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LAB TECHNICIANS

DARIA BARTLOVÁ

Fields of research

- Atmospheric aerosols
- Indoor/outdoor aerosols
- Nucleation phenomena
- Synthesis of nanoparticles *via* aerosol processes
- Heat and mass transfer in aerosol systems
- Interaction of aerosols with electromagnetic radiation
- Emissions sampling
- Nanoparticles and health
- Aerosol technology
- IR and UV laser induced chemistry
- Chemical vapor deposition of novel C-, Si- and Ge-based nanostructured materials
- IR laser-induced carbothermal reduction of oxides
- IR and UV laser photopolymerization in the gas phase
- UV laser chemical liquid deposition of metal nanosols and nanocomposites
- CVD of nanostructured objects (nanowires, nanoplatelets)
- IR and UV laser deposition of TiO₂-based materials
- IR and UV laser ablation for deposition of thin films

Research projects

Aerosols, Clouds, and Trace gases Research InfraStructure Network

(V. Ždímal, zdimal@icpf.cas.cz; supported by EC, project No. INFRA-2010-1.1.16 ACTRIS, as “initial associated partner”)

ACTRIS (Aerosols, Clouds, and Trace gases Research InfraStructure Network) is an European Project aiming at integrating European ground-based stations equipped with advanced atmospheric probing instrumentation for aerosols, clouds, and short-lived gas-phase species. ACTRIS will have the essential role to support 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. ACTRIS is funded within the EC FP7 under "Research Infrastructures for Atmospheric Research".



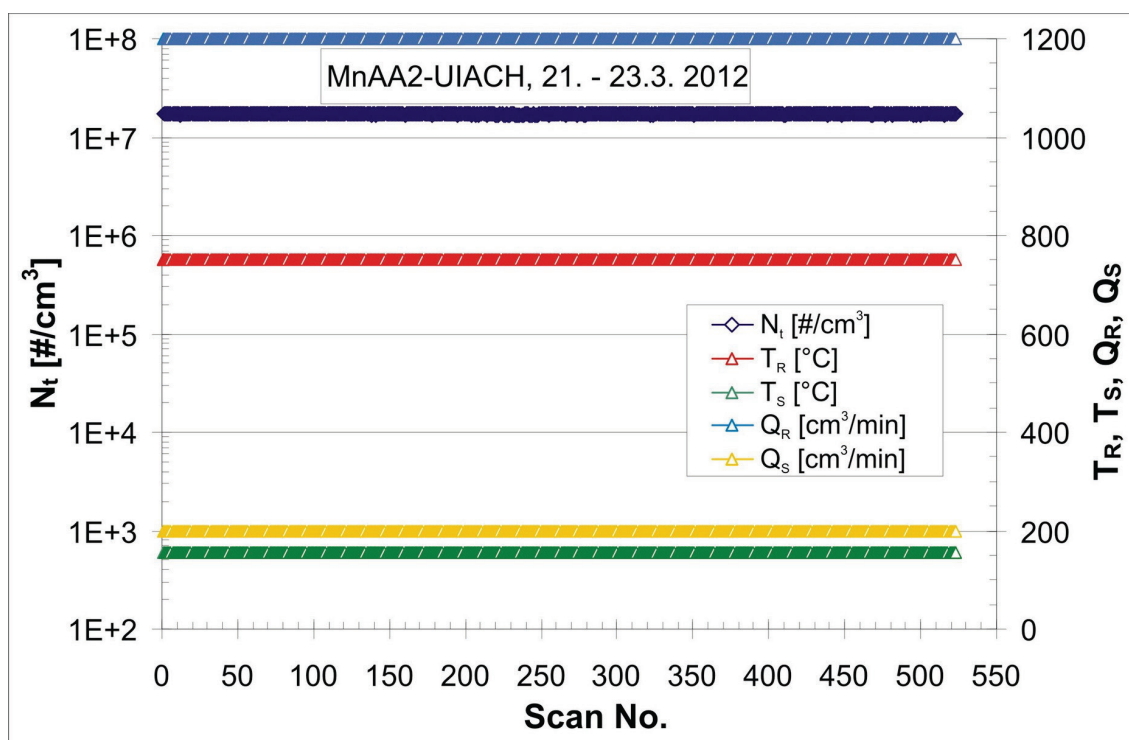
Photo of the scanning mobility particle sizer measuring size distribution of particles at background site Košetice

Centre for studies on toxicity of nanoparticles

(P. Moravec, moravec@icpf.cas.cz; supported by GACR, project No. P503/12/G147)

The rapid expansion of nanomaterials production and their use in many products create a need for understanding the mechanisms of nanomaterial interactions with living systems. This need is above all given by unique properties of nanoparticles related to their dimensions and

by their ability to penetrate into various tissues and cells in organism. Nanoparticles are also formed unintentionally as a result of the anthropogenic activities (industry, local heating). The proposed interdisciplinary centre of basic research will integrate laboratories capable to perform complex studies on mechanism of the toxicity of important and widely used engineered nanoparticles, as well as anthropogenic nanoparticles in the environment with a special attention paid to heavily polluted areas of the Czech Republic. The studies will be performed on thoroughly characterized nanoparticles to obtain valid and comparable results on biological action and toxicity of nanoparticles.



Time dependence of number concentration N_t of MnO_x nanoparticles generated in purified nitrogen at given T_R , T_S , Q_R , Q_S . 1 scan = 5 minutes. Notice a stable output concentration during 45 hours of the experiment

Thermophysical properties of water in unexplored, technologically significant regions

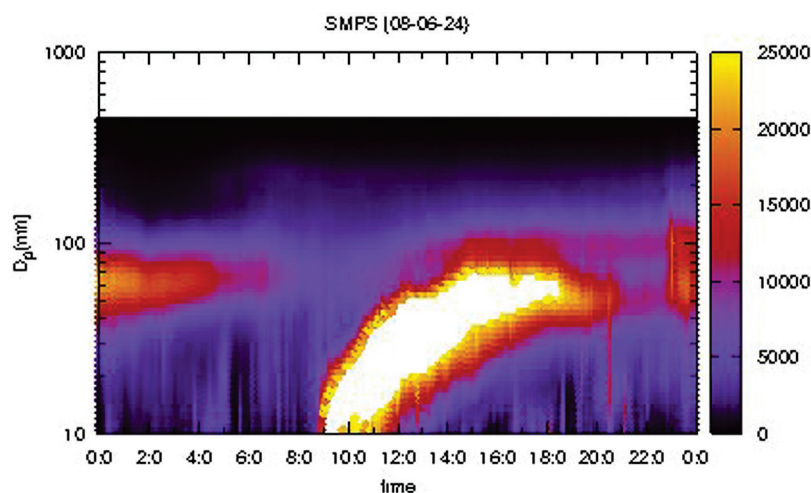
(V. Ždímal, zdimal@icpf.cas.cz; joint project with Institute of Thermomechanics of the ASCR, v. v. i., CTU, and University of West Bohemia, Plzeň, supported by GA ASCR, project No. IAA4200760905)

This project focuses primarily on liquid water and solutions of selected salts below the freezing point (supercooled water), and water in nano-droplets. Existing hypotheses include the possibility of phase separation of supercooled water into two liquid phases below the second critical point. Density of supercooled water is only known at 0.1 MPa. Suggested measurements up to 100 MPa will provide first data. A new method and apparatus will be developed. The surface tension of supercooled water and a salt solution will be measured. The surface tension of nano-droplets will be estimated from nucleation experiments. A range of theoretical approaches including phenomenological methods, simplified microscopic models, and molecular simulations, will be used with experimental data to obtain fundamental findings and engineering models. [Refs. 7, 8]

Advanced study of physical and chemical properties of atmospheric aerosols in high time resolution

(V. Ždímal, zdimal@icpf.cas.cz; supported by GACR, project No. 209/11/1342)

Advanced physical and chemical properties of Central European atmospheric aerosol at rural background and urban background sites will be studied in high time and size resolution. Parallel measurement of aerosol volatility will be carried out using a C-ToF-AMS equipped with a thermodenuder inlet, aerosol hygroscopicity using an Hygroscopic Tandem Differential Mobility Analyser (HTDMA), and particle number size distribution using an Scanning Mobility Particle Sizer (SMPS). The information about aerosol particle density will be extracted from the SMPS and AMS. Hygroscopicity closure will be obtained from the combined HTDMA and AMS chemical composition data allowing to study the influence of organic aerosol on particles' hygroscopicity. The content of primary and secondary organic aerosol and the extent of aerosol ageing will be determined using AMS data at each site. In addition, at least a year-long time evolution of number size distributions obtained using the SMPS and OC/EC concentrations from the OC/EC analyzer will be delivered to the EBAS database, to be available for global atmospheric modeling groups. [Refs. 2, 10, 13]

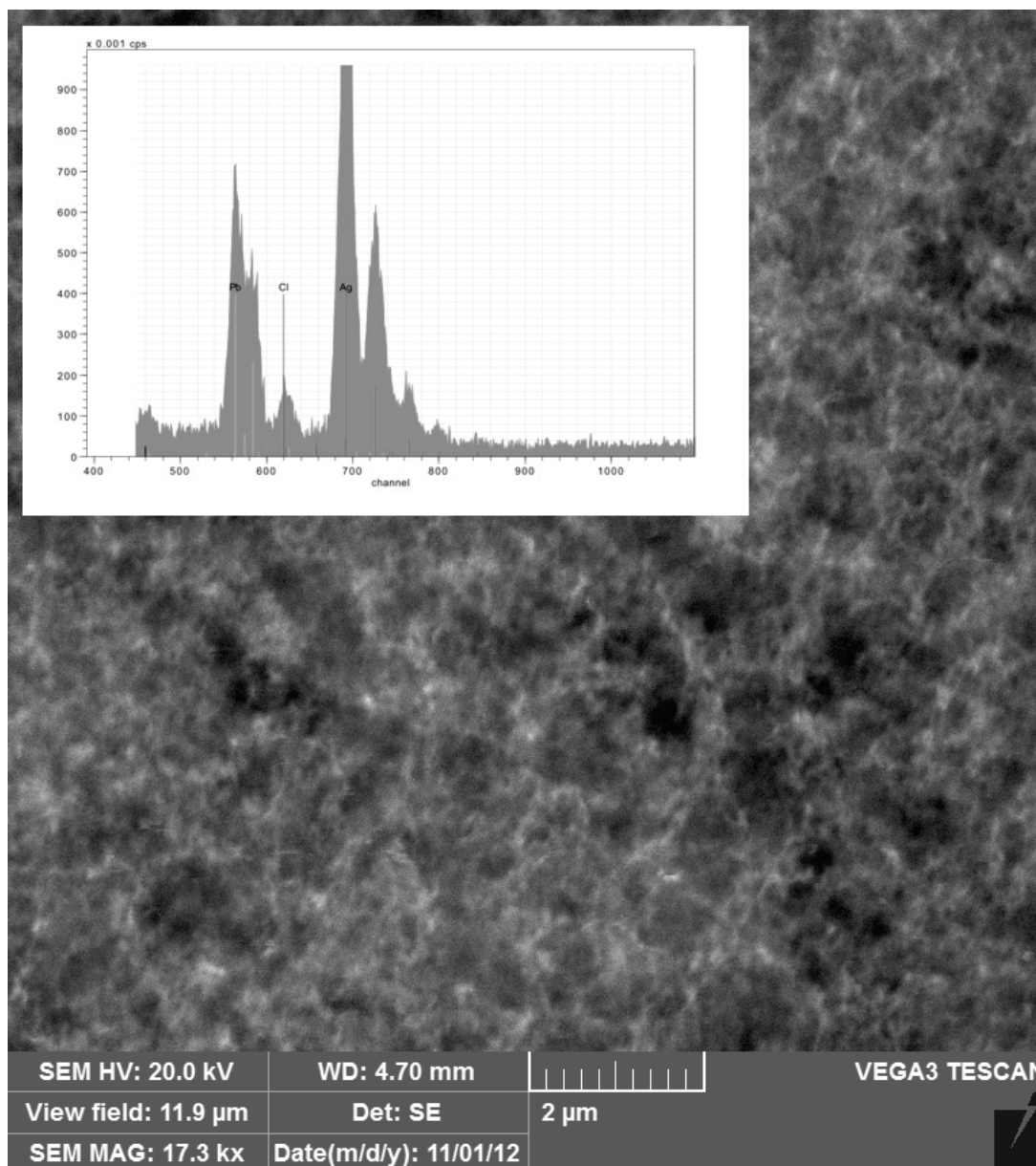


New particle formation event “banana type” recorded by aerosol spectrometer SMPS at rural background station Košetice

Study of transport of inhaled nano-sized particles (Pb, Cd) and their allocation in organs

(J. Smolík, smolik@icpf.cas.cz; supported by GACR, project No. 503/11/2315)

All of the evidence from animal and human studies showed that there are risks associated with inhalation of nano-sized particles (NSP). The alveolar translocation of NSP is likely the pathway how NSP can be transposed from air to the blood vessels, and distributed throughout the body to organs. In spite of the fact that an extrapulmonary translocation is highly dependent on particle surface characteristics/chemistry, in addition to particle size, the study of transport of inhaled nano-particles Pb, Cd (elements, oxides), their allocations in organs, as well as study of toxicity these nanoparticles will be carry out with nanoparticles (10, 20 and 60 nm). The nonbiogenous elements (Cd, Pb) have been selected as products of technological processes and due to their presence in ambient aerosol. The research will give us more information for a proper understanding of risks of technologies producing Cd and Pb nano-sized particles and ambient aerosol risk.



Pb nanoparticles and their EDS spectrum (inset) generated by PVD method for inhalation experiments

Development and application of new experimental methods to measure heterogeneous particles in superheated steam

(V. Ždímal, zdimal@icpf.cas.cz; joint project with CTU and Institute of Thermomechanics of the ASCR, v.v.i.; supported by GACR, project No. 101/09/1633)

The aim of the project is to determine some properties of heterogeneous nuclei present in the superheated steam of steam turbines. In this project, the sampling device, coupled to advanced aerosol instrumentation (condensation particle counter, scanning mobility particle sizer), will be used to measure heterogeneous particles at selected power stations. To enable measurements of particles down to about 1 nm, a fast expansion chamber will be developed, enabling resolution of particle size by variable supersaturation. Collected data will serve as a basis for understanding the transport and the state of agglomeration of chemicals present in the steam circuit, for quantifying their effect on condensation, and, consequently, on the efficiency and reliability of steam turbines. [Refs. 7, 8]

Methodology of evaluation of air quality effect on library and archival collections

(J. Smolík, smolik@icpf.cas.cz; supported by the Ministry of Culture of the CR, project No. DF11P01OVV020)

The aims of the project are: a) development of evaluation methods for indoor air quality in libraries and archives, targeted at reduction of damages on library and archival collections caused by adverse effects of environment and b) gaining detailed knowledge of direct dependences between damage of library and archival collections and surrounding environment, leading to precautions reducing the adverse effects of deteriorated environment.

Black and elemental carbon at two European urban sites – site specific similarities and differences in method intercomparability

(J. Schwarz, schwarz@icpf.cas.cz; supported by MEYS, program MOBILITY, project No. 7AMB12AT021)

The method intercomparison studies will be conducted both under summer and winter conditions at both sites lasting 2 weeks each. By pooling the instruments and expertise of the two partners, BC will be measured on-line with the MAAP and the aethalometer techniques and from filter samples with the integrating sphere technique; EC will be investigated both from bulk samples with a Sunset Analyzer set both in reflection and transmission modes with three thermal protocols (NIOSH, DRI, EUSAAR2) and quasi on-line with two Sunset Field Analyzers set to two different temperature protocols. BrC will be analyzed with the modified integrating sphere technique. Background information on the aerosol will be obtained in parallel.

Preparation of thin layers of ferromagnetic semiconductors

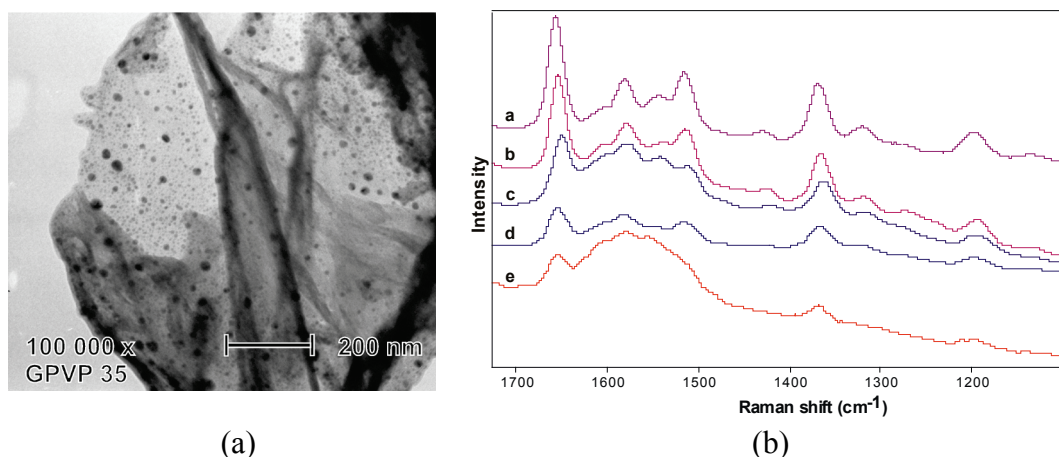
(R. Fajgar, fajgar@icpf.cas.cz; supported by ICPF)

Manganese atoms diluted in silicon or germanium matrix are potential ferromagnetic semiconductors. Thin layers have been prepared by reactive excimer laser ablation of elemental manganese target under low pressure of volatile precursors (silane or germane). Ablated atoms with high energy (estimated initial temperature 1 mm above the Mn target surface is 1.9 eV) interact with gas and amorphous thin layers of Mn/Si or Mn/Ge are deposited. The prepared layers contain up to 40 % of Mn atoms. Successful crystallization was achieved by annealing of Mn/Si at as high temperatures as 1100°C or rapid laser annealing using TEA CO₂ laser. Magnetic properties were studied by SQUID technique, and weak ferromagnetic properties have been revealed so far.

Novel sensors based on laser ablated graphene

(R. Fajgar, fajgar@icpf.cas.cz; supported by NATO, project No. 984399)

Nanocomposites of poly(BA/MMA) reinforced with up to 3 wt. % graphene sheets were used as targets for laser ablation. The target was ablated using TEA CO₂ laser with fluence of 1.00 J/cm² and thin films of crosslinked polymer with embedded graphene sheets with large specific surface area were obtained. The polymer-graphene deposit was covered with silver nanoparticles by excimer laser ablation in order to prepare active substrates for Surface-Enhanced Raman Scattering (SERS). In vacuum, Ag nanoparticles reaching the polymer/graphene substrate graphitized the graphene as revealed by Raman spectroscopy. Optimized ablation in helium atmosphere was used to preserve graphene covered with silver nanoparticles. The nanocomposites were characterized by means of spectroscopies, microscopies and diffraction technique. The SERS substrate performance was tested using Rhodamine 6G as a probe compound. Highly enhanced signal was observed and sensoric properties of the novel substrates were demonstrated.

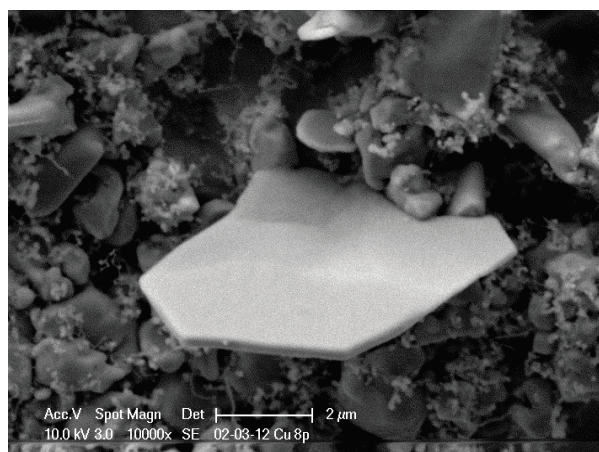


(a) SEM image of the SERS active substrate (Ag nanoparticles on the graphene surface)
 (b) Raman spectra of Rhodamine 6G on Ag/graphene support (lines a- 10^{-4} , b- 10^{-5} , c- 10^{-6} , d- 10^{-7} mol/l) and Ag alone (line e- 10^{-5} mol/l)

Formation of Cu_xGe_y nanoplatelets using LPCVD of hexamethyldigermane (Ge_2Me_6) and tetraethyllead (PbEt_4)

(V. Dřínek, drinek@icpf.cas.cz; supported by ICPF)

Low Pressure Chemical Vapor Deposition (LPCVD) of Ge_2Me_6 and PbEt_4 allows decomposition of both gaseous compounds and leads to deposition of nanoplatelets along with Ge nanowires, and nanoparticles. In agreement with analytical techniques (Raman spectroscopy, ED, EDX, SEM and HRTEM) the nanoplatelets up to several tens of mm in length have been prepared in solid solution of Ge in Cu cubic lattice. Thickness of the nanoplatelets ranges from 100-400 nm. Nanowires which are composed of cubic Ge have a diameter of about 30 nm and length of several tens of micrometers. Lead was detected in amorphous phase of around dispersed nanoparticles. [Ref. 5]



Ge/Cu platelet prepared by CVD process

IR laser photochemical deposition of amorphous Fe/Si nanocomposite films and thermal evolution of nanocrystalline grains of ferrisilicate, carbon-encapsulated iron disilicide and rare high-pressure ambient conditions-surviving hexagonal iron

(J. Pola, pola@icpf.cas.cz; no support)

IR laser-induced gas-phase co-photolysis of $\text{Fe}(\text{CO})_5$ - SiH_4 mixtures occurs as SiH_4 -photosensitized $\text{Fe}(\text{CO})_5$ decomposition enhanced by products of $\text{Fe}(\text{CO})_5$ decomposition and

it results in deposition of amorphous Si/Fe nanocomposite films. The analyses of the deposited and subsequently annealed solid films were made by FTIR, Raman and X-ray photoelectron spectroscopy, X-ray diffraction and electron microscopy. The deposited films are amorphous, undergo atmospheric oxidation in topmost layers to iron oxide and hydrogenated silicon oxide and contain crystalline nanostructures of iron silicide FeSi_2 . Upon annealing they develop nanocrystalline structures of ferrisilicate $\text{Fe}_{1.6}\text{SiO}_4$, carbon-encaged iron disilicide FeSi_2 and very rare hexagonal (high-pressure) Fe surviving ambient conditions. Mechanism of formation of these nanostructures is discussed in terms of gas-phase and solid-phase reactions. [Refs. 11, 12, 14]

Quantum size effect in semiconductor nanostructures for optoelectronics

(R. Fajgar, V. Dřínek fajgar@icpf.cas.cz; drinek@icpf.cas.cz cooperation with Institute of Physics of the ASCR, supported by MEYS, project No. LH12236)

Thin layers of non-hydrogenated and hydrogenated silicon were prepared by excimer laser ablation of silicon target in vacuum and silane (SiH_4) atmosphere. Optical and electrical properties were studied for potential applications in light emitting devices and photovoltaic cells. Introducing of inorganic nanoparticles (PbS , Mg_2Si) into silicon layers was studied with aim to increase light scattering and absorption in solar cells. Reflection and fluorescence spectra confirm the improved light scattering of layers with embedded nanoparticles. Enhancement of optical absorption, especially at lower wavelengths was demonstrated.

International co-operations

Division of Nuclear Physics, Department of Physics, Lund University, Lund, Sweden

Finnish Meteorological Institute, Helsinki, Finland: Studies on homogeneous nucleation using diffusion chambers

Ghent University, Institute for Nuclear Sciences, Ghent, Belgium: OC/EC in urban and suburban PM10 aerosol in Prague, Hygroscopic properties of urban and suburban carbonaceous aerosols

Institute of Environmental Engineering, National Chiao Tung University, Hsinchu, Taiwan
Laboratory of Atmospheric Chemistry, Paul Scherrer Institut, Switzerland

Norwegian Institute for Air Research, Kjeller, Norway: Indoor aerosol behavior

Southern Illinois University Carbondale, Carbondale, IL, USA: Friction materials based on polymer matrix containing metals and their impact on environment

Technical University of Crete, Chania, Greece: Aerosols in the environment

University of Helsinki, Division of Atmospheric Sciences, Helsinki, Finland

Tampere University of Technology, Tampere, Finland: Synthesis and characterization of nanosized metal/ceramic particles

University of Eastern Finland, Kuopio, Finland: Novel aerosol generation processes focused on medical treatment and nanotechnology

University of Vienna, Faculty of Physics, Dept. of Aerosol physics and Environmental Physics, Vienna, Austria: Black and elemental carbon analysis, aerosol optical properties

Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Lodź, Poland: UV laser-induced cross-linking of polysiloxanes

Faculty of Technology and Metallurgy, University of St. Cyril & Methodius, Skopje, Republic of Macedonia: Novel preparation and photocatalytic study of titania-based catalysts

Instituto de Estructura de la Materia, CSIC, Madrid, Spain: Studies on IR laser deposition of nanosized metal chalcogenides and polycarbosilathianes

King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia: Laser degradation of contaminants in fuel oils

National Institute for Lasers, Plasma and Radiation Physics, Bucharest, Romania: Laser-induced CVD of Fe/polymer nanocomposites

National Institute of Advanced Industrial Research and Technology, Tsukuba, Japan: Laser control of organic reactions

POLYMAT, Institute for Polymer Materials, San Sebastian, Spain: Laser ablation of graphene-based composites

University of Crete, Heraklion, Greece: Laser induced chemical vapor deposition of polycarbosilathianes

AC2T, Wiener Neustadt, Austria: Tribological study of nanostructured materials (nanowires, nanoplatelets)

Visits abroad

D. Brus: Finnish Meteorological Institute, Helsinki, Finland (12 months)

L. Krabáč: AC2T, Austria (4 months)

Visitors

T. Hussein, University of Helsinki, Helsinki, Finland

V. Nororos, University of Helsinki, Helsinki, Finland

J. Blazevska-Gilev, University of St. Cyril & Methodius, Skopje, R. Macedonia

Radmila Tomovska, POLYMAT, Institute for Polymer Materials, San Sebastian, Spain

Nicole Doerr, AC2T, Wiener Neustadt, Austria

Josef Brenner, AC2T, Wiener Neustadt, Austria

Ulrike Cihak – Bayr, AC2T, Wiener Neustadt, Austria

Teaching

V. Ždímal: Faculty of Mathematics and Physics, Charles University in Prague, undergraduate course: “Aerosol Engineering”

V. Ždímal: ICT, Faculty of Chemical Engineering, graduate course “Aerosol Engineering”

Publications

Original papers

- [1] Blazevska-Gilev J., Urbanová M., Pokorná D., Šubrt J., Pola J.: IR Laser-Induced Breakdown in Thiirane for Gas-Phase Deposition of Conjugated Organosulfur Polymer Incorporating Cycloheptasulfur. *J. Anal. Appl. Pyrol.* 93, 165-169 (2012).
- [2] Borsós T., Řimnáčová D., Ždímal V., Smolík J., Wagner Z., Weidinger T., Burkart J., Steiner G., Reischl G., Hitzemberger R., Schwarz J., Salma I.: Comparison of Particulate Number Concentrations in Three Central European Capital Cities. *Sci. Total Environ.* 433, 418-426 (2012).
- [3] Duchek P., Urbanová M., Pokorná D., Kupčík J., Šubrt J., Pola J.: Laser-Induced Ablative Amorphisation of Montmorillonite. *J. Non-Cryst. Solids* 358(23), 3382–3387 (2012).

- [4] Hussein T., Smolík J., Kerminen V.-M., Kulmala M.: Modeling Dry Deposition of Aerosol Particles on Rough Surfaces. *Aerosol Sci. Technol.* 46(1), 44-59 (2012).
- [5] Krabáč L., Klementová M., Šubrt J., Fajgar R., Kupčík J., Bastl Z., Stuchlíková The Ha, Dřínek V.: Preparation of Si/O/C Nanotubes Using Ge Nanowires as Template. *J. Anal. Appl. Pyrolysis* 97, 94-98 (2012).
- [6] Křenek T., Murafa N., Bezdička P., Šubrt J., Masoudi H.M., Pola J.: IR Laser-Induced Breakdown in Tetramethyltin Adjacent to Ag or Au: Deposition of beta-Sn Nanograins-Containing Amorphous Au-Sn/C and Ag-Sn/C Films. *Appl. Organometal. Chem.* 26(3), 135-139 (2012).
- [7] Levdansky V.V., Dragun V.L., Ždímal V.: Vliyanie elektromagnitno izlucheniya na fiziko-khimicheskie protsessy v geterogennykh sistemakh. (Russ) *Vestci Nat. Ak. Nauk Belarusi, Ser. Fyz.-Tekh. Navuk* 1, 70-74 (2012).
- [8] Levdansky V.V., Smolík J., Ždímal V.: Razmernye efekty pri fazovykh prevrascheniyakh v nanoobjektakh. (Russ) *Inzh.-Fyz. Zh. [J. Eng. Phys. Thermophys.* 85(5), 1092-1096 (2012)] 85(5), 1006-1010 (2012).
- [9] Matějová L., Matěj Z., Fajgar R., Cajthaml T., Šolcová O.: TiO₂ Powders Synthesized by Pressurized Fluid Extraction and Supercritical Drying: Effect of Water and Methanol on Structural Properties and Purity. *Mater. Res. Bull.* 47(11), 3573-3579 (2012).
- [10] Novák J., Šilhavý J., Ždímal V., Ondráček J., Ziková N., Dostál M., Pastorková A.: Projekt UFIREG - Central Europe. Měření ultrajemných částic a analýza dopadu expozice na lidské zdraví. (Czech) Project UFIREG - Central Europe. Monitoring of Ultrafine Particles and Analysis of Health Effects of Exposure to UFP. *Ochrana ovzduší* 24(6), 31-34 (2012).
- [11] Pola J., Gondal M.A., Urbanová M., Pokorná D., Masoudi H.M., Bakardjieva S., Bastl Z., Šubrt J., Siddiqui M.N.: Laser Photochemical Deposition of Magnetite Nanograins in a-Fe/C/O Composite: High-Pressure Metal Oxide Polymorph Surviving Ambient Conditions. *J. Photochem. Photobiol., A* 243, 33-40 (2012).
- [12] Pola J., Urbanová M., Pokorná D., Bakardjieva S., Šubrt J., Bastl Z., Gondal M.A., Masoudi H.M.: IR Laser Photodeposition of a-Fe/Si Films Developing Nanograins of Ferrisilicate, Iron Disilicide and Rare Hexagonal Iron upon Annealing. *Dalton Trans.* 41(6), 1727-1733 (2012).
- [13] Schwarz J., Štefancová L., Maenhaut W., Smolík J., Ždímal V.: Mass and Chemically Speciated Size Distribution of Prague Aerosol Using an Aerosol Dryer - The influence of Air Mass Origin. *Sci. Total Environ.* 437, 348-362 (2012).
- [14] Urbanová M., Kupčík J., Bezdička P., Šubrt J., Pola J.: Room-Temperature Sulfidation of Copper Nanoparticles with Sulfur Yielding Covellite Nanoparticles. *C. R. Chim.* 15(6), 511-516 (2012).
- [15] Urbanová M., Pokorná D., Šubrt J., Kupčík J., Bastl Z., Pola J.: IR Laser-Irradiation of Metals in Vacuum and Hydrocarbons: Gas Phase Deposition of Metal-Carbon Nanocomposites. *J. Adv. Microsc. Res.* 7(1), 14-20 (2012).
- [16] Vacík J., Lavrentěv V., Horák P., Fajgar R.: Structural Variation of Transition Metal - Fullerene Thin Films Modified by Ion Beam Bombardment and/or Thermal Annealing. *Adv. Mater. Res. J.* 463-464, 1387-1391 (2012).

Patents

- [17] Ždímal V., Slezák J., Goliáš J., Pušman J.: Zařízení k ředění aerosolů. (Czech) Aerosol Diluter. Pat. No. CZ24340 / PUV 2012-26049. Applied: 12.05.15, patented: 12.09.24.