measurement of the output level in optical fibres and amplifiers, laser emitted energy, laser pulse width, laser beam diameter, intensity distribution, deviation from Gaussian distribution, divergence). The measurement of the components parameters that form the basis of optoelectronic systems and parts is necessary for the development of devices that incorporate lasers, optical fibres, optical amplifiers, optoelectronic materials, in accordance with European quality standards. INDICO aims to create in Romania the necessary framework for the manufacture of components and systems in accordance with European Union quality certification requirements.

The certification of INDICO by RENAR accreditation authority has allowed the infrastructure to reach a European level of testing requested by legal and individual entities interested in optoelectronic devices. INDICO is grouped into the following areas of activity: a) characterization of the laser beam: waist, divergence, M^2, energy/power distribution; b) measurement of the energy/power of the laser beams and laser pulse width; c) characterization of optical components: focal lengths, radii of curvature, flatness of components with flat surfaces, angles of optical prisms; d) characterization of propagation through optical fibres: attenuation as a function of travelled distance and measurement of optical power at the exit of the fibre (Fig. 17).

The infrastructure assigned activities refer to: development of the technical capacity of INDICO through the efficient purchase of equipment; development of Quality Management System documents for the laboratory; development, testing and demonstration of the functionality of test methods; training of personnel in quality management; demonstration of the implementation of new methods through internal audit; preparation and registration of documents for laboratory certification.

Fig. 17. The INDICO facility.

In addition, INDICO allows high-precision determinations for the quality evaluation of subassemblies and systems with laser and fibre optics, and the characterization by optical methods of the composition of materials for optoelectronics in order to determine the non-conformities that have arisen as a result of non-compliance with the technical specifications/ or non-compliance with the instructions for use with repercussions on those who use them.

3.2. MOCA

The Laboratory for Optospectral Methods for the Evaluation of Water Quality is the only infrastructure in the country that allows a comprehensive approach to investigate dissolved and particulate organic matter and emerging pollutants in aquatic systems. The establishment and modernization of MOCA laboratory sprung from the society's need to have varied and sustainable ecosystem services. National and international policies are moving towards the development of smart cities for a resilient and sustainable society, considering the continuous urbanization of the planet. Blue infrastructure plays an essential role in keeping a balance by ensuring ecosystem services for health maintenance, climate regulation and provision of cultural benefits. MOCA laboratory contributes to the development, at national level, of the capacity to detect and characterize a wide range of compounds through state-of-the-art complementary methods, improving the quality of ecosystem services in the urban environment. It also stimulates collaboration between researchers and the public in the assessment of aquatic ecosystems quality and the detection of surface waters accidental pollution.

The core concept of the laboratory is to provide rapid, qualitative and quantitative information on water quality using fluorescence spectroscopy in tandem with chromatography and microbiology techniques (Fig. 18). MOCA offers a unique combination of instruments for the characterization of environmental components, such as dissolved organic matter, polyaromatic hydrocarbons, natural and engineered nanoparticles. Therefore, MOCA laboratory is intrinsic to the advancement of scientific research on ecosystem quality considering the ever-increasing number of emerging pollutants in the environment and the constant need of finding better techniques for pollution detection, characterization, monitoring and early warning.

Fig. 18. MOCA Laboratory.

3.3. Current collaborations

The Department of Technological and Constructive Engineering has established long-term collaborations with many prestigious institutions, such as the National Institute for Laser, Plasma and Radiation Physics, National Institute or Materials Physics, National Institute of Earth Physics, University of Bucharest, University Politehnica Bucharest, Technical University of Civil Engineering Bucharest etc. At international level, the department has established collaborations with institutions from Australia, Bulgaria, Estonia, France, Greece, Italy, Russia, Spain, United Kingdom, United States of America etc. In addition, important collaborations were created with national and international SMEs to effectively exploit the commercial potential of the systems developed within the department. Long-standing partnerships were formed with WING Computers and Apel Laser, from Romania.

Recent collaborations of the department relate mainly to the latest research projects. Thus, the team cooperated with WING Computers and Grado Zero Innovation to develop methods and optoelectronic devices for medical applications, which resulted in two European funded projects. Moreover, the department collaborated with University Politehnica Bucharest and Apel Laser SRL to develop plasmonic materials for innovative memory devices.

Recently, MOCA laboratory performed studies in collaboration with the Centre for Environmental Research and Impact Studies (UB-CCMESI), University of Bucharest and the Centre for Research and EcoMetallurgical Expertise (ECOMET), University of Politehnica Bucharest. The collaborations targeted both scientific research activities and the implementation of student internships in the MOCA laboratory. The cooperation is based on the expertise gained by MOCA team regarding the application of optoelectronic methods for investigating water quality. Thus, the team carried out studies, together with UB-CCMESI, for the characterization of organic matter in aquatic systems, as part of annual campaigns to collect and measure water samples from Bucharest lakes, the lakes on the island of Ostrov (Caraș-Severin) and the Danube River (Brăila). The team also characterized, together with ECOMET, the size distribution of micro- and nanoplastics in water samples collected from various aquatic systems in Europe.

4. Recent results and transfer of results

The department continues its research and development of devices and sensors for medical applications. In the past 5 years, it undertook two European projects, ECOLISENS and SensAssist, in collaboration with SMEs from Romania and Europe, for the transfer of results. ECOLISENS project led to the design of a long period grating fibre sensor (LPGFS) demonstrator for real time detection of pathogen bacteria E. Coli [19]. LPGFS operation was based on the detection of ambient refractive index variation induced by the presence of E. coli bacteria. The demonstrator had a small volume measuring chamber where liquid phase sample, suspected to be infested with E. coli, was placed. It consisted of a Sensor Interrogation Module (SIM LPGFS and Optoelectronics) and a Data Acquisition and Processing Unit (DAPU). The system was low cost, portable and highly sensitive and could provide a result in 5 to 10 min. (Fig. 18). With increasing public recognition of threats from bacteria induced diseases and their outbreak potential among densely populated communities, an intrinsic, low-cost biosensor device that can perform quick and precise identification of the infection type is in high demand to respond to such challenging situations and control the damage induced by those diseases. The device based on LPGFS could be used for other types of pathogenic bacteria strains or chemical substances present in gaseous or liquid phase samples.

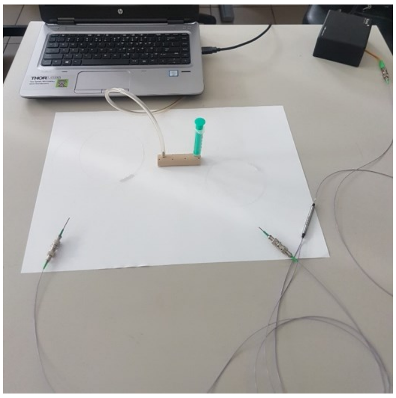

Fig. 18. The set-up of the ECOLISENS device

The SensAssist project, which started in 2019, was also made in collaboration with SMEs for technological development and transfer of results [20]. During this project, the team designed a system for automatic monitoring of 3 biological parameters (EEG, ECG and pulse oximetry), permanently wearable by the patient. This wearable solution monitored the patient's health 24 hours a day, transmitting the collected data via mobile phone (Android and iOS platforms) to a monitoring centre, where an eHealth platform managed the patient's health status information (Fig. 19). From the monitoring centre, the patient was managed by an automatic assistance platform. The systems developed within the ECOLISENS and SensAssist projects were patented and, in 2020, were awarded gold medals at the Inventions and Innovations International Exhibition from Timisoara, Romania.

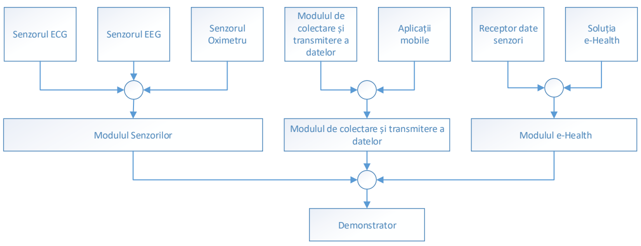

Fig. 19. Diagram of the SensAssist solution.

Plasmonic research is also continued with the development of memory devices and health related solutions. In a recent project, FOMAN [21] designed an innovative fast plasmonic optical memory based on photo-induced optical anisotropy. It was based on a technology already validated in the laboratory, during project MEMOPLAS, and took this solution from experimental demonstrator level (TRL3) to a validated technology (TRL4). The technology will be transferred in the future to economic agents. Plasmonic technology will also be applied to the team's latest project ISens-Chip, which will end in 2024. The project aims to develop an innovative surface plasmon resonance (SPR) multi-sensor concept based on grating coupling in four layer's SPR configuration with plasmonic wave guide made of high refractive index amorphous chalcogenide film for detection of chemical and biological pollutants in liquids.

Hazard research has been undertaken in the recent complex project VESS - Extensive capitalization of experience in Space and Security activities. The department participated in subproject 3, Integrated geospatial and in-situ monitoring platform of the lithosphere-low atmosphere coupling- ionosphere for monitoring and predicting moderate and strong earthquakes in the Vrancea area in Romania (PIMS), VESS 3-PIMS. The aim of the project was to increase the institutional performance of the partners in the field of space and security, supporting the Romanian involvement in the activities of European Space Agency.

The department also strengthened the research in the environmental field, considering the upgrade of the MOCA laboratory. Consequently, the team, in a collaboration with the Remote Sensing Department from INOE, led by UB-CCMESI, assessed the potential changes in urban ecosystem services supplied by urban lakes under land use and climate change, based on the Smart Cities principles. Thus, a series of innovative and traditional methods (e.g., spatial modelling, scenarios, fluorescence, sensors, remote sensing) were used to determine the evolution of ecosystem services for urban lakes, under the pressure of urbanisation and climate change. At the end of the project, a multicriteria spatial model was proposed to validate and generate an integrative overview of urban lake ecosystem services supply.

Another recent project, ELMINA, focussed on the main characteristics and the behaviour of microplastics in wastewater and drinking water. The studies helped the team to gain new insight on the interaction of microplastics with water components, microplastics weathering processes and their removal during treatment stages. Also, the role of the public in monitoring the levels of pollution in aquatic ecosystems was evaluated in the recent project ECOMORE [22]. During the project, the team developed a user-friendly and free platform, Aqua S.O.S. (Fig. 20) for collecting water related data [23]. This platform allowed the team to collect large data sets, from two campaigns, with qualitative and quantitative information regarding the quality of water systems in Romania. Based on the results, research reports were sent to the Ministry of Research, Innovation and Digitalization and the Ministry of Environment, Water and Forests.

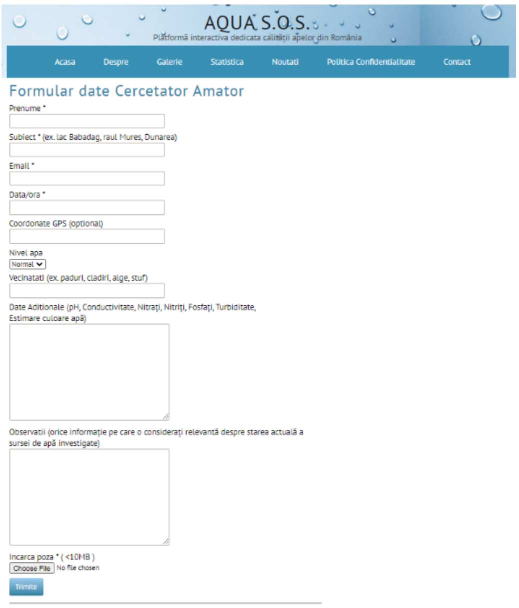

Fig. 20. The Aqua S.O.S. platform used by the public to send water quality data.

Finally, the department also supported research on the connection between anthropogenic stressors and COVID-19 pandemic. The team analysed observational and geospatial data to determine how much certain environmental parameters, such as air particulate matter, radon, nitrogen dioxide or sulphur dioxide, affected the incidence and mortality of SARS-CoV-2 virus [24,25]. These studies were made to provide useful information to public health authorities and decision makers in managing future pandemics and urban pollution.

5. New directions of research

The department's new directions of research relate to the recent projects and collaborations. Thus, the team will focus on applying the SPR technique for sensors development. Another recent direction for research relates to a system for determining the dielectric parameters of the saline environment, useful in the detection of cosmic radiation and in telecommunications. Moreover, MOCA laboratory opens new horizons in Romania regarding the concept of citizen science. International citizen science programs have had significant successes in the field of environmental quality monitoring. A productive partnership between researchers and the public can increase the temporal and spatial resolution of environmental data, providing complementary information on aquatic ecosystems. Science with citizens is an effective framework for exchanging knowledge on environmental issues, raising awareness, reconnecting people with nature and promoting an ecological attitude. Essentially, citizen science activities led to the democratization of the environment and science, in general.

6. Perspectives

The department aims to expand the Institute's capacity in the development of techniques and technologies based on sensors, optical fibres or electromagnetic wave detectors, useful in creating new state-of-the-art photonic devices with applications in medicine, environmental protection, industry, security and aerospace. Thus, the department will overcome frontiers in the research of photonic devices, by answering to some of the current scientific problems. New concepts of multilayer plasmonic structures coupled to optical fibres will be developed, LPG and optical micro/nanofiber types sensors will be developed. Also, technologies for the production and use of fibre optic lasers doped with Yb ions will be developed. Moreover, various fibre sensors will be used to detect water contamination with pathogens, after extreme weather events.

Acknowledgements

The department acknowledges the dedication and support of Eng. Sorin Miclos and Dr. Eng. Laurentiu Baschir. Sorin Miclos was one of the main pillars of this department. His innovative vision led to development of most of the systems described in this chapter. Laurentiu Baschir brought enormous enthusiasm and leadership skills to the team and helped establish new collaborations and open new areas of research. Sorin and Laurentiu will be greatly missed. The department also acknowledges the support of Dr. Gabriela Pavelescu, who, with immense dedication and guidance, established and modernized the MOCA laboratory.

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Optoelectronic developments with impact in Heritage Science

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The activity of the Center of Restoration by Optoelectronic Techniques (CERTO) is focused for over 20 years on the development of new remote sensing methods, technologies and systems for Cultural Heritage conservation and restoration, as well as new concepts for scientific approach and data processing.

Keywords: Heritage Science, Optoelectronics, laser, remote, in-situ

1. Introduction

CERTO's activity combines perfectly the science and art fields (with an emphasis on valorization), pioneering in developing non-contact, non-invasive, remote equipment and methods for *in situ* investigation and diagnosis of Cultural Heritage, but most importantly - a new research field: **Heritage Science**. The scientific progress, obtained in over 20 years of activity, is internationally appreciated and it directed the group to participation in major national and international committees, projects and shared infrastructures.

Following a visionary path, in 2006 CERTO developed a **mobile laboratory for *in-situ* investigation, diagnosis, analysis and intervention on heritage, ART4art** - a complex infrastructure, unique in the region due to its original architecture that generates complex data packages covering the full cycle of needs: *monitoring, documentation, analysis and diagnosis, intervention*.

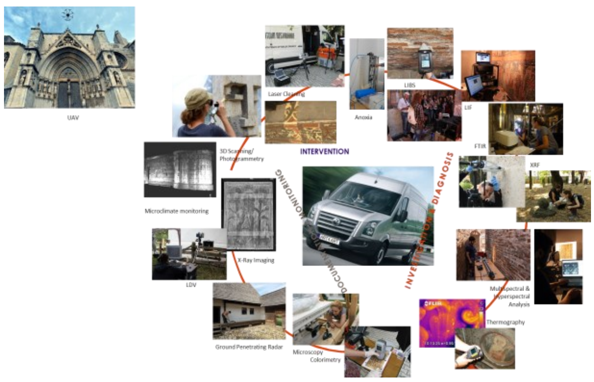

Fig. 1. ART4art mobile lab – 2022

The ART4art mobile-laboratory has remote operation capability, high autonomy and can collect and correlate data without sampling or sample preparation, related to volume, positioning, structure, pollutant deposits, physico-chemical characteristics, identification/ discrimination and charting of specific materials (pigments, binders, consolidants, underlayers, preparatory drawings etc.), chemical stratigraphy of multilayer structures, detection and mapping of hidden defects/compositions, underground objects and structures, and more of the sorts.

ART4art, described in *Fig. 1*, has also an aerial feature: an Unmanned Aerial Vehicle (UAV) with photogrammetry, thermography, multispectral imaging analysis and LIDAR sensors, that was added in 2015 together with handheld X-Ray Fluorescence Spectroscopy (XRF), mobile X-Ray, and a mobile hyperspectral system, under the European Regional Development Fund project: INOVA OPTIMA.

CERTO is authorized by the Romanian Ministry of Culture [1] since 2014 as restoration and conservation laboratory for investigation and diagnosis of CH and it is the initiator of the ASRO/CT Technical Committee 380 – "Conservation of cultural assets", a decisive innovative action utterly necessary for the standardization of the field in Romania.

The group is focused on research for new solutions to solve acute problems in the cultural heritage field and contributes with chapters on research methods and procedures for large UNESCO dossiers, but also for evaluation, identification of fraud and forgeries, along with traditional collaborators from museums, art galleries, national and international authorities (heritage police).

The group documented numerous monuments and archeological sites, and has the expertise in order to detect what are the needs and necessities in the studied casuistic, and thus propose a new development in the matter. Also, INOE implements together with the national authority – National Heritage Institute - the tools for scientific monitoring of heritage assets and archiving of information (historical interventions and digital models).

The group has over 100 articles in the field of scientific research for heritage (from national and international collaborations) and over 10 patents which were mostly focused on finding and proposing innovative solutions for different casuistic.

[1] MC authorization nr. 64 from 27.05.2014

2. Historical Landmarks

CERTO's interests in the Cultural Heritage field are strongly bonded with INOE's first steps, starting in the late 20th century[1]–[3]. A selection of the most important activities and breakthroughs achieved by the group in national and international landscape are presented, as follows:

1999 EUREKA E! 2094 – CLEANART - the first international project elaborated and coordinated by Romania, with UK and Greece as partners, that resulted in the development of a laser microscope for micro-precision laser cleaning. [4] (see *Fig. 2)*

Fig. 2. MicroLASER x-y with Nd:YAG laser

2000 COST G7 „Artwork Conservation by Lasers” - the first COST action under Romanian proposal; 21 states: Austria, Belgium, Cyprus, Denmark, Finland, France, Germany, Greece, Hungary, Israel, Italy, Latvia, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovenia, Spain, United Kingdom.[5]

2000 Member in the most outstanding Scientific Committee (SC) in the field **Lasers in Artwork Conservation – LACONA**.

2003 Advanced On-Site Restoration Laboratory for European Antique Heritage Restoration - the first CULTURE 2000 international restoration campaign coordinated by Romania was focused on four hypogeum-type funeral monuments from Tomis and Basarabi-Murfatlar in Dobrudja region, see *Fig. 3*.

Fig. 3. Painted hypogeum (Tomis)

2004 The first laser cleaning campaign in S-E Europe - laser cleaning of the stone columns and decorations from the atrium of Biserica Doamnei, Bucharest, developed in collaboration with The National Arts University and under the monitoring of The National Historical Monuments Office - see *Fig. 4*.

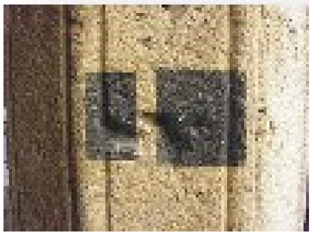

Fig. 4. Laser cleaning on a column from Biserica Doamnei

2006 ART4Art - development of a unique complex mobile laboratory for *in situ* investigation, analysis and diagnosis of CH using non-invasive methods. Its initial design is presented in *Fig. 5*.[6]–[8]

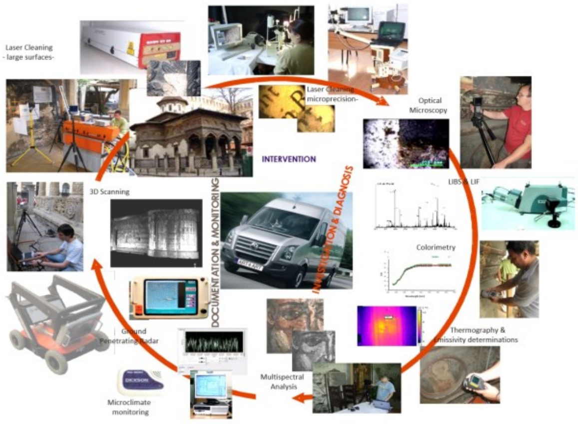

Fig. 5. The original 2006 ART4art setup

2007 Development of **portable Laser Induced Breakdown Spectroscopy (LIBS)** and **portable Laser Induced Fluorescence Scanning (LIFS)** systems for *in situ* analysis of CH (see *Fig. 6*).[9]–[19]

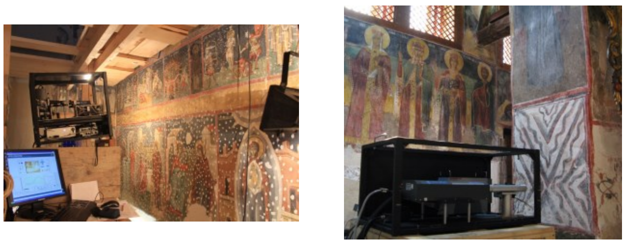

Fig. 6. LIF (right) and LIBS (left) portable setups

2008 India campaign was focused on 3D scanning and **thermal** imaging and emissivity determinations for UNESCO sites from India and Tibet.[20], [21]

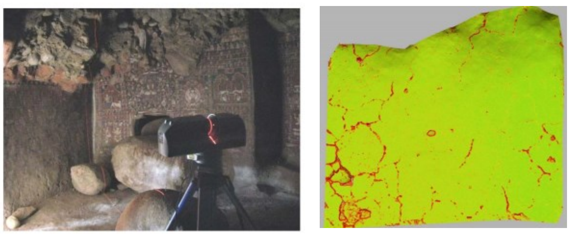

Fig. 7. 3D laser scanning - Sasspol Main Temple (left) and 2nd temple degradation identification (right)

2008 Joining the funding members of **The Balkan Archaeometry Network**.

2010 Slovenia campaign was focused on demonstrations of 3D Scanning, portable LIBS and laser cleaning of stone artefacts.

2010 Onion model - development of an advanced methodology for diagnosis of CH corroborating the data acquired by different techniques (such as: LIBS, LIF Scanning, 3D Scanning, Thermal imaging, multispectral imaging, LDV etc.) in a multi-layered 3D digital model. An example is presented in *Fig. 8*.[22]–[26]

2011 VisART - Contemporary Art Conservation – the first national research project dedicated to innovative methods for conservation of contemporary artworks.[27]–[29]

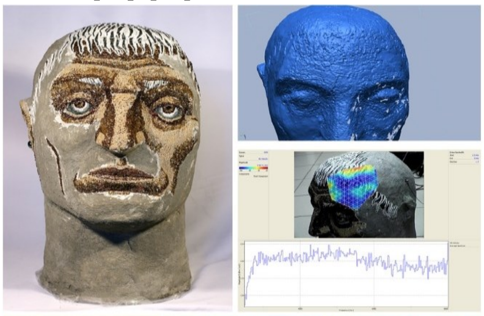

Fig. 8. Onion model applied on a contemporary statue, within VisART project

2011 World Wide Open Workshop with Advanced Techniques for Cultural Heritage - WWWwATCH, project developed the **first platform in SE Europe that works as an open laboratory or open restoration workshop**.[30]–[32]

2014 Bulgaria Campaign was focused on *in-situ* investigations and diagnosis of UNESCO sites from Nessebar using non/micro destructive portable techniques, in a context of an international workshop that allowed **specialists and students from across the world to remotely access and operate the LIF Scanning equipment** placed in St. Stephan's church from Nessebar.

2015 The real scale reconstruction of painted Hypogeum from Tomis (see *Fig. 9*), made based on 3D Scanning, now donated to National Museum of History and Archaeology from Constanta.

Fig. 9. Hypogeum reconstruction exhibit @Memory of Light event

2015 The first aerial investigations made in Romania dedicated to HS: UAV with LIDAR, multispectral and thermal sensors, see *Fig. 10*.[33]

Fig. 10. The first UAV investigations were made at the Heroes' Path from Târgu Jiu

2016 Spain Campaign was focused on application of advanced non-invasive techniques on several objectives: Great Mosque of Cordoba; Apostles` Gate, Morella, Santa Maria Magdalena, San Roman, San Julien, San Marco, Santa Marina and Omnium Sanctorum Churches from Seville.

The Spanish restoration project for Apostles` Gate, Morella (see *Fig. 11)* won EUROPA NOSTRA award for Research in 2019[2].

Fig. 11. Non-invasive techniques applied at the Apostles' Gate from Morella cathedral

2015 Started the **multi-annual monitoring program of the monumental ensemble of "The Heroes Path"** from Târgu-Jiu, created by Constantin Brâncuși.

2016 CERTO infrastructure is included in the **European Research Infrastructure for Heritage Science E-RIHS** and INOE is appointed coordinator of the national hub.

2017 INOE adds **E-RIHS** RO to the **Romanian Research Infrastructures Roadmap** in the 2017 selection.

[2] https://www.europanostra.org/2019-european-heritage-awards-europa-nostra-awards-special-mentions/

3. A glance on current activities and interests

The current researches pursued by CERTO group are dedicated to Heritage Science, focused on developing new equipment and methods for non-invasive *in-situ* analysis and diagnosis, with a major emphasis on **association and corroboration of the imagistic and the analytic results**, in order to obtain powerful tools for conservation, restoration, authentication, but also for studies related to the artist/creator's touch.[34]–[36]

The last years in the field of 3D documentation and digitization have seen the re-emergence on large scale of an old method for recording and measuring physical surfaces: photogrammetry. INOE integrated photogrammetry along with the two other 3D laser scanners that were already part of our infrastructure, almost 10 years ago, and important results have been obtained within research projects and studies, but also in long term documentation of architectural complexes and archaeological sites (such as The Heroes Path from Târgu Jiu, Basarabi-Murfatlar chalk churches complex, etc.). [37]–[39]

Year by year, the processing algorithms used in photogrammetric reconstruction evolved rapidly, catching up the laser scanning precision and accuracy, but with the advantage of having high resolution and calibrated color textures. Versatility of photogrammetry allowed us to use it and test in different scenarios like textile documentation[31] or physical damage documentation on polychrome wood panels at macro level, as can be seen in *Fig. 12*.[40]

Fig. 12.Macro-photogrammetry: left-St Nicholas icon on wood panel, right- digital elevation model

The method was also integrated in airborne systems for aerial photogrammetry survey together with other imaging sensors like thermal imaging, multispectral imaging or LIDAR, since 2015. The airborne system acquired data were associated and corroborated using the ***onion model*** that provided ***GIS documentation*** for sites and cultural landscapes (such as, the Golești museum or the caves site from Aluniș-Bozioru, see *Fig. 13*).

Fig. 13. Photo taken during the flight over the area in the vicinity of the rupestrial monument Iosif's Church, Buzău Mountains

The study published on a rare bronze vessel unearthed in a Roman fort from Mălăiești, Vâlcea, România, from the collection of National History Museum of Romania, is an example of a recent data association that ***integrated analytical spectral data from LIBS, XRF and Fourier Transformate Infrared (FTIR), with imaging data, 3D documentation and 3D virtual reconstructions hypothesis,*** as can be seen *in Fig. 14.* [41], [42]

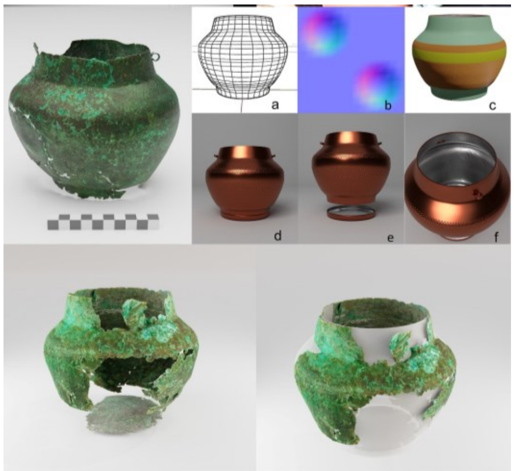

Fig. 14. Military Roman rare bronze vessel - physical restoration and virtual reconstruction and restoration[41]

Another interesting study was dedicated to ***revealing a hidden early composition by Hans Máttis-Teutsch*** using corroborated imagistic and spectroscopic techniques[3].

Shaping his artistic training as a sculptor and extracting his roots right from the center of the artistic world – Paris, Berlin, Vienna – after Fin-de-siècle, Hans Máttis-Teutsch was an exemplary case of peripheral artist that spent his entire life in the native town and experimented in a diversity of modern styles, as they were reflected in the Eastern and Central Europe at the beginning of 20^{th} century. Marked at the beginning by the Jugendstil, Expressionism and Abstract art, Máttis-Teutsch established his art at the intersection of three major avant-garde movements: the Magyar Aktivizmus[4], Berlin's „Der Sturm“, and Romanian avant-garde group. After the outbreak of World War II, the historical context and the ideological pressures lead his art on the territory of Socialist-Realism, while repainting many of his canvases made during the Romanian avant-garde period.

Two paintings from this latter period *The scientists* (1946) and *Past, Present, Future* (1947), belonging to a private collection, were documented and investigated using complementary imaging and spectroscopic techniques. The results obtained using hyperspectral imaging and high-resolution digital radiography revealed the initial compositions, depicting a specific *Constructivist style*, which was developed by Máttis-Teutsch after 1925, when he becomes more active in the Romanian avant-garde scene. XRF analysis was able to highlight the presence in the under-layers of pigments that were often used by the artist at

[3] 1^{st} Intl. conf. MUNCH 2022 - Understanding Munch and the Art at the turn of the Centuries Between the Museum and the Laboratory, Oslo, Norway, 21-23 March 2022)
[4] Hungarian Activism

that time. By corroborating the data obtained from the imaging and spectroscopic analysis with the art historical documentation of the avant-garde period of Máttis-Teutsch, a virtual digital polychrome reconstruction of the initial painting was conceived, as can be observed in *Fig. 15.*

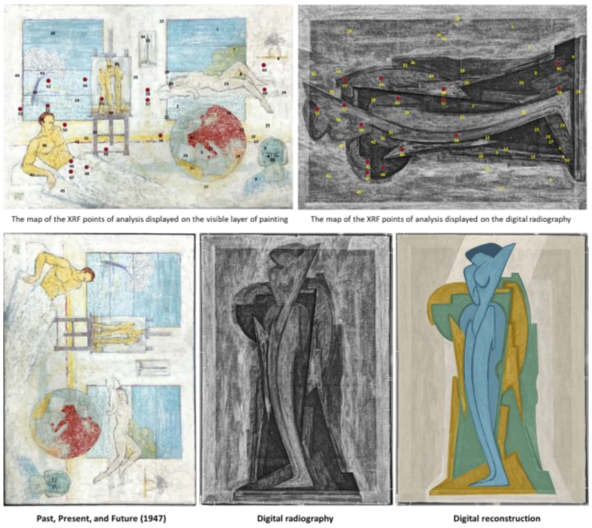

Fig. 15. Virtual digital polychrome reconstruction of the hidden composition discovered under "Past, Present, Future" (1947) by Hans Máttis-Teutsch

The complex documentation obtained by corroborating the results from investigations made using complementary, is extremely useful for the restoration practices. An interesting case was brought to our attention by IORUX Restoration that was working on a complex project focused on a 19th century Brancovan iconostasis from the "Holy Trinity" church in Măgureni, Prahova, România. The iconostasis was repainted during previous restorations and a thick metallic paint was covering the wooden frame decorations, that was also affected by deposits of dirt, strong oxidation of the silver paint, cracks, dislocations and loss of sculptural elements. (see *Fig. 16*)

Chemical cleaning tests were not very efficient on the thick layer of metallic paint, thus further investigations and tests were needed. The spectra from XRF, FTIR and stratigraphy LIBS, were interpreted and associated to the imagistic data obtained using digital microscopy, hyperspectral imaging and photogrammetry.

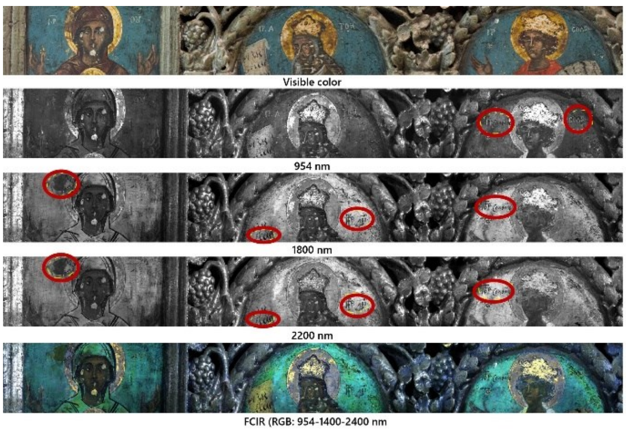

Fig. 16. Hyperspectral imaging revealed the presence of the original inscriptions that were later covered and repainted differently

The cleaning tests were made evaluating several methods, in order to find the proper regime that would help preserve as much as possible from the underlying polychrome layers and it was decided that the best solution was to use ***laser cleaning guided by the HIS images*** for the rough removal of the metallic paint overlayers and finalize with ***chemical cleaning***.

As it was mentioned before, our research takes into consideration the specificity introduced by contemporary artworks media and materials, contributing in the preventive conservation strategies, and creating a documentation flow through the years that will have a major impact, when needed. General public is used to attribute graffiti to acts of vandalism, but ***what do you do when the graffiti is art and it is vandalized***? [43], [44] A study was published on the efficiency of the laser cleaning of black permanent marker tags from a contemporary graffiti painting. The major issues addressed were the complex and often similar composition of the material to be removed and the one to be preserved, as well as their usually light-sensitive nature. The cleaning tests were performed by a Q-switched Nd:YAG laser operating at 1064 nm and 532 nm and it was supported by characterization of the chemical composition of the materials using ATR-FTIR, XRF and colorimetric measurements (see *Fig. 17*).[45]

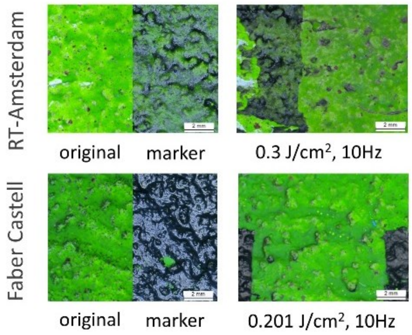

Fig. 17. Microscopic images of the areas before and after the laser cleaning using 1064 nm wavelength

Optoelectronic techniques have a big contribution to the characterization of archaeological objects [46], [47]. As, it is the case of the multi-analytical study of archaeological pottery excavated in the Early-Neolithic settlement of Chavdar, performed in the frame of the international scientific inter-academic cooperation between the Romania and the Bulgaria. The pottery was analyzed applying different spectroscopic techniques (FTIR, LIBS, and XRF) and digital microscopy. The outcome of the research shed light not only on the compounds of the decoration and the ceramics body, but also on ***the temperature and the atmospheric conditions at which the pottery has been fired***, as well. This collaboration is still ongoing as the investigation of the decoration of a large set of archaeological pottery fragments from different regions in Bulgaria is planned. [48]

Also, exciting results have been obtained in the preliminary study regarding the classification of metal archaeological artefacts from Hallstatt period using LIBS technique. The artefacts are part of a very important discovery made a decade ago, by one of our most valued collaborators from the National History Museum in Romania, on sites located on the middle Mureș Valley at Tărtăria – Podu Tărtăriei Vest (the hoards Tărtăria I and Tărtăria II). In *Fig. 18* there are presented two representative adornments that were studied. The discrimination of the archaeological objects, was achieved using multivariate analysis on the complementary data acquired by LIBS and Raman, that grouped them according to similarities, obtaining a ***detailed classification of the objects extracted by archaeological excavation (or from other random discoveries) based on the elemental composition of the original material***. A comparison between several statistical methods of analysis is in progress.[49]–[51]

Fig. 18. Glasses Fibulae with knot (left) and bracelet (right) from Tărtăria sites

In the recent years, part of our work has been devoted to maximizing the capitalization of the high-level scientific outputs, with immediate application in the vast field of *Heritage Sciences*. The projects developed within CERTO cover in a large extent the heritage science interests, ranging from developing equipment, IT tools, data bases to exploratory researches and shared infrastructures. The projects described in the following are a selection based on the category of results provided.

The complex project **Implementation and exploitation of the scientific research results in the restoration and conservation practice of cultural goods - IMPLEMENT** coordinated in partnership with top universities and research institutes, but also with the national public authority responsible for managing the cultural heritage, our long-term partner - National Heritage Institute, has successfully shaped new teaching directions, implemented in the national universities' curricula. [5] Besides the scientific results generated[52]–[54], one of the main tools developed within the frame of this partnership was ***a platform for the transfer, access and exploitation of data in the national cultural operators' network***.[6]

Fig. 19. IMPLEMENT platform

This platform (*Fig. 19*) allows registered specialists to report scientific data, in order to store, administer and generate personalized datasheets of both mobile and immobile cultural heritage items. The platform, properly operated, can offer the user tools related to authentication, crafting technique, material discrimination, validation, restoration, conservation, expertise, documentation, and also, aspects pertaining to malpraxis.

Spectral data mining for material identification, chemical fingerprinting and forgery detection of painted works of art - INFRA-ART is a postdoctoral research project that was running for 2 years now, that is aimed to foster innovation and knowledge advancement in the field of heritage science, with a specific focus on the scientific examination of painted works of art.[7]

One of the main results obtained within the post-doctoral research project is the development, implementation and optimization of the ***INFRA-ART Spectral Library***, an open access resource, available on-line[8], which was designed as a useful digital resource tool for researchers and other specialists in the field of heritage science, art history, conservation, and materials science. [55] The INFRA-ART spectral database is a constantly growing collection of spectra that now contains over 1000 XRF, ATR-FTIR and Raman spectra, linked to over 500 known reference materials.

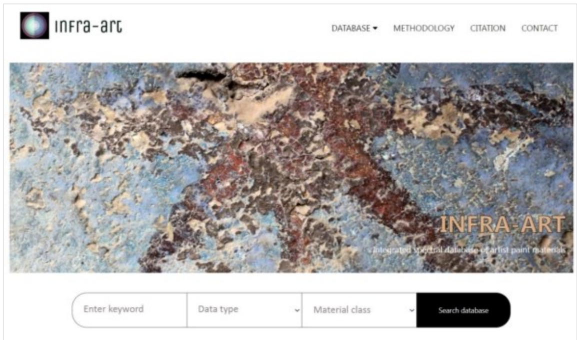

Fig. 20. INFRA-ART Spectral Library interface

Another important result includes an in-depth study carried out on a large group of earth pigments, of various hues, from different geographical regions[56]. The pigments were investigated by means of complementary spectroscopic techniques (FTIR, XRF, Raman) and principal component analysis, with the aim to identify distinctive mineralogical and chemical characteristics of natural pigment sources. The study demonstrates the value of using easily-accessible complementary spectroscopic techniques as a preliminary step for the characterization and differentiation of earth pigments and how chemometric analysis can inform and enhance the interpretation of spectral and chemical trends. ***The results obtained contribute to the knowledge and understanding of the complex chemistry of earth pigments, including of pigments never studied before***.

Important results were also obtained in terms of the

[5] UEFISCDI, PN-III-P1-1.2-PCCDI-2017-0878/NR.55PCCDI/2018, https://https://implement.inoe.ro/
[6] http://certo.inoe.ro/implement_ppta

[7] UESFISCDI, PN-III-P1-1.1-PD-2019-1099, https://certo.inoe.ro/infraart
[8] https://infraart.inoe.ro/

materials and painting techniques used by various artists and masters, by investigating diverse archaeological artefacts (surviving pieces of decorative polychrome painting on plaster from the former Roman province of Dacia[57]), as well as a series of easel paintings. By integrating multiple spectral and imaging techniques, in-plane information as well and in-depth data could be obtained on the various materials that were originally used to produce the painting, allowing a better understanding of the creative process[9]. Technical features (execution of the preparatory drawing), characteristic patterns (color palette, specific pigment mixtures) or typical fingerprints (chemical signature of the identified pigments) that may be used for attribution and forgery detection were also investigated.

Product for smart correlation of airborne GPR and imagistic data in to a multi-layered package - PEGASUS is a transfer to economy targeted project that ran for two years.[10] The project proposes the creation of a pilot product for the correlation of aerial imaging and geophysical data (GPR), capable of characterizing with high accuracy not only the surface of the soil but also the subsoil, resulting in a product with wide applicability in the field of cultural heritage, see *Fig. 21*. The correlated and precisely mapped aerial data can be used in the investigation of archaeological sites, historical monuments, civil engineering, etc.[58]–[60]

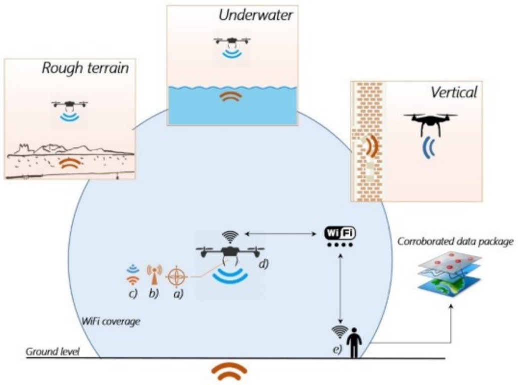

Fig. 21. Correlation of aerial imaging and geophysical data concept

The product is obtained by using the data delivered by an ***innovative system that includes two main elements: an UAV,*** with remote sensing capabilities (LIDAR, multispectral & thermal sensors, high-resolution camera) ***and a radar system (GPR)*** that was modified within the project for ***aerial acquisitions***. The *in-situ* measurements are carried out on specific locations that involve particular casuistic requiring remote investigations.

The project ensures the unity with the economic environment by assimilating the RDI results of the research organization and transferring these results to the market. The project is based on an original software solution, identified by CERTO's extensive involvement and experience in this field (long-lasting investigation/ documentation campaigns on archaeological sites and historical monuments).

Another interesting application of the Optoelectronics in Cultural Heritage, is developed within the project **Biocleaning of the mural painting with new ecological products based on microbial metabolites - BioCleanMur**, coordinated by one of our most valued partners, Institute of Biology Bucharest, Romanian Academy.[11]

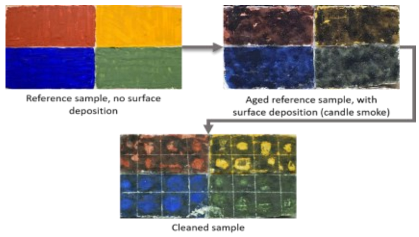

Fig. 22. BioCleanMur tests

The biocleaning made with bacterial esterases immobilized in polysaccharides-type gels and micro-fungi cultures was evaluated using ***corroborated spectroscopic, imagistic and chemometric techniques***, in order to assess from the physical-chemical point of view their potential to remove Paraloid B72, transparent dispersion of casein (TDC), candle soot, sunflower oil and beeswax. [61]–[65]

On international scale, CERTO is partner in HORIZON 2020 project **Integrating Platforms for the European Research Infrastructure ON Heritage Science - IPERION HS -** a consortium of 24 partners from 23 countries that contributes to establishing a distributed pan-European research infrastructure, opening key national research facilities of recognized excellence in heritage science. IPERION HS offers cross-border access to a wide range of high-level scientific instruments, methodologies, data and tools for advancing knowledge and innovation in heritage science, offering more than 180 services from 52 access providers, divided in 3 access platforms: ARCHLAB, FIXLAB and MOLAB.[12]

CERTO is included in the MOLAB, together with other key laboratories from across 10 European countries, providing coherent access, under a unified management structure, to a set of mobile equipment and related competencies, for in-situ non-destructive measurements of artworks, collections, monuments and sites, see *Fig. 23*.

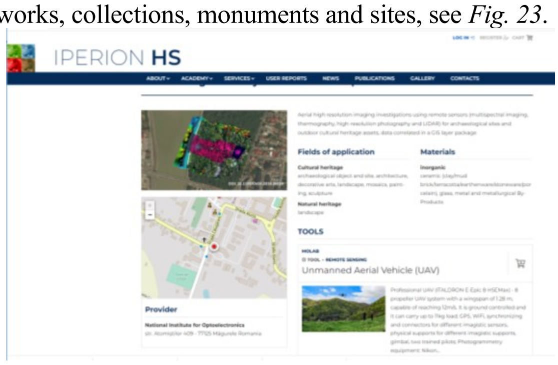

Fig. 23. UAV entry in the MOLAB catalogue of services

[9] I.M.Cortea, L. Ratoiu, R. Rădvan, The secrets of old masters: investigating the pigment mixtures and layering techniques in two paintings by Lucas Cranach the Elder and his workshop, Lasers in the Conservation of Artworks, 12-16 Sep 2022, Florence
[10] UEFISCDI, PN-III-P2-2.1-PTE-2019-0492, https://certo.inoe.ro/pegasus

[11] UEFISCDI, PN-III-P2-2.1-PED2019-0082, https://www.ibiol.ro/proiecte/PNIII/BioCleanMur/obiective.html
[12] H2020-INFRAIA-2019-1, Grant nr. 871034, http://iperionhs.eu

Go-on-target in art – GoT in art is an exploratory research project that just began this year, and has as main objective the development of a portable hybrid system featuring Hyperspectral Analysis, LIBS and RAMAN Spectroscopy, that will improve the characterization and discrimination of materials (mapping) by providing a complete stratigraphic profile. The results will guide the restorer and the investigator in the micro/nanoscopic universe of the hidden layers of the compositions, and will serve as ***a unique tool for preservation, restoration, evaluation of interventions or authentication of cultural heritage***.[13] Although yet a fresh project, promising results have already been obtained, as can be seen in *Fig. 24*.

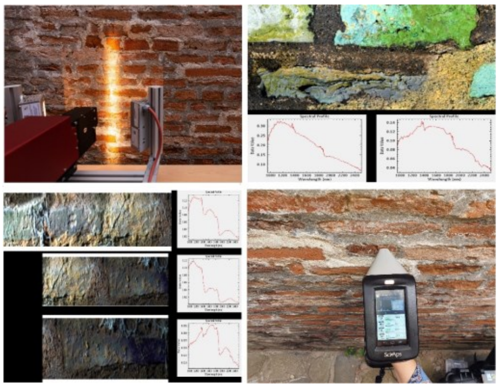
Fig. 24. HSI and LIBS correlated in situ during the analyses of the bricks and mortars from the Turkish Bath from Golești museum

European Research Infrastructure for Heritage Science Implementation Phase – E-RIHS IP, is another project based on distributed infrastructure funded through the Horizon Europe Framework Programme, that has the following main objectives:

✓implement the E-RIHS governance structure and finalize its distributed architecture;

✓support the E-RIHS management with strategies and related implementation plans regarding HR, procurement, risk management and quality system

✓maintain and build upon the established E-RIHS excellence in user access and foster FAIR open access with the design of the DIGILAB platform

✓strengthen international cooperation, cultivate synergies and consolidate the HS community around E-RIHS, while establishing E-RIHS in the landscape of EU RIs and global initiatives

✓***secure the ERIC*** sustainability and unlock its socioeconomic impact potential by providing E-RIHS with an updated business plan and a marketing strategy tailored for its new lifecycle phase.[14]

Other recently won research grant, **Innovative analytical methodology for in-situ identification and real-time mapping of organic binders used in ancient wall paintings - artMAP**, combines two complementary highly specific molecular techniques, namely Laser Induced Fluorescence Spectroscopy (LIF) and Fourier-Transform Infrared (FTIR) Spectroscopy looking for a solution for a difficult problem of the international scientific community: ***the identification and mapping of organic binders present in low concentrations in ancient painted surfaces***.

Fig. 25. artMAP

As can be observed, the current research activities of CERTO are addressing specific needs and gaps identified in the field, alongside long-term partners, but also opening new directions of collaboration within a wide range of the stakeholders involved in the heritage domain (museums, universities, art galleries, foundations, restoration firms, academy and state institutions), as beneficiaries of specific services (see *Fig. 26*) or partners in research projects (see *Fig. 27Fig. 27*).

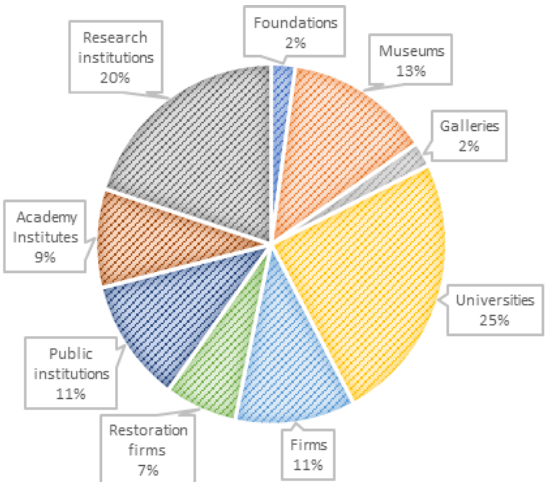

Fig. 26. CERTO's beneficiaries

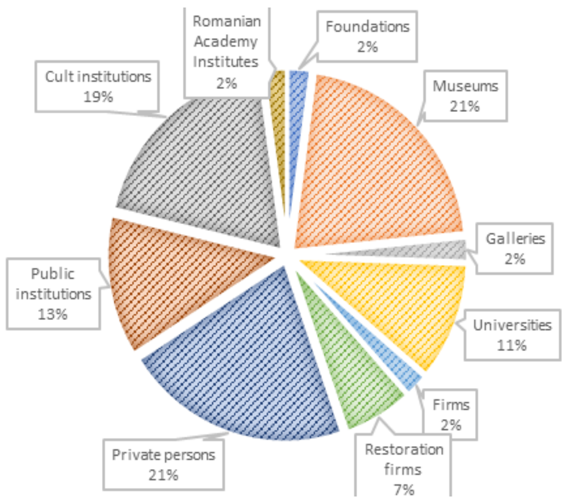

Fig. 27. CERTO's partners

[13] UEFISCDI, PN-III-P4-PCE2021-1605, http://GoT.inoe.ro
[14] HORIZON-INFRA-2021-DEV-02-02, grant nr.101079148, http://e-rihs.eu

4. Distributed Research Infrastructures

A national distributed research infrastructure that INOE developed in partnership with the National Institute for Research & Development in Chemistry and Petrochemistry ICECHIM has been included in the Romanian Research Infrastructures Roadmap in 2021: **The integrative infrastructure for the fusion of complex digital data for the identification, mapping and evaluation of Cultural assets - DATAFUSIONART**.

The protection of tangible heritage normally requires complex multi-disciplinary documentation. Most of the time the raw data obtained from such documentations are processed and evaluated separately both spatially and temporally. This usually leads to accumulations of data, of various types and formats, that are not associated. This is how the DataFusionArt distributed infrastructure was born, with an integrative, intelligent approach that considers any type of data and that can merge them into a new, much more complete approach, for shortening times in conservation decisions, implicitly, reducing the costs on long term basis.

The purpose of this infrastructure is to facilitate the fusion of any type and format of digital data (imaging or spectral) in an integrative characterization model of a cultural or artistic good. The model can have different forms of presentation: complex database, multi-layer referenced model for mapping surfaces, 3D digital model accessible on-line with surface projections and distributions of compounds/elements/characteristics (e.g. Time-lapse thermography 3D viewer- see *Fig. 28Fig. 28*). This type of service adapts accordingly to the request, the casuistic, but especially to the types of data input in the model. The proposed infrastructure has an *open access* character, being based on *FAIR data* principles.

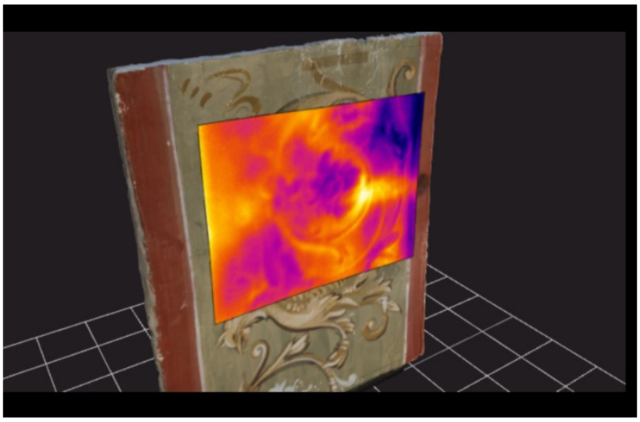

Fig. 28. Visualization of a time lapse of thermal imaging data on the 3D digitized model of the investigated object [66]

E-RIHS is the **European Research Infrastructure for Heritage Science** that supports research on heritage interpretation, preservation, documentation and management. The mission of E-RIHS is to deliver integrated access to expertise, data and technologies through a standardized approach, and to integrate world-leading European facilities into an organization with a clear identity and a strong cohesive role within the global heritage science community.

INOE joined E-RIHS ESFRI in 2016, during the Preparatory Phase, initially as observer, and one year later succeeded to add it in the Romanian Roadmap of Research Infrastructures. Now a partner in the consortium and coordinator of the Romanian hub (see *Fig. 29*) formed from Horia Hulubei National Institute for R&D in Physics and Nuclear Engineering - IFIN HH and National Heritage Institute, with over 15 affiliated institutions such as museums, universities, research and academic institutes, INOE prepares E-RIHS RO[15] to pursue the establishment of the ERIC, as a funding state.

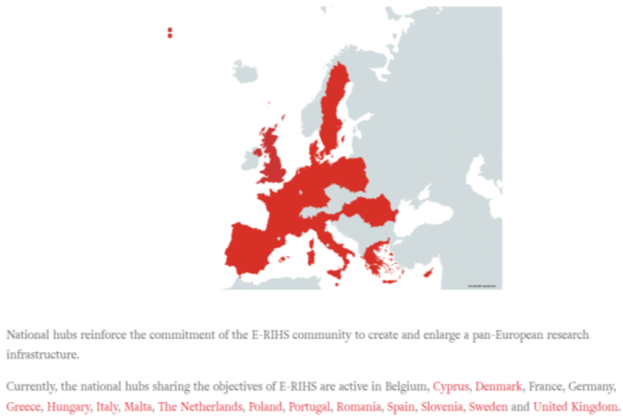

Fig. 29. E-RIHS national hubs

The objectives of E-RIHS ESFRI are the following:

- ➢ Catalyzing new cross-disciplinary research by mobilizing expertise and researchers in the humanities and natural sciences.
- ➢ Integrating world-class facilities across Europe to connect the global community of heritage science.
- ➢ Building state-of-the-art tools and services for research communities and the heritage industry.
- ➢ Driving scientific excellence and innovation through visionary research projects.
- ➢ Leading the way in the development of digital platforms for the improved understanding, visualization and use of heritage.
- ➢ Developing skills and capabilities to build strong science and to foster collaboration.[16]

E-RIHS provides access to the services through four integrated platforms:

- **ARCHLAB** (archives) offers access to specialized knowledge and organized scientific information – including technical images, analytical data and conservation documentation – in datasets largely unpublished from archives of prestigious European museums, galleries and research institutions.
- **DIGILAB** is related to virtual access to scientific data concerning tangible heritage, making them FAIR (Findable-Accessible-Interoperable-Reusable). It includes searchable registries of multidimensional

[15] http://e-rihs.ro
[16] http://e-rihs.eu

images, analytical data and documentation from large academic as well as research and heritage institutions.

- **FIXLAB** offers a unique expertise to users in the heritage field, for sophisticated scientific investigations on samples or whole objects, revealing their microstructure and chemical composition, giving essential and invaluable insights into historical technologies, materials, alteration and degradation phenomena or authenticity, by means of large-scale and medium-scale facilities such as particle accelerators and synchrotrons, neutron sources and other non-transportable analytical instruments.
- **MOLAB** brings out an impressive array of advanced mobile analytical instrumentation for non- invasive measurements on valuable or immovable objects, archaeological sites and historical monuments. The MObile LABoratory allows its users to implement complex multi-technique diagnostic projects, permitting the most effective in situ investigations.

INOE – example of services provided	Techniques	Platform
Non- invasive in situ Elemental & Molecular characterization of CH materials	LIF, XRF	MOLAB, FIXLAB, ARCHLAB
Micro-invasive Molecular characterization of CH materials	FTIR	FIXLAB
Non-contact micro- invasive elemental analysis and stratigraphy, in situ & in lab	LIBS	MOLAB, FIXLAB
Non contact, in situ laser cleaning of organic and anorganic materials	Q, switched Laser YAG:Nd, 1064-266 nm	MOLAB, FIXLAB, ARHILAB
Non-invasive comparative analysis by X-Ray radiography, multispectral and hyperspectral imaging	X-ray station, Artist system, hyperspectral camera	ARHILAB, FIXLAB, MOLAB
Complex 2D and 3D digital models for investigation and characterization of multilayer surfaces	3D Scanning, Laser Doppler Vibrometry, Photogrammetry, Thermography, Colorimetry, 3D Printer	DIGILAB, ARHILAB, MOLAB
Aerial documentation of archaeological sites, urban areas and outdoor monuments	LIDAR, Thermography, Photogrammetry, multispectral imaging	ARHILAB
Archaeologic site underground mapping	GPR	ARHILAB
Microclimate monitoring	Intelligent monitoring system	MOBILAB, FIXLAB
Anoxic based disinfestation for CH objects	Veloxi	MOBILAB, FIXLAB
Fluorescence microscopy analysis	Optical and digital microscopes	FIXLAB
Accelerating ageing tests	Microclimate chamber, UV lamps	FIXLAB

Fig. 30. A glimpse at some of the services provided by INOE

The services provided by INOE cover a wide range of techniques, a selection being presented in Fig. 30, and count numerous national and international accessions per year, more than 10 % being international solicitations, as can be visualized in *Fig. 31.*

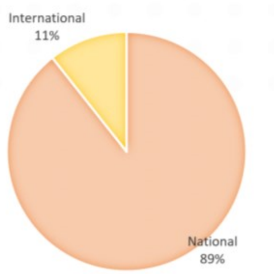

Fig. 31. Services provided on national and international level

5. Perspectives

Where will the future take us?

We will keep following our dreams and use the best of our knowledge into the service of Heritage Science.

We will quest for finding solutions to integrate and make data compatible to spectral hypercubes, in order to obtain complex data packages that can contribute to the conservation of inorganic and organic materials, understanding and finding a way to mitigate the degradation mechanisms, or fight fraud.

Another important goal we will pursue is to extract high accuracy data from multiple analytic and imagistic techniques in order to recreate or reconstruct hidden or missing decorations or compositions, as well as use advanced chemometrics for developing dating techniques focused on laser spectroscopy data, that can help overcome the Carbon dating limitations that may be induced by the rising fossil-fuel emissions[67].

As for perspectives in the field of 3D documentation, an important step would be the integration of BIM/HBIM (Heritage Building Information Modelling) methodology with our current imaging and 3D documentation methods.

Our future developments are constantly adapting to the foreseen challenges, promoting sustainability, researching new ecological solutions focused on pollution monitoring and reduction, encouraging the circulation of technology and products (through open access, FAIR data, shared researched infrastructures), and taking as step further the tele-operation, thus supporting reducing the expenses of access to infrastructure and expertise.

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Research Centre for Advanced Surface Processing and Analysis by Vacuum Technologies - ReCAST: a multidisciplinary R&D centre

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The Research Centre for Advanced Surface Processing and Analysis by Vacuum Technologies (ReCAST) is a multidisciplinary research centre that combines knowledge from three areas: vacuum technologies, plasma physics and material engineering. In this contribution a short description of the history of centre is presented, pointing the most representative results obtained over the years. Examples of research projects and applications are given, describing the main activities of the centre.

Keywords: research centre, vacuum, plasma, material science, thin films, applications

1. Introduction

The Research Centre for Advanced Surface Processing and Analysis by Vacuum Technologies (ReCAST) [1] is part of the National Institute of Optoelectronics. In this multidisciplinary centre the vacuum technologies, plasma physics and materials engineering are joining to tackle a large variety of applications.

The main mission is to provide an interdisciplinary environment that includes all the steps, starting from vacuum technologies, including thin film deposition and surface processing, going through advanced characterization of the thin films and surfaces, to finally reach the ultimate step of developing multifunctional materials and structures. The cornerstone of our activities lies in the development of technologies, having vacuum at their core. This includes the design and configuration of various processes and geometries such as: thermochemical treatment, mass spectrometry analysis (applied to leak detection), cathodes for magnetron sputtering and cathodic arc. Physical vapor deposition techniques are implemented, applied and optimized, using as main tools: magnetron sputtering, cathodic arc and thermal and e-gun evaporation.

The thin film characterization infrastructure includes techniques that provide knowledge on the morphology (1D, 2D and 3D imaging), structure, composition of the thin films, as well as complex characterization of optical, electrical, mechanical and functional properties. The range of applications tackled over the years is quite diverse , including:

i) Materials and devices for solar energy conversion
ii) Photovoltaic and thermoelectrical systems
iii) UV-VIs-IR radiation detectors
iv) Optical coatings
v) Protective coating in industrial environments
vi) Multifunctional materials and systems for prosthetics

2. Hystorical development

The ReCAST centre, as it is known today, was renamed in 2007, as a development of the former Tehnoprof centre. Over the years the centre has grown in terms of number of staff , topics and domains of specialty, and also complexity of the infrastructure. There were two main periods of accelerated growth. In 2011-2012 the size of the team increased with the addition new members, that are part of the team until today. In 2014-2015 due to the implementation of the INOVA Optima Project [2] we had a boost in terms of new, high-end infrastructure for coatings characterization techniques. The centre and the research group was lead until 2020 by its founder, Dr Viorel Braic. Since then the position of head of department was taken by Dr. Catalin Vitelaru, ensuring that the knowledge and infrastructure acquired over the years is kept and the continuity of our activities is ensured.

Historically, the centre was built around the vacuum technologies. In the first years some important achievements were made, even from before the renaming of the centre into ReCAST. In the following, some of the most relevant examples of such developments will be given.

In the frame of the collaboration between the Institute of Atomic Physics (including all the institutes in Magurele) and the Joint Institute for Nuclear Research (JINR) in Dubna (Russia), JINR explored the possibility to get from the Romanian partner a leak detection system (**LDS**) to be used during the in line checking of the Monitored-Drift Tube chambers (MDT). JINR was manufacturing the MDT, but they needed a system to check its properties. The requirement form CERN, the final beneficiary, was to maintain inside the 400,000 tubes the gas filled mixture (Ar, CH_4, CO_2) at 3 atm internal pressure.

Figure 1: The LDS system with mass spectrometer, vacuum system, system for gas mixing and computer

INR representatives chose the project presented by Tehnoprof Centre and a mass-spectrometry based leak detection system (**LDS**) was developed. The radiofrequency mass spectrometer can detect masses in the 1-100 amu range. The trace gas is helium (10% in mixture with air). LDS is provided with specific accessories for Al tube testing (vacuum inside, He spraying outside) and MDT (He/air mixture inside, vacuum around end-plugs). LDS can measure leak rates in the range: 10^{-4} - 10^{-7} mbar.l/s with an accuracy of 10%. The minimum flow rate yet detected is 10^{-8} mbar.l/s. The LDS system is computer controlled, and the stand-by and test sequences are automated. However the final decision pass/fail is done by the operator. Usually the test cycle duration is less than 5 minutes, including data accumulation for statistics.

The system was installed and successfully operated at JINR for MDT mass production. The MDT system was successfully installed in CERN, as part of the largest muon spectrometer of the ATLAS system.

Figure 2: The UHV system for forming and transport of positrons and electrons in LEPTA, installed at JINR Dubna.

Due to excellent results obtained in LDS-MDT project, JINR representatives chose Tehnoprof Centre for the design, mounting, testing and installing at JINR the ultra-high vacuum (UHV) system for forming and transport of positrons and electrons in the Low energy Positron Toroidal Accumulator (**LEPTA**).

The UHV system, Figure 2, was delivered with a computer controlled outgassing procedure up to 350^0 C, providing an internal pressure less than 10^{-9} mbar while in function. Apart from other applications, the LEPTA system is also used for positronium generation needed in positron annihilation spectroscopy, a non-destructive spectroscopy technique to study voids and defects in solids and thin films.

Improvement of low voltage vacuum circuit breaker on the basis of vacuum switching electric arc investigation was the topic of the LOVARC, a NATO-SfP project. The foreseen improvement was the replacement of the quenching chamber (QC) filled with the non-ecological gas SF6 by a vacuum chamber.

Figure 3: Images of the QC: from the design, to the fabrication, parts before assembling and the prototype

The technological approach of the QC prototype manufacturing was to get a sealed off device with extremely low out-gassing yield of the component materials. Oxygen free copper, stainless steel and an adequate ceramic used in high voltage devices were selected as materials to be used. The bonding of these materials in one vacuum tight assembly implied the ceramic bonding by active metal method, combined with metal – metal brazing in vacuum, such as the QC sealing and outgassing under high vacuum conditions was obtained in a single technological step. The images of the prototypes are presented in Figure 3.

The pressure measurement inside the sealed off QC was done by applying a high voltage and an axial magnetic field over the chamber's electrodes and measuring the discharge current measured versus the true pressure (mbar) indicated by the Bayard-Alpert vacuum gauge.

The functional parameters of the two prototypes of QC are:

- rating a.c. voltage: 660 V.; 1000 V.;
- insulating rating a.c. voltage: 1500 V.;
- thermal stability current: 50 kA;
- dynamic stability current:100 kA_{peak};
- breaking capability:
    - 660 V at 65 kA;
    - 1000 V at 40 kA.

Related to the coatings deposited by physical vapor deposition (PVD), ReCAST team developed coatings resistant to harsh environments, always a research priority, being recurrent demand from industry. Such coatings were used as resistant coatings on the rotor blades of the centrifugal air compressors (TURMO IVC). The coating consisted of a multilayer composed of four different layers: Ti/TiN/TiAlN/Al2O3, as described in the RO122133 (B1)/2009 patent "Multilayer material for covering rotors for turbomotors" [3]. Figure 4 shows the rotor blade inside the deposition chamber after deposition, a section of the coatings obtained by scanning electron microscope, the rotor blade before being installed on the bench test at the beneficiary and the couple of two rotors on the bench test. The centrifugal air compressors with the coated rotor blades were given to the S.C. Petrom Service S.A. beneficiary.

Figure 4: Images of the rotor blades after deposition, before and after being mounted on the bench test of the centrifugal air compressor. The image in the right up corner is presenting a transversal section of the multilayered coating.

Going forward, in 2014-2015 the INOVA Optima project [2], in the frame of Sectoral Operational Program "Increasing Economic Competitiveness, Investments for your future", brought an opportunity for growth, by completing the already available infrastructure with new equipment for coatings characterization. It was also the moment when the structure of the centre was reorganized, in 5 laboratories.

First two laboratories, for plasma and vacuum processing and for film deposition, relate to the traditional activities of our group.

Indeed, the ***The Laboratory for plasma and vacuum processing of materials (LaP)*** includes:

i) High and ultra-high vacuum technologies
ii) Vacuum leak detection systems
iii) Clean High Vacuum brazing unit
iv) Equipment for thermal cycling in vacuum*

The ***Laboratory for thin film deposition by PVD methods (PVD Lab)*** includes:

i) Magnetron sputtering systems with 1, 3 and 5 cathodes
ii) Cathodic arc deposition system with 3 cathodes
iii) Thermal evaporation/ electron gun deposition system
iv) Plasma diagnostics systems (emission spectroscopy, electrical probes)

The activities in these two laboratories are related to the processes and technologies used for thin film deposition and surface processing. Once the thin films are obtained, their characterisation is performed in the other 3 laboratories.

These laboratories gather complementary characterization techniques, for elemental and morphological analysis, for structural analysis and for functional analysis, as follows.

The Laboratory for elemental and morphological analysis (LanE) includes:

- ✓ Ultra-performant elemental analysis equipment NanoSAM LAB**(high resolution SEM coupled with Auger electron Spectroscopy (AES)
- ✓ Scanning Electron Microscope (SEM) coupled with Energy Dispersive X-ray Spectrometry (EDS)
- ✓ Atomic force microscope (AFM/STM)

The Laboratory for structural analysis (LanS), includes

- ✓ System for structural characterization at micro and mesoscopic scale by high resolution X ray diffraction (HR-XRD)
- ✓ Structural analysis system for powders

The laboratory for functional analysis (LaC), includes:

- ✓ Modular system for mechanical and electrochemical characterization of materials (nano, micro and mesoscopic level **)
- ✓ Systems for measuring the surface energy, contact angle, electrical resistivity and Hall mobility, optical transmittance, reflectance and absorbance
- ✓ Optilayer Software for optical modelling

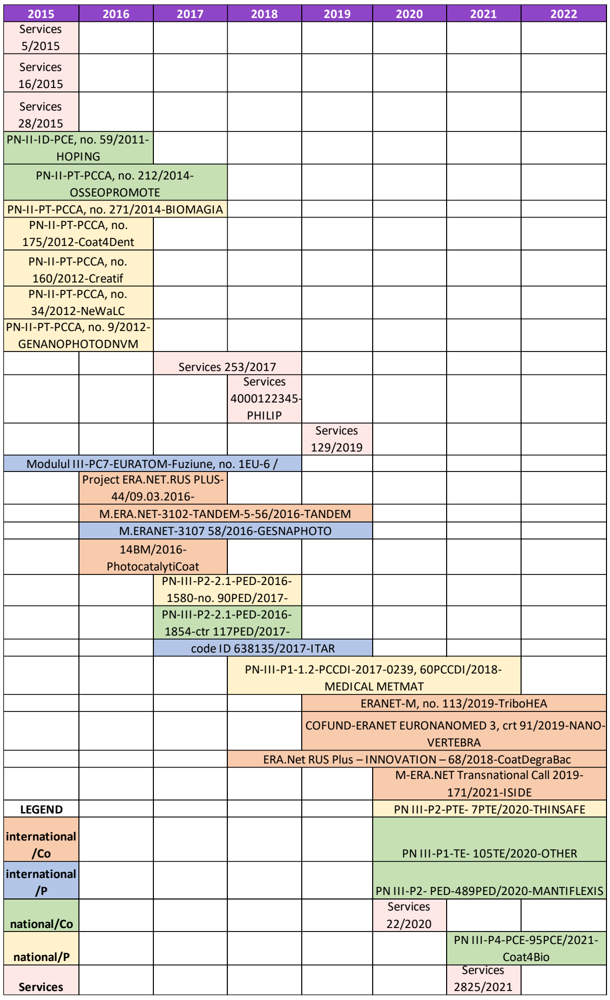

Figure 5 Time distribution of research project managed by the ReCAST centre in the past 7 years [4]

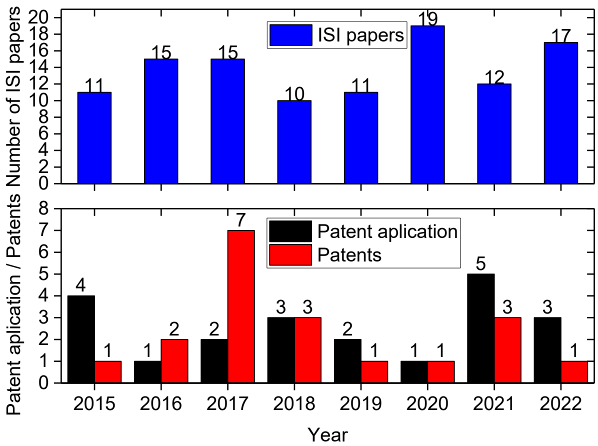

Fig 6. Time evolution of number of ISI papers and Patent applications and patents of ReCAST center members in the past 7 years [5].

In the past 7 years, since the end of Inova Optima project, the activity of the department and the research centre was focused around research projects, both national and international. In Figure 5 an overview on the recent years activities is given, regarding the projects that were conducted in our department. A continuous flow of projects over the past years was maintained, managing simultaneously a number of projects that is typically higher than 5. By implementing these projects we had a quite high scientific production, with ISI papers and patent applications and patents. The evolution over the years can be seen in Figure 6, showing a good continuity of results.

3. Research projects, applications and relevant results

In the following, a few examples of the more recent projects and applications will be given, emphasising one project for each major research direction that we pursue.

The research direction related to the coatings for harsh environments was continued in a national project, CREATIF: Complex Carbon and Titanium based nanocomposites for industrial applications (2012-2016) [6]. The project was realised in a partnership with Ovidius University from Constanta, National Institute for Laser, Plasma and Radiation Physics and the private company NOVUS.

Recent investigations of TiSi based carbide [7,8] or carbonitride coatings [9,10] have demonstrated that these materials are attractive candidates for a variety of industrial applications due to their high hardness, low friction, enhanced wear-corrosion resistance and high thermal stability.

The goal of CREATIF project was to study the effects of additions of Zr or Cr elements into TiSiC coatings. The coatings prepared were envisaged to be used for the protection of irrigation water pump components, working under high wear and corrosion conditions. According to the considered application, the tribological tests were carried out on uncoated and coated C45 steel substrates. TiSiC, TiSiC-Zr and TiSiC-Cr coatings, with Zr and Cr added to TiSiC base coating system, were prepared by cathodic arc method in a CH_4 reactive atmosphere on Si and 316 L substrates. The corrosion and wear resistance of the coatings in 0.9 % NaCl solution was evaluated. The TiSiC coatings were taken as reference. Additional film characterization concerning the elemental and phase composition, chemical bonds, morphology, residual stress, hardness, and adhesion was performed.

All the coatings exhibited nanocomposite structures, mainly consisting of a mixture of crystalline face-centred cubic (FCC) carbide solid solutions, with a preferential (220) texture, and amorphous carbon phases. The coatings showed compact, homogeneous and featureless cross-sectional microstructures. Cr and Zr incorporation in TiSiC resulted in lattice distortion (from a lattice parameter of 0.4358 nm for TiSiC, to 0.4536 nm and 0.4320 nm for TiSiC-Zr and TiSiC-Cr, respectively) and grain refinement. Also, alloying TiSiC led to a reduction of stress in the films, from -3.12 GPa (TiSiC) to -2.37 GPa (TiSiC-Cr) and -2.58 GPa (TiSiC-Zr), and to film hardness changes (TiSiC: 35.2 GPa; TiSiC-Zr: 42.1 GPa; TiSiC-Cr: 31.4 GPa). When compared to the uncoated substrate (316 L steel), all the coatings exhibit more electropositive corrosion potential, lower corrosion current densities and higher polarization resistances, which is indicative of a more noble character. Nevertheless, metal addition to TiSiC led to an improvement of the corrosion resistance of TiSiC in NaCl solution. For the uncoated specimen, the coefficient of friction remained practically constant during the tribological test, at a value of ~ 0.3. In the case of the coated samples, the friction coefficient show an unstable behaviour, presumably due to the formation and destruction of passive films on the surface, It appears that Zr addition to TiSiC lends to a diminution of friction coefficient of about 2 times. Of the investigated coatings, TiSiC-Zr exhibited the lower dry friction coefficient (~ 0.2) and the lowest wear rate (~ $3.2 \cdot 10^{-6}$ $mm^3N^{-1}m^{-1}$).

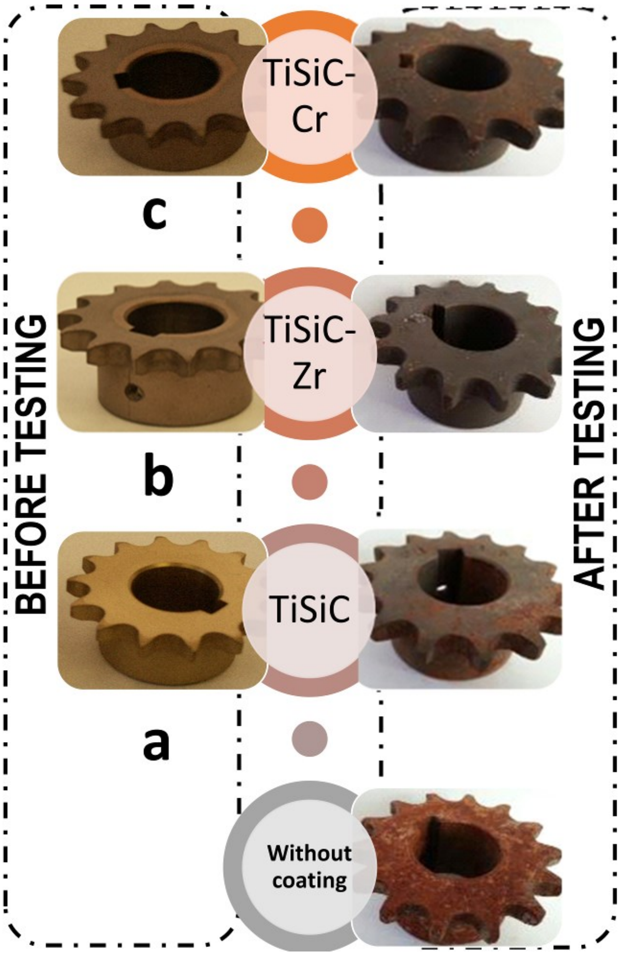

Figure 7: Optical images of irrigation pumps gears before and after testing (working in 3,5 % NaCl; at 30 rot/min; for 30 days and 6 h/day) [6]

Complex carbon and titanium based nanocomposites were obtained, on 3D pieces, and were tested inside irrigation pumps produced by the private company Novus, partner in the project. The advantage of using such coatings, as compared with uncoated samples is evident from the images of the gears, before and after testing in corrosive solution 3,5 % NaCl; at 30 rot/min; for 30 days and 6 h/day, as seen in Figure 7

Another important research direction is related with optical coatings in general, more specifically, multi-layered coatings with tuneable properties. This direction was developed in the frame of Core programme over the years, tackling various applications. These kind of multilayers are obtained using magnetron sputtering as a deposition tool, coupled with optical design and optimization. One of the examples of applications is related to selectively reflective coatings. In Figure 8 the optical transmittance and reflectivity of a multilayer consisting in 7 layers of SiO_2 and TiO_2 is represented [11]. A good match between the optical characteristics of designed and experimentally obtained multilayer can be seen, demonstrating both the accuracy of the design and the ability to experimentally obtain such a structure. In this case the purpose was to obtain a selectively reflective coating in narrow spectral interval, having a visual appearance in the yellow-green part of the spectrum. There are several applications that can be approached as a development of these structures, such as use into solar panels for architectural integration, hybrid solar concentrators, use in the optics for multispectral imaging.

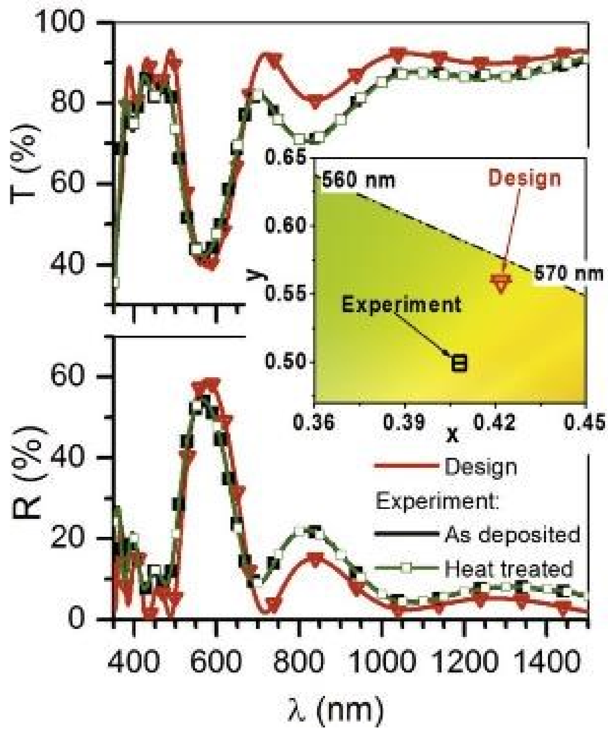

Figure 8. Transmittance and reflectivity spectrum of designed an experimental multilayer structure, consisting of 7 layers of SiO2 and TiO2 [11]

Our research in the field of novel materials for optoelectronics and microelectronics focuses on design, preparation, characterization and testing in applications of novel thin film materials prepared primarily by (hybrid) magnetron sputtering techniques, seeking to develop materials which can facilitate new technologies or to significantly enhance the existing optoelectronics technologies.

During two consecutive projects [12, 13], our attention was dedicated to group III nitrides such as InN materials, high-In-content ternary nitride-based materials, searching for the engineering of the electronic and optical properties of single-layers of InN for applications including photovoltaics, lighting, light detecting, fast microelectronics, optical devices, etc. For example, Figure. 9 illustrates the improvement on electron mobility of InN material by alloying with yttrium [12, 13,14].

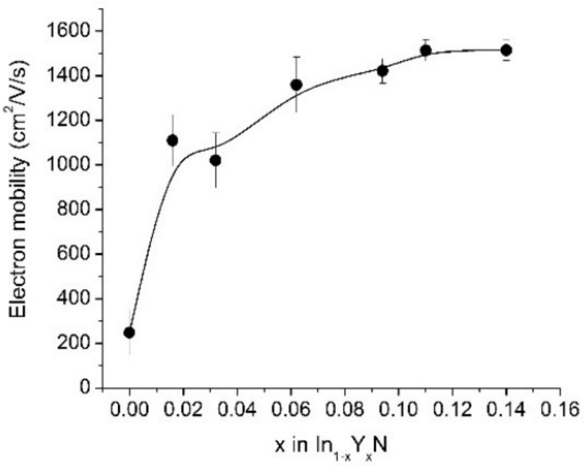

Figure 9 Electron mobility of InYN films

Studies on the magnetron sputtering hetero-epitaxial growth conducted to development of high crystallinity layers with improved electronic and optical properties (ex: monocrystalline layers of TiC and TiN grown for contacts of SiC-based high power devices [15,16,17]), to facilitate preferential growth directions of functional layers (ex: AlN(0001) and AlScN(0001) epitaxial grown on TiN(111)/MgO(111) and TiN(111)/Si(111) templates for piezoelectric energy harvesting MEMS – Figure . 10 [18]), to integrate device layers on cost-effective substrates, to develop functional multilayer devices or templates for further processing by other techniques. Examples include the development of SWIR ITO/(nc-GeSn)(SiO2)/GeSn(100)/Ge(100)/Si(100) photodetectors [19, 20], development of TiN(001)/MgO(001) (figure 11) and TiN(100)/Si(100) (Figure 12) templates for fabrication of UV-VIS NiO- and DUVGa_2O_3-based photodetectors [21,22, 23].

Our research also focuses on the fabrication and characterization of advanced nano-structures and materials and related devices. Examples include development of GeSn nanocrystals (NCs).

Lately the progress of short-wave infrared (SWIR) photonics domain was observed because it addresses many and various topics, such as environment in pollution monitoring or the new and most needed IoT (Internet of Things). The detectors based on Ge nanocrystals and crystalline GeSn are specific for SWIR photonics. However, the low miscibility of Ge and Sn make the manufacturing of GeSn a difficult problem. However, the magnetron sputtering technique proved again to be an effective and versatile deposition technique, suitable to solve this intricate provocation. We obtained nanocrystals of GeSn embedded in silica, and by selecting the deposition conditions we obtained the best growth condition.

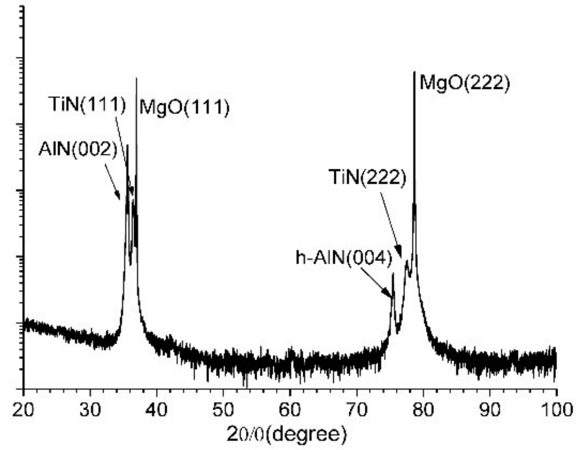

Figure 10 XRD profile of AlN(0001)/TiN(111)/MgO(111) structure

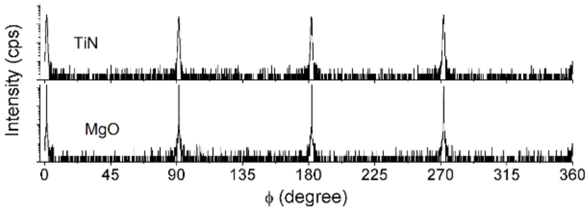

Fig. 11. 360° ϕ-scans over the (-202) planes corresponding to TiN films and MgO substrate [21]

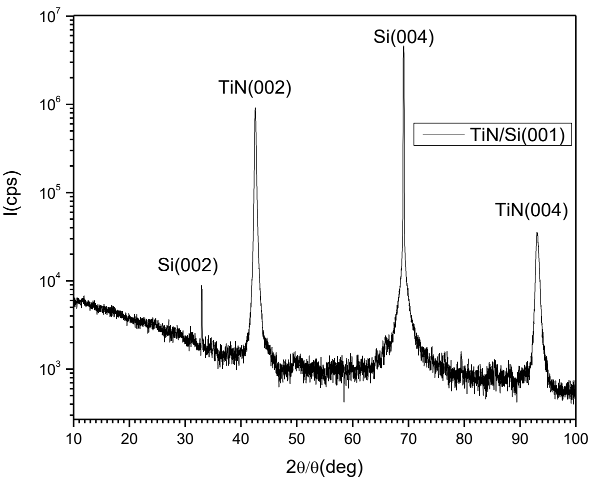

Figure 12. XRD spectrum of the epitaxial grown TiN film on Si (001) substrate used for Deep-UV photo detectors on industrial integrated silicon platform [22,23]

Three types of diode structures were obtained and investigated in the frame of M-Era Net project GESNAPHOTO [20]. Magnetron sputtering was used as deposition method, and the high power impulse magnetron sputtering was used for GeSn epitaxial deposition.

i) GeSn Nanocrystals in $GeSnSiO_2$ deposited by Magnetron Sputtering [24]

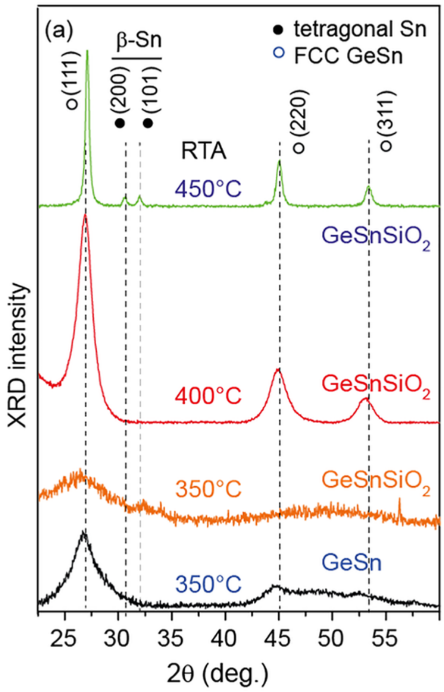

Figure 13: GeSn NCs embedded in SiO_2 are formed either by post-deposition annealing (350 °C – 450 °C), or during growth by deposition at high temperatures (300 °C – 370 °C.) [24]

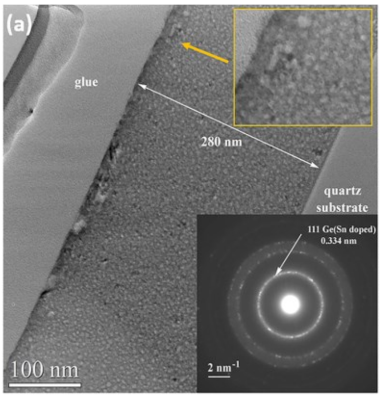

Figure 14: TEM image with the SAED of $(Ge1-xSnx)1-y(SiO2)y$ with $x = y = 9\%$ after RTA at 400 °C pattern as inset [24]

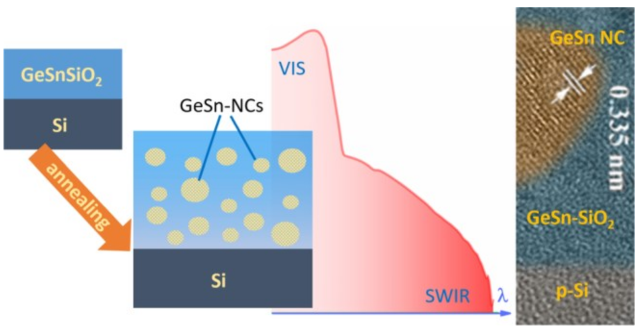

Figure 15: Photosensitivity of GeSn NCs in SiO_2 [24]

ii) $GeSn/SiO_2$ Multilayers deposited by Magnetron Sputtering [25]

The electrical contact of the diode was made of ITO conductive oxide, also deposited by magnetron sputtering.

The photosensitivity in SWIR of the ITO/20×(GeSn NC/SiO2)/p-Si/Al diodes exhibits the maximum value for a reverse voltage of 0.5 V. The sensitivity was observed also for wavelengths longer than 2200 nm (Figure 16).

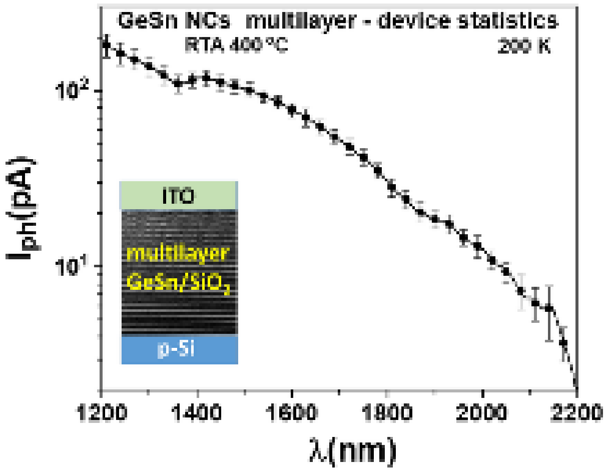

Figure 16:The diode photosensitivity [25]

It is to be noted that the multilayered stack produced photodiodes with higher photocurrent efficiency assessed in comparison with diodes fabricated with GeSn NCs films.

iii)Epitaxial GeSn layer Obtained by High Power Impulse Magnetron Sputtering for SWIR Heterojunction with Embedded GeSn Nanocrystals [19]

The stacking of these layers in one run of deposition formed a p−n GeSn NCs layer/GeSn epilayer hetero-junction diode. The diode has high photosensitivity in SWIR (1.2−2.5 μm), up to 2 × 10^5 %, compared to diodes based only on embedded GeSn NCs.

The epitaxial GeSn layers by high power impulse MS (HiPIMS) was obtained for the first time by ReCAST team.

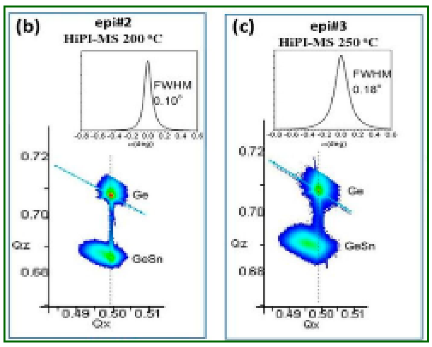

Figure 17: Rocking Curves of the epitaxial GeSn films [19]

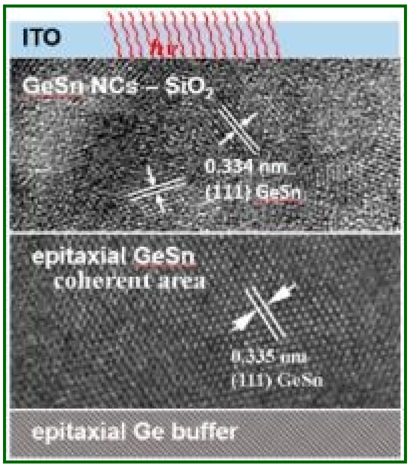

Figure 18: TEM image of the GeSn NCs embedded in oxide as $(Ge_{1-x}Sn_x)_{1-y}(SiO_2)_y$ layers[19]

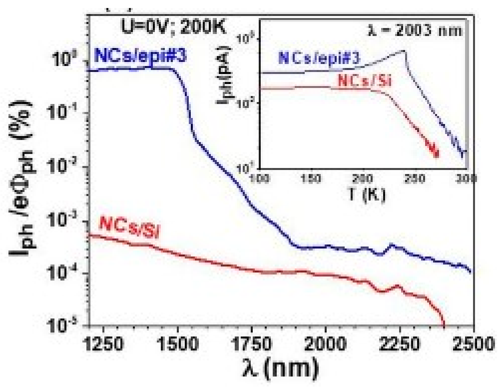

Figure 19: The photosensitivity in SWIR of the diode [19]

Another field of applications approached in our centre relates to medicine. Nowadays, there is a major concern on the health issues related to prolonged life expectancy of people. Therefore, the enhancement of quality and lifetime of different type of prosthetics is of great importance. Bactericidal coatings were obtained on biodegradable and non-biodegradable implants of different types, during the project ERANET-RUS-PLUS-CoatDegraBac68/2018: *Biodegradable and non-biodegradable orthopaedic implants with bactericidal coatings and controllable degradability*, 2018-2021 [26]

CoatDegraBac aimed to significantly reduce failure of implants made of biodegradable Mg alloys and nonbiodegradable Ti-based alloys by specially designed antibacterial and bioactive coatings. Coated implants accelerated osseointegration and improved bone bonding ability, reduced local inflammation, and guaranteed the long-term the antibacterial abilities. The project applied a multidisciplinary approach using advanced physical, chemical and biological methods to design innovative coating and to examine their interaction with cells and tissues in ex vivo and in vivo models. We engineered surface modification of the Ti-based and Mg alloys to control topography, roughness and blind porosity to enhance the adhesion, spreading, growth and differentiation of the osteoblastic cells, leading to the improved osseointegration. Beyond state-of-the art results were achieved by the design of calcium phosphate (CaP) coatings with the controlled dissolution rate of Zn or Cu and/or Sr, ensuring optimal release kinetics of the antibacterial agents provide the antibacterial properties for up to six months post-implantation. The innovative properties of developed surfaces were tested in functional test systems for the biocompatibility, for the first time the effect of the controlled dissolution rate of Zn or Cu and/or Sr on the essential innate immune responses were examined. To demonstrate the proof-of-concept, we developed a coated implant prototype for validation in the animal model. CoatDegraBac exhibited a significant impact on the international scientific community by intensifying the interdisciplinary research in regenerative medicine. During the project, a novel technology for surface functionalization of Ti and Mg -based alloy was developed by bioactive and antibacterial coatings. The result obtained during the project, were widely disseminated in: 1 book, 13 ISI Papers, 5 patent applications, 18 lectures in international conferences, 1 and interview in Radio Romania Cultural. Moreover, the young researchers were strongly involved in this project in the frame of 7 bachelor and 1 master degree projects.

Some of the prototypes, produced by the company that was partner in this project, TEHNOMED IMPEX CO S.A, and coated with our technologies are presented in Figure 20.

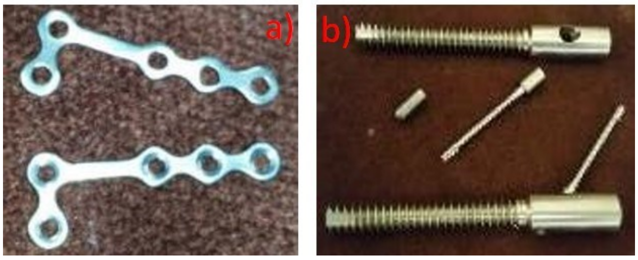

Figure 20 maxilo facial implants coatd with CaP+Mg (a), and screws coated with CaP+Ag

The international cooperation helped to understand obtained scientific data from many points of view and through the expertise of many collaborators during the discussion which essentially makes conclusions more complete and justifiable.

An important component that is visible in the activities of ReCAST centre is the relation with the industry. Therefore, industrial partners are included in the project consortiums, so that a transfer of technology and knowledge becomes possible. One example of such collaboration was the M-ERA Net project "Thick, adherent stress-free DLC coatings for demanding applications M.ERANET-3102-TANDEM-5 56/2016" [27], taking place between 2016-2019 inside an international consortium with partners form Sweden (Uppsala University, Ionautics AB, Linkoping University, Romania (INOE-2000, S.C MGM Star Construct SRL) and Portugal (University of Coimbra). Thick adherent DLC coatings were obtained, first in laboratory scale conditions and then in industrial conditions, Figure 21.

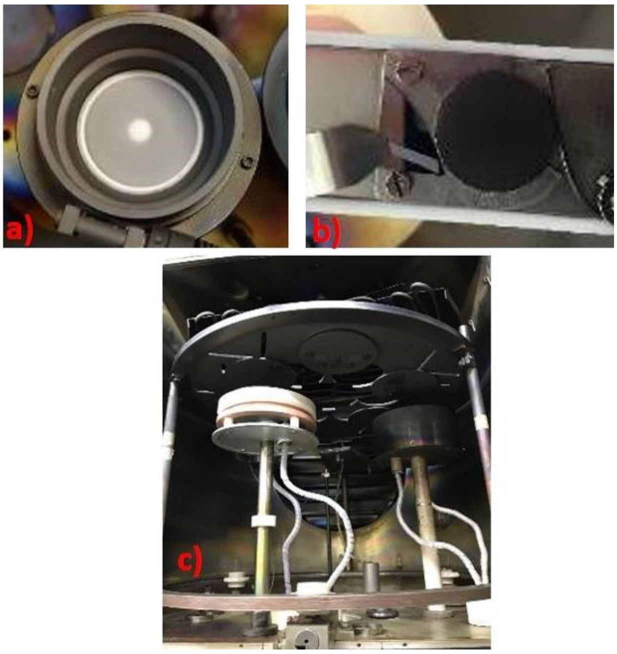

Figure. 21. a)Laboratory scale magnetron target, 5 cm diameter, b) typical sample of laboratory scale conditions, diameter 2.5 cm, c)industrial scale setup with 15 cm diameter target, for the deposition of DLC coatings in TANDEM project [27]

By combining the knowledge of academic partners we managed to provide a viable solution for a deposition technology, implemented and validated by the industrial partner. Coatings with hardness up to 30 GPa were obtained both on flat samples, used for testing under laboratory conditions, and on diesel injector pins, user for testing in industrial relevant conditions. It was proven that the DLC coatings have a protective role and can enhance the lifetime of the injector pins.

Another example of this type is the M-ERA Net project TriBOHEA, "High entropy alloy coatings for tribological applications", that is still in progress. The project is realized in a consortium composed by partners form Romania (INOE and - SC MGM Star Construct SRL) and Spain (GOIZPER, S. Coop end-user which subcontracted Tekniker (research institute). The main objective of the project was the development of thick high entropy alloy (HEA) based coatings for applications requiring high friction and wear resistant surfaces The targeted application is coatings for clutch friction discs. The project started by development of thin films by Hybrid HiPIMS/DCMS/RFMS of metallic high entropy alloys and high entropy ceramics (high entropy carbides - HEC and high entropy carbo-nitrides -HECN) in order to test different high entropy material compositions for the targeted application. A selection of compositions was made and tested for powder fabrication by mechanical alloying technic, starting from mixtures of elemental powders. We developed the technologies for fabrication of single crystallographic phase of metallic HEA powders, high entropy carbide powders and high entropy composites (TiC and WC reinforced HEA). These technologies have been transferred to MGM Star Construct SRL. The powder materials produced by these technologies were used as raw material for development of thick HEA-based coatings on clutch disc substrates by Atmospheric plasma spray process.

XRD spectra of three versions of HEA alloys obtained on clutch discs by atmospheric plasma spray are shown in Figure 22

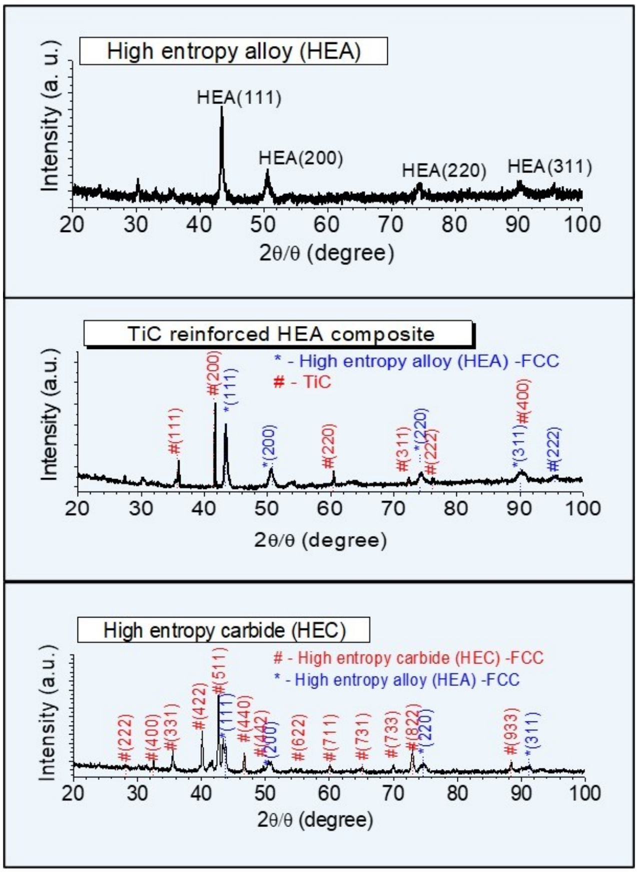

Figure 22. XRD spectra of the this HEA alloys obtained by plasma spray on clutch discs, in the frame of TRIBOHEA project [28]

Complementary to the main activities of thin film deposition and characterization, in our group there is also a solid expertise for developing our own tools for the sputtering technologies. One such tool is the power supply for High Power Impulse Magnetron Sputtering, known as HIPIMS. A prototype of such power supply was entirely developed and build in our laboratory, in the frame of the Core Programme [18], a picture of the power supply in the experimental setup being presented in Figure 23.

The main technical characteristics of the power supply are:

- Maximum voltage: 1000 V
- Pulse frequency: 1 ÷ 250 Hz;
- Single or double pulse;
- Pulse delay : 25 μs ÷ 1 ms;
- Pulse width: 50 ÷ 300 μs;
- Maximum current : 125 A;
- Maximum average power: 750 W;
- Short circuit and arc protection;
- Remote controlled

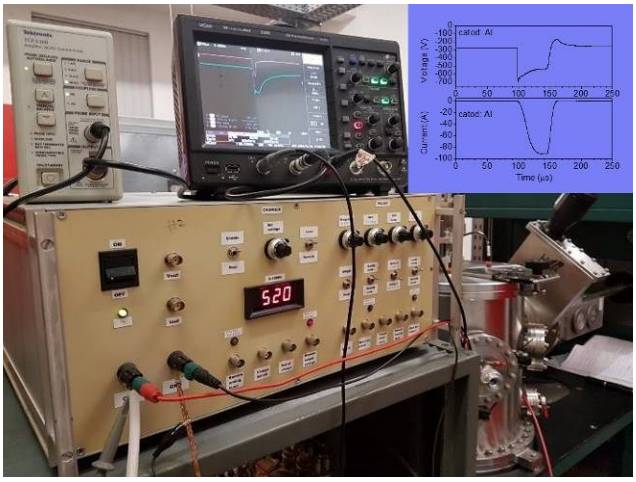

Figure 23. Front panel of HIPIMS power supply developed in-house, on the experimental setup with Oscilloscope, Current probe and vacuum chamber. Typical pulse characteristics on the top right corner of the image

The main advantage, compared with commercially available power supplies, is that we can design our own control knobs. Therefore we have a greater versatility in controlling the process, using single or multi-pulses, different delays, fine control of the duration and frequency.

In the broader frame of vacuum technologies, we recently developed a facility for vacuum testing and thermal cycling. This can be used for testing materials or even objects in conditions that can mimic the conditions in space, such as vacuum or controlled atmosphere and thermal cycling.

Figure 23. Facility for high vacuum testing and thermal cycling (TVAC)

The picture of the equipment is presented in Figure 23, showing to the left the PC-DAQ and TVAC controller, and the testing chamber to the right.

The technical parameters of the testing facility are the following:

-temperature interval -175° ÷ 200°C

-adjustable temperature slope

-continuous monitoring of temperature and pressure

-base pressure < $1x10^{-6}$ Torr

-vacuum chamber size: diameter 700 mm, length 550 mm

4. Summary and conclusions

To summarize, the ReCAST research centre and the department staff have a solid expertise in all the fields, going from the technological processes, through the characterization of the thin films and finally tackling a large variety of applications. The applications come from different research fields, that can be summarized as follows:

i) Bioactive coatings, based on hydroxyapatite with different doping elements were obtained for applications in medicine. The main types of coatings are Hydroxyapatite doped with:

- •Zn, Cu, Ag with anti-microbial properties;
- •Sr, Mg – for increased osteointegration;
- •Si, Ti, Zr for increased mechanical performance.

ii) Super hard coatings, based on nitrides, carbides, carbonitrides and oxynitrides were developed for various industrial applications. The main types of coatings developed are:

- •Nitrides: MeN, MeAlN, MeSiN, HEAN;
- •Carbides: MeC, MeSiC; HEAC;
- •Carbonitrides: MeCN, MeSiCN, HEACN;
- •Oxynitrides: MeNO; MSiNO;
- •Diamond like carbon (DLC)

where Me = Ti,Zr,Nb,Cr,W, Fe,Al, etc; HEA = High Entropy Alloy

iii) Decorative coatings were obtained on different types of substrates, such as plastics, ceramic and glass. The main types of coatings in thi category are:

- •Nitrides: e.g. TiN, ZrN;
- •Oxides: CuO, TiOx, TiZrOx.

iv) Finally, tunable properties of a large variety of coatings are achieved , for applications in optics and optoelectronics. The main types of coatings are;:

- •Multilayer collection optics for SOARING EUV lithography system
- •Optical system for laser beam transmission @ 15 km on Mars, with almost constant beam diameter
- •Coatings with high reflectivity coefficient in VIS, UV, EUV, XUV;
- •Optical coatings, filters;
- •Epitaxial and polycrystalline thin films and structures based on GeSn, TiC, SiC, InN, AlN, TiN for opto and micro –electronics.

An intense activity in these directions is foreseen in the future. The preparations starts with the project proposals that are already under consideration or were evaluated in the past 2 years. Besides the national competitions, where project submission is constant, the European competitions are also target. Among the most important calls for proposals, where projects were submitted in the past years, are M-EraNet, Eurostars 3 - Call 3, LEAP-RE 2021, HORIZON-CL4-2022-RESILIENCE-01-13, ERA-MIN2021, ERC.

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Special optoelectronic and optospintronic materials with targeted functionalities

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Abstract The activity of the department is focused in the direction of the development of multifunctional materials with optoelectronics and optospintronics applications in commercially significant technologies for optical and photonic components, process monitoring and control, communication technology, energy, health and environment protection and control. The department carries out research to develop synthesis technologies for special materials with optical, magnetic, magneto-optical and non-linear optical properties, for targeted applications. Structural, morphological techniques are used to investigate materials and nanostructures for information technology, medicine, food, environment and the non-conventional energy.

Keywords: Optospintronics, Optoelectronics, Heusler compounds, Oxide materials, Graphene, Magneto-optical effect, Non-linear optical effect, Quantum dot semiconductors, Sensors, Food, Environment protection, Health, solar cells.

1. Introduction

1.1. Brief description and personnel

The department "Optospintronics" has been christened through merging the names of two main research fields, i.e. "optoelectronics" and "spintronics", taken over along with the building of the team. Activity on spintronics has started in 1999, with Access To Research Infrastructures at the European Facility at IESLHeraklion, Crete,Greece, when PLD of the first known spin polarized half Heusler alloy NiMnSb has been deposited on InSb at moderate temperature and issued a WO patent Application. Further on, the department evolved following the initiative of the institute in setting up a European network focused on the development of spin-polarized half-Heusler and Heusler alloys as contacts for narrow gap semiconductor structures. The network eventually turned in a FP5 R&D project with 16 partners (FENIKS, G5-RD-CT-2001 00535 EC), where INOE 2000 played a foremost role through leading one of the 7 work packages, i.e. "Magnetic Alloy DepositionTo date the group Optospintronics counts two physicists (condensed matter, biophysics), two chemical engineering scientists (1 silicate engineering and 1 organic chemistry engineering), one physical-chemistry scientist, one specialist in electronic engineering. In addition, two technicians give their best support in experimental work. The actual activity of the group advances around hot topics in materials science, physics, and chemistry, focused on photonics, spintronics, sensors and their wide applications.

1.2. Main elements of infrastructure

The infrastructure has been gathered according to the goings-on of the group. The multidisciplinary skills of the scientists as mentioned above have made sprung a few strands of research with a focus to advanced materials with improved properties, such as complex metal alloys, semiconductor oxides, metal-organic compounds, group III-nitrides, phosphate glasses. These materials have been developed as either bulk or thin films, and subsequently characterized on site for their structural, optical and magnetic properties.

Thin films are mainly produced by pulsed laser deposition (PLD) and sol-gel, depending on the material. Metal alloys and oxides are usually grown by PLD from metal targets using the high-tech PLD 2000 workstation (PVD Products, USA), that employs either the 193nm or the 248nm wavelength of a COHERENT 201 excimer laser. Sol-gel films of phosphate glasses and organo-metallics embedded in polymers from various precursors are prepared on site using a spin processor WS 650 (Laurell).

Preparation of samples with a view to their characterizations is mainly the task of the technicians. On this purpose a MECATOME I 201 A (PRESI) cutting machine is used to first make slices of the bulk samples, which are then polished on the MECAPOLE P260 (PRESI).

Characterizations are made through: FTIR, with a Perkin Elmer Spectrum 100 Spectrometer holding an UATR accessory; UV-VIS-NIR spectrometer Perkin Elmer, Raman spectroscopy, using a LABRAM HR UV-VIS-NIR instrument (Horiba Scientific) that presently performs at 4 wavelengths (785nm, 632nm, 514nm, 488nm); fluorescence spectroscopy run with a Fluorolog spectrometer (Horiba Scientific).

The main research domain of Optospintronics Department is related to advanced research on the synergy between the structures that emit, transmit and interact with optical radiation and development of materials with applications in optoelectronics and optospintronics. The main application fields for the materials developed in Optospintronics Department are (i) Optical & photonic components, (ii) Process monitoring & control, (iii) Communication technology (iii), Energy, (iv) Health and Environment protection & control.

The developed activities were financed based on projects granted at national and international competition calls. The Table 1 presents a selection of projects developed since the establishment of the institute till nowadays.

Table 1. Selection of projects granted at national and international competitions of calls

Program	Title-Acronym
MANUNET-Transnational Call 2020	Smart optical device for temperature sensing, based on innovative luminescent IV-VI quantum dots-doped complex nano-structured thin films **(TEMSENSOPT)** **(2020-2022)**
PNCDI-III P2. The development of the national research and development system	Ultrasensitive gas sensor array for green house environment assessment **(GREHSEN)** **(2020-2022)**
PNCDI-III P1. Increasing the competitiveness of the Romanian economy through CDI	E-tongue like sensor for food safety **(FOODESENS)** **(2020-2022)**
MANUNET-Transnational Call 2017	Optical Limiter Device Based on Innovative Graphene Derived Materials **(OLIDIGRAPH)** **(2018-2020)**
PNCDI- III P2. The development of the national research and development system	Nanostructured carbon materials for advanced industrial applications **(CARBON+)** **(2018-2021)**
	Component project P2-Oxidic nanocomposites with nanocarbon materials with applications in photonics (photovoltaic systems and lasers) **(NANOCOMPOZITCARB)**
	Component project P4- Composite photocatalytic coatings: metallic oxide – nanocarbon materials with applications in environment technologies: self-cleaning properties and advanced treatment of organic pollutants **(FOTOCAT-CARBONCOMP)**
PNCDI- III P2. The development of the national research and development system	New advanced nanocomposites. Technological developments and applications **(AdvanceNano)** **(2018-2021)**
M-ERA.NET Transnational Call 2015	High-performance tandem heterojunction solar cells for specific applications (**SOLHET)** **(2016-2019)**
PNCDI-II Partnerships in priority areas	Nanostructure-based system for real time detection of malignant tumor margins (**NANOMARDET)** **(2014-2017)**
PNCDI-II Partnerships in priority areas	Nanostructrures based on new organometallic compounds for electronic applications (**NANOCEA)** **(2012-2016)**
PNCDI-II Partnerships in priority areas	New vitreous magneto-optical materials applied in optoelectronics **(MOVITOPT)** **(2012-2016)**
PNCDI-II Partnerships in priority areas	Sensors for Metals Based on Azulenes Modified Electrodes for Water Quality Monitoring (**SEMEMA)** **(2014-2017)**
COST ACTION MP1406	Multiscale in modelling and validation for solar photovoltaics **(Multiscale Solar)** **(2015-2018)**
PNCDI-II Ideas	Quantum confinement effect of CdS/CdSe quantum dots in phosphor aluminosilicate matrix as a promising new temperature sensing material **(TEMPSENSGLASS)** **(2011-2016)**
MNT-ERA.NET Transnational Call 2010	Innovative optical microsensors based on rare-earth-doped phosphate glass **(SENSGLASS)** **(2011-2014)**
PNCDI-II Capacities	Correlation sinthesis-microstructure-properties for aluminophosphate vitreous bulk materials with application in magnetooptics **(MAGFOMEC)** **(2013-2014)**
PNCDI-II Resurse umane	Chemical and optical characterization of atmospheric suspended particles **(CHEMOP)** **(2011-2013)**
PNCDI-II Resurse umane	Contributions to the development of in-situ Laser Induced Breakdown Spectroscopy

	applications on submerged archaeological artifacts (under-water) **(2011-2013)**
PNCDI-II Capacities	Mechanical properties of rare-earth-doped phosphatic glassy materials used in optoelectronics **(MECANOFOSGLASS) (2010-2012)**
PNCDI-II Partnerships in priority areas	Advance phosphate materials with vitreous structure, doped with rare-earth ions, for optoelectronic applications **(OPTOGLASS) (2007-2010)**
PNCDI-II Partnerships in priority areas	Advanced organometallic materials for optoelectronics (**MOMAOPT) (2008-2011)**
PNCDI-II Partnerships in priority areas	Monitoring the behavior of metal construction structures to mechanical actions (**SISMET**) **(2007-2010)**
PNCDI-II Partnerships in priority areas	Development of clean technologies for glass industry in the context of the sustainable development **(CLEANTECHGLASS) (2007-2010)**
PNCDI-II CEEX	Research on obtaining some vitreous phosphate-potassium fertilizers with controlled solubility and establishing the parameters for use in plant production **(AGROFERTIGLASS) (2008-2011)**
PNCDI-II CEEX	Non linear functionalities in nanostructured photonic materials for IT applications" **(FUNFOTON) (2008-2011)**
PNCDI-II CEEX	Ecological glasses obtained through nanotechnologies, for mitigating, adapting and restoring natural environmental factors **(FRIENDLY GLASS) (2005-2008)**
PNCDI-II CEEX	Interdisciplinary network dedicated to the synthesis and study of semiconducting and conducting nanostructures for the purpose of obtaining photonic and optoelectronic devices and for use in biology and medicine **(NANOCRYSTALNET) (2005-2008)**
PNCDI-II CEEX	Obtaining of nanopigments for digitized vitreous decorative coatings **(DIGIDECOR) (2006-2008)**
PNCDI-I CEEX	Non-destructive method for evaluating the characteristics of road layers (**MNSR) (2005-2008)**
PNCDI-I CEEX	Synthesis of calcium carbonate with predetermined properties through non-conventional processes (**SONOCARB) (2005-2008)**
PNCDI-I CEEX	Advanced Knowledge on Spintronics by Developing the Physics of Tailored-Heusler Alloys **(ASPIDHA) (2005-2008)**
PNCDI-I CEEX	The experimental method for the study of materials with magnetic properties by KERR magneto-optical effect (**MAGNE-KERR) (2005-2008)**
PNCDI-I CEEX	Interactions Mechanisms and New Phenomena In 2D, 3D Systems Based on Nitrides of 3d and 4f Transition Elements **(TRANZEL) 2006-2008**
PNCDI-I CERES	Advanced structured materials for microelectronic microsystems (**ASMOM) (2005-2007)**
PNCDI-I CERES	The behavior of emerging states in heavily correlated electronic systems **(COSTEMSEC) (2006-2008)**
PNCDI-I CERES	Advanced research concerning preparation of photonic structures based on nano-crystalline GaN (**SFENG) (2004-2006)**
PNCDI-I CERES	Obtaining and characterization of thin photo and electroluminescent layers **(LUMILUX) (2004-2006)**
PNCDI-I MATNANTECH	Uniformly distributed pinning nanocenters produced by doping and irradiation in high critical temperature semiconductor materials **(2004-2006)**
PNCDI-I CERES	Phosphate glasses doped with transition ions. Correlation of microscopic properties with structural, electronic and local interaction properties **(STIFOSDOP) (2003-2005)**
PNCDI-I Grant CNCSIS	Ceramic/polymer composite materials for applications in the field of intelligent structures **2006**
FP5-EC-R&D	Ferromagnetic Semiconductors and Novel Magnetic-Semiconductor Heterostructures for Improved Knowledge on Spintronics

	(**FENIKS)** **(2001-2005)**
PNCDI-I CERES	Study of the influence of spatial-temporal variable thermal fields on phase processes in binary and ternary systems **(2001-2004)**
PNCDI-I RELANSIN	System for the study of vibration behavior and multiparametric analysis of construction elements **(2001-2003)**
Grant CNCSIS	Complex methods of characterizing the specific parameters of ultrasonic piezoceramic transducers in the medical field **(2000-2002)**

2. History

The high scientific potential of our department is ensured by the accumulated professional experience and the greatly improved endowment during years through the development of "large infrastructure" projects and by allocating a generous percentage of the developed research project costs for the "Equipment" chapter. The activity of the department is carried out in line with the most investigated subjects worldwide in the field of materials for applications in optoelectronics and optospintronics and the elucidation of the mechanisms of interaction of light with them. From the department establishment till around 2008 year, some activities were directed towards semi-Heusler compounds, e.g. NiMnSb, Heusler Co2Mn(Si, Ge, Ga, Sn, Sb) and Heusler with adjustable composition-Co2Mn X(1-x)Yx, new diluted magnetic semiconductors from the chalcopyrite family -MnxGe1-xSby :(Fe, Co). A selection of published papers is presented [1-15].

Starting with 2007 (the financial periods 2005-2013 and 2014-2020), the department was oriented towards new directions of research due to the significant increase of research infrastructure for synthesis (chemistry laboratory for sample preparation, PLD (pulsed laser deposition) and investigations (FTIR, UV-VIS-NIR). Thus, since 2007 there were continuously developed synthesis technologies (sol-gel, PLD and conventional methods) for special oxide materials with optical [16-25], magnetic, magneto-optical properties (eg: alumina-phosphate glasses doped with rare-earth, transition, post transition ions) [26-31], nonlinear optic characteristics (silico-phosphate films doped with organic compounds) [32-34] and electrical properties [35-38] for target applications in the field of optoelectronics. Bulk materials and films were investigated in the department's laboratories from the point of view of structure and morphology, as well as optical properties (spectroscopy studies: FTIR, Raman, ellipsometry, fluorimetry, UV-VIS-NIR), with application for **optical and photonic components**. The references are a selection of our published results in each area.

The continuous improvement of equipment endowment made possible the development of advanced research oriented towards the field of sensors based on photonic materials and nanostructures for **communication technology** [39-41], medicine [42-43], **process monitoring and control** [44, 45] **environmental protection and control** [46, 47] and the non-conventional way of obtaining electricity. The references represent a selection of our published results.

Recent and current research activities of the department are in line with the main challenges at European and International level. Thus, in the **health field**, modern technologies propose the development of complex methods of diagnosis and monitoring, based on the exploitation of the optical properties of nanostructures in their interaction with biological tissues/fluids when they are investigated with electromagnetic radiation. Recently, in the **energy sector**, advanced graphene-based materials represent the solution to many challenges, especially in **energy** storage applications. Due to the transparency and high conductivity, the integration of graphene materials in photovoltaic devices is a challenge and it is still being explored. Faraday rotators as magneto-optical components for the laser systems and IV-VI semiconductor-doped vitreous thin films for temperature sensing systems are recent and current research directions implemented in department. Also, research investigations are in progress, referring to silicon-based tandem solar cells incorporating low-cost, abundant, and non-toxic metal oxide materials, increasing the conversion efficiency of silicon solar cells beyond their conventional limitations with obvious economic and environmental benefits.

3. Recent results and transfer of results

3.1. Vitreous phosphate materials doped by rare earth ions (Dy^{3+}, Tb^{3+}, Nd^{3+} for Faraday rotators) for optical and photonic components

Magneto-optical phenomena occur as a result of the interaction of optical radiation with the material, in the presence of the magnetic field. The size of the magneto-optical effect of a material is given by the size of the rotation angle of the polarized light, transmitted or reflected by the material, placed in a magnetic field. In the case of the transmitted light, there is Faraday effect and in the case of the reflected light, there is Kerr effect (Fig.1). Diamagnetic materials show a positive rotation angle, having negative magnetic susceptibility whereas paramagnetic materials show a negative rotation angle and positive magnetic susceptibility. Both the Faraday rotation angle and Verdet constant are decreasing with visible wavelength and are correlated with magnetic susceptibility of the materials as well as with the thickness of the sample and the applied magnetic field [48].

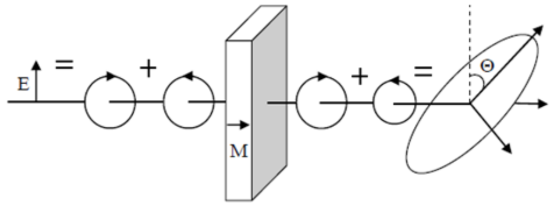

Fig.1 Faraday magneto-optical effect

Two directions were developed in the frame of magneto-optical materials domain:

3.1.1. Vitreous phosphate materials doped by rare-earth ions (Dy^{3+} and Tb^{3+}) for Faraday rotators

Rare-earths and transition ions-doped glasses prepared by wet melt-quenching non-conventional method are paramagnetic materials. These glasses have negative Verdet constants of high values, inversely proportional to the temperature.

In the case of Dy-doped phosphate glass, the magnetic susceptibility is positive and it is increasing with magnetic field, with positive slope and the inverse of susceptibility is increasing linearly with temperature [49]. The magnetic susceptibility, χ is 5.3 $\times 10^{-5}$ cm^3/g, at 300 K and Curie constant, C is 0.01598 Kcm^3/g. The Faraday rotation angle, θ_F is decreasing with wavelength, being 1.25° at 400 nm and 1.05° at 500 nm. Dy-doped phosphate glass shows multiple absorption bands in the visible domain as well as a decreasing of Verdet constant with wavelength. Thus, Verdet constant, V is 0.17 min/Oe/cm at 400 nm and 0.1 min/Oe/cm at 500 nm [49].

3.1.2. A new zinc phosphate-tellurite glass belonging to the $45ZnO$-$10Al_2O_3$-$40P_2O_5$-$5TeO_2$ system, having magneto-optical properties, applied in Faraday rotators

A Zn-containing phosphate-tellurite glass was synthesized, showing two absorption bands in the visible domain, at 420 nm and, respectively, at 580 nm, assigned to clusters of tellurium diatomic molecules that are formed during the glass fabrication, due to reduction processes during the glass melting stage (Fig.2) [50] The band gap of the glass is graphically determined, based on the absorption spectrum, being 3.18 eV (Fig.3). The diamagnetic character of phosphate-tellurite glasses is mainly given by the clusters of tellurium diatomic molecules. The magnetic susceptibility is negative and it is increasing with magnetic field, with negative slope. Zn^{2+}, Al^{3+}, P^{5+}, Te^{4+} from the vitreous network determine a diamagnetic rotation of the polarization plan of the transmitted light. Faraday rotation angle and Verdet constant are positive of relative small values, mostly independent of temperature (Figs. 4 and 5).

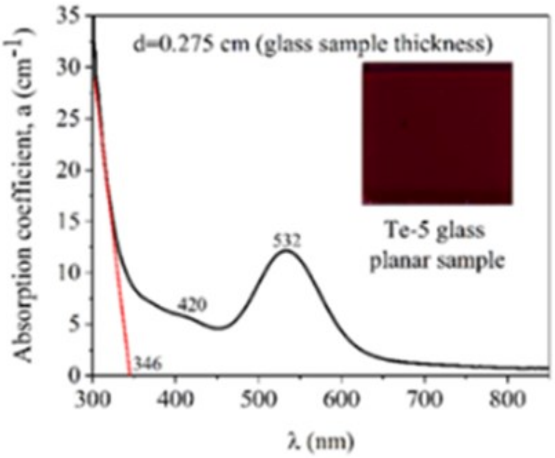

Fig.2. Optical absorption of zinc phosphate-tellurite glass [50]

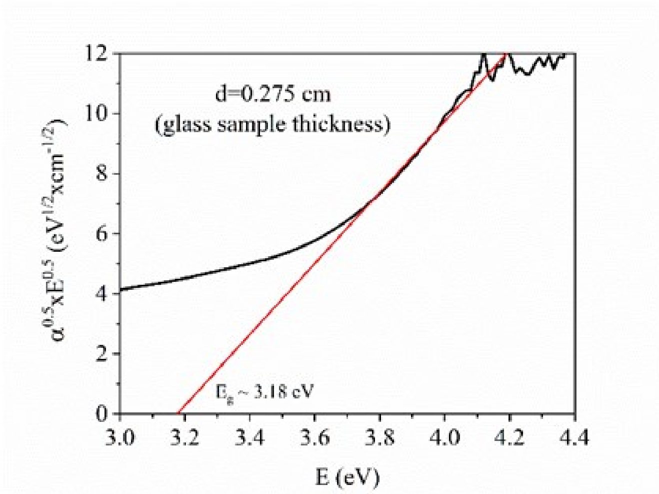

Fig.3. Optical band gap of zinc phosphate-tellurite glass [50]

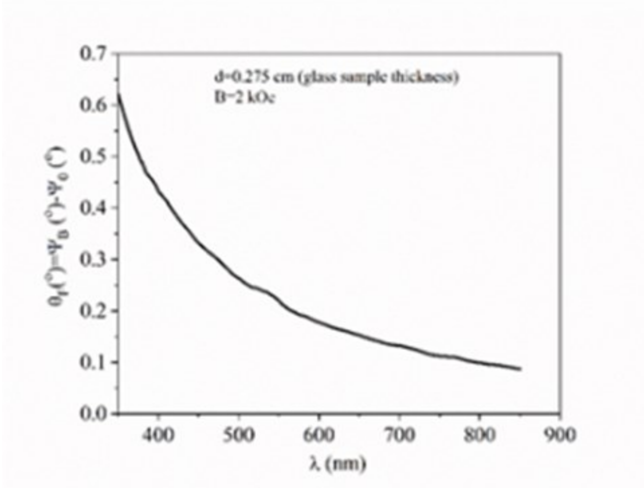

Fig.4. Faraday angle versus wavelength for zinc phosphate-tellurite glass [50]

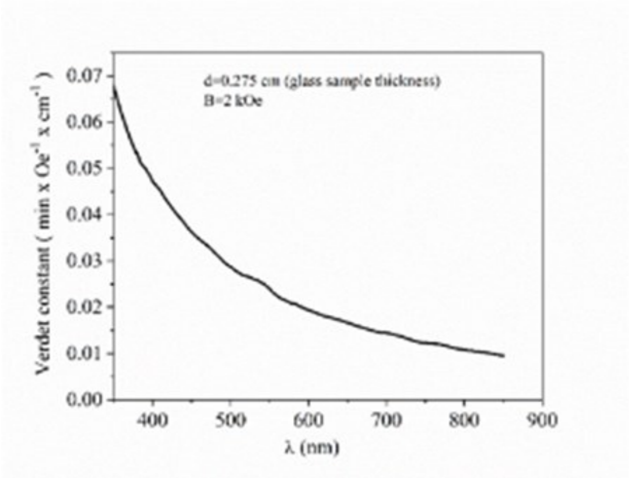

Fig.5. Verdet constant versus wavelength for zinc phosphate-tellurite glass [50]

3.2. Oxide nanocomposites ($ZnO-P_2O_5$) with nano-carbonic materials with applications in photovoltaic systems for energy field

The addressed objective of our research activities, was the development of sol-gel technologies for synthesis of new materials: ZnO-GO/rGO and $ZnO-P_2O_5$-GO/rGO, as transparent electrodes, with applications in photovoltaic systems. We have investigated these new composites as transparent electrodes for photovoltaic solar cells based on: (i) the high optical transparency, low resistivity, ability to be deposited at low temperatures, nontoxicity, wide availability, low cost and chemical stability of zinc oxide; (ii) the remarkable electrical, optical, mechanical and chemical properties, tunable band gap, high mobility, and high flexibility of graphene oxide and on (iii) the phosphate-based glasses (P_2O_5) that can improve the conductivity and increase graphene oxide (GO)/reduced graphene oxide (rGO) concentration and the homogeneity distribution in the films, preserving the good transparency.

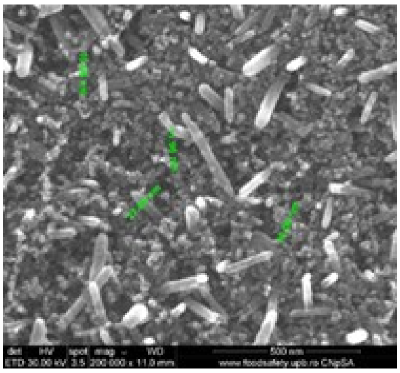

Fig. 6 SEM image of a $ZnOP_2O_5$rGO sol-gel film on ITO substrate

Our results (Figs. 6 and 7) were published [52] and [53] and the technology was the object of a patent application [54] awarded with Silver Medal, at EUROINVENT 2022 Iasi, Romania.

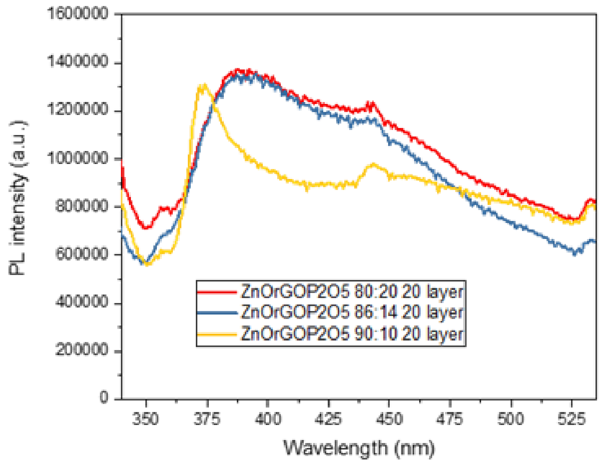

Fig. 7 Photoluminescence of 20 layers films at λ excitation=325 nm, at different $ZnO:P_2O_5$ rations: 80:20; 86:14; 90:10 and 1%rGO

3.3. Titanium based oxide nanocomposites ($TiO_2-P_2O_5$) with nano-carbonic materials, for photocatalytic applications for environment protection & control domain

Photocatalysts for environmental remediation are extensively studied and $TiO_2–P_2O_5$ glasses were reported to exhibit photocatalytic oxidation activity and highly photo-induced hydrophilicity under UV irradiation.

Graphene, with its large surface area is a good adsorbent for organic pollutants through the combination of electrostatic attraction and π-π interaction and having a high electron mobility it reduces the electron-hole pair recombination, improving the photocatalytic activity. TiO_2-P_2O_5-rGO and TiO_2-rGO glassy films with different concentrations of rGO (reduced graphene oxide), were prepared using the sol-gel method, aiming at exploiting both P_2O_5 and graphene oxide capabilities to meet the photocatalytic requirements and enlarge the light absorption domain of TiO_2. SEM image of a representative 1.5 % rGO-$TiO_2P_2O_5$ film on ITO substrate is presented in Fig.8. The results obtained in these conditions are promising and show that solar active photocatalytic thin films can be obtained using common temperatures [55]. The developed technology was the subject of a patent application [56] awarded with Golden Medal at PRO INVENT, Cluj-Napoca 2021, Romania.

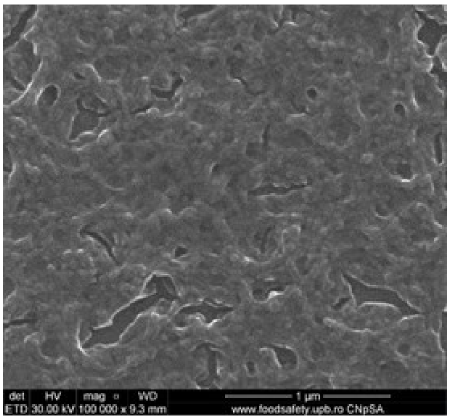

Fig. 8 SEM image of the 1.5%rGOTiO$_2$P$_2$O$_5$ film on ITO substrate

3.4. Optical Limiter Device Based on Innovative Graphene Derived Materials for optical & photonic components

Recently laser and related technologies developments led to rapidly growing applications in the fields of military, medicine, scientific research and manufacture/processing industries. The potential damages of laser to human eyes and delicate optical instruments stimulates the developments of laser protecting materials. Optical limiting (OL) materials are the most recently developed laser protection materials. Their OL behavior is based on nonlinear optical (NLO) effect and therefore can be expected to fulfil the requirements of efficient laser protection: high linear transmittance; short response time; high damage threshold; low limiting threshold; broadband spectral response. Graphene is theoretically consisted of a single layer of hexagonally arranged sp2-hybridized carbon atoms and has a unique electronic structure with linear dispersion of Dirac electrons, the interband optical transitions independent of frequency over a wide range and depend only on the fine-structure constant making it a promising broadband NLO material. The fine structure constant is the parameter that describes coupling between light and relativistic electrons and that is traditionally associated with quantum electrodynamics rather than materials science) and poor solubility. In terms of practical applications, it has to be a compromise between: synthesis costs of suspensions (GO/rGO) and enhancement of OL properties due to the morphology-dependent bandgap of graphene materials. We have investigated the sol-gel SiO_2-P_2O_5 matrix as it has high linear transmittance in visible region, thermostability, mechanical characteristics and may enhance the NLO properties of the material.

These new proposed materials have the role to lower their optical transmittance when incident laser beam intensities are increasing above a threshold value, ensuring a constant intensity of the transmitted laser beam and preventing, thus, the damages to human eye and different optical sensors.

We have developed a laboratory synthesis technology for composite silico-phosphate films doped with rGO and GO. Films deposited on ITO with properties of optical limiting for laser beam with ultrashort pulses (~fs) at λ=1550 nm and at λ=750. The best materials were integrated into 2 variants of optical limiter device [57].

The schematic representation of the optical limiting functionality of graphene-based silico-phosphate film is presented in Fig.9.

Fig.9 Schematic presentation of the optical limiter [57]

3.5. Optical analysis of ZnO/Cu$_2$O structures in silicon-based tandem solar cell for energy field

The COST ACTION MP1406 (Multiscale Solar): "Multiscale in modelling and validation for solar photovoltaics" that ran during the period (2015-2018) http://multiscalesolar.eu/ (MC member, WG2 Mesoscopic Dynamics Meso, Workgroup 3: Macroscopic Device Characteristics) [58] was the starting point of further research activities developed in the frame of different projects.

The semiconducting metal oxides ZnO and Cu$_2$O are promising candidate materials for implementation in photovoltaic applications, since they are earth-abundant, non-toxic and have the potential for low production cost.

Rapid progress of thin film solar cells has resulted in the development of tandem solar cells based on crystalline silicon with conversion efficiencies beyond the c-Si single-junction limit. We have investigated ZnO and Cu$_2$O materials for optoelectronic applications and new materials and structures for photovoltaic applications [59, 60]. Further investigation of Cu$_2$O-based solar cells is still needed in order to realize their full potential in photovoltaic applications.

ZnO is a high energy excitation (60 MeV) high-energy (3.37 eV) semiconductor material that provides ultra-violet emission exciton regions efficiently at room temperature. This bandgap corresponds to a wavelength of 328 nm, within the UV light range and it is transparent to visible light as well as to the most widely used wavelengths in optical technologies.

The incorporation of nitrogen into the Cu$_2$O thin films did not significantly affect surface morphology or the optical properties, and thus the nitrogen-doped Cu$_2$O thin films remained phase pure [61].

Semiconducting metal oxides such as ZnO and Cu$_2$O are promising candidate materials for implementation in photovoltaic applications (Fig. 10). The Aluminium doped ZnO (AZO) thin films indicate a high transparency in the visible region and these transparent AZO films may open a new avenue for optoelectronic and photonic devices applications in near future [62].

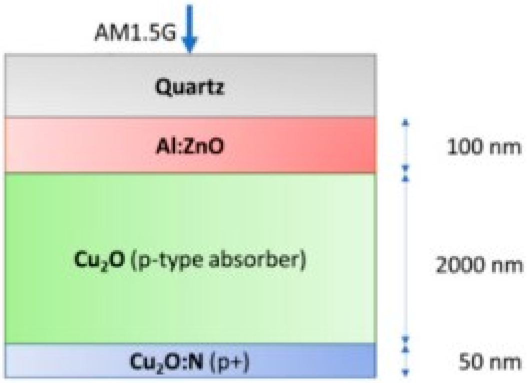

Fig. 10 Simplified diagram of the simulated metal oxide solar cell [63]

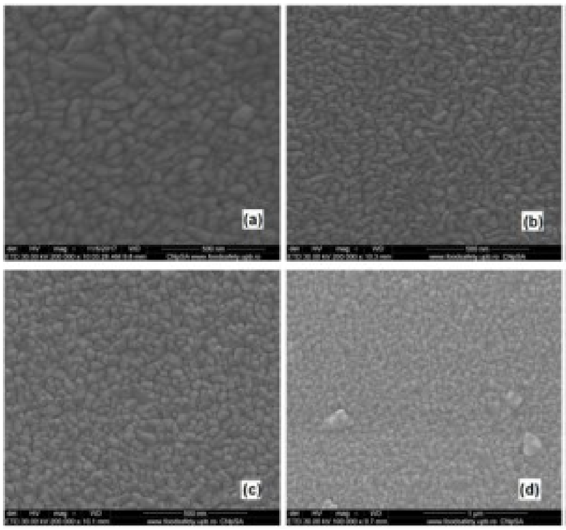

Fig.11. SEM images of Cu_2O:N thin films deposited on quartz substrate by the DC magnetron sputtering under different gas flow conditions : (a) Sample 0, (b) Sample 1, (c) Sample 2, and (d) Sample 3 [63]

Experimental measurements for the determination of surface morphology were performed on Cu_2O:N thin films deposited by the DC magnetron sputtering on the quartz substrate under different gas flow conditions (Figs. 11 and 12) [63].

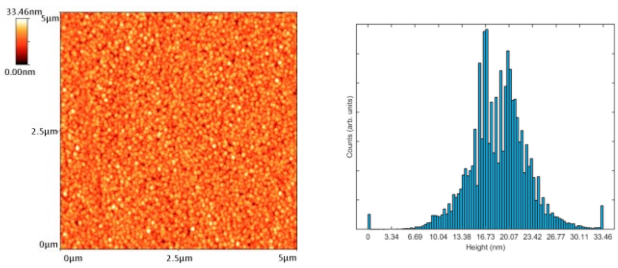

Fig.12. 2D AFM images of Cu_2O thin film and its 2D corresponding histogram [63]

3.6. High-performance tandem heterojunction solar cells for specific applications for energy

Silicon-based tandem solar cells incorporating low-cost, abundant, and non-toxic metal oxide materials can increase the conversion efficiency of silicon solar cells beyond their conventional limitations with obvious economic and environmental benefits [62].

Research on silicon-based tandem heterojunction solar cells (STHSC) incorporating metal oxides is one of the main directions for development of high-efficiency solar cells [64].

The tandem solar cell is constituted from two subcells: the top subcell based on the heterojunction ZnO/Cu2O and the bottom one based on c-Si (Fig.13).

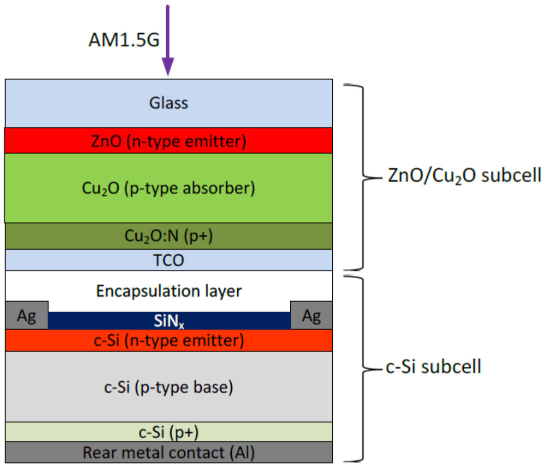

Fig.13. Schematic device design of a four-terminal tandem heterojunction solar cell combining a conventional crystalline silicon bottom subcell with a metal oxide top subcell based on ZnO and Cu_2O layers [64].

ZnO/Cu_2O sub-cell is realized by reactive magnetron sputter deposition of metal oxides on a transparent glass substrate (quartz), enabling low-energy photons to be transmitted through the ZnO/Cu_2O top sub-cell for subsequent absorption in the c-Si bottom sub-cell. The ZnO/Cu_2O sub-cell, deposited on glass, could serve, in this architecture, as the module glass encapsulating the c-Si subcell, requiring insignificant changes to the design of the bottom cell [62, 64].

At INVENTICA 2022 Iasi, Romania, the patent application [65] related to heterojunction structure based on non-toxic metal oxides, was awarded with Diploma of Honor, Gold Medal.

3.7. Electrochemical sensors for environmental protection, health

The research activities address key issues in the field of food safety, such as assessment of food freshness, quality control and food waste limitation by introducing a novel e-tongue like sensor for histamine evaluation with fast and ultra-sensitive response. We focus on knowledge-based engineering for developing a sensor for histamine evaluation in meat products, since they seem to be subject to more improper hygiene during production and processing. Three metalloporphyrins were selected to develop the e-tongue: (1) Mn-porphyrin, (2) Zn-porphyrin and (3) Co-porphyrin. These metalloporphyrin were dispersed in chloroform and drop casted onto screen-printed electrodes [66]. Based on our results we decided to further test two metalloporphyrins together on the same sensor array. For this purpose, we developed in association with MGM Star Construct, a double working electrode sensor support (Fig.14).

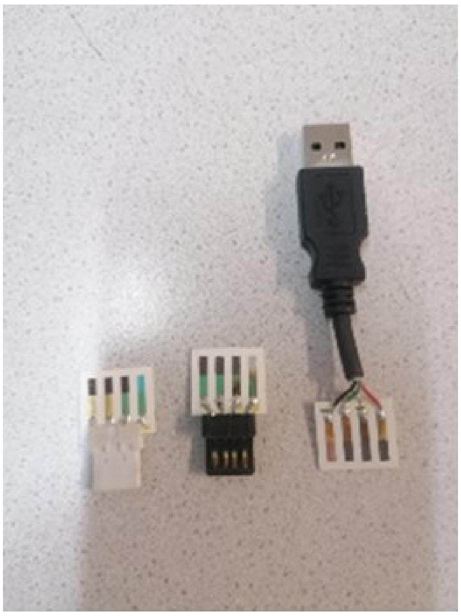

Fig.14. Experimental models of the final support sensor

4. Current developments and collaborations

4.1. Thin films based on PbS semiconductor quantum dots embedded into the Al_2O_3-SiO_2-P_2O_5 host matrix, synthesized by sol-gel method, candidate materials for potential application in NIR (Near Infrared) temperature sensor systems for environment protection & control

A new PbS-doped silicate-phosphate film was prepared by sol-gel method spin coating technique [67]. The doped film shows optical absorption that is decreasing from UV to the visible domain with two absorption bands (580 nm and 1254 nm) (Fig. 15). The surface of the film is nanostructured with small grains attributed to the dopant that agglomerates forming islands with the size between hundreds of nanometers to microns.

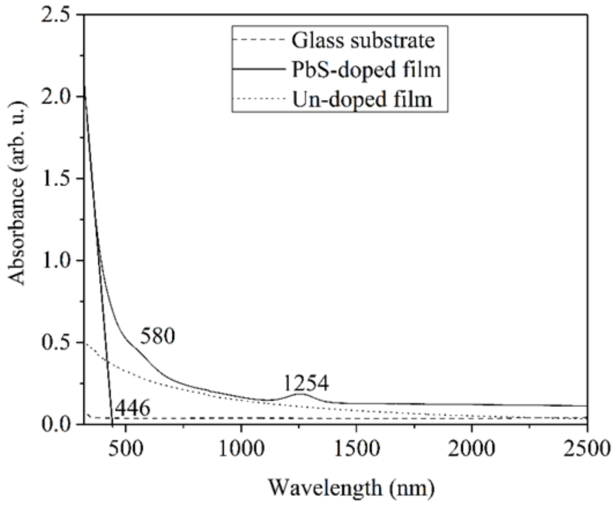

Fig.15. Optical absorption of PbS-doped film [67]

Optical band gap of PbS-doped film was graphically determined, based on absorption spectrum, being 2 eV (Fig.16).

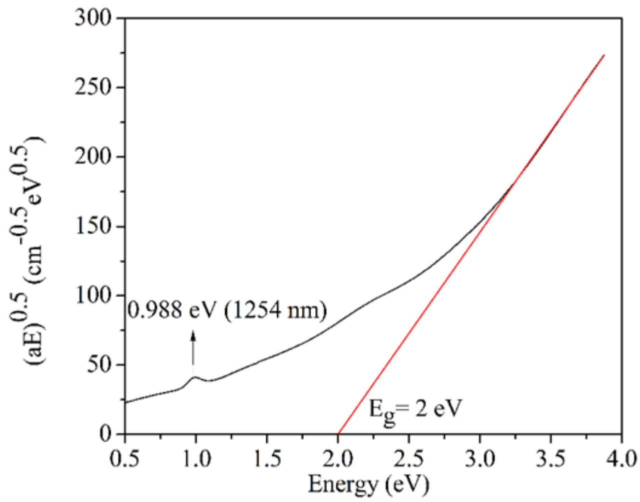

Fig.16. Optical band gap of PbS-doped film [67]

Figure 17 shows the EDX elemental composition of the Pb-doped film deposited on the glass substrate. It is noticed that specific elements to both the film and the glass substrate are found, such as: Si and O, together with elements specific to the deposited film such as Al, P, Pb, and S.

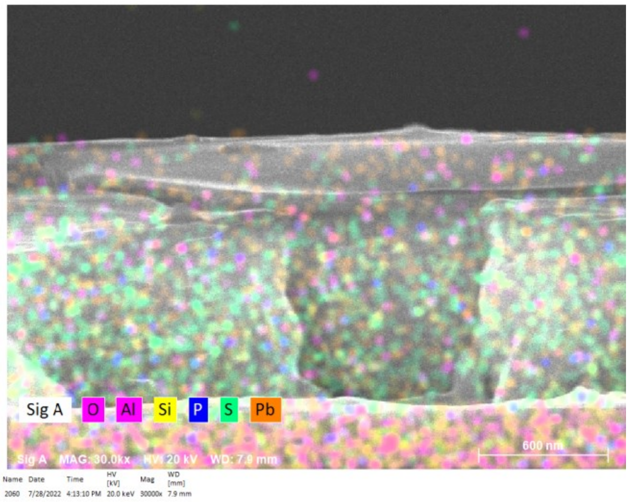

Fig. 17. SEM (Scanning Electron Microscopy) cross-section elemental mapping of PbS-doped film [67]

The low roughness value indicates an uniform and smooth surface of the film. (Fig.18). The dependence of the NIR emission on environmental temperature is applied in temperature sensing systems.

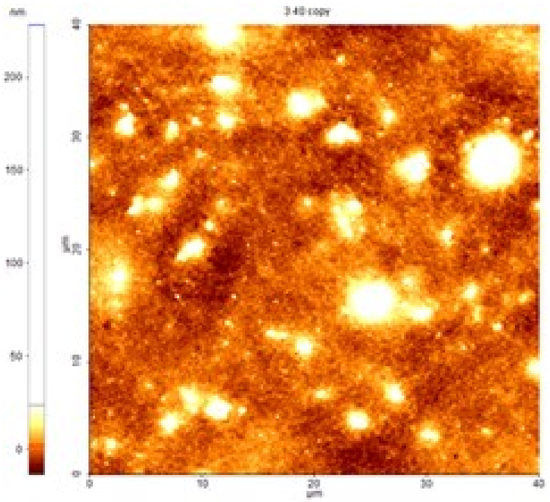

Fig. 18. AFM images of the surface layer of PbS-doped film [67]

4.2. Ultrasensitive gas sensor array for green house environment assessment for environment protection and control

We aimed at developing a monitoring sensor which can specifically evaluate the level of gases produced inside of greenhouses. The demonstration model is an experimental model consisting in an integrated gas sensors array and an appropriate data acquisition system. The integrated gas sensors array based on functionalized graphene allows amplification of the detected electrical signals (Fig.19). The detection mechanism is based on the variation of resistivity/conductivity and interfacial properties of the active semiconductor layer (in our case the modified graphene layer) when exposed to different gases [68-70].

Fig. 19. Different types of gas sensors developed for the analysis of CO_2 from atmosphere (graphene and polypyrrole).

4.3. Au@Fe_3O_4 nanoparticles for Raman spectroscopy/SERS measurements through the skin for health domain

Collaboration between INOE 2000 and RoxyVeterinary SRL and HistoVet SRL produced Au@Fe_3O_4 core-shell nanoparticles for SERS substrates with spin-plasmonic interfaces used for blood vessels traceability in skin. We studied the traceability of blood vessels through surface enhanced Raman spectroscopy. The Au shell provides protection for the Fe_3O_4 against oxidation and prevents aggregation of the magnetic nanoparticles. The plasmon properties refer to the magnons in the magnetite and gold that diverge from equilibrium and generate a spin current at the magnetite/plasmonic metal interface. This is as proved by the shifts in the measured Raman spectra. Also, we observed that transmittance of skin containing only Au@Fe_3O_4 nanoparticles is higher than of the raw skin itself. Solutions of Fe_3O_4/Au core-shell nanoparticles with or without fluoresceine were injected into fresh ex-vivo animal tissues in order to check the traceability of blood vessels and to prove the penetration of Raman excitation sources through the dermis and other skin layers (Fig. 20). The blood vessels are picking up the Fe_3O_4/Au core-shell nanoparticles and produce fluorescence/fluoresce, thus becoming traceable. This is a major contribution to the field of health specially to post bariatric surgery [71].

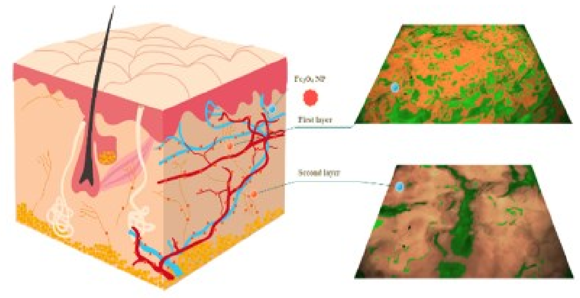

Fig. 20. Graphical representation of the distribution of Fe_3O_4/Au nanoparticles inside blood vessels re-used with permission from [71]and under Copyright notice 978-1-5386-5541-2/18/$31.00 ©2018 IEEE

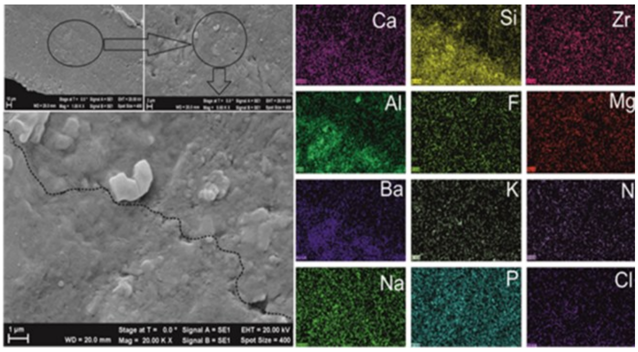

Fig. 21. SEM and mapping images of the interface between tooth and reconstructive composite material, with permission from [72]

4.4. Raman Spectroscopy as Spectral Tool for Assessing the Degree of Conversion after Curing of Two Resin-Based Materials Used in Restorative Dentistry for health field

The collaboration with Carol Davila University of Medicine and Pharmacy produced an extensive study of two of the most used dental materials, commercialized as "nano" and "micro", which are photopolymerizable and revealed its behavior at the boundary between dentin and enamel. Light-cured composites consisting of inorganic fillers and a polymer matrix are increasingly used as dental restorative materials or dental cements. The major problems that affect their performance is the intrinsic polymerization shrinkage and interface adhesion. This volumetric shrinkage causes stress in confined environments such as tooth cavities. Polymerization shrinkage and the resulting shrinkage stress play an important role in influencing the forces acting on the tooth-restoration interface. Strength and toughness are usually investigated by SEM-EDS (Fig.21), micro fractography and macro/micro hardness. To understand the process on the above-mentioned properties, a series of investigations with SEM revealed local stresses and their dynamics for different conditions of polymerization. Results from this study accomplished with a Raman investigation could predict a model for dentin interface bonding with application as a functional biomaterial.

4.5. Scientific agreement on Research Cooperation between Institute of Solid-State Physics, University of Latvia (ISSP UL), Riga and National Institute of Research and Development for Optoelectronics INOE 2000, Romania (2020-2023) in the field of optical & photonic components

The object and purpose of the cooperation is the research in the domain of synthesis and optical characterization of rare-earth (RE)-doped vitreous materials applied in optoelectronics. The vitreous bulk materials are synthesized by conventional melt-quenching-annealing route.

The cooperation is based on the techniques developed at INOE 2000 and ISSP UL for synthesis and, respectively, optical characterization of the vitreous materials.

The purpose of the cooperation is: (i) to improve the technical, working and personal capacities in the two institutions, in complement of the resources offered by the respective national programs and/or other bilateral agreements; (ii) exchange of expertise in synthesis/optical characterization of the vitreous materials based on RE-doped vitreous materials by performing complimentary synthesis/testing methods on the agreed materials; (iii) reciprocal information and consultation on the problems encountered in the above mentioned field and on the relevant subjects to the common activities of the groups involved; (iv) reciprocal information of the preparation and measuring techniques and exchange of documentation; (v) better utilization of the experimental techniques and acquisition of new experimental skills, knowledge and know-how by means of short or long term visits; (vi) preparation of mutual publications and international projects based on the results of the common research.

Photoluminescence measurements in the VIS-NIR domain were performed on phosphate glass samples doped with RE ions: Eu, Dy, Er, Yb-Er, Yb-Ho and Yb-Tm, by UV-VIS excitation.

Table 2. Excitation and emission wavelengths of the RE-doped phosphate glasses.

Sample	Excitation wavelengths (nm)	Emission wavelengths (nm)
Eu-doped glass	318; 393; 464	592; 612; 701
Dy-doped glass	350; 452	485; 574
Er-doped glass	378; 520	545
Yb-Er-doped glass	378; 520	545
Yb-Ho-doped glass	360; 448	544
Yb-Tm-doped glass	285; 357	349; 451

Eu-, Yb/Tm, and Dy – doped samples exhibit the highest luminescence intensity in the visible range whereas Er, Yb/Er and Yb/Ho-doped samples shows relatively weak luminescence in the visible range. The excitation and emission characteristics of the RE-doped phosphate glasses are presented in Table 2.

5. New and ongoing directions of research

The research works of the Optospintronics department fall under the top directives of the European Union, the worldwide international community as well as under the National Strategy for Research, Innovation and Smart Specialization 2022-2027. Our New and ongoing research directions are summarized below:

- Exploring the synthesis of new materials and structures with special characteristics for photovoltaic, communication technology and environment applications (graphene-based materials)
- Investigating novel tandem structures for high efficiency photovoltaic technologies targeting low-cost production
- Synthesis and investigation of new oxide materials as temperature sensors for environment control (rare-earth-doped phosphate glasses and glass ceramics, semiconductor-doped films)
- Exploring new materials as sensors for health (bio-compatible composites based on carbonic structures) and sensors for energy (ultra-porous materials)
- Investigation of some special materials for spintronic applications (based on Fe_3O_4)
- Increasing and diversifying the capacity to characterize the new obtained materials

5. Perspectives

Development of temperature sensing materials used in severe environmental applications (corrosive/toxic environment, oil refineries, power stations, heating plants, coal mines, building fire detection, etc) represents a challenge and a need for many industrial fields. Thus, new perspectives are open for a faster design and development of a new generation of sensors as a front line of European research area, with the aim of overall improvement of human and environmental well-being.

Moving towards renewable energy resources instead of fossil fuels should be the ultimate goal of modern civilization and alternative solar fuel generation by applying heterogenous photocatalysis is one of the major approaches in renewable energy research. Graphene based materials are some of the most promising materials for efficient photocatalysis in terms of solar water splitting and CO_2 photo-reduction.

Photovoltaic power generation in the transition to a clean energy system, the achievement of the zero-emissions target and the development of new materials and structures for photovoltaic applications represent the nowadays challenges.

Microbial contamination management is a crucial task in the food industry, which requires the achievement of dedicated sensors in this field as a current need/demand. Undesirable microbial spoilage in a modern food processing plant poses a risk to consumers’ health, causing severe economic losses to the manufacturers and retailers, contributing to wastage of food and a concern to the world’s food supply.

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Fluid Power in the Context of Reconstruction and Resilience

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Hydraulic and pneumatic drives can be found in most industrial fields, due to advantages not discoverable in other types of drive, although there is constant competition, mainly with electric drive. Thus, hydraulic drive provides a much higher power density, and pneumatic drive is environmentally friendly. Fluid power systems have high complexity, given that in the current context in which precise, reliable and energy-efficient drives are required, electrical, electronic and automation components and systems can be found in fluid power systems, and adapting to IoT requirements involves the existence of numerous sensors to communicate information about the status of components. The chapter presents several recent achievements of Hydraulics and Pneumatics Research Institute, as well as the history of the Institute, the future directions of action and short- and medium-term work prospects, taking into account the advanced applied nature of our activity.

Keywords: Hydraulics, pneumatics, fluid power, efficiency, energy

1. Introduction

The Hydraulics and Pneumatics Research Institute (IHP) subsidiary joined the structure of INOE 2000 in 1996, bringing along a history of almost 40 years, at that time, of expertise and achievements in the field of Fluid Power systems. As the name suggests, the main field of activity is in the area of hydraulic and pneumatic drives, a field that interferes with most economic sectors. Hydraulic drives provide large forces, unmatched by any other type of drive (currently and in the future), while pneumatic drives provide convenient, non-polluting solutions for achieving small and medium-sized forces and torques, both in the machine building industry, as well as in sectors such as the food industry, health, etc.

Hydraulics is present both in the applications of drive systems of fixed machines and equipment, in enterprises, in installations for obtaining energy from classic or renewable sources (industrial hydraulics), as well as in the fields of transport, construction, agriculture, for maintenance operations in various locations, etc. (mobile hydraulics).

The development of components and the increase of working parameters, also supported by the emergence of new materials and manufacturing processes, have made hydraulics and pneumatics enter current applications of great interest such as energy recovery and storage, and the association with modern sensors and transducers recommends them as areas of interest for the Internet of Things (IoT) and Industry 4.0 (I4.0).

Another current constant endeavour in the field is the transformation of hydraulics and pneumatics into the most "green" drive systems, in which industrial air is obtained by mixing with ecological lubricants, and mineral hydraulic oils compete for the market of working fluids with biodegradable fluids, whose market share increases annually.

Even though electric drives, mainly, are an important competitor and penetrate some traditional areas of Fluid Power, each step forward (of the type mentioned above) in the direction of better compatibility with the environment, in parallel with the increase in performance, offers us new opportunities [1, 2].

2. History of Fluid Power in Romania

The history of Hydraulics begins in antiquity, when the first technical books were written containing chapters related to water drive, such as Archimedes' work related to the floating objects. Closer to the modern period, Leonardo da Vinci's work on "The Motion and Measurement of Water" should be mentioned. A real technical explosion occurred in the 16th and 17th centuries. At that time in countries (or regions of these countries) such as Italy, France, Germany, England or Russia, research was conducted, books were written and many machines and equipment were invented, many of which, over time, entered the history of the field of hydraulic drives, such as the writings of Galileo and Newton.

In the middle of the 20th century, in Romania, the first achievements in hydraulics belonged to professors such as Dorin Pavel, Aurel Bărglăzan, Ioan Anton, Elie Carafoli, etc. They had in mind, predominantly, water science and applications. Later, in the 60s and 70s, the first theoreticians and practitioners of the field of hydraulic and pneumatic drives using fluids other than water appeared. In our country, their activity was correlated with the introduction of hydraulic and pneumatic equipment into production. During that period, the first specialized factories appeared, such as those in Sibiu, Plopeni, Bucharest, Focsani, Ramnicu Valcea, Bistrita, Braila, and Galati. Nowadays, the field is kept alive by several production units in Bucharest, Iasi, Ramnicu Valcea, Sibiu, and Brasov, and by several research centres within institutes in Bucharest (INOE 2000 through its subsidiary IHP Bucharest), Iasi, Cluj-Napoca, Timisoara, etc.

Hydraulics and Pneumatics Research Institute (INOE 2000 Subsidiary IHP Bucharest) is part of the design and research units with a predominantly applied character that laid foundations between 1950 and 1965. They were intended to be involved in the introduction of various products into manufacturing, from the design stage to homologation.

Initially having the structure of a design and research "workshop" for hydraulics and pneumatics, created between 1958 and 1962 within the ITCM institute (later known as ICTCM), the institute went through various forms of organization. In June 1980, it was integrated into CCSITMFS, transformed into a sector and then into a subsidiary of the new institute, while keeping the activity profile. Since 1983, it has been operating in the building located in Cutitul de Argint Street, specially built as a recognition of the importance of the field and its object of activity.

Two major design and research directions were developed between 1975 and 1990. The first direction was the assimilation of hydraulic and pneumatic equipment in series production. 300-bar equipment (directional control valves and other valves) were introduced in the production at Balanta Sibiu, hydraulic power steering and orbital motors - at HESPER Bucharest, pneumatic devices and equipment - at Bistrita, monoblock directional control valves - at Focsani, hydraulic cylinders, filters, pneumohydraulic accumulators, and the first electrohydraulic servo components - at Ramnicu Valcea. The second direction was the design and commissioning of facilities of major importance for the national economy. On this line, the first hydraulic installations for tractors and motor trucks manufactured in the country were made, as well as the continuous casting plant at Galati, and many other metallurgy and steelmaking facilities at Galati, Targoviste, Campia Turzii, etc. Other outstanding achievements are the railway tunnel-boring machine used in the construction of the subway, the machine intended for technological operations at the railway, the 120-tf mobile crane, etc.

After joining the structure of INOE 2000, the institute maintained its profile, emphasizing collaboration with existing economic units in order to develop products required on the market. In parallel, by collaboration with technical universities and institutes in the country and abroad, advanced research is carried out in the field of fluid power, with applications in topical areas such as renewable energy, IoT or the circular economy.

3. Current developments and collaborations

The current research endeavours of IHP aim at the development of competitive research at the national and European level in the context of establishing research networks with competitive and transferable results; these networks shall be capable of being integrated into European technology platforms oriented towards the following topics:

• Environmental monitoring/rehabilitation
• Integrated processes for the development of new renewable energy sources
• Research on physical phenomena and processes in the field of hydraulic pressures; development of mechatronic systems.

Over the last few years, IHP, analysing the requirements of the economy and the research directions at the European and international level, also taking into account the existing infrastructure and the professional experience of its research scientists, has mainly addressed applied research and design issues, especially at the level of systems, in the following directions:

• Hydrotronic and mechatronic technologies for automating and robotizing complex technical systems
• Environment, ecology and green energy
• Hydrotronics, mechatronics and tribology – main elements of increasing the functional performance and life span of complex automation systems based on hydraulic and pneumatic drive equipment.

IHP has research endeavours and achievements in areas that can fit into the European research programmes H2020 and HORIZON EUROPE related to Transport, Disaster Prevention and Mitigation, Energy and Resources.

On these lines, IHP maintains a permanent and direct relationship with most manufacturers and users of hydraulic equipment and systems; the institute has collaborated before and is currently collaborating with them in revamping their products and technologies. Among the companies with which we collaborate, we would like to mention S.C. Caloris Group S.R.L., S.C. ROLIX IMPEX SERIES S.R.L., S.C. PROFLEX SERVICE S.R.L., S.C. GRADINARIU IMPORT EXPORT S.R.L., S.C. HESPER S.A., S.C. CORNER PROD S.R.L., S.C. DELTAROM S.R.L., S.C. TEHNOLOGICAL BRAND S.R.L., etc.

Moreover, there is a close collaboration of IHP with technical universities in Romania - among which we mention Politehnica University of Bucharest, Technical University of Cluj-Napoca, Politehnica University of Timisoara, "Gheorghe Asachi" Technical University of Iasi, and "Dunarea de Jos" University of Galati. Collaboration with research stations - such as The Research and Development Station for Plant Culture on Sands in Dabuleni, The Research and Development Station for Fruit Growing in Constanta, etc. - has also been established.

Other collaborating partners in our projects are various research institutes within our institute's fields of interest, such as I.N.C.D.M.T.M, I.N.M.A., and I.C.P.E.-C.A.

On an international level, the last few years have given rise to very good collaborative partnerships of IHP with Technical University of Moldova in Chisinau, Wroclaw

University of Science and Technology and KOMAG Institute of Mining Technology in Poland.

4. Recent results and transfers of results

4.1. Recent research projects

Several most representative research projects implemented by INOE 2000 Subsidiary Hydraulics and Pneumatics Research Institute over the past few years are presented below.

The project **ESTABLISHING A HIGH LEVEL PROFICIENCY NUCLEUS IN THE FIELD OF INCREASING RENEWABLE ENERGY CONVERSION EFFICIENCY AND ENERGY INDEPENDENCE BY USING COMBINED RESOURCES - CONVENER**, carried out in the period 2016 - 2021 and financed from structural funds under the POC 2014 – 2020 programme, capitalized on the experience in the field of renewable energy of a high-level specialist from abroad and laid the foundations of a team specialized on this topic within the INOE 2000 subsidiary IHP.

Going beyond current solutions, the project resulted in two conversion systems that use renewable energy with superior efficiency, as each system uses two sources that complement each other.

For the production of ***thermal energy***, an assembly of thermal solar panels has been associated with a thermal energy generator that gasifies biomass and uses the resulting gas to heat water. The energy produced by both sources is stored in a bivalent boiler [3].

Solar photovoltaic panels (fig. 1) combined with a special construction wind turbine - consisting of a Savonius turbine, acting as a starter at low wind speeds, and a Darrieus turbine, efficient at higher speeds (fig. 2) - have been used to produce ***electricity***. The electricity is stored in batteries, and with the help of a management unit, the system can be used both in isolated locations and in households that have electricity from the grid.

Fig. 1. Assembly of photovoltaic solar panels

Fig. 2. Combined turbine with start at low wind speed

The project **ECO-INNOVATIVE TECHNOLOGIES FOR BIOMASS WASTE CAPITALIZATION - ECOVALDES**, carried out in the period 2016 - 2022 and financed from structural funds under the POC 2014 – 2020 programme, is a project of great complexity, through which thermotechnic elements are combined with mechanics, hydraulics, pneumatics, electronics and informatics, thus resulting, from the five equipment groups on which the project is focused, combinations of technological lines for the capitalization of vegetal biomass, adaptable according to the objective and the type and quality of biomass available.

The five equipment groups under the project (fig. 3) [4] are as follows:

- Chopping equipment
- Drying equipment
- Compaction (pelletization and briquetting) equipment
- TLUD principle-based gasification combustion equipment
- Vegetal biomass transport equipment.

The general objective of the policy on the capitalization of the energy potential of biomass is the integration and consolidation of the technical-scientific, informational, and educational potential and the implementation of the agricultural and forestry practices regarding the use of biomass as a raw material for the production of compacted biofuel or thermal energy, in the conditions of preserving the quality of the environment.

Technological lines can use wood biomass from secondary agricultural production, residues from urban biomass or from green area and park periodic maintenance operations, wood residues from timber processors (including sawdust), biomass materials from periodic pruning of vineyards and orchards, or biomass waste from forest holdings.

The project has developed with the help of partner companies 16 prototypes of equipment that can be integrated so as to result in complete production lines for processing vegetal biomass.

Fig. 3. Equipment for vegetal biomass processing lines developed under ECOVALDES project

The project **DEVELOPMENT OF ENERGY-EFFICIENT TECHNOLOGIES IN SOME APPLICATIONS OF ON-DEMAND MECHANICAL - HYDRAULIC SUBASSEMBLIES MANUFACTURING AND MOBILE HYDRAULIC EQUIPMENT MAINTENANCE - MENTEH** has aimed to support companies interested in assessing the performance of hydraulic equipment undergoing maintenance processes. In Romania, there are many companies that deal with the maintenance of hydraulic equipment, but very few have the technical possibility to certify the operation at the appropriate parameters.

In order to capitalize on this opportunity, the project offers interested companies the opportunity to design, from the draft phase to the approved product phase, complex test means such as benches (fig. 4) or simpler ones such as mobile devices for assessing the main parameters such as pressure, flow rate, forces and torques (fig. 5).

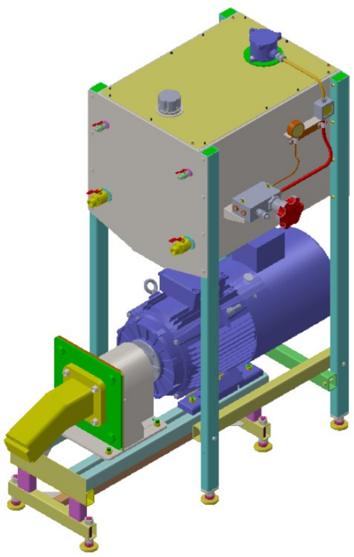

Fig. 4. Hydraulic pump maintenance bench - a 3D sketch

Fig. 5. Control and data acquisition panel

On the other hand, the project can develop new products in the mechano-electro-hydraulic field, at the request of potential interested partners, through projects fully implemented by IHP or in partnership with the companies [5]. An example is the company S.C. HIAROM INVEST S.R.L., which is developing a multi-functional vehicle with hybrid drive in partnership with the institute.

Other opportunities for companies, under this project, are related to the improvement of the professional knowledge of their employees (through professional training), the development of feasibility studies for introduction of new products into production, in very advantageous financial conditions.

The project **DIGITAL MECHATRONIC SYSTEMS FOR GENERATING 1000 BAR PRESSURE USING HYDRAULIC PRESSURE INTENSIFIERS - SMGP** has the general objective of diversifying the manufacturing nomenclature of the company S.C. HESPER S.A. Bucharest by introducing new products into production, referred to as ***high-pressure pumping units and systems***, comprising ***low-pressure pumping units*** equipped with ***oscillating hydraulic pressure intensifiers*** (miniboosters). These products are useful for activities carried out in confined spaces (subway tunnels, mining, etc.), interventions in case of car accidents (extrication), testing pipelines at high pressure rates, etc.

The project is being implemented in a partnership consisting of S.C. HESPER S.A., project beneficiary and coordinator, INOE 2000-IHP, partner 1 in the project, and UPB, partner 2 in the project. The project is an opportunity for the beneficiary to confer a greater use value in the market to some of the most representative products in its own manufacturing range, namely ***the gear pumps*** (which are part of the structure of high-pressure pumping units and systems).

So far, the following (fig. 6) have been achieved under the project: **three pumping units** with pressure rates of 1000, 1320, and 1520 bar, respectively; **1 test bench** for high-pressure pumping units and systems. The project further aims to achieve **two** high-pressure **pumping systems**, one of which has two and the other has three oscillating hydraulic pressure intensifiers [6].

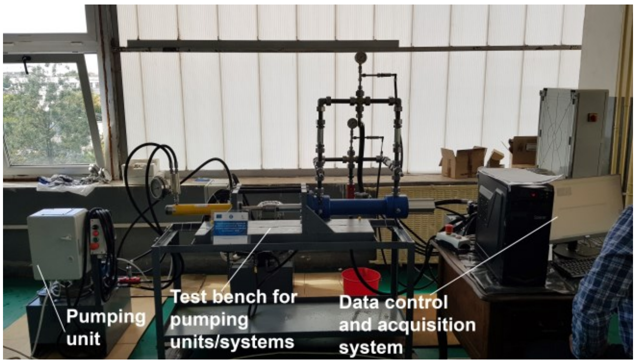

Fig. 6. Products developed under SMGP project

4.2. Recent results achieved and transferred

Many of the results presented below (4.2.1 … 4.2.5, 4.2.9 and 4.2.11) fall under the category Equipment for security or improving professional skills; the rest are under the categories Equipment for the production of renewable energy (4.2.6 and 4.2.7), Agricultural equipment (4.2.8), Marine equipment (4.2.10), and Industrial use equipment (4.2.12 and 4.2.13) - and this illustrates only part of the wide range of areas where one can find fluid power systems.

4.2.1. Mobile assault ramp with hydraulic drive

The assault ramp (fig. 7) is a transportable equipment that allows users' access, from the outside, to the upper levels of buildings. The riot police use this equipment in specific missions.

The product has been developed within the R&D Sectoral Plan of the Ministry of Internal Affairs.

Main features:

- It is based on two ramps with independent operation, supplied with hydraulic energy from a hydraulic unit with an independent internal combustion engine. The control of this hydraulic system is done remotely.
- Maximum lifting height of the access ramps is 10 m.
- Maximum distributed load on an access ramp is 1500 kg (10 fully equipped police officers).

Fig. 7. Hydraulically actuated assault ramp - a 3D sketch

For this product, the institute has received the self-propelled platform, and carried out the design, development and assembling of the mechanical-hydraulic structure [7].

4.2.2. Hydrostatic drive bench designed and built for Politehnica University of Timisoara (UPT)

The structure of the bench has been designed to fulfil two purposes, one educational and one lucrative. Thus, a complex structure has been built (fig. 8), which would provide information about several types of devices - pumps, motors, directional control valves. This bench enables the testing of several types of hydraulic devices, such as pumps, linear (cylinders) and rotary motors, directional control valves, etc.

Fig. 8. Bench for hydrostatic drives

As the bench has been built at the request of a technical higher education entity, it can also be used in the educational process, in order to impart with students specific knowledge in the field of hydrostatic drives. Due to the high values of pressure and flow rates that one can achieve, one can use the bench for testing industrial equipment, as well [8]. For this purpose, the bench has been designed in a modular structure, consisting of four parts (fig. 9):

1. SAH / SBS – bench basic structure
2. SAH / MHL – subassembly for linear hydraulic motors
3. SAH / MHR – subassembly for rotary hydraulic machines
4. SAH / BAE – equipped auxiliary tank.

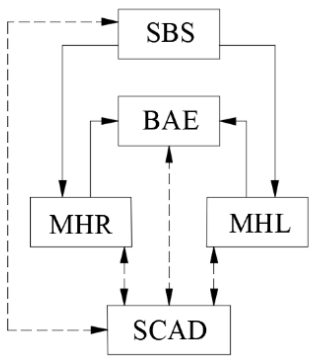

Fig. 9. Bench subassemblies and their interconnections

4.2.3. Mobile side skid simulator

The skid simulator (fig. 10) is a piece of equipment that is attached to a car and enables drivers to train in order to acquire instinctive reactions in the event of a car skidding caused by low ground adhesion.

Main features:
- Structure: metal frame with four swivel wheels, compatible with Dacia Logan, mini hydraulic pumping unit, electronic control box, trainer remote control.
- Electrohydraulic drive: 150 W electric motor, maximum pressure: 150 bar, pump flow rate: 0.5 l/min.
- Manual/automatic control of the operating mode, 8 stored program settings (wheel grip adjustments).

The product has been developed within the R&D Sectoral Plan of the Ministry of Internal Affairs.

Fig. 10. Skid simulator

For this product, our institute received the documentation for the frame and carried out the automation and electro-hydraulic drive project, the development and assembling of the mechanical-hydraulic structure [9].

4.2.4. Movement system with hydraulic drive for flight attendant training

The flight attendant training system (fig. 11) enables the movement of a Boeing 737 aircraft body, using two hydraulic cylinders, to simulate flight situations (take-offs, landing, turning, air gaps, and turbulence).

Fig. 11. Flight attendant training system

Main features:
- 16 training scenarios with vertical/horizontal movements with variable frequency and speed rates.
- Two hydraulic cylinders with stroke encoders (max. 400 mm).
- Hydraulic system power: 8 kW, maximum pressure: 100 bar, V_{max} 200 mm/s.
- Maximum load on each hydraulic cylinder: 2500 kgf.

The movement system has been developed within the framework of an economic financing agreement signed with S.C. REGIONAL AIR SERVICES Tuzla, Romania.

Fig. 12. Control panel

Fig. 13. Electro-hydraulic side tilt subassembly

For this product, our institute has designed and implemented the automation project (fig. 12) and the electro-hydraulic installation (fig. 13) for the movement system [10].

4.2.5. Expandable, remote-controlled portable barrier for stopping vehicles by a controlled deflation of the tires

The equipment (fig. 14) is intended for the efficient and safe stopping of the vehicles with tires, by rapidly extending a barrier with removable pins, on the transverse direction of the roadway on which the target vehicle moves (fig. 15); this produces the controlled perforation and deflation of at least one of vehicle tires, when it crosses over the barrier. Afterwards, the barrier has to be retracted to clear the roadway and allow emergency crew vehicles access to the target vehicle [11].

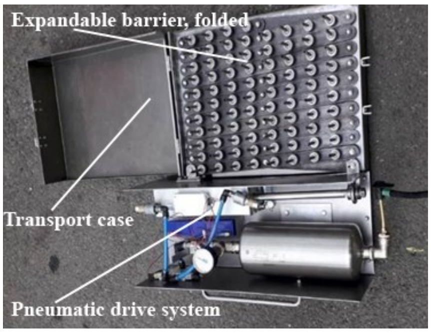

Fig. 14. Expandable barrier, folded

Fig. 15. Barrier in operating position

Main features:
- Overall dimensions (L x w x h): approx. 500 x 300 x 150 mm.
- The equipment can be transported and used by a single person, since total mass is 23.4 kg.
- In the extended position, the barrier with pins covers the width of one traffic lane (about 3.6 m).
- The barrier extension/retraction time is 3 seconds.
- Remote control - The barrier can be controlled from a distance of at least 60 m.
- Working fluid is compressed air.
- Working pressure is 10 bar.
- Pneumatic cylinder stroke is 200 mm.

Funding has been provided through the R&D Sectoral Plan of the Ministry of Internal Affairs.

4.2.6. Renewable energy system for mooring pontoons

Fig. 16. Mooring pontoon equipped with two types of solar panels

The renewable energy system enables the operation of facilities (lighting, water supply, water purification, refrigerator, naval traffic surveillance, etc.) on a mooring pontoon (fig. 16) located in an isolated area [12].

Main features:
- Number of photovoltaic panels: 32 pcs.
- Storage capacity in lead batteries: 31 kWh.
- Installed electricity power: 8 kW.
- Number of thermal panels/evacuated tubes: 2/20 pcs.
- Thermosolar boiler capacity: 80 l.

The product has been developed within the R&D Sectoral Plan of the Ministry of Internal Affairs.

For this product, our institute has designed, built and commissioned the electrical energy and domestic hot water supply system for a mooring pontoon located in the Chilia Veche Border Police Sector in the Danube Delta.

4.2.7. Vertical hot air generator with gasifier

The equipment (fig. 17) is intended for heating of production spaces (> 200 m^2). The aim is to increase energy independence, by heating, of the solariums and mini greenhouses in order to increase their duration of use, by using local residual biomass micro-gasified by the TLUD process.

Main features:
- Thermal power: 24 kW.
- Operating pressure (max): 2.5 bar.
- Dimensions: Height (mm): 1950
  Width (mm): 900
  Depth (mm): 900
  Weight (kg): 800.
- Maximum load capacity (kg): 10-14.
- Efficiency: 85%.
- Fuel: vegetal biomass, pellets.
- Adjustable primary and secondary air intake flap.

Fig. 17. Hot air generator, 24 kW

Funding has been provided through Financial agreement no. 67/214 - *Using renewable energy resources to increase the energy independence of mini greenhouses and solariums* under PNCDI II (2014-2017).

Beneficiaries could be farmers, small households, guesthouses, etc. [13].

4.2.8. Motorized farming platform used for spraying works, with remote guidance automation system

The platform is a piece of equipment designed for horticultural spraying works. It is intended to carry out "spatial spraying" works, meaning spraying in several directions during the same passage, up and down, but also to the left and right of the vehicle. Moving on soft ground is facilitated by the crawler track system of the platform [14].

The equipment (fig. 18) can be guided by manual commands, but also by automatic commands / remote control, which will enable, in a future stage, the platform to work in a computerized mode, based on the use of the computer and GPS.

Fig. 18. Self-contained spraying platform - a 3D sketch and actual equipment

Main features:
- Type of spatial spraying: a) side, with vertical arms, and b) horizontal.
- Spraying distance: maximum 3 m.
- Spraying flow rate: maximum 20 l/min.
- Spraying pressure:maximum 20 bar.
- Fluid tank capacity: 100 l.
- Travel speed: 0 – 7 km/h.

4.2.9. Access road blocker

The equipment is intended to restrict access to various areas, by blocking pedestrian crossing on a street or part of the street, with a width of maximum 10 m. One can pass through the blocked area by way of an access gate controlled by law enforcement officers.

Main features:
- Maximum width of the served access path: 10 m.
- Number of fences: 5.
- Fence height: 2.5 m.
- Maximum folding time of the fence package: 1 min.
- Maximum time to block the street: 5 min.

Compared to existing systems, the road blocker comes in the form of a compact package of five overlapping fences, which are unloaded from a truck by means of a quick and convenient hydraulic drive.

Fig. 19. Road blocker, unfolded

Since 2015, the equipment has been in the possession of the Romanian Gendarmerie and is used in specific missions to maintain public order (fig. 19), for example, on the occasion of sports, cultural events, parades, etc.

4.2.10. Active heave compensator test bench

The product, which can simulate the vertical motion of the waves, is used in the demonstration of the operation / experimental testing of the dynamics of hydraulic servo cylinders dedicated to active heave compensators or the active component of hybrid heave compensators, which equip floating cranes and drilling rigs [15].

The bench (fig. 20) has in its structure a mobile assembly (a welded construction, made of equal-angle iron, on which a Moog servo cylinder is fixed), a fixed assembly (a welded construction, made of equal-angle iron, on which the body of a Parker servo cylinder is fixed), a connecting part (a coupling for clamping the rods of the two servo cylinders), an electrical panel and a programmable logic controller (PLC), connected to a PC, to control the servo cylinders and acquire data from the stroke transducers.

Main features:
- Bench dimensions (L x w x h) (mm): 368x412x1740.
- Testing parameters:
    - Idle (no load) working pressure: maximum 40 bar (bench safety valve control pressure).

- Under load working pressure: maximum 310 bar (bench safety valve control pressure).
- Maximum working flow rate: 50 l/min (for each pressure branch).
- Useful power required by the pumping unit (at p=40 bar and Q=100 l/min): 7 kW.
- Maximum power required by the pumping unit (at p=300 bar and Q=100 l/min): 50 kW.
- Working range of hydraulic servo cylinders' displacement transducers: -10V…+10 V.

Fig. 20. Test bench for servo cylinders as part of an active heave compensator

4.2.11. Heart simulator bench

The equipment (fig. 21) is intended for the teaching and training of medical students. An animal heart, similar to the human one, is used, and open heart operations are practiced with the simulation of arrhythmia, fibrillation or other situations occurring during the operation. The product is currently in use.

Fig. 21. Cardio surgery teaching bench

Main features:
- Volume of pumped fluid: 0-120 ml.
- Filling factor: 10%-90%.
- Pulse rate: 50-150 bpm.

4.2.12. Computerized system for the thermal treatment section

The system is used in industry, in thermal treatment sections; it computerizes the thermal treatment process by monitoring and controlling the temperature of furnaces by means of a database [16].

It consists of two software components, which run on a PC under the WINDOWS or LINUX operating system (fig. 22), namely an operator application and an application for generating operation reports. It uses a programmable logic controller as a bridge between the RS485 network of temperature controllers and the Ethernet network where the computers running the software applications and the database server are connected. The product is currently in operation.

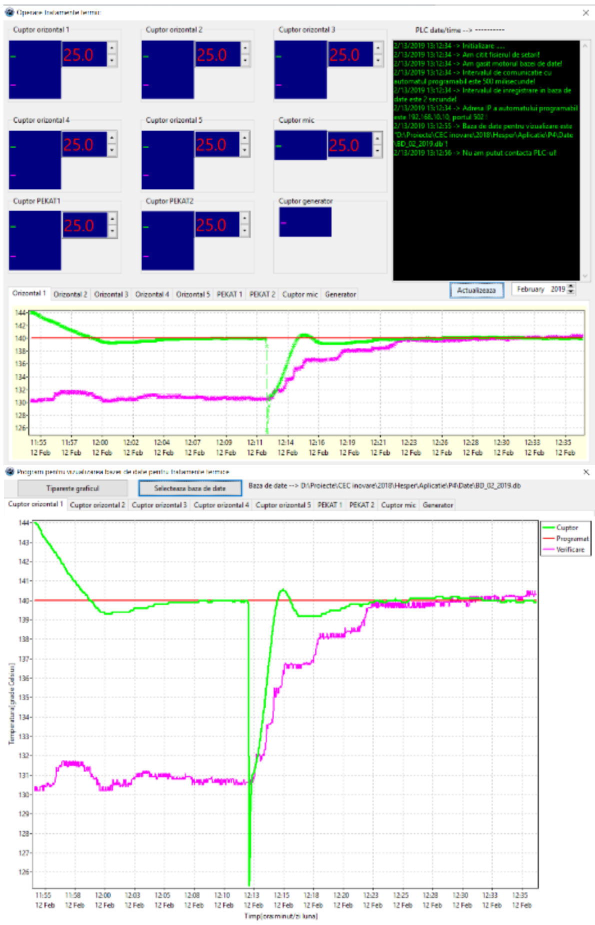

Fig. 22. Application interface and thermal treatment process results

Main features:
- Number of monitored furnaces: up to 254.
- Database type: local or remote.

- It enables configuring the communication and database parameters using a configuration file.

4.2.13. Computerized system for testing steering gearboxes on cars

The system enables the acquisition of the mechanical-hydraulic operating parameters of a test bench (fig. 23) for hydraulic steering gearboxes, as well as the issuing and archiving of test reports. The product is currently in operation.

Fig. 23. Hydraulic steering boxes test bench

Main features:
- Number of transducers: 5 (2 pressure, 1 flow rate, 1 stroke, 1 temperature transducer).
- Data acquisition board: NI USB – 6008.
- Transducer power supply: 24 V; 4A.
- Software application: issuing and printing test reports.

5. New directions of research

In the current context of research globalization and interdisciplinarity, the research directions of IHP are in close connection both with the general topics of interest on an international level and with the specificity of the Romanian economy. Thus, the most important directions considered for the next period involve the following:

- Improved energy efficiency, achievable by promoting new types of systems that combine mechanical or electrical drives with hydraulic ones. Digital Hydraulics and Direct Driven Hydraulics are among the directions that can be considered.
- Digitalization of systems, achievable by introducing electronic components able to convey information in order to make decisions remotely by human operators or even Artificial Intelligence.
- Introducing new materials (ceramics, plastics, etc.) or manufacturing techniques, such as additive manufacturing, which will increase the performance and at the same time will place us in the circular economy paradigm, by consuming reduced amounts of materials or remanufacturing in various ways.
- Reducing the share of primary energy produced from burning fossil fuels, used especially for mobile drives, and replacing it with energy from renewable sources.
- Accelerating research for the involvement of hydraulics and pneumatics in systems that convert renewable energy, during the production, storage or supply stages.
- Extensive use of modeling and simulation tools specific to the Fluid Power domain, in order to reduce product development costs at various levels and the time required to develop solutions.
- Preserving, expanding and disseminating specific technical knowledge to the personnel directly involved in the field, with the aim of turning them into specialists; persistently promoting the need for specific knowledge in higher technical education.

6. Perspectives

The institute shall carry on its activity in accordance with its mission, as a support institution for the industrial and services sector in Romania. On this line, the institute will have to meet the requirements and overcome the challenges coming from companies that integrate hydraulic and pneumatic systems in their products. Nowadays, one can mainly find these systems only in a functional connection with other systems, such as electronic/IT systems, data processing systems, and so on.

The development of such systems through interdisciplinary collaboration has to be based on 3 aspects, as synthesized by Professor Wolfgang Backé back in 1993: using the specific advantages of fluid power, compensating for disadvantages and leveraging advantages of other technologies for the benefit of fluid power [17].

To this end, some of the energy has to be directed to approaching of present-day and forward-looking advanced research topics, either through in-house research or through national and especially international collaborative projects.

The current and prospective major topic in the field of Fluid Power is the development of devices / systems with improved energy efficiency and requiring a minimum amount of materials. The concern for a minimum consumption of resources must also be found at the level of (hydraulic) fluid volumes in the system - in devices, pipes, tanks.

Energy efficiency is also attainable by increasing the level of working pressures, both in pneumatics and, most of all, in hydraulics. While today we adapt to pressure levels of 400…420 bar, the perspective of this decade is the value of 500 bar for average pressure.

Fluid power systems need to become more friendly to the environment and their operators; related to compatibility with the environment, development perspectives consider the use of biodegradable fluids, compatible with the seals so that fluid losses are reduced, if not eliminated. Regarding the health of the operators, first of all we must act to reduce the noise in operation.

Last but not least, a fluid working system must be kept in operation for as long as possible, with minimum costs; this forces us to promote predictive maintenance in the context of IoT - a large number of sensors that would provide as much information as possible about both the components and the fluid working environment.

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OMBA Group – Pioneers of medical hyperspectral imaging in Romania

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Abstract

Hyperspectral imaging is an optical method that provides a large amount of information about the investigated object. Its medical applications are presented in this book chapter, including tumor delimitation and identification, assessing tissue perfusion and its pathological conditions (including some complications like diabetic foot ulceration). Many of the results presented show very promising results. It is clear that choosing the appropriate hyperspectral imaging analysis method for each medical field are the main goals of the OMBA group and also to try answer some questions on this topic and set up some directions for future research.

Keywords: Hyperspectral imaging, Supervised and unsupervised classification methods, Chemometric methods, Index-based metric for burn depth assessment.

1. Introduction

Hyperspectral imaging (HSI) is a new technology applied in medical field that offers the possibility of extracting spatial and spectral information in each pixel of the image. The usefulness of this information is highlighted by the large number of applications in characterization, identification, and classification of various pathological and non-pathological biological tissue for diagnostic purposes and medical treatment monitoring. The principle of this method is to acquire a set of images in a large number of adjacent narrow spectral bands from which it can be obtained the reflectance spectrum for every pixel inside the image. The resulting data is a so-called hyperspectral hypercube which is a three-dimensional matrix containing both the spectral dimension and the two spatial dimensions, data which can be extracted and analyzed for different medical needs.

HSI has found its utility in a wide array of applications in numerous fields such as: remote sensing [1] , agriculture [2], mining and geology [3], chemistry [4], and astronomy [5]. In the medical field, the use of hyperspectral imaging is in its infancy, but different studies have shown that this method can be considered as a valuable tool in the medical field for noninvasive detection of cancer, diabetic foot ulcers, peripheral vascular disease or to assess levels of tissue blood oxygenation during surgery [6].

Since 2013, the OMBA group has been concerned with the implementation of the HSI method in certain medical fields, especially for diagnostic purposes, but also as a method for monitoring medical treatments, being among the pioneers of this scientific field. The main activities of the OMBA group were related to the development of the HSI applications to: burn characterization [7–9], cancer detection [10], tissues viability monitoring [11]and skin color assessment [12], wound assessment [13,14]. The greatest attention, within each HSI application, was paid to the processing and analysis methods of the data contained in the hyperspectral images, aiming at extracting the most important information about the investigated pathological areas.

2. HSI image processing methods

The OMBA group has implemented different algorithms for processing medical hyperspectral images to improve their quality by eliminating noise and reducing the large volume of data contained and speeding up the analysis process. Minimum Noise Fraction (MNF), Principal Component Analysis (PCA) and Independent Component Analysis (ICA) are the most important processing algorithms used by the OMBA group in various medical applications (Fig. 1). In addition, new processing algorithms were developed by researchers from this group, the best performing one for the medical field being an algorithm based on Wavelet transformation. Wavelet transformation is one of the image processing methods commonly used in computed tomography (CT) or magnetic resonance imaging (MRI), but until now, to our knowledge, it has not been applied in the field of medical hyperspectral imaging. Our group proposed for the first time this method for processing hyperspectral images of rabbit liver and burn wound [15]. However, among all these processing methods, the results obtained by our research group demonstrated that the MNF transformation performs best in medical hyperspectral imaging.

The OMBA group aims to further identify new ways to improve the performance of current HSI image processing methods and to persevere in the development of new ones dedicated to medical hyperspectral images.

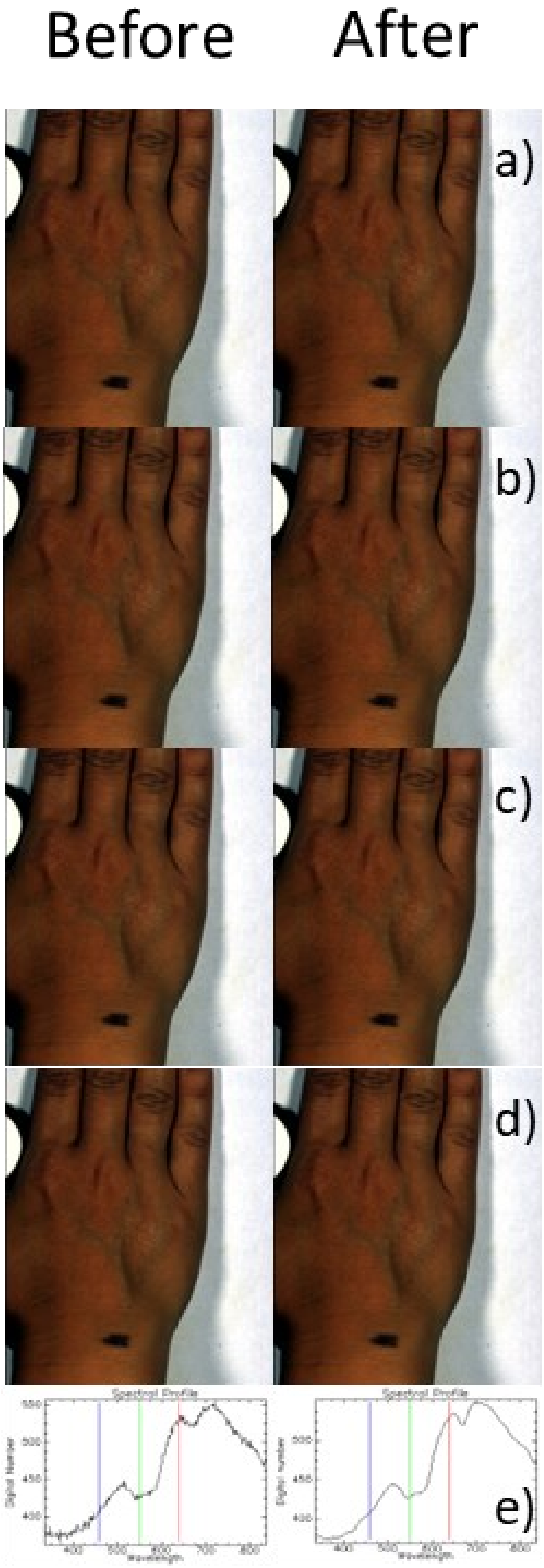

Figure 1. Processing hyperspectral image of a skin nevus using different algorithms. a) MNF algorithm; b) PCA algorithm; c) ICA algorithm; d) Wavelet transform algorithm; e) spectra noise removal

3. HSI image analysis methods

Hyperspectral data analysis is a continuous challenge for this field and different supervised or unsupervised data classification methods or chemometric analysis methods have been proposed so far, especially for the remote sensing field. Taking inspiration from this field, the OMBA group implemented some of these classification methods in the medical field, but at the same time proposed new specific approaches to solve some diagnostic difficulties.

The supervised and unsupervised classification methods investigated by the OMBA group performed well in the diagnosis of burns, wounds, and tumor margins detection. The chemometric analysis methods developed by the OMBA group in the last decade aimed at assessment of tissue oxygenation, the skin flaps viability, the hypoxic state, the skin melanin content, as well as the effects of mud therapy on the skin. Also, among the achievements that OMBA group is proud of is the index-based metric for burn depth assessment which was proposed for the first time by our group for a better differentiation of different skin burn degrees.

3.1. Supervised and unsupervised classification methods

The most important supervised and unsupervised methods approached by the OMBA group to solve the medical diagnostic problems mentioned above were the following: Linear spectral unmixing (LSU), Spectral Angle Mapper (SAM), Support Vector Machine (SVM), Minimum Distance (MD), Spectral information divergence (SID), and K-Means. A brief description of these methods is presented below.

3.1.1. Linear spectral unmixing (LSU) supervised algorithm

Linear spectral unmixing (LSU) supervised algorithm assumes that, when each component located in the pixel area is large enough so that multiple scattering between the different components is insignificant, the reflectance spectrum of each pixel can be expressed as a linear combination of ‘‘pure’’ spectra of the different components (usually called endmembers) weighted by their corresponding fractional abundances. This algorithm has been used for the characterization of skin burns [16].

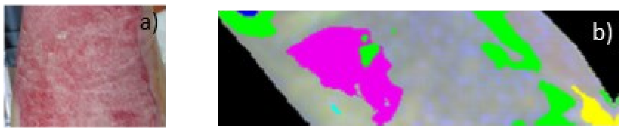

Figure 2. Linear Spectral Unmixing classification of burn types in an affected leg area. a) original HSI image; b) classified image

3.1.2. Spectral Angle Mapper (SAM) supervised algorithm

Spectral Angle Mapper (SAM) supervised algorithm measures the spectral similarity between each pixel spectrum from the hyperspectral medical image and the reference spectra of each endmember extracted from the same image. Each spectrum is considered as a spectral vector in an n-dimensional space and the angle between the spectral vector of the investigated pixel and the spectral vectors of the references is calculated, resulting in a color-coded image that has areas where the investigated pixels have the same spectral angle as the reference pixels. The smaller the spectral angle, the higher the similarity between a pixel spectrum and a reference spectrum. The Spectral Angle Mapper has been shown to be effective in evaluating diabetic foot ulcers and mapping skin burns [9,13].

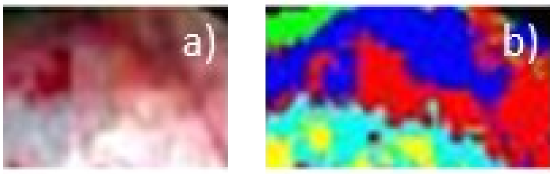

Figure 3. Spectral Angle Mapper classification of a burn wound located on upper arm area. a) original HSI image; b) classified image

3.1.3. Support Vector Machine (SVM)

Support Vector Machine (SVM) is a supervised machine learning algorithm that performs the task of classification by setting an optimal separating hyperplane between the classes by maximizing the distance between the nearest points of each class (named support vectors) and the hyperplane. This approach typically yields a high-accuracy classification of linearly separable data. However, there are many situations where the data are nonlinear separable, and a simple hyperplane cannot be a sufficient separation criterion to solve the binary classification problem. For these cases, a combination of SVM with different kernel functions (polynomial, radial basis function or sigmoid kernels) allows the data to be transformed into a higher dimensional feature space so that linear separation is possible. Support Vector Machine was used in the assessment of wound in diabetic leg and skin burn characterization [8,9,13].

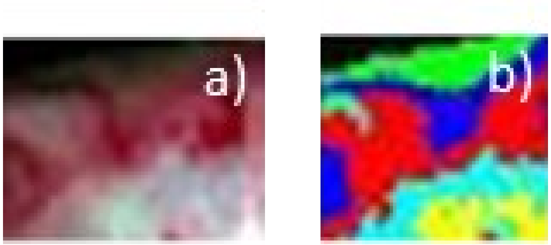

Figure 4. Support Vector Machine classification forearm burned skin wound. a) original HSI image; b) classified image

3.1.4. Minimum Distance (MD)

Minimum Distance (MD) is a supervised approach that uses the mean vectors of each class and calculates the Euclidean distance from each unknown pixel to the mean vector of each training class. Our group implemented this method for the diabetic leg ulcer assessment [13].

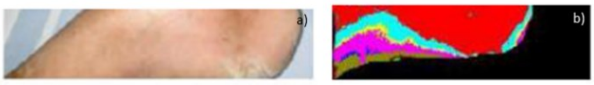

Figure 5. Minimum Distance classification of a diabetic leg wound. a) original HSI image; b) classified image

3.1.5. Spectral information divergence (SID)

Spectral information divergence (SID) is a supervised spectral classification algorithm that uses a divergence measure to compare the spectral similarity between a given pixel spectrum and a reference spectrum. In this method, each spectrum is treated as a random variable and the SID measures the divergence between two spectral vectors that can be extracted either from ASCII files/spectral libraries or directly from a hyperspectral image. The lower the SID value, the more likely the pixels are spectrally similar. In the studies carried out so far, SID was successful in characterizing a diabetic foot wound [13].

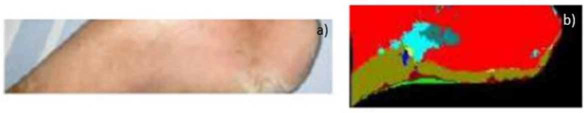

Figure 6. Spectral information divergence classification diabetic foot wound. a) original HSI image; b) classified image

3.1.6. K-Means

K-Means is an unsupervised algorithm that calculates the initial mean values of pixels of all classes in a medical hyperspectral image and iteratively groups pixels into the closest class using a minimum distance technique. At each iteration, the mean values of the classes are recalculated, and the pixels are reclassified according to the new calculated mean values. The iterative process continues until the maximum number of iterations is reached. In oncology, the detection of the edges of a mammary tumor using this method proves that hyperspectral imaging offers the hope of providing non-invasive methods for detecting optimal incision areas [17].

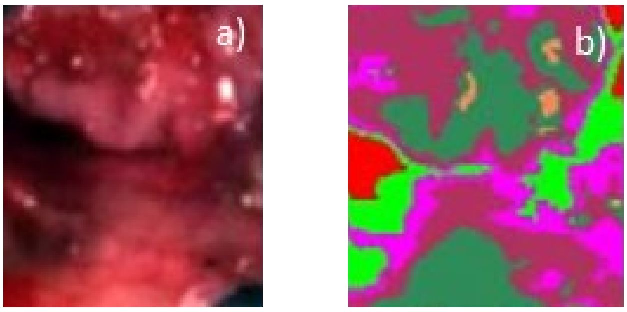

Figure 7. K-Means classification of mammary tumor margins. a) original HSI image; b) classified image

3.2 Chemometric methods

Chemometric methods in hyperspectral imaging have gained importance in the mapping of the concentration's distribution of different chemical constituents of the investigated samples. Chemometric methods in the hyperspectral imaging field have gained importance in mapping the concentration distributions of different chemical constituents of the investigated samples. In the medical field, only a few studies have reported, until now, the use of chemometric methods for hyperspectral data analysis, especially for extracting information about the oxygenation status of biological tissues [18]. OMBA research group, as pioneers in medical hyperspectral imaging field, developed in the last five years, two new chemometric methods (ROMA and MelSkin software) that allows the detection of some skin chromophores, such as: oxyhemoglobin, deoxyhemoglobin, oxygen saturation and melanin [11,19–22].
ROMA software uses a spectral unmixing model based on modified Beer–Lambert law to generate the oxyhemoglobin and deoxyhemoglobin distribution maps as well as the oxygen saturation maps from hyperspectral absorbance data. This software was mainly applied for the assessment of tissue oxygenation in normal and pathological conditions, such as: simulated altitude hypoxia, viability of skin flaps, monitoring of the mud therapy and the photobiomodulation therapy, [11,19–21,23,24].

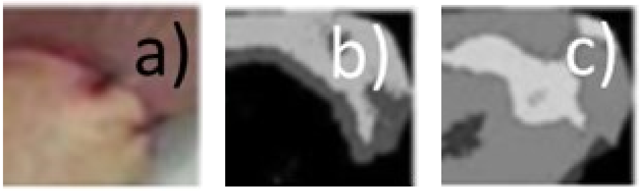

Figure 8. Mapping of oxyhemoglobin and deoxyhemoglobin for a skin flap located on the foot of a patient. a) Original HSI image; b) deoxyhemoglobin map; c) oxyhemoglobin map

MelSkin software is similar to ROMA, the difference is that instead of generating oxygenation maps it will generate a melanin concentration color-coded map of the investigated human skin area. MelSkin method is reliable for the first four Fitzpatrick skin types, how it was proved in our study [22]. This type of software is from our knowledge the first to exist, making OMBA group pioneers in the hyperspectral data analysis for the medical field.

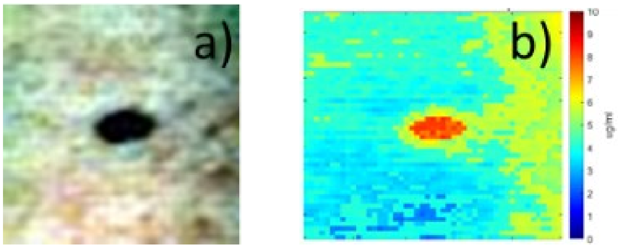

Figure 9. Example melanin concentration map for a nevus in the forearm area. a) original HSI; b) melanin concentration map

3.3 Index-based metric for burn depth assessment (SBSI)

SBSI was defined, as a modified version of relative delta normalized burn ratio index proposed and was proposed for the first time by Miller and Thode [25], the authors used this method with the scope of determining forest burn severity using hyperspectral satellite data. A combination of wavelengths was used to calculate the SBSI, wavelengths which they were derived from an analysis of the normal skin and burned skin hyperspectral data. After finding the optimal wavelengths and obtaining the SBSI, the resulting image was converted from continuous scale of burn degree to distinct burn degree classes to create a burn classification map can be created.

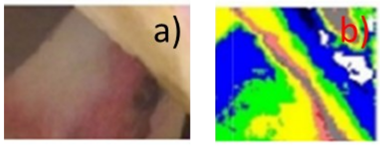

Figure 10. SBSI generated mapping of burn skin in the thorax area. a) original HSI image; b) SBSI final resulting skin burn map

For some time now hyperspectral imaging is in the spotlight of numerous researchers in various fields. With the advancement in imaging technology, it produces a much higher dimensionally images with hundreds of spectral bands thus the rich amount of information is exactly what made HSI to be taking in consideration seriously for various utilizations. The OMBA group have specialized in HSI image processing and data analysis algorithms further improving the medical act into more and more non-invasive region. The OMBA group obtained very good results until now hoping that in the near future the algorithms developed here will replace traditional medical invasive equipment or prevent medical complications in useful time. As scientific researchers, OMBA group strives to open new pathways for non-invasive medical solutions for as many as possible pathologies and advanced monitoring for present treatment and therapies.

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Two decades of research on atmospheric composition using optoelectronic techniques

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Abstract

With a history of not even two decades, the Remote Sensing Department in INOE is currently conducting high quality research in the field of atmospheric composition. The state-of-the-art infrastructure combining remote sensing and in situ optoelectronic instruments, along with the consolidated international and national partnerships enabled the experienced team to become an important contributor to the Aerosol, Clouds and Trace gases Research Infrastructure (ACTRIS), as well as a reliable collaborator of the European Space Agency. This paper presents a short overview of the history, achievements and perspectives.

Keywords: remote sensing, aerosol, clouds, trace gases, air quality, climate change, satellite Cal/Val

1. Introduction

The environment is a complex structure continuously analyzed by researchers. One of its main components, the atmosphere, makes life possible on our planet. The atmosphere is directly involved in general environmental problems, in all its processes and at all time scales. In the short term (on a local scale) the acute problem of air quality is highlighted, but in the long term (on a global scale) the problem of disrupting the Earth-Sun radiation budget becomes important. Between the two temporal scales, especially in the case of the atmosphere, many important physical processes must be taken into account because they direct the effects of regional air pollution and can themselves be influenced in magnitude and frequency by climate changes.

There are multiple in situ techniques for characterization of the atmospheric composition, but they cannot provide information about the distribution in the atmospheric column unless they are placed on board airborne platforms (airplanes, UAVs), which increases the cost of investigations and reduces the amount of data. The most used for this purpose today are passive and active light-based remote sensing techniques. These techniques are extremely sensitive but involve a series of assumptions and parameterizations that increase the uncertainty of the final products. In general, the difficulty of determining optical and microphysical parameters of the atmospheric components from remote sensing observations resides in the fact that the signal from aerosols and molecules is mixed, for their separation various software methods are applied which are never infallible. Passive and active remote sensing techniques each have limitations that make it impossible to accurately determine the composition of the atmosphere. That is why modern science uses synergistically data from several instruments, in situ and remote sensing, generally located at complex atmospheric observatories.

In this paper we present the not so long history of the Remote Sensing Department, its recent achievements and near future perspectives. This overview covers the development of the infrastructure and international collaborations which stay at the foundation of recent scientific and technological results obtained by the team in the field of atmospheric composition, with significant relevance for air quality, quantification of the essential climate variables, and Cal/Val of satellite atmospheric missions.

2. History/Landmarks

In the last two decades, the Remote Sensing Department (RES) from National Institute of Research and Development for Optoelectronics - INOE 2000 has conducted atmospheric studies operating a complex research infrastructure and having multidisciplinary expertise spanning from laboratory/in-situ chemical analysis to Earth Observation (EO) techniques and applications.

Starting 2004, the first lidar system was installed in Romania, at our institute. First measurements, first active remote sensing results were published by INOE's team in 2005 and the first Ph.D thesis in this field was earned in

2006 by Mrs. Doina Nicolae and was entitled “Lidar techniques for characterization of aerosol in the lower troposphere”. Our lidar station was accepted as a full member of the EARLINET (European Aerosol Research LIdar NETwork) in November 2005 and is regularly contributing to the enhancement of this European data base since then.

In 2007 INOE was accepted as an associate partner to the FP6 EARLINET-ASOS (http://www.earlinet.org), a networking project for integration of lidar stations in aerosol measurements by following standardized procedures for measurements, data processing and reporting and also development of a common data base.

With the support of the EXIST project - PNCDI2 Capacities development (http://inoe.inoe.ro/EXIST) RES purchased and installed additional instruments, making important steps towards becoming an atmospheric composition observation site in East Europe: the multi – wavelength Raman Lidar (RALI) which is even now used for retrieving the aerosol optical and microphysical parameters, the ozone lidar (OLI) for measuring tropospheric concentrations, and other complementary instruments for measuring aerosol and gaseous compounds near-surface.

However, to become a supersite and prove to be an advanced active remote sensing center in Europe, INOE station needed to fulfill some performance criteria, including training of the personnel and implementation of chemical speciation of aerosols. A new project has been conceived and submitted to FP7-REGPOT-2008-1 and it was funded, in 2009: DELICE “DEveloping the emerging research potential of romanian LIdar CEntre". DELICE (http://inoe.inoe.ro/DELICE) allowed the purchasement of an aerosol mass spectrometer - unique in Romania (for aerosol chemical composition and size distribution), a microwave radiometer (to measure the vertical profiles of temperature and humidity) and a sodar (for vertical profiles of wind directions and speed). All come along with dedicated training sessions in collaborations with international partners.

Experience from within EARLINET, new instruments and expertise gained through projects like EXIST and DELICE, but a very clear need to expand spatially our measurements determined INOE’s team to promote a new project, for installing 4 new lidar stations at Timisoara, Iasi, Cluj and Baneasa. ROLINET, a partnership program PNCDI2 (http://inoe.inoe.ro/ROLINET), formed a consortia of research institutes and universities open to start a new research direction - laser remote sensing: University "Al. I. Cuza"-Iasi, University "Babes-Bolyai" -Cluj, University "Politehnica" - Timisoara, National Meteorological Administration (ANM) and University of Bucharest, Faculty of Physics. In ROLINET a prototype Romanian lidar system has been developed (Published patent no. RO125055-A0) and constructed by ESYRO company, project partner. This instrument was set up at ANM. The design of the lidar was especially for use near the airport, but then it was improved to study the planetary boundary layer (0- 3Km) and free troposphere aerosol (up to 10 km). Three identical lidars have been installed at Iasi, Cluj and Timisoara. ROLINET ended in 2010, but Romanian lidar network continued to develop.

We have to emphasize that projects like EARLINET-ASOS, EXIST, DELICE and ROLINET overlapped in time partially, their objectives and tasks being different, but together these projects have laid the foundation for a nation-representative atmospheric observatory which uses active remote sensing for detecting and characterizing atmospheric components and processes in the low atmosphere (0 – 10 Km altitude). This foundation was further consolidated through Norwegian funds (2008-2011), which were used by INOE in collaboration with the Norwegian Institute for Air Research (NILU) to improve relations between science and society, through development of a new infrastructure, RADO-Romanian Atmospheric 3D research Observatory. With this project the relevance of the measurements was extended to the free troposphere, and a small Science Centre was established for combining research education and practical training. Since then, thousands of children have learned about the atmosphere and how light propagates through it, and hundreds of master and PhD students have been trained in lidar and photometry at the RADO Science Centre.

Several events and series of events were organized by RES department during its existence. During 2006 - 2013 Optoelectronic Techniques for Environmental Monitoring OTEM workshop was organized in several cities across Romania having the aim to encourage the exchange of ideas and knowledge between various groups of the scientific community concerned by current issues in environmental science, engineering, management and policies. In 2009 OTEM workshop was organized together with EARLINET meeting in Bucharest and few times was coupled with “Atmospheric Remote Sensing” ARS Summer School. ARS-ss comprises training classes in the scientific modules introducing concepts, practice and caveats of the different instrumental techniques, algorithm concepts and the atmospheric processes. Special focus is on hands-on training using available instrumentation at RADO. Each summer school is complemented by courses and practice on complementary skills, e.g., presentation & communication, project management, ethics and IPR.

An important landmark for RES department was the involvement in ACTRIS - Aerosol, Clouds and Trace Gases Research Infrastructure (https://www.actris.eu/). All started in 2011 with the ACTRIS INFRA project (2011 – 2014) financed by the European Framework Programme 7 and continued with ACTRIS H2020-INFRAIA project (2015 - 2019). The group was involved in both projects, with increasing responsibilities: from providing Trans-National Access to the RADO infrastructure in ACTRIS-1, to the leadership of the Lidar Calibration Laboratory in ACTRIS-2. The main goal of these two projects was to create the European infrastructure/network having the aim to study short-lived atmospheric compounds, more precisely aerosols, clouds and minor gases, using complex scientific equipment and state-of-the-art laboratories. The ACTRIS projects series continued with ACTRIS PPP (2017-2019, https://cordis.europa.eu/project/id/739530) and ACTRIS

IMP (2020 – 2023, https://cordis.europa.eu/project/id/871115).

ACTRIS-PPP, as a Preparatory Phase project, brought together a wide community of research performing organizations, research funding organizations and ministries needed to take the decisions and actions to move forward in the implementation of the ACTRIS. The main objectives of ACTRIS PPP were to develop the organizational, operational and strategic frameworks of the Research Infrastructures (RI). This was a major milestone for RES because at this point INOE was given the responsibility to lead one of the 8 Central Facilities of the pan-European research infrastructure, more precisely the Centre for Aerosol Remote Sensing.

The implementation of ACTRIS structures, policies and activities is now ongoing through the ACTRIS Implementation Project (IMP), which builds on the achievements of the successful ACTRIS PPP and on the scientific and technical deliveries of the ACTRIS, ACTRIS-2 and EUROCHAMP-2020 projects. The series of ACTRIS projects had a significant role in enabling the transition from a project-based network of research facilities to a centrally coordinated integrated pan-European RI. ACTRIS has been selected on the ESFRI Roadmap in 2016 and has already reached the ESFRI Landmark in 2021.

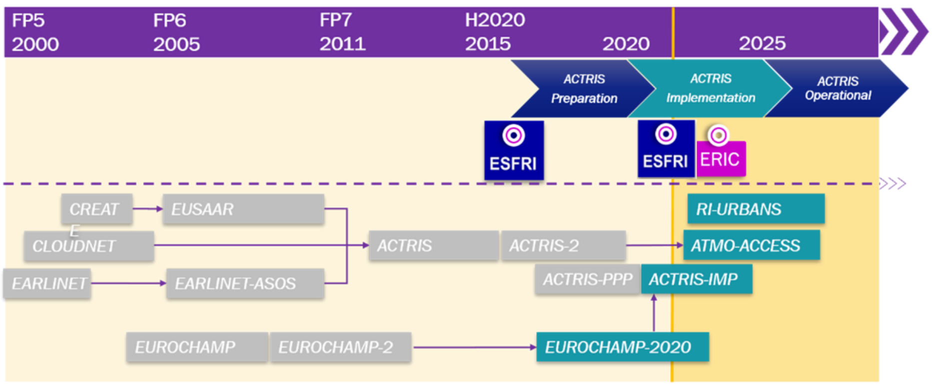

Fig. 1 European projects building and consolidating ACTRIS

In ACTRIS, INOE is leading the Centre for Aerosol Remote Sensing (CARS), unique worldwide, and is hosting one unit of the aerosol high

power lidars. CARS mission is to offer operation support to ACTRIS National Facilities operating aerosol remote sensing instrumentation, more specifically aerosol high-power lidars, ceilometers and sun/sky/lunar photometers. Romania also participates with 3 observation stations for aerosol remote sensing, 3 for cloud remote sensing, 1 for aerosol in situ and 2 exploratory platforms. These National Facilities operated by the “Babes-Bolyai” University of Cluj-Napoca, “Al. I. Cuza" University of Iasi, “Dunarea de Jos” University of Galati, and the National Institute for Aeronautical Research "Elie Carafoli" inherited from the previous collaborations in ROLINET and RADO projects.

One of the National Facilities offered by Romania as contributors to ACTRIS is operated by INOE. In order to complete the infrastructure needed, INOE has successfully applied to, and implemented an ERDF project for building up large infrastructures, CEO-TERRA (A1.1.1-F-2015/ 108109/152). Although many instruments have been installed at RADO over the years, the location proved to be not ideal because is small, and is surrounded by high buildings and trees. The 13.5 mil EUR brought by CEO-TERRA were invested therefore in modernizing several existing laboratories, but mostly in building up a new observation site, Măgurele centre for Atmosphere and Radiation Studies (MARS), which was put into operation in 2021. MARS is now similar to the major European Observatories (JOYCE (Germany), CESAR (Netherlands), CIAO (Italy) participating to the European environmental research infrastructures ACTRIS and ICOS.

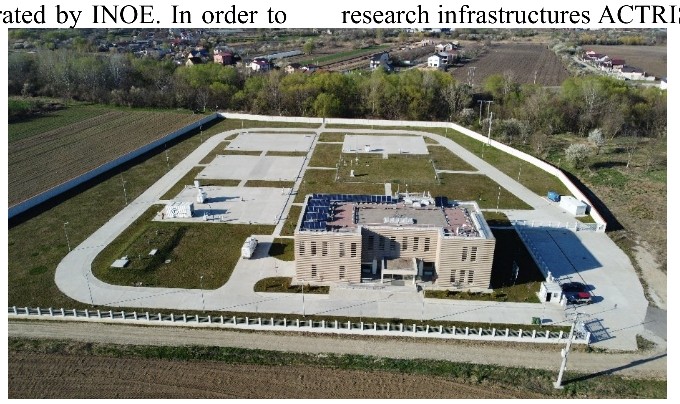

Fig. 2 Aerial view of the Măgurele centre for Atmosphere and Radiation Studies (MARS)

The Magurele Center for the Study of the Atmosphere and Radiation (MARS) is an experimental center for observing, studying and understanding the exchanges and interactions between climate-relevant atmospheric variables and climate components. MARS hosts a brand-new cloud remote sensing laboratory, an upgraded aerosol in situ measurements laboratory, the Lidar Calibration laboratory, as well as many complementary instruments spanning from meteorological sensors to trace gases and greenhouse gases remote sensors. The main research directions are: the study of clouds, aerosol-cloud interactions, quantification of the radiative effects of aerosols and clouds, microscale studies of the planetary boundary layer, the study of turbulence and flows, studies on the physical and chemical properties of aerosols. The instruments operated at MARS are connected to a node, equipped with high-performance IT systems (application servers, supercomputers, data storage systems) within the MARS data center.

In addition to the major contribution to the research infrastructures, this investment opens up extraordinary prospects for long-term participation in the European Space Agency's Earth observation space programs (Copernicus and Earth Explorers). Since 2014 until now, European Space Agency signed with INOE more than 15 projects (http://environment.inoe.ro/category/80/international-projects).

Fig. 3 The Aerosol in situ measurements laboratory

Fig. 4 The reference lidar and the MIRA-35 cloud radar

3. Current developments and collaborations

The approach of knowledge, understanding and control of the state of the environment (air/water/soil) is based on the collection of coherent data and information at various spatial scales (local to global, from the ground to the upper atmosphere), and centralized analysis of them through international programs and initiatives. In this sense, the international community developed several large-scale initiatives and programs in recent decades such as: WMO GAW (Global Atmosphere Watch Programme), Copernicus (European Earth Observation Programme), ACTRIS (Aerosol, Clouds and Trace Gases Research InfraStructure) or ICOS (Integrated Carbon Observation System).

Within this framework, the goal of RES was always to become an important contributor to the relevant databases for atmospheric composition, while adding scientific and technological value as part of the continental and global research. Today, the Remote Sensing Department contributes to global and European profile networks (AERONET, EARLINET, MWRNET, ACTRIS) and to Earth observation activities from space carried out by the European Space Agency (Cal/Val campaigns for Aeolus, EarthCARE and TROPOMI). This community joins more than 350 research institutions world-wide, with whom INOE collaborates as part of various project consortia.

RES operates a GAW regional station and contributes to the following joint European and global climatological database as part of international networks:

European Aerosol Research Lidar Network EARLINET (www.earlinet.org) is the first network of advanced lidar stations which provides a quantitative climatological database of the horizontal, vertical, and temporal distribution of aerosols over Europe. Lidars are powerful tools for providing quantitative measurements of the optical properties of aerosols with high spatial and temporal resolution and with a high level of accuracy. The objectives of EARLINET are reached by operating a network of presently 31active stations distributed over most of Europe, using advanced quantitative laser remote sensing to directly measure the vertical distribution of aerosols, supported by a suite of more conventional observations. Special care is taken to assure data quality, including intercomparisons at instrument and evaluation levels. A major part of the measurements is performed according to a fixed schedule to provide an unbiased statistically significant data set. Additional measurements are performed to specifically address important processes that are localized either in space or time. Back-trajectories derived from operational weather prediction models are used to characterize the history of the observed air parcels, accounting explicitly for the vertical distribution. INOE is part of EARLINET since Nov. 2005 providing data three times per week and during alerts as well as during specific satellites overpass, conforming to the protocol, and participating in all important associated events, campaigns and projects.

Aerosol Robotic Network AERONET (https://aeronet.gsfc.nasa.gov/) program is a federation of ground-based remote sensing aerosol networks established by NASA and PHOTONS (University of Lille 1, CNES, and CNRS-INSU) and is greatly expanded by collaborators from national agencies, institutes, universities, individual scientists, and partners. The program provides a long-term, continuous and readily accessible public domain database of aerosol optical, microphysical and radiative properties for aerosol research and characterization, validation of satellite retrievals, and synergism with other databases. The network imposes standardization of instruments, calibration, processing and distribution. INOE is part of AERONET since Jul. 2007.

International Network of Ground-based Microwave Radiometers MWRNET (http://cetemps.aquila.infn.it/mwrnet/) is a network connecting people working with ground-based microwave radiometers. MWRnet aims to facilitate the exchange of information in the MWR user community – beginners, experts, and manufacturers – fostering participation to coordinated international projects. In the long run, MWRnet mission is the set-up of an operational network sharing knowledge, software, procedures, formats, quality control, etc., similarly to other successful networks such as CWINDE, EARLINET, AERONET. INOE is part of MWRNET since Dec. 2009 providing continuous data (automatic data collection and transfer), and participating to associated events and campaigns.

European Supersites for Atmospheric Aerosol Research *EUSAAR* (https://cordis.europa.eu/project/id/26140) is an EU-funded I3 (Integrated Infrastructures Initiatives) project carried out in the FP6 framework of the specific research and technological development programme "Structuring the European Research Area - Support for Research Infrastructures". The objective of EUSAAR is the integration of measurements of atmospheric aerosol properties performed in a distributed network of 20 high-quality European ground-based stations. This integration contributes to a sustainable reliable operational service in support of policy issues on air quality, long-range transport of pollutants and climate change. INOE is associated partner to EUSAAR since Nov. 2007.

A network of stations for the continuous evaluation of cloud and aerosol profiles in operational NWP models CLOUDNET (https://cloudnet.fmi.fi). The main objective of the network is to provide accurate observations from a synergy of ground-based instruments in order to obtain continuous records of cloud microphysical and macrophysical parameters (e.g., reflectivity, cloud base height, liquid water content, Doppler velocity) and their associated errors, to develop and validate cloud remote sensing synergy algorithms and use these algorithms to enhance the quality of forecast models. Datasets collected inside the network are provided by three essential instruments: a Doppler cloud radar, a ceilometer and a microwave radiometer and a set of non-essential instruments: Doppler wind lidar, and disdrometer. INOE is a CLOUDNET member since 2019 providing continuous data and participating in the development and implementation of CLOUDNET algorithms.

E-PROFILE is the EUMETNET Profiling Programme (wind observations from weather radars and dedicated wind profilers and Lidar/Ceilometer observations). E-PROFILE coordinates the measurements of vertical profiles of wind from radar wind profilers (vertically pointing Doppler radars) and weather radars from a network of locations across Europe and provides the data to the end users. The main goal is to improve the overall usability of wind profiler data for operational meteorology and to provide support and expertise to both profiler operators and end users. To make available the information on the vertical distribution of aerosols derived from the backscatter profile, E-PROFILE is developing a framework to produce and exchange profiles of attenuated backscatter profiles. Automatic lidars and ceilometers of stations across Europe are added to the operational network (https://www.eumetnet.eu/activities/observations-programme/current-activities/e-profile/). The operational data can be visualized in real time (https://e-profile.eu/). INOE is part of the Automated Lidars and Ceilometers (ALC) network since 2018.

Recently, the above networks have agreed to become part of, or to be linked with, the ACTRIS research infrastructure. As a consequence, these databases are in process of being integrated under one single data portal operated by ACTRIS.

ACTRIS - Aerosol, Clouds and Trace Gases Research InfraStructure (www.actris.eu) has an essential role to support the building of new knowledge as well as policy issues on climate change, air quality, and long-range transport of pollutants. ACTRIS is building the next generation of the ground-based component of the EU observing system by integrating three existing research infrastructures EUSAAR, EARLINET, CLOUDNET, and a new trace gas network component into a single coordinated framework. INOE is part of ACTRIS since the beginning, in 2011, offering trans-national access to infrastructure and participating in networking and joint research activities. Recently, the consortium of Romanian institutions (ACTRIS-RO) led by INOE has been included in the ACTRIS research infrastructure. INOE operates *The Lidar Calibration Center (LiCal),* a unit of the ACTRIS Center for Aerosol Remote Sensing (CARS), and also leads the entire Central Facility. The mission of CARS is to offer operation support to ACTRIS National Facilities operating aerosol remote sensing instrumentation: aerosol high-power aerosol lidars, automatic low-power lidars and ceilometers, and automatic sun/sky/polarized/lunar photometer. Additionally, CARS offers specialized services for the above instruments and related ACTRIS variables, to ACTRIS users of various types: academia, business, industry and public services.

The infrastructure and the expertise covered by RES goes, nevertheless, beyond ACTRIS. The resources provided by the RADO and MARS facilities are also used in support of Cal/Val satellite missions (e.g., intensive campaigns, participation in fiducial reference measurement systems, and development of retrieval algorithms for designing and developing new instruments). INOE's team has already completed several validations and multi-instrument inter-comparison campaigns related to the ESA Cal/Val program and instrument-oriented validation campaigns. Over the past years, the team at INOE in collaboration with ESA has developed a set of tools and equipment designed to test and optimize remote sensing instruments. The successful collaboration with ESA derived from several research projects such as NATALI – Neural network Aerosol Typing Algorithm based on LIdar data, MULTIPLY - Development of a European HSRL airborne facility, FRM4RADAR - 94 GHz Miniature Network for EarthCARE Reference Measurements, RAMOS - Technical Assistance For A Romanian Atmospheric Observation System, SAMIRA - SAtellite based Monitoring Initiative for Regional Air quality, and other (http://environment.inoe.ro/category/80/international-projects).

4. Recent results and transfers of results

Over the last years, a series of fruitful collaborations took place between our department and various international and national institutes and universities. ACTRIS-only embeds more than 100 research performing organizations in 22 European countries. With its leading role at the ACTRIS Centre for Aerosol Remote Sensing, RES coordinates 8 institutions (the so-called CARS Units) located in Germany, Italy, France and Spain, is in permanent contact with more than 40 aerosol remote sensing National Facilities, and collaborates on daily basis with the aerosol remote sensing Unit of the ACTRIS Data Centre (ARES) located in Italy. This extended network of collaborators allowed us to realize many joint studies and technical developments shortly described below.

Recent scientific results refer to **aerosol typing** aiming to determine which kind of aerosol we measure (e.g., dust, smoke, volcanic ash, local pollution). D. Nicolae et al. [1][2] have developed an aerosol typing algorithm based on artificial neural networks, able to retrieve up to 14 aerosol mixtures from multiwavelength Raman lidar observations. The algorithm was further implemented in a Python software and distributed to the ACTRIS community for further use. With this software, V. Nicolae et al. [3] evaluated the typology of LRT aerosols over Europe during 2008-2018 by means of EARLINET and AERONET data. The authors found that the typical aerosol particles observed in that period were medium-sized, medium-absorbing particles with low spectral dependence. Smoke (37%) and Continental (25%) aerosol types were the predominant aerosol types in Europe, followed by Continental Polluted (17%), Dust (10%), and Marine/Cloud (10%) types. K.A. Vadouri et al. [4] compared the NATALI software with another aerosol typing method. The authors considered four major types of aerosols: Dust, Maritime, Polluted Smoke and Clean Continental. The analysis showed that the two algorithms, when applied to real atmospheric conditions, provide typing results that are in good agreement regarding the automatic characterization of Polluted Smoke, while there are some differences between the two methods regarding the characterization of Dust and Clean Continental. These disagreements are mainly attributed to differences in the definitions of the aerosol types. Later, M. Mylonaki et al. [5] performed aerosol typing introducing a new aerosol type method, comparing the results with the methods analyzed by Vadouri et al. (2019). The NATALI software was also used by V. Nicolae et al. [6] to identify the changes in the aerosol types and properties during pandemic restrictions in Romania. The study showed that in Magurele the reduced traffic and industrial activity determined a decrease of small aerosol particles in the low troposphere, more precisely that continental polluted aerosols and smoke decreased as proportion in the total aerosol load. A new method of identifying and analyzing oil smoke plumes based on MODIS and CALIPSO satellite data was presented by A. Mereuța et al. [7].

The **aerosol climatology** in Magurele was assessed using solar and lunar photometers between 2007-2016 [8]. The site is characterized by high intra-annual and inter-annual variability of the total aerosol optical depth (AOD), which has two peaks, during March and August. For half a year, from May to November, Magurele is affected by the transport of aerosols from the nearby city of Bucharest, since the dominant winds are from this direction. Thus, the predominant is the fine mode of aerosols. Negative statistically significant trends at all AOD wavelengths, the order of 20–40% per decade, have been calculated. J. Vasilescu et al. [9] studied the seasonal variation of the aerosol chemical composition using the Aerosol Mass Spectrometer. Proportions of chemical species, concentration time series, mass range distribution and aerodynamic size distribution of aerosols have been analyzed. Mass spectrometry measurements proved that the organics, nitrate, sulphate and ammonium, with small amounts of chloride were the main species at ground level during the investigated period. The fine particle mode consisted typically of organics, sulphate and ammonium during summertime, with size distribution centered at about 400-500 nm.

Aerosol speciation has been studied using near-surface observations. L. Marmureanu et al. [10] studied the chemical characterization and the source identification of the summer and winter aerosols at our site. Approximately 50% of the organic fraction contribution to the total submicron particulate matter sampled by aerosol mass spectrometer was evidenced during both seasons. For warm (summer) and cold (winter) seasons, more than 50% of total organics was represented by oxidized factors. Regional contributions were characterized by lower traffic and biomass burning. During winter, local non-traffic sources were dominant, with residential heating as important source. Hoffer at al. [11] investigated the emission factors for PM10 and polycyclic aromatic hydrocarbons (PAHs) from illegal burning of different types of municipal waste in households. It was found that the PM10 emission factors from the combustion of wood-based waste samples were about twice that of firewood, whereas emission factors in the range of 11–82 mg g−1 (a factor of 5–40 times higher than that of dry firewood under the same conditions) were obtained for different types of plastic waste. The authors proposed novel tracers for the burning of PET and furniture plates (LDF), which are among the most widely used waste types burned in households.

Source apportionment methodologies applied on data collected with the Aerosol Chemical Speciation

Monitor showed that organic aerosols (OA) present in submicron particles (PM1) are important due to the diversity and complexity of its primary sources and secondary formation processes. M. Via et al. [12] compared the source-receptor seasonal Positive Matrix Factorization (PMF) model and the recently developed rolling PMF technique for retrieving the organic aerosols from a synthetic dataset and nine European ACSM datasets (including ours) in order to spot the main output discrepancies. Results proved that the rolling PMF performed better than seasonal PMF globally for the ambient datasets, especially in periods between seasons.

Microphysical properties of sub-micronic aerosols were studied by S. Samaras et al. [13] using the Raman-lidar-based regularized inversion. The authors extracted the microphysical properties of aerosols for a collection of measurement cases with low volume depolarization ratio originating from fire sources captured by the Raman lidar located at INOE. The algorithm was tested not only for pure smoke but also for mixed smoke and urban aerosols of variable age and growth. A direct quantitative comparison of the retrieved microphysical properties with measurements from the Aerosol Mass Spectrometer showed remarkable similarities for the retrieved size distribution of the fine mode, and a good correlation between the aerosol effective radius and particle age.

A series of studies involving lidar measurements focused on the **characterization of the biomass burning.** By using the synergy between lidar and the Aerosol Mass Spectrometer, D. Nicolae et al. [14] have studied the changes of the optical and microphysical properties of long-range transported biomass burning (BB) aerosols and their variation with atmospheric evolution (ageing). The authors found that the relevant optical parameter for the ageing process is the Ångström exponent, with a decrease from 2 for fresh to 1.4–0.5 for aged smoke particles. The ratio of lidar (extinction-to-backscatter) ratios (LR_{532}/LR_{355}) changes rapidly from values <1 for fresh to >1 for aged particles. The synergy between lidar and photometer was used by B. Kokkalis et al. [15] for comparing the LIRIC (Lidar-Radiometer Inversion Code) aerosol concentration retrievals with airborne measurements. The study showed that LIRIC retrievals of the biomass burning aerosol concentration in the fine mode are in a good agreement with the measured airborne in-situ data (Aerosol Mass Spectrometer and Passive Cavity Aerosol Spectrometer Probe) from 2 to 4 km, while significant discrepancies were found below 2 km due to the spatial and temporal variability of the aerosol load within the area measured by plane. I.S. Stachlewska et al. [16] studied the influence of long-range transport of biomass burning aerosol on local urban aerosol properties. Within the synergetic approach, air mass transport models and satellite images were used to identify biomass burning sources. The authors observed an increase in aerosol optical depth and Ångström exponent as well as the surface PM_{10} and $PM_{2.5}$. Intrusions of advected biomass burning particles into the urban boundary layer affected also the top height of the boundary layer, by moderating its increase. H. Baars et al. [17] investigated the long-range transport of stratospheric smoke during 2017-2018. Six months of observations within EARLINET (including INOE's lidar station) were analyzed. The depolarization values decreased in time, consistent with the smoke particles aging. The authors found ascending aerosol layer features over most of southern European stations, especially over the eastern Mediterranean at 32–35° N, that ascended from heights of about 18–19 to 22–23 km from the beginning of October to the beginning of December 2017 (about 2 km per month). M. Adam et al. [18] presented a data analysis methodology of the EARLINET measurements. Three directions were described: analysis of a BB event observed by several lidar stations, analysis of LRT from North America and statistical analysis of various European geographical regions. M. Adam et al. [19] published a methodology for lidar monitoring of biomass burning smoke in connection with the land cover. Using a synergy with backtrajectories models and satellite data for land cover and fires, the authors identify the contributing smoke sources to the measured smoke layer by lidar. Newly developed methods estimate the vegetation type of the contributing fires.

Few studies referred to the **dust investigation.** The assessment of aerosol's mass concentrations from lidar measured linear particle depolarization ratio and simulations was published by A. Nemuc et al. [20]. For this study 11 months of lidar measurements performed at INOE were analyzed. The authors found that calibrated depolarization measurements are critical in distinguishing between smoke-rich aerosol during the winter and dust-rich aerosol during the summer, as well as between elevated aerosol layers having different origins. Good agreement was found between lidar retrievals and DREAM (Dust REgional Atmospheric Model) forecasts in cases of Saharan dust, but also with LIRIC retrievals. L. Marmureanu et al. [21] investigated the unusual event of Saharan dust intrusion over Romania during 2018 winter using in-situ and remote sensing measurements. The chemical analysis of the dust and its optical properties confirmed the dust source. A. Tsekeri et al. [22] described a polarization lidar to detect dust orientation. M.J. Granados-Muñoz et al. [23] studied the radiative effect of two mineral dust events using CALIPSO observations over Europe. The radiative fluxes obtained are first validated in terms of radiative efficiency at a single point with space-time collocated lidar ground-based measurements from EARLINET. The methodology is then applied to the full orbit. The strong dependence of the radiative effects on the aerosol load (and to a lesser extent on the surface albedo) highlights the need for accurate AOD measurements for radiative studies. The calculated dust radiative effects and heating rates below the orbits are in good agreement with previous studies of mineral dust. The results demonstrate the validity of the method presented to retrieve 2-D accurate radiative properties with large spatial and temporal coverage.

Lidars and ceilometers are used for **Planetary Boundary Layer (PBL) studies**. D. Wang et al. [24] looked at the variability of PBL over an urban site over ten years of measurements using ceilometer and lidar, operating at 1064 nm. Three methods were involved to determine PBL height while radiosonde measurements were used complementary. There was a relatively good agreement between methods. For the whole period, the PBL heights below 1 km constituted more than 60% of the retrievals. The monthly mean PBL height had a strong seasonal change: a mild weakly autumn diurnal cycle, followed by a flat winter diurnal cycle, then a sharp transition to a spring diurnal cycle, and a high bell-like summer diurnal cycle.

As a step forward towards public awareness, L. Levei et al. [25] studied the **human health risk associated with PM10 exposure** (monthly averages) for the residents in Cluj-Napoca city for a decade, considering the best and the worst scenario. In general, the monthly PM_{10} concentrations were higher from October to March than in the rest of the year. The monthly air quality index (AQI) showed a good to moderate quality of the air during the whole decade; however, there were days when the air quality was unhealthy for sensitive population groups.

Based on the synergy between the cloud radar, ceilometer and microwave radiometer at our new established CLOUDNET station, a recent study by R. Pirloaga et al., [26] presents the first **cloud properties** over 18 months (2019-2021), following target classification based on the Cloudnet algorithm. According to the authors, clouds were more frequently observed during winter (45% of all profiles). Ice clouds were the most frequent type of cloud during the study period, followed by mixed phases and mixed phased precipitable clouds. The geometrical thickness varied from a median value of 244 m for liquid clouds during summer to 3362 m for mix phased precipitable clouds during spring. The complementary meteorological sensors at MARS enabled several studies referring to hail and convective clouds. T. Púčik et al. [27] present several statistics based on reports of large hail that had been submitted to the European Severe Weather Database (ESWD). Thus, the authors studied the diurnal and seasonals trends, the impact of hail on various damages, injuries and casualties, looked at the economic losses associated with hailstorms occurring in central Europe and looked for long-term changes. S. Andrei et al. [28] shows the main characteristics of two convective events that occurred in Romania in order to emphasize the similarities and disparities between a tornado event and a non-tornado event, from the warning perspective. Also, the authors investigated for the first time in Romania, the general public's comprehension, risk perception and reactions regarding the tornado events. By means of lidars and radars, E. Marinou et al. [29] studied the **clouds properties in the presence of dust**. The significant presence of Mixed-Phase Clouds was observed in all the clouds formed at the top of a dust layer, with three times higher abundance than the mean conditions (26% abundance at $-15\,^{\circ}C$). The low-level clouds were formed in the presence of sea salt and continental particles with ice abundance below 30%.

Trace gases and greenhouse gases are also under observation at our site. The study by C. Marin et al. [30] shows the results of a winter intensive campaign for measuring gas concentrations of NO_x, SO2, CO, O3 and CH4. The long-range transport of SO2 and two hotspots for CO from traffic and from residential heating emissions were emphasized. The values for NO2, CO and SO2 concentration were at least two times lower than the European Union pollution limits. The concentration of O3 was only twice higher than the established limits.

For a more practical approach, RES has worked also to **setup of early warning systems for atmospheric hazards**. For example, N. Papagiannopoulos et al. [31] developed an NRT (near real time) warning system for aviation hazards. The methodology is based on backscatter coefficient and depolarization values provided by a lidar. The method was implemented for two different aerosol types: desert dust and volcanic ash. Based on mass concentration values (derived from backscatter coefficient), various alarms (low, medium and high) are issued. M. Adam et al. [32] setup an alarm system based on ceilometer and photometer values. In addition, backtrajectories models help identify the potential sources. The aerosol transport events are considered to be major when various optical properties provided by the photometer are found outside the climatological values.

Lidars coupled with other ground-based observations are heavily employed in the **validation of the satellites' sensors.** E. Proestakis et al. [33] presented the EARLINET evaluation of Cloud-Aerosol Transport System (CATS) level 2 aerosol backscatter coefficient. Three ground-based EARLINET stations are used for correlative measurements. The results show that under cloud-free, relative homogeneous aerosol conditions, CATS is in good agreement with EARLINET, independent of daytime and night-time conditions. CATS low negative biases (~6%) are observed during night, while during day it increases to ~ 22%. RES was involved in two campaigns related with the satellite validation: the AROMAT (the Airborne ROmanian Measurements of Aerosols and Trace gases) campaigns focused on validation strategy for NO_2, H_2CO and SO_2 [34], and SAMIRA (SAtellite Based Monitoring Initiative for Regional Air Quality) proved the use of satellite data for regional and urban-scale air quality monitoring in terms of gases (NO_2, SO_2) and PM ($PM_{2.5}$, PM_{10}) [35].

A few collaborations have been established within the **modelling of various aspects of either gases or aerosol in atmosphere**. D. Konsta et al. [36] use the CALIPSO dust extinction profiles as a tool for examining the performance of the regional dust model BSC-DREAM8b in space and time. Thus, the model overestimates the dust extinction coefficient above dust source regions in Sahara Desert or transported over Mediterranean while it underestimates the transported dust over Europe and Atlantic Ocean and Middle East. V. Nicolae et al [37] have used Calipso data and FLEXPART model in order to analyze the seasonal variability, for the hot and cold seasons, of biomass burning aerosol observed over Romania. The model was set up to use as input the MODIS fire data with a degree of confidence over 25% after transforming the emitted power in emission rate. Distribution in the upper layers were compared to Calipso retrieval. The authors concluded that the model correctly represent, on average, the BBA distribution, but its performance for simulating vertical profile structure and the exact amount of BBA is still not sufficiently good. C. Talianu and P. Seibert [38] studied the sulfate aerosols over an air quality background station in Austria in April 2014 based on the synergy of instruments measurements and aerosol modelling and transport. The excess of SO_2, $PM_{2.5}$, PM_{10}, and O_3 observed were analyzed using in situ data, lidar measurements, CAMS near-real-time data, and aerosol and atmospheric transport modelling. This excess was associated with the transport of sulfate aerosols, mixed with dust during the transport. By correlating the local information with a trajectory analysis and an analysis of aerosol potential sources, the pattern of sulfate contributions was found. The lower layers (below 2000 m) and middle-altitude layers originated mainly from central Europe. The high-altitude layers (above 5000 m) originated from sources from northwest Africa and from the southern and eastern US, as transported secondary sulfate mixed with dust. S. Solomos et al. [39] established a time-dependent dust source map for DREAM v1.0 model based on AOD values from MODIS and AERONET. Consequently, the modelled (forecasted) AOD improved.

An important goal at RES is the **development of the measurement technology**. L. Belegante et al. [40] presented experimental techniques for the calibration of lidar depolarization in EARLINET. These techniques are currently implemented in ACTRIS to all lidar stations. RES has also participated in the second inter-comparison for aerosol chemical speciation monitors (ACSM) where 15 instruments participated [41]. The authors state that the work illustrates the benefits of integrating new calibration procedures and artifact corrections and highlights the benefits of these intercomparison exercises to continue to improve our knowledge of how these instruments operate, and assist us in interpreting atmospheric chemistry.

In 2014, European Space Agency granted a vote of confidence to researchers from INOE, together with Max-Planck Institute for Meteorology, National Observatory of Athens, the Netherlands Airspace Agency and the National Institute for Aeronautical Research "Elie Carafoli", for the implementation of MULTIPLY project “Development of an airborne HSRL system". The aim of MULTIPLY project is the development of a novel multi-wavelength HSRL system for airborne operation, capable of retrieving the aerosol extinction, backscatter and depolarization profile distributions. INOE was especially involved in the development of the High-Speed Photon Counting System [42]. This project is still ongoing, currently at the status of the integration of components. The lidar system was designed to be especially compact and robust, both optically and mechanically. Soon it will be shipped to INOE for testing. The next step includes the integration of the HSRL system on board of a EUFAR (EUropean Facility for Airborne Research) research aircraft. The new lidar system operation will then be tested for in flight operation and further validated during a dedicated experimental campaign that will take place over a number of European lidar stations.

5. New directions of research

In addition to the well-known warming effect due to greenhouse gases, aerosols, clouds and trace gases also influence regional and global climate through their interactions with clouds, precipitation, and radiation. Understanding this interaction is of the utmost importance, especially in the context of climate change and its impacts. The data collected by a suite of state-of-the-art remote sensing instruments installed at the Măgurele Center for Atmospheric and Radiation Studies (MARS) allows a step-change in our ability to observe, study and understand the exchanges and interactions between climatically relevant atmospheric variables and climatic components and their interaction. The automatic instruments that are located at MARS operate continuously (24/7), thus ensuring the collection of high-quality datasets that will be used for various studies. MARS can also provide the required infrastructure for the organization of international campaigns, such as those for intercomparison or for calibration/validation.

The new research directions for the **study of clouds and their interactions with aerosols and radiation** were opened with the installation at MARS of two cloud radars. Together with a microwave radiometer and a ceilometer, these represent the nucleus of the Cloud Remote Sensing station from MARS. One of the new directions of research facilitated by these instruments is the study of macrophysical and microphysical characteristics of clouds. This is an important topic given the role played by the cloud in meteorology, climate change from a global perspective and the climate variability at the regional scale.

The **boundary layer processes** exert a great influence on the formation and evolution of clouds. The installation at MARS of wind lidar in 2020 allows the study of clouds in conjunction with boundary layer processes. Other research directions facilitated by the wind lidar are the study of dynamic and turbulent processes and atmospheric dynamics in particular for air quality and greenhouse gas studies.

The radiation station (i.e., a system that monitors solar radiation) installed at MARS is state-of-the-art equipment providing continuous measurements of short-wave and long-wave solar radiation (i.e., direct, total and diffuse), global horizontal solar irradiance (i.e., diffuse horizontal solar irradiance from space and solar irradiance directly from the sun) and diffuse solar radiation. Starting from May 2021, the MARS radiation station is part of the Baseline Surface Radiation Network (BSRN) a project of the Data and Assessments Panel from the Global Energy and Water Cycle Experiment (GEWEX) under the umbrella of the World Climate Research Programme (WCRP). Thus, the MARS radiation station is opening new directions of research such as **detecting changes in the radiation field at the surface** of the Earth which can be related to climate changes (in accordance with the aim of the BSRN), calibration/validation studies of satellite-based estimates of the surface radiative fluxes, comparison to climate models, development of regional radiation climatologies, and study of the cloud–aerosol–radiation interaction and forcing.

Other new research directions based on the data collected at MARS are **calibration/validation activities for satellite-based observations** and the **improvement of numerical weather prediction models** through verification of model outputs and the development of new aerosol-cloud-related parametrizations.

All these are adding-up to the continuous work for ACTRIS-related research directions: **characterization of optical and microphysical properties of aerosol, clouds and trace gases**, at near-surface and on the vertical. It covers not only valuable scientific studies but also horizontal issues such as coordination with the major players in our field (i.e. international organizations and stakeholders, instrument manufacturers), optimization of access to research infrastructures, and transfer of expertise and technology towards the operational services. Our involvement in ACTRIS activities as the leader of the Centre for Aerosol Remote Sensing and also as a 3-component National Facility will enlarge collaborations and will consolidate our position within the international atmospheric science community. Building on previous experience and achievements, RES is currently involved in two major European projects in which 3 European research infrastructures (ACTRIS, ICOS and IAGOS) work together for harmonizing their procedures for atmospheric observations, as well as for pushing further the science and technology in the field of atmospheric composition.

ATMO-ACCESS (H2020-IA, GA no. No 101008004, https://www.atmo-access.eu/) is the organized response of distributed atmospheric research facilities for developing a pilot for a new model of Integrating Activities. The project will deliver a series of recommendations for establishing a comprehensive and sustainable framework for **access to distributed atmospheric Research Infrastructures** (RI), ensuring integrated access to and optimized use of the services they provide. ATMO-ACCESS mobilizes extensive resources in the atmospheric RIs communities to engage into harmonizing access procedures in relation to policies, financial regulations and conditions for access. ATMO-ACCESS will open physical and remote access to 43 operational European atmospheric research facilities, including ground-based observation stations, simulation chambers, but also mobile facilities and central laboratories that are fundamental elements in distributed RIs. In ATMO-ACCESS, INOE is responsible to develop and implement the pilot TNA (trans-national access) for international stakeholders, more specifically to setup a framework for long-term collaboration between ESA, EUMETSAT, Copernicus and others alike (on one side) and the research infrastructures (on the other side). Enabling TNA to the research infrastructures for the space agencies, in a coordinating manner, will optimize the Cal/Val of satellite atmospheric missions but will also make the use of the European facilities more efficient.

RI-URBANS (H2020-LC-GD-2020, GA no. 101036245, https://riurbans.eu/) focus on demonstrating how **service tools from atmospheric research infrastructures** can be adapted and enhanced in air quality monitoring networks in an interoperable and sustainable way. The project intends to better address the challenges and societal needs related to air quality in European cities (and industrial, harbour, airport, and traffic hotspots). It responds to the urgent need to substantially reduce air pollution across the EU and to engage in a strategy to evaluate the health impacts of air pollution on citizens. RI-URBANS is based on the premise that advanced monitoring and modelling tools developed in research infrastructures, by air quality experts and advanced monitoring networks can be used to supplement current networks of regulated pollutants. In RI-URBANS, INOE is responsible to organize pilot studies in Bucharest, in order to demonstrate how modern techniques are able to measure and model ultra-fine particles at street level, and to estimate the contribution of medium and long-range transported pollutants to the measured near-surface concentrations.

In the field of **technology development**, it is worth highlighting the recently finalized HELENA project, and its continuation PALT project, both financed by ESA. *HERA lidar engineering model altimeter* was focused on the development of an altimeter for the HERA mission, based on a Laser Landing Altimeter Engineering Model previously developed by EFACEC, Portugal. The laser source of this altimeter is a compact low power consumption microchip laser that emits 1.5μm light pulses. This laser technology enables rangefinder compact designs, but the prototype was not able to meet the more demanding requirements for a measurement range of 0.5 - 14 km range, an accuracy of 0.5m and mass below 1.5kg. This design was optimized by INOE and the HELENA consortium (http://environment.inoe.ro/article/243/about-helena), and is now under implementation in the PALT prototype.

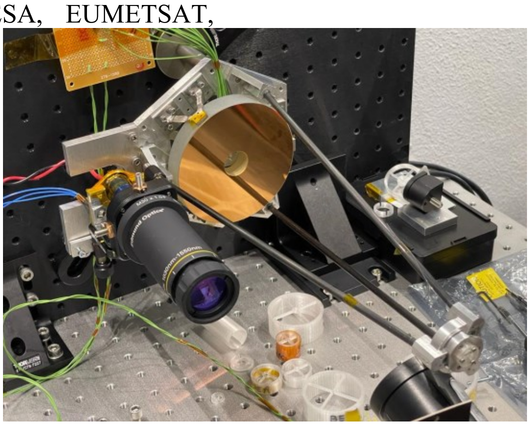

Fig. 5 The Helena altimeter aligned by INOE and Synopsis Planet, October 2022

Summing up, RES has almost two decades of history and expertise in using and developing optoelectronic techniques for observing the composition and the properties of the atmosphere. Our work is strongly linked with the European and global research in the field, as many joint publications demonstrate it. With a journey starting in 2004 when the first lidar was installed in Romania, we are now a well-recognized team, operating a state-of-the-art infrastructure, providing data to open databases, and contributing to the advancement of the measurement technology and retrieval algorithms. Our future is with ACTRIS, through which we contribute to air quality and climate change research.

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