

Characteristics of main research directions investigated at the institute and the achievements 2010–2014

Institute	Institute of Inorganic Chemistry of the CAS, v. v. i.
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The main research directions investigated have been:

New materials and their applications
New compounds and their properties
Methods and special techniques

1.1. New materials and their applications

- nanostructured and nanocomposite materials based on graphene, metal oxides, and chalcogenides; applications in environmental photocatalysis and degradation of warfare chemical agents and pesticides.
- nanoporous, layered, and polymer materials with bactericidal, luminescent, and photocatalytic properties.
- nanocomposites with ferromagnetic and thermoelectric properties and multifunctional magnetic nanocomposites with catalytic properties.
- materials based on aluminosilicate matrices for intelligent applications.

In the field of **materials chemistry** a number of synthetic routes leading to nanomaterials and composites bearing specific functions have been developed. At the forefront of our interests have been (and continue to be) photocatalytic materials, reactive sorbents, graphene and graphene-like materials. Considerable attention has been paid to the developing area of hybrid materials, polymer nanofibers, and nanocomposite films with an emphasis on their photophysical properties and potential use in constructing multifunctional platforms with photobactericidal, photovirucidal, and photooxidative properties. Other achievements have been registered in the area of magnetic and thermoelectric materials. The in-house availability of contemporary scientific equipment and instrumentation, accompanied by skilled operating personnel, has enabled the majority of characterization procedures to be carried out locally, however, some specialist methods were conducted in cooperation with other research institutes and universities.

1.1.1. Photocatalytic materials

In the period here evaluated, the research performed on photocatalytic materials has primarily been focused on the study of doped titania, and of nanocomposites based on graphene oxide. The method of homogeneous hydrolysis has been successfully applied to the production of titania doped with boron, tungsten, indium, selenium, tellurium, germanium, or gallium. These new materials show good photocatalytic performance, with operating activities achievable under visible-light irradiation. Photocatalysts doped with molybdenum, niobium, tantalum, iodine, tin, and bismuth were prepared using the method of thermal hydrolysis of peroxo-complexes. The doping affected the absorption spectra of the resultant photocatalysts, as well as their particle sizes, morphology, surface area, and porosity, leading to an increase in the degradation rates of azo dyes in aqueous solutions. The optimal concentrations of individual dopants were determined, and the effects of high or insufficient doping levels were evaluated.

Selected papers:

V. Štengl, S. Bakardjieva, *J. Phys. Chem. C* 114 (2010), 19308-19317.

V. Štengl, D. Popelková, P. Vlášil, *J. Phys. Chem. C* 111 (2011), 25209-25218.

V. Štengl, J. Henych, P. Vomáčka, M. Slušná, *Photochem. Photobiol.* 89 (2013), 1038-1046.

1.1.2. Photofunctional materials

Here efforts have been concentrated on delineating the photophysical parameters of certain photosensitizers (PS) in complex environments, and correlating these parameters to their photosensitizing efficacy. Understanding these relationships and, in particular, the interactions between PS and their chemical environments, has enabled us to explain the differences in the photophysical and photochemical properties of free PS molecules and corresponding complex materials. This effort has led to the synthesis of new intercalated materials composed of PS (mostly of the porphyrinic type), and a host (layered simple or double hydroxides, clay materials or polymer nanofibres). PS were studied in solutions, dispersions, and embedded in photofunctional materials. Some of the studied PS have excellent brightness, high yields of singlet oxygen ($^1\text{O}_2$) production, and emission in the red region. The structural aspects, absorption spectra, luminescence, and sensitizing properties of the materials were determined and evaluated. It was found that in these materials the hosts play an active role in controlling the photophysical and photochemical properties of the introduced PS. Some of the investigated materials act as solid-state sensitizers that produce $^1\text{O}_2$, and, as a result, they have bactericidal, virucidal, and photooxidation properties with the potential of applications as photoactive surfaces, catalysts, and oxygen sensors.

Selected papers:

K. Kirakci, K. Fejfarová, M. Kučeráková, K. Lang, *Eur. J. Inorg. Chem.* (2014), 2331-2336.

K. Kirakci, V. Šícha, J. Holub, P. Kubát, K. Lang, *Inorg. Chem.* 53 (2014), 13012–13018.

J. Demel, K. Lang, *Eur. J. Inorg. Chem.* (2012), 5154-5164.

E. Káfuňková, K. Lang, P. Kubát, M. Klementová, J. Mosinger, M. Šlouf, A.-L. Troutier-Thuilliez, F. Leroux, V. Verney, C. Taviot-Guého, *J. Mater. Chem.* 20 (2010), 9423-9432.

P. Henke, K. Lang, P. Kubát, J. Sýkora, M. Šlouf, J. Mosinger, *ACS Appl. Mater. Interfaces* 5 (2013), 3776-3783.

J. Demel, P. Kubát, F. Millange, J. Marrot, I. Císařová, K. Lang, *Inorg. Chem.* 52 (2013), 2779-2786.

1.1.3. Reactive sorbents for chemical warfare agents (CWAs) and environmental pollutant degradations

In recent years, suitable methods have been developed for the preparation of metal oxide powders with tuneable control of their primary particle size as well as the size of their crystallite agglomerates. Many synthesized sorbents - pure single component oxides (e.g., MnO_2 , TiO_2) or mixed oxides (e.g., Ti-Fe, Fe-Mn) or oxides doped with indium, germanium and/or zirconium - were used for the degradation of sulphur mustard, soman and agent VX and/or volatile organic compounds (VOC) pollutants. Similarly to the photocatalytic materials, doped systems proved to have better degradation abilities. Detailed studies of these materials showed that the introduction of other elements into the crystal structure of the parent oxide not only affects the particle size and morphology, but it also produces nonstoichiometric defects, and initiates the formation of new highly reactive sites, which results in the acceleration of the heterogeneous reactions on the surface. These efforts have recently extended to the use of sorbents in the civil sector. Aspects of this research have been carried out in long-term cooperation with Uppsala University, Sweden and the Czech Military Technical Institute.

Selected papers:

V. Štengl, T. M. Grygar, F. Opluštil, T. Němec, *J. Hazardous Mater.* 192 (2011), 1491-1504.

V. Štengl, D. Králová, F. Opluštil, T. Němec, *Micropor. Mesopor. Mater.* 156 (2012), 224-232.

V. Štengl, T. M. Grygar, F. Opluštil, T. Němec, *J. Hazardous Mater.* 227-228 (2012), 62-67.

1.1.4. Low-dimensional materials

Low-dimensional materials have become a hot topic since the discovery of **graphene**. Our team has developed an original, relatively easy and low-cost synthesis to this material using a high-intensity ultrasonic reactor. Using this method, graphene flakes can be produced from natural or synthetic graphite by exfoliation. We also demonstrated an easy conversion of thus prepared graphene to **graphene oxide**. Additionally, we found that by refluxing sonicated graphene in ethylene glycol or other solvents **graphene quantum dots** (GQDs) could be prepared. Contrary to other inorganic materials (e.g., CdSe QDs), GODs are non-toxic and relatively easy to prepare. The same method as for graphite exfoliation was used for the preparation of inorganic analogues of graphene (MoS₂, WS₂, BN, and BCN nanosheets). Similarly to graphene, these materials were fragmented to produce quantum dots. Recently, the attention was also focused on graphene-ionic liquid interactions for the preparation of polymer composites.

Another significant family of low-dimensional materials studied during the evaluated period is that of the **layered metal hydroxides**. These materials compose of positively charged metal hydroxide layers separated by a wide variety of intercalated anions. The controlled packing of inorganic and organic entities in the same material allow for the tuning of the material's final properties. Our team reported the preparations and spontaneous delaminations in water of layered **cobalt hydroxide**, **nickel hydroxide**, and nickel-cobalt hydroxide intercalated with lactate anions. The assembled nanosheets form layers with an adjustable thickness and flexibility. These hydroxide nanosheets can be restacked to form transparent self-standing films with the original layered structure. These electrochemically active ultrathin films with reproducible and stable charge-discharge properties show promise for use in nanocomposite materials for energy storage applications. **ZnO nanosheets** flattened along the [001] direction were prepared via delamination of layered zinc hydroxide intercalated with dodecyl sulphate and subsequent solvothermal transformation. The procedure is a scalable one-pot reaction and produces stable ZnO nanosheet dispersions with the thicknesses of 0.6–0.7 nm, which corresponds to 2 or 3 stacked ZnO tetrahedral layers. Printing ZnO nanosheet dispersions ("ZnO ink") on suitable supports can provide a facile means for fabricating large area transparent films. The high photocatalytic activity of the ZnO nanosheets compared to common morphologies was found in coordinated cooperation with external groups.

Selected papers:

V. Štengl, *Chem. Eur. J.* 18 (2012), 14047-14054.

V. Štengl, J. Henych, *Nanoscale* 5 (2013), 3387-3394.

A. C. Kleinschmidt, R. K. Donato, M. Perchacz, H. Beneš, V. Štengl, S. C. Amico, H. S. Schrekker, *RSC Advances* 4 (2014), 43436-43443.

B. Schneiderová, J. Demel, J. Pleštil, P. Janda, J. Bohuslav, D. Ihiawakrim, O. Ersen, G. Rogez, K. Lang, *J. Mater. Chem. A* 1 (2013), 11429-11437.

B. Schneiderová, J. Demel, J. Pleštil, H. Tarábková, J. Bohuslav, K. Lang, *Dalton Trans.* 43 (2014), 10484-10491.

J. Hynek, V. Kalousek, R. Žouželka, P. Bezdička, P. Dzik, J. Rathouský, J. Demel, K. Lang, *Langmuir* 30 (2014), 380-386.

1.1.5. Magnetic and thermoelectric materials

Here the focus was on the application of soft chemistry synthetic methods to the preparation of multiferroic hexagonal ferrites, thermoelectric layered cobaltates and multifunctional nanocomposites. We prepared epitaxial hexagonal ferrite thin films with M - and Y - type magnetic phases, performed chemical, structural, and microstructural characterization and suggested a model of orientation growth of bulk layer onto the seed layer. Then, layered cobaltates Ln_xCoO₂ (Ln = La, Pr, Nd), isostructural with thermoelectric Na_xCoO₂, were prepared with the aim to introduce a strong magnetism into the structure by insertion of rare earths ions and to stabilize the long-range magnetic ordering. Effort was also put into the development of synthetic procedures for CoFe₂O₄ monodispersed nanoparticles embedded in

oxide matrices. This method allows the preparation of new types of nanocomposites constituted of uniform nanoparticles of the desired type (magnetic, luminescent etc.) embedded in the favoured oxide matrix.

Selected papers:

J. Buršík, R. Kužel, et al., *J. Solid State Chem.* 203 (2013), 100-105.

K. Knížek; Z. Jiráček, J. Buršík, et al., *J. Appl. Phys.* 111 (2012), 07D707.

S. Kubickova, J. Plocek, A. Mantlikova, J. Vejpravova, *RSC Adv.*, 4 (2014), 5113-5121.

1.1.6. Advanced inorganic materials for industry

In the field of applied research our team has been primarily engaged in the development of technologies for the production of (a) inorganic pigments based on natural aluminosilicates with a low content of Fe; (b) TiO₂ and ZnO₂ nanosols for thin layers and combined optical materials; (c) inorganic matrices based on aluminosilicates matrices for the preparation of materials with a shielding effect to neutron radiation for nuclear power plants; (d) photocatalytic TiO₂ active in the UV and visible spectral regions for application in paints;

Selected outputs:

a) ČLUZ, plc., licence agreement 2012.

b) OPTAGLIO, Ltd., licence agreement 2011.

c) Ankaba Ltd., joint project assigned 2014.

d) Rokospol, plc., licence agreement 2012

1.2. New compounds and their properties

In the evaluated five-year period the team of Dpt. Of Syntheses successfully contributed to several areas of boron cluster chemistry. Efforts were focused on basic synthetic chemistry of boron cages, carborane and metallacarborane chemistry directed towards (i) biologically active compounds and (ii) the treatment of high level nuclear wastes (HLW), on 'macropolyhedral' large cluster chemistry and interactions of light with borane molecules, on metal surface protection using carborane and borane thiols and on theoretical chemistry of polyhedral boron compounds. However, the borderlines between these areas are flexible with broad overlaps for solutions and mobility of team members. The research was directed towards emerging applications based on new knowledge gained from our basic research.

1.2.1. Targeted development of reactive metallacarborane building blocks

We have continued our investigation in the area of tricarbollides (11-vertex *nido* tricarbaboranes), in which we have achieved a world-leading status. This particular class of carboranes was discovered by scientists from our team, and the continuation of this topic has been priority since then, with emphasis on so-called "tricarbollide" (C₃B_xH_y) analogues of the cyclopentadienide anion and ferrocene. We have shown these tricarbollide analogues to be chemically versatile, extremely stable in air and toward heating, and as such may become potential candidates for a variety of technical purposes in which the cyclopentadienide anion or ferrocene play a traditional role.

Associated with this tricarbollide area is a recent breakthrough in which we have shown the *arachno*-6,9-C₂B₈H₁₄ carborane to react with acyl chlorides (RCOCl) in the presence of amine bases to generate a series of alkylated and arylated tricarbollides of type 8-R-*nido*-7,8,9-C₃B₈H₁₁ in high yields. These so-called skeletal alkylcarbonation (SAC) reactions are reminiscent of organic aldol condensation reactions, and as such represent a new type of cross-coupling reactions between R and the tricarbaborane cage, and a new approach to carbon insertion into borane clusters generally. These advancements in generic synthetic procedures for borane/carborane chemistry provide a sound basis for more application-driven research on these compounds.

Selected papers:

B. Štíbr, M. Bakardjiev, J. Holub, A. Růžicka, Z. Padělková, R. Olejník, Švec P., Chem. Eur. J. (2011), 13156-13159.
M. Bakardjiev, B. Štíbr, J. Holub, A. Růžicka, Z. Padělková, Inorg. Chem. 52 (2013), 9087-9093.

1.2.2. Biologically active borane clusters focused on the design of viral enzyme inhibitors or cytostatics

Systematic research into the synthesis of metallaborane building blocks for use in the design of novel biologically functional molecules has been a team priority. Although initially intended for the specific and efficient inhibition of HIV-PR enzymes, these molecular systems have happily also proved useful in the inhibition of carbonic anhydrase IX, relevant to cancer therapy. The majority of our attention has been focused on the chemistry of the cobalt bis(dicarbollide) anion - the stable metalladecaborane sandwich, which is structurally similar to ferrocene. Our team has developed a number of synthetic methods for the derivatization of this cobalt bis(dicarbollide) anion with functional organic moieties that increase the therapeutic potency and target specificity of the molecule. We showed that newly designed compounds efficiently inhibit mutated HIV strains isolated from infected patients. The refinement of the structures for the HIV PR enzyme containing cobalt bis(dicarbollide) anion inhibitors (performed at IOCB) helped to explain the mechanism of activity of these compounds. The structures revealed a unique binding mode within the active site of the enzyme, and, along with NMR studies, shed light on the mechanism of the inhibition of resistant variants of the virus.

We have also discovered the great potential of carborane and metallacarborane derivatives as specific and selective inhibitors of the carbonic anhydrase IX (CA IX) enzyme. This isoenzyme is overexpressed on the surface of the cells of hypoxic solid tumours and responsible for the exchange of CO₂ in cancer tissues. The inhibitor's design is structurally based on the tailored bonding of sulfamide, sulfamoyl or sulfonamide headgroups to the relevant carborane and metallacarborane clusters, typically *via* a short aliphatic chain. The key synthetic steps to the designed structures consisted in critical experimental revisions of the reactions leading to the carborane alkylamine precursors and development of completely novel synthetic routes that furnished carbon substituted cobalt bis(dicarbollides) by alkylammonium groups.

Supported by unpublished toxicology and pharmacokinetic studies carried out jointly with IMTM Olomouc (our team performed the analytical assays), stable metallacarborane ions have great potential to serve as novel hydrophobic pharmacophores. We believe that these compounds can offer distinctly different properties from typically used organic scaffolds.

Selected papers:

P. Řezáčová, P. Cígler, P. Matějček, M. Lepšík, J. Pokorná, B. Grüner, J. Konvalinka, *Boron Science- New Technologies and Applications*, N.S. Hosmane, Ed., CRC Press: New York, ISBN-978-1-4398266-3-8.

J. Plešek, B. Grüner, V. Šícha, v. Böhmer, I. Císařová, *Organometallics*, 31 (2012), 1703-1715.

J. Brynda, P. Mader, V. Šícha, M. Fábry, K. Poncová, M. Bakardiev, B. Grüner, P. Cígler, P. Řezáčová, *Angew. Chem., Intl. Ed. Eng.*, 52 (2013) 13760-13763.

J. Nekvinda, V. Šícha, D. Hnyk, B. Grüner, *Dalton Trans.*, **43**, 2014, , 5106-5120.

1.2.3. Development of a new generation of agents for selective extraction of radionuclides from nuclear wastes

We have also continued in the development of synthetic methods leading to new families of exceptionally robust extraction agents useful for isolation of the lanthanides and highly radiotoxic minor actinides from high activity nuclear waste. Our research team has contributed to technological developments in this field from early stages by the design and synthesis of new types of extraction agents for the main fission products (former industrial dicarbollide process for Cs⁺ a Sr²⁺ partitioning). Recently, a series of new extractants for actinide and

lanthanide family of fission products, based on ionic diamides composed of a N,N'-dialkyl diglycolyl complexing group and two cobalt bis(dicarbollide)(1-) anions has been synthesized. The research team has been also involved in technological process development for actinide partitioning using bis(triazinyl) bipyridines as selective organic ionophores, supported by European Collaborative research projects ACSEPT and SACSESS (F.P. 7). The main results, in close collaboration with Chalmers Univ., Sweden (C. Eckberg), led to the determination of stabilities of modified bis(triazinyl) bipyridide molecules after hydrolysis and irradiations by high doses and detailed elucidations of degradation pathways. The search for interferences with other metal cations present in fission mixtures was another studied task. A deeper understanding of such factors plays an important role in the process development.

Selected papers:

B. Grůner, M. Kvíčalová, P. Selucký and M. Lučaníková, *J. Organomet. Chem.* 695 (2010), 1261-1264.

B. Grůner, P. Švec, P. Selucký, M. Bubeníková, *Polyhedron*, 31 (2012) 103-112.

B. Grůner, V. Böhmer, C. Dordea, P. Selucký, M. Bubeníková, *J. Organomet. Chem.* **747**, (2013) 155-166.

1.2.4. Macropolyhedral large cluster chemistry and the interaction of light with boron hydride molecules

The unlocking of the full potential of boron-containing cluster chemistry requires the development of cluster architectures larger than the twelve-boron icosahedron. The high molecular boron content and stability of such species makes them commercially interesting compounds for several applications. For example, there is particular interest in the use of large boron hydride clusters, such as B₁₈H₂₂, as dopant agents in the manufacture of *p*-type semiconductor devices. Our team has developed new and improved syntheses to this and other large cluster boron hydrides, like the [B₁₉H₂₂]⁻ anion. We are also interested in the photophysical properties of B₁₈H₂₂. We have shown that the *anti*-B₁₈H₂₂ isomer shows an intense blue fluorescence with a high quantum yield, Φ_F = 0.97, which is very rare amongst molecular inorganic compounds and unique amongst the binary boron hydrides. We subsequently established that this emission withstands the stringent conditions of high-energy pump excitation necessary for functioning as a laser material – the first boron hydride laser known. The new borane laser material irradiates efficient laser emission in the blue, a spectral region of interest in applications such as spectroscopy or materials processing, and shows a resistance against degradation that is superior to many of the commercially available state-of-the-art blue laser dyes.

Additionally, we have been developing the capacity of the metallaborane system L₄M₂B₁₀H₁₀ (where M = Pt, Pd and L = phosphine or other ligand) to selectively and reversibly uptake various small molecules of gases (O₂, SO₂, CO, NO_x, acetylene, ethylene, etc.). There are numerous potential ways to tune the properties of this system according to requirement – e.g. choice of cluster metal, metal ligand, and substitution of the borane cluster. These alterations allow us to control the reversibility of small-molecule uptake, and the conditions by which molecule-release is affected; for example, reduction in pressure, heating, or irradiation with UV light. With the use of UV irradiation we also observed, in the case of the reversible uptake of O₂, that oxygen release from the L₄M₂B₁₀H₁₀ cluster also involves a transfer of energy to the oxygen molecule and its excitation from triplet to singlet states, and thus the evolution of highly reactive and bactericidal singlet-oxygen.

Selected papers:

M. G. S. Londesborough, J. Bould, T. Baše, D. Hnyk, M. Bakardjiev, J. Holub, I. Císařová, J. D. Kennedy, *Inorg. Chem.*, 49 (2010), 4092-4098.

M. G. S. Londesborough, D. Hnyk, J. Bould, L. Serrano-Andres, V. Sauri, J. M. Oliva, P. Kubát, T. Polívka, *Inorg. Chem.*, **51**, 1471-1479, (2012).

L. Cedran, J. Braborec, I. Garcia-Moreno, A. Costelo, M. G. S. Londesborough, *Nature Commun.*, 6 (2015), Article Number 5958.
J. Bould, T. Baše, M. G. S. Londesborough, L. A. Oro, R. Macias, J. D. Kennedy, P. Kubát, M. Ficiman, T. Polívka, K. Lang, *Inorg. Chem.*, **50**, 7511-7523, (2011).

1.2.5. Metal surface protection using borane and carborane derivatives

Carborane-thiol derivatives, functionalized inorganic cage molecules with the structure of nearly regular icosahedra, were introduced by our team as a new type of stable molecules for self-assembled monolayers (SAMs) and monolayer-protected colloids (MPCs). The carborane-based SAMs have been proved to possess a number of unique features including lower concentration of defects, higher thermal stability heating, and anti-corrosive properties. These species have been proved to form densely packed and well-ordered 2D arrays on flat metal surfaces, and a special aspect addressed within our studies was the effect of their dipole moment orientation on work function changes of gold and silver surfaces.

Selected papers:

T. Baše, Z. Bastl, V. Havránek, J. Macháček, J. Langecker, V. Malina, *Langmuir* 28 (2012), 12518-12526.

J. Bould, J. Macháček, M. G. S. Londesborough, R. Macias, J. D. Kennedy, Z. Bastl, P. Rupper, T. Baše, *Inorg. Chem.* 51 (2012), 1685-1694.

1.2.6. Theoretical chemistry focused on polyhedral boron compounds

Here we are concerned with the theoretical and computational treatises of the building blocks of boron cluster chemistry useful to our team. For example, we computationally predicted five possible tricarbaborane icosahedral cations together with their ^{11}B NMR spectra, thus supplementing the experimentalists with a means to correlate spectroscopic measurements with the computed values to determine liquid phase structures. In this way, unknown molecular structures are easier to determine, and synthetic targets can be suggested by relatively quick computational practices, providing a more effective synthetic strategy.

Computational work aimed at electronic structures and paramagnetic ^{11}B NMR spectroscopy was additionally conducted on a range of other fused polyhedra boranes, including, for example, the large boranes $\text{B}_{21}\text{H}_{18}^{(-)}$ and $\text{B}_{20}\text{H}_{16}$ that contain four and three joint vertices respectively. Computational analysis of the structural dimensions of the former species, and comparison of this data with other known biologically-active borane species, led to the finding of $\text{B}_{21}\text{H}_{18}^{(-)}$ to be a potent inhibitor of HIV protease.

Selected papers:

Hnyk, D., Jayasree E. G., *J. Comput. Chem.* 34 (2013), 656 – 661.

Fanfrlík, J., Přáda, A., Padělková, Z., Pecina, A., Macháček, J., Lepšík, M., Holub, J., Růžička, A., Hnyk, D., Hobza, P., *Angew. Chem. Int. Ed.* 53 (2014), 10139 – 10142.

1.3. Methods and special techniques:

- advanced investigation of materials (Centre of Instrumental Techniques, CIT); electron microscopy, X-ray diffraction, thermal analyses, Mössbauer spectroscopy
- analysis of sediments for paleoenvironmental reconstructions (Laboratory of Environmental Geochemistry Analysis, LEGA)
- integrated materials analysis of artworks (Academics Materials Research Laboratory of Painted Artworks, ALMA))

1.3.1 Advanced investigation of materials

In the evaluated period the members of CIT have participated in scientific studies in collaboration with many Czech and foreign (Slovakia, Spain, India, Ukraine, Russia, France, Japan, Germany, South Africa, etc.) scientific groups.

The team developed an original method for the synthesis of highly **photoactive anatase foams**. Aggregates of planar nanoparticles were prepared from lyophilized aqueous colloids of peroxo-polytitanic acid with subsequent annealing. The product demonstrated significantly higher activity in comparison with the commercially available Degussa P25 photocatalyst.

Selected papers:

E. Pližingrová, L. Volfová, P. Svora et al., *Catalysis Today*, 240 (2015), 107-113.

J. Šubrt, P. Pulišová, J. Boháček, P. Bezdička et al., *Mat. Res. Bull.* 49 (2014), 405-412.

In the field nanostructured materials for application in photocatalysis and energy conversion, the CIT team contributed to studies focused on controlling particle size and shape during formation, and the effect of nanoparticle aggregation on catalytic activity by performing microscopic and crystallographic characterization of particular phases as well as, in some cases, also by the synthesis of new materials (**sulphur doped TiO₂ nanoparticles**, **nanocrystalline PrFeO₃** perovskite-type orthoferrite).

Selected papers:

L. Szatmary, S. Bakardjieva, J. Šubrt, P. Bezdička et al., *Catalysis Today* 161 (2011), 23-28.

S. N. Tijare, S. Bakardjieva, J. Šubrt et al., *J. Chem. Sci.* 126 (2014), 517-525.

The CIT team also participated in an international cooperation aimed at problems associated with severe nuclear accidents, in particular with the formation and **properties of corium** including characterization of phases present, the reaction of corium melts with concrete, etc. The team performed microscopic and crystallographic characterizations of particular phases as well as emissions formed during formation of corium and interactions of corium melts with materials used in the construction of reactors.

Selected papers:

S. Bakardjieva, et. al., *Ann. Nucl. Energy*, 74 (2014), 110-124.

Y. B. Petrov et.al., *Glass Phys. Chem.*, 37 (2011), 212-229.

V. Tyrpekl, et.al., *Ann. Nucl. Energy*, 75 (2014), 210-218.

Mainly in cooperation with external subjects, **Mössbauer spectroscopy** was applied in characterization of various nanostructured magnetic materials. In addition to Mössbauer spectroscopy measurement and interpretation, the CIT team ensured thermoanalytical, microscopic and crystallographic characterization of particular phases.

Selected papers:

J. Z. Msomi, H. Abdallah, T. Moyo, A. Lančok, *J. Magn. Magn. Mater.*, 323 (2011), 471-474.

H. Abdallah, J. Z. Msomi, T. Moyo, A. Lančok, *J. Supercond. Nov. Magn.*, 25 (2012), 2619-2623.

The CIT team was also involved in the research oriented to the **treatment of strongly acidic waste waters** coming from extractions of sulfide materials. The team suggested the use of urea precipitation method for the treatment of these waste waters and carried out microscopic and crystallographic characterization of particular phases.

Selected papers:

E. Michálková et.al., *Pol. J. Environ. Stud.*, 22 (2013), 1111-1118.

J. L. Perez-Rodriguez et.al., *Appl. Clay Sci.*, 51 (2011), 274-282.

P. Pulišová et.al., *J. Therm. Anal. Calorim.*, 116, (2014), 625-632.

1.3.2. Analysis of sediments for paleoenvironmental reconstructions

A series of case studies on Czech rivers (the Morava, Jizera and Ploučnice) was focused on the development of a methodology for research of **pollution chemostratigraphy in floodplains**. The methodology comprises methods for the sampling of sediment, its complex analysis, data processing, the use of geographical information systems (GIS) and fluvial geomorphology. This broadly multidisciplinary approach is indispensable for the correct interpretation of element compositions (including risk elements) with respect to the internal structure of the floodplain architecture. The outputs of these studies were robust interpretations of floodplain sediments in a historical context of past fluvial development and pollution history, where natural and anthropogenic contributions to risk element concentrations in sediments were distinguished.

Selected papers:

T. Grygar et al., *CATENA* 80 (2010), 106-121.

T. Matys Grygar et al., *Sci. Total Environ.*, 452 (2013), 233-245

T. Matys Grygar et al., *Appl. Geochem.*, 48 (2014), 1-15.

Stratigraphy of the Miocene Most Basin fill was studied in a long-term collaboration with the North Bohemian Mines, the largest coal-mining company in the Czech Republic. The research resulted in an improvement of the local stratigraphy, identification of orbitally driven changes in element composition induced by climate change, and dating of the sediment. Furthermore, the results allow geologists in the North Bohemian Mines to rationalise variable behaviour of the clastic strata above the coal seam in individual opencast mines.

Selected papers:

T. Matys Grygar et al., *Bull. Geosci.* 88 (2013), 557-571.

T. Matys Grygar et al., *Geol. Mag.* 151 (2014), 1013-1033

The know-how concerning element analyses of sediment profiles, developed in the laboratory, was successfully used in **sedimentary research** carried out in co-operation with GeoForschungsZentrum Potsdam, Germany, faculties of sciences of the Charles University in Prague and universities in Olomouc and Brno. Since 2014 similar works have also been performed in the frame NSF project with the Denver University is PI in this project).

Selected papers:

Oberhänsli et al., *Global Planet. Change* 76 (2011), 95-104.

Kumpan et al., *Sediment. Geol.* 311 (2014), 43-59.

1.3.3. Integrated materials analysis of artworks

The main effort of the ALMA team was focused on the testing and implementation of non-destructive micro-analytical techniques and methodologies in the field of materials research of paintings. Consequently, experimental research of painting pigments was focused also on the historical methods of preparation and processes of degradation in the colour layer.

Within the **methodological research**, methods of X-ray micro-diffraction (micro-XRD) were developed for micro-samples (*i.e.* fragments of paints). The research was followed by several comparative analytical studies combining either micro-XRD with synchrotron-based micro-XRD (SR-XRD, cooperation with Helmholtz-Zentrum Berlin, Germany) or micro-XRD with micro-Raman (cooperation with the Faculty of Science, Charles University in Prague). In this way structural characterizations of various clay-based pigments in painted artworks were carried out with the aim to help in the evaluation of works of art in terms of their originality, age and provenance. The team participated in the development and testing of the methodologies of **non-invasive survey** of works of art. Analytical limits of hand-held instruments were shown.

Selected papers:

S. Švarcová et al., *Anal. Bioanal. Chem.* 399 (2011), 331-336.

V. Košařová et al., *J. Raman Spectrosc.* 44 (2013), 1570-1577.

S. Švarcová et al., *Spectrochim. Acta A* 132 (2014), 514-525.

To understand fully historical painting technologies and the materials used, the team has been also involved in **materials research** focused on the description of properties of these materials, specific signs of their origin and pathways of degradation in painting layers caused by internal or external agents. The team developed a way of distinguishing between green earths imported from the historical sites in northern Italy and from deposits in Northern Bohemia. A close attention was paid to vivianite, a rare mineral pigment, which can be profitably used in authorship ascription or copy identification, and to its degradation processes. Recently, another rare mineral pigment, antonozite, was investigated for its distinguishing in microanalysis and provenance-related studies.

Selected papers:

D. Hradil, *et.al.*, *Archaeometry* 53/3 (2011), 563-586.

Z. Čermáková, *et.al.*, *Archaeometry* 56 Suppl. 1 (2014), 148-167.

Z. Čermáková, *et.al.*, *Spectrochim. Acta A* 140 (2015), 101-110 (*in press*).

Z. Čermáková, *et.al.*, *J. Raman Spectrosc.* 46 (2015), 236-243 (*in press*).

Unique pre-Romanesque murals, belonging to the oldest **wall paintings** in Central Europe, were investigated in Kostol'any pod Tribečom, Slovakia. The identification of original pigments and bindings as well as the explanation of degradation processes became valuable leads for future restoration. Other mural paintings of exceptional quality were investigated in Kuřívody, Northern Bohemia and in Lidzbark Warminski, Poland. The ALMA team was also involved in international cooperation focused on material and technological characteristics of early Renaissance altars in Transylvania.

Selected papers:

D. Hradil, *et.al.*, *Archaeometry* 55/4 (2013), 691-706.

C. Serendan, D. Hradil, J. Hradilová, J. Cannataci, In.: Saunders D., Spring M., Meek A. (Eds.): *The Renaissance Workshop*, Archetype Publications Ltd., London, 2013, pp 199, ISBN: 978-904982-93-7, p 60-71.

Research Report of the team in the period 2010–2014

Institute	Institute of Inorganic Chemistry of the CAS, v. v. i.
Scientific team	Department of Syntheses

General

In the period 2010-2014 the team of the Dpt. of Synthesis has continued to build on its record of significant contributions to boron chemistry, both in its basic research and on its potential applications, by pursuing clearly defined research targets and objectives focused on boron hydride cluster chemistry.

The specific contribution of the team in this five-year period falls within several areas of boron cluster chemistry, and for purposes of clarity may be divided into five main directions according to research domains and the principal investigators responsible for each respective domain.

1. Basic synthetic chemistry of boron cages; new types of carboranes and metallacarboranes (B. Štíbr).
2. Carborane and metallacarborane chemistry directed towards (i) biologically active compounds and (ii) the treatment of high level nuclear wastes (HLW) (B. Grüner).
3. 'Macropolyhedral' large cluster chemistry and the useful interaction of light with boron hydride molecules. (M.G.S. Londesborough).
4. Metal surface protection using carborane and borane thiols (T. Baše).
5. Theoretical chemistry focused on polyhedral boron compounds (D. Hnyk).

The above distribution of research domains reflects success in attaining support for these particular areas from national and international Grant Agencies. In addition to these individual grants covering distinct areas of research, a Joint Centre of Basic Research with the University of Pardubice "New Inorganic Materials" ("Group of Excellence" programme from the Ministry of Education, running up to 2011) enabled the merging of boron and material chemistry in several new areas.

However, it must be emphasized that the borderlines between these domains are subtle, flexible and are often with broad overlaps and interchanges for ideas and solutions as well as for mobility of team members between these areas. All areas of research are directed towards emerging applications based on new knowledge gained from our basic research.

We believe that our Team has proven over the last five years its viable ability to carry out research at a level of high international standards, and indeed to have pioneered several novel directions in international boron chemistry i.e., the design of biologically active boron hydride species, modifications of metal surfaces with monolayers composed of boron clusters, gas-trapping metallaboranes, and laser light-emitting fused boron polyhedra. This success is demonstrated by the large number of 89 high-quality original articles published in peer-reviewed international journals. The trend to publish in high-impact journals and the number of citations per article has visibly increased over last five years.

Summary of main results achieved in the period 2010-2014.

1. Systematic synthetic chemistry of boron cages: New types of carboranes and metallacarboranes.

We have continued our investigation in the area of tricarbollides (11-vertex *nido* tricarbaboranes), in which we have achieved a world-leading status. This particular class of carboranes was discovered by scientists from our Department in 1995, and the continuation of this topic has been priority since then, with emphasis on so-called “tricarbollide” ($C_3B_xH_y$) analogues of the cyclopentadienide anion and ferrocene. We have shown these tricarbollide analogues to be extremely stable in air and toward heating, and as such may become potential candidates for a variety of technical purposes.

a) Carboranes and tricarbollides - analogues of the Cp^- anion. The structures and alternative syntheses of generic tricarbollide compounds, such as $[nido-7,8,9-C_3B_8H_{11}]^-$, $[7,8,10-C_3B_8H_{11}]^-$ and $[1-Cp-closo-1,2,4,10-FeC_3B_8H_{11}]$, were unambiguously established and complemented with X-ray diffraction analyses. In keeping with this research line, a series of aminotricarbollides was prepared, each of which exhibited tautomerism between zwitterionic ($7-t-BuNH_2-8,9-R,R'-nido-7,8,9-C_3B_8H_8$) and neutral ($7-t-BuNH-8,9-R,R'-nido-7,8,9-C_3B_8H_9$) molecules. The tautomeric behaviour was strongly affected by the nature of the substituent.

Associated with this tricarbollide area is a recent breakthrough that we have made: reactions between the *arachno*-6,9- $C_2B_8H_{14}$ carborane and acyl chlorides ($RCOCl$) in the presence of amine bases were found to generate a series of alkylated and arylated tricarbollides of type $8-R-nido-7,8,9-C_3B_8H_{11}$ in high yields. These so-called skeletal alkylcarbonation (SAC) reactions are reminiscent of organic aldol condensation reactions, and are consistent with an insertion of the carbonyl carbon into the structure of 6,9- $C_2B_8H_{14}$. These SAC reactions indeed represent a new type of cross-coupling reactions between R and the tricarbaborane cage, and a new approach to carbon insertion into borane clusters generally.

Graphene-oxide modified with the extremely stable *o*-carboranyl 1,2- $C_2B_{10}H_{11}$ unit was prepared leading to a new carborane-grafted material. Carboranyl-functionalized graphene oxide was synthesized from $Li[1,2-C_2B_{10}H_{11}]$ and $COCl$ -functionalized graphene-oxide.

b) Iron complexes of the tricarbollide ferrocene analogue. To probe the assumed similarities of tricarbollide ligands and the cyclopentadiene ion, isomeric twelve-vertex ferratricarbollide complexes of the general structure $[1-Cp-12-t-BuNH-2,4-R,R'-closo-1,2,4,12-FeC_3B_8H_8]$ and $[1-Cp-10-t-BuNH-2,4-R,R'-closo-1,2,4,10-FeC_3B_8H_8]$, and ferrocenyl substituted derivatives of *nido*-5,6- $C_2B_8H_{12}$ (the tautomeric tricarbollide complexes $7-t-BuNH_2-8-Fc-7,8,9-C_3B_8H_9$ and $[1-Cp-2-Fc-10-t-BuNH-1,2,4,10-FeC_3B_8H_9]$ (Fc = ferrocenyl)) were prepared and characterized. A series of novel monoaryl-substituted 12-vertex ferratricarbollide complexes of a general constitution $[1-(CpFe)-closo-ArC_3B_8H_{10}]$ (where $Ar = C_6H_5$, $1'-C_{10}H_7$, $2'-C_{10}H_7$) with three different aryl substituents and arrangements of cluster carbon vertexes was isolated and fully characterized. Fe complexation was accompanied by the extensive rearrangement of the cluster carbon atoms over the 12-vertex tricarbollide cage.

We also developed original routes to a complete series of novel arene complexes $[1-(\eta^6-Me_nC_6H_{6-n})-closo-1,2,3-FeC_2B_9H_{11}]$ (for $n = 1-6$) with strictly linear correlations between 1H and ^{11}B NMR parameters, $Fe^{II/III}$ redox potentials and the number of arene methyls. These results evidenced the strictly additive character of electron donation by the methyl substituents to the arene ring and to the Fe center and the dicarbollide ligand. In connection with this work, it was found that heating of selected $[1-(\eta^6\text{-arene})-closo-1,2,3-FeC_2B_9H_{11}]$ complexes resulted in their thermal rearrangement and isolation of the corresponding 1,2,4-, 1,2,7-, and 1,2,8-cage isomers.

The results achieved in this field are based on original synthetic methods designed and developed exclusively in our Department. The University at Pardubice (Team of Prof. Ruzicka) contributed by X-ray diffraction studies and the team of the Charles University in Prague performed electrochemical studies. Two students from the University of Pardubice, involved in some of these studies, had part time employment at the Institute.

2. Carborane and metallacarborane chemistry directed to biologically active compounds and treatment of high level nuclear waste (HLW).

The team of the Dpt. of Synthesis performed systematic research into the synthesis of metallaborane building blocks for use in the design of novel radionuclide extractant agents and biologically functional molecules. Regarding this latter purpose, these molecules were initially intended for the specific and efficient inhibition of HIV-PR enzymes, however, and happily, these molecular systems also proved useful in the inhibition of carbonic anhydrase IX, relevant to cancer therapy.

a) New modification of the metallacarborane cages - design of molecular “building blocks”. The majority of our attention has been focused on the chemistry of the cobalt bis(dicarbollide) anion - the stable metalladicalcarborane sandwich, which is structurally similar to ferrocene. Derivatization of this cobalt bis(dicarbollide) anion with functional organic moieties has proved a considerable challenge due to the absence of suitable synthetic methods for direct cluster-substitution. Concordantly, our work focused on several principally new ways for the direct substitution of the cobalt bis(dicarbollide) cages, enabling functionalization (hydroxy, carboxy, ammonium or cleavable rings containing the oxonium atom) at both boron and carbon sites of the cluster molecules. In addition to the development of such synthetic procedures, we have also been concerned with the structural characterization of all new compounds, delineation of their physico-chemical properties and reaction pathways, and their application to more sophisticated systems. The synthetic results (published in a range of peer-reviewed journals) were achieved exclusively at our Department; Dr. I. Čísařová from the Charles University in Prague and Dr. Z. Padělková from the University of Pardubice contributed to the published papers by means of X-ray crystallographic studies. These results have opened up new opportunities for the construction of novel molecules for biomedicine and radionuclide extraction.

b) Inhibitors of HIV-Protease enzyme. In 2005, we successfully designed synthetic pathways leading to the first members of inorganic, non-peptidomimetic inhibitors of the HIV protease (HIV-PR), the key enzyme of the HIV virus life cycle. A joint project of the Grant Agency of the Academy of Sciences of Czech Republic (2009-2013, the team led by B. Grůner as a principal investigator) resulted in significant extensions of the library of dicluster metallacarborane inhibitors of the HIV-PR enzyme and in a deeper understanding of their properties. The synthesis and design of molecules have been carried out at the Department. The HIV-PR inhibitors have been developed and tested in cooperation with the Institute of Organic Chemistry and Biochemistry, CAS (IOCB; team leader: J. Konvalinka). Physico-chemical aspects were studied at the Dpt. of Physical and Macromolecular Chemistry, Charles University (P. Matejíček). The structures composed of two (or more) cobalt bis(dicarbollide)(1-) cages have shown high antiviral activities. The new modifications introduced selectively into the inhibitor-molecule structures followed closely the progress in synthetic methods, and aimed at modifying the central organic moiety and improving the water solubility of the compounds. The synthetic results consisted of original methods for derivatization of cobalt bis(dicarbollide) and other boron species, opening new routes to rational design and structural optimizations. We showed that newly designed compounds efficiently inhibit mutated HIV strains isolated from infected patients. The refinement of the structures for the HIV PR enzyme containing the dicluster inhibitors (performed at IOCB) helped to explain the mechanism of activity of these compounds. The structures revealed a unique binding mode within the active site of the enzyme, and, along with NMR studies, shed light on the mechanism of the inhibition of resistant variants of the virus. A tendency of cobalt bis(dicarbollide) derivatives to aggregate in aqueous solutions and its strong influence on biological activity was delineated. The study of interactions of metallacarboranes with biocompatible systems serving as carborane-based drug transporters was performed. This research reached the stage of toxicology and pharmacokinetics tests performed on animals in close collaboration with the Laboratory of Experimental Medicine, Palackého University, Olomouc, (M. Hajdúch; later transformed into the Institute of Molecular and Translational Medicine, IMTM). The results from pharmacokinetic

studies are promising. It should be pointed out that the inhibition mechanism of clusters towards the HIV-PR is completely different from those of the ten organic peptidomimetic inhibitors which are currently on the market. The clusters have a good ability to treat HIV infection because of their unique mechanism of inhibition and ability to withstand the resistance pressure, which is known to be extremely high in the case of the HIV-PR enzyme. The outputs of this project were evaluated by the Grant Agency as excellent.

c) Boron compounds designed for cancer therapy. The results from the previous studies on metallacarboranes that exhibited specific action towards the HIV protease enzyme, prompted us to consider the wider applicability of carboranes and metallacarboranes as hydrophobic pharmacophores in drug design. Our team, together with the teams of structural biologists from IOCB and the Institute of Molecular Genetic, CAS (dealing with *in vitro* enzymatic assays and enzyme-inhibitors structures), discovered the great potential of carborane and metallacarborane derivatives as specific and selective inhibitors of the carbonyl anhydrase IX (CA IX) enzyme. This isoenzyme is overexpressed on the surface of the cells of hypoxic solid tumors and responsible for the exchange of CO₂ in cancer tissues. The inhibitor's design is structurally based on the tailored bonding of sulfamide, sulfamoyl or sulfonamide headgroups to the carborane and metallacarborane clusters, typically *via* a short aliphatic chain. The key synthetic steps to the designed structures consisted in critical experimental revisions of the reactions leading to the carborane alkylamine precursors and development of completely novel synthetic routes that furnished carbon substituted cobalt bis(dicarbollides) by alkylammonium groups. These intermediates can be then easily converted into active inhibitors. The structure-activity relationship (SAR) in the enzyme inhibition towards the CA-IX isoform has been elucidated. The best compounds of this series have proven specific action towards the CA-IX with IC₅₀ values in the nanomolar, or according our recent results, even in picomolar range and high selectivity factors. We believe that these novel types of the CA IX carborane inhibitors may be further developed into important tools for cancer therapy and diagnostics. The results were covered by a joint PCT International Patent. The first pilot study on the carborane-alkylsulfamide series of compounds was published in *Angew. Chem., Intl. Ed. Engl.* in 2013. This has demonstrated that carboranes can be successfully used to replace the 'ring' moiety in classical CAs inhibitors and that the nature of the cluster, its size and/or the exo-skeletal cluster substitution can be in principle used in fine tuning the specificity of compounds toward the CA-IX isoenzyme.

Supported by unpublished toxicology and pharmacokinetic studies carried out jointly with IMTM Olomouc (our team performed the analytical assays), stable metallacarborane ions have great potential to serve as novel hydrophobic pharmacophores. We believe that these compounds can offer distinctly different properties from typically used organic scaffolds.

d) Chemistry of extractants of radionuclides for the HLW treatment. We have also continued in the development of synthetic methods leading to new families of exceptionally robust extraction agents useful for isolation of the lanthanides and highly radiotoxic minor actinides from high activity nuclear waste.

Our research team has contributed to technological developments in this field from early stages by the design and synthesis of new types of extraction agents for the main fission products (former industrial dicarbollide process for Cs⁺ a Sr²⁺ partitioning). Recently, a series of new extractants for actinide and lanthanide family of fission products, based on ionic diamides composed of a N,N'-dialkyl diglycolyl complexing group and two cobalt bis(dicarbollide)(1-) anions has been synthesized. Also the development of compounds based on covalent bonding of diphenyl-N-*tert*-octyl-carbamoyl methyl phosphine oxide groups (CMPO) to cluster anion has been continued from previous periods, particularly with the aim to further improve solubility in low polar solvents and re-extraction. Both these series of compounds enabled highly efficient and selective liquid-liquid extraction of polyvalent cations, i.e., lanthanides and actinides from highly acidic HLW to low polarity auxiliary solvents without presence of synergic or other

additives in the extraction system. Simultaneously, another even more efficient family of extractants emerged from the designed prearrangement of CMPO groups and cobalt bis(dicarbollide)(1-) anions on the calixarene platform. The new developments in area of calixarene chemistry have been achieved in close cooperation with the group of V. Böhmer (Johannes Gutenberg University, Mainz, Germany), which provided us with starting calixarene precursors for introduction of both types of functional groups. Extraction tests carried out in macro quantities from synthetic mixtures of fission products and tests of re-extractions have been performed at the Nuclear Research Institute, plc. Řež (NRI, P. Selucký). Under this collaboration, the methods of re-extraction of the Ln/An group have been found for all types of ionic ligands. The recently performed cycle experiment proved feasibility of the selected members of extractants for the efficient recovery of the Ln/An group from a simulated PUREX fission products mixture. This procedure may be considered as a further step forward to the existing industrial technology of Cs⁺ and Sr²⁺ extraction using cobalt bis(dicarbollide). The results have been published in a series of original papers and as a summary in a book chapter.

Our research team has been also involved in technological process development for actinide partitioning using bis(triazinyl) bipyridines as selective organic ionophores, supported by European Collaborative research projects ACSEPT and SACSESS (F.P. 7). The main results, in close collaboration with Chalmers Univ., Sweden (C. Eckberg), led to the determination of stabilities of modified bis(triazinyl) bipyridide molecules after hydrolysis and irradiations by high doses and detailed elucidations of degradation pathways. The search for interferences with other metal cations present in fission mixtures was another studied task. A deeper understanding of such factors plays an important role in the process development.

3. 'Macropolyhedral' large cluster chemistry and the useful interaction of light with boron hydride molecules.

The unlocking of the full potential of boron-containing cluster chemistry requires the development of cluster architectures larger than the twelve-boron icosahedron. The high molecular boron content and stability of such species makes them commercially interesting compounds for several applications in, for example medicine and materials. We are interested in the targeted syntheses of new large, macropolyhedral boron hydride clusters and in delineating their chemical and physical properties, in particular their luminescent aspects.

a) Semi-conductor doping agents. There is particular interest in the use of large boron hydride clusters, such as B₁₈H₂₂, as dopant agents in the manufacture of *p*-type semiconductor devices. Our team has developed new and improved syntheses to this and other large cluster boron hydrides, like the [B₁₉H₂₂]⁻ anion.

By using the [B₁₉H₂₂]⁻ anion as an intermediate, we successfully effected the first isomerisation pathway between *anti*-B₁₈H₂₂ and *syn*-B₁₈H₂₂. As the major synthesis of B₁₈H₂₂ results in the formation of both isomers, the isomerisation route we describe could be useful in individual isomer enrichment. This work was published in *Inorg. Chem.*, 2010, **49**, 4092-4098. All authors were from our Department apart from I. Císařová from Charles University in Prague, who performed the necessary X-ray crystallographic studies, and J. Kennedy from Leeds University in the UK, who contributed to important discussions.

b) High quantum-yield fluorescence. We are also interested in the photophysical properties of B₁₈H₂₂. We have shown that the *anti*-B₁₈H₂₂ isomer shows an intense blue fluorescence with a high quantum yield, $\Phi_F = 0.97$, which is very rare amongst molecular inorganic compounds and unique amongst the binary boron hydrides. Conversely, isomer *syn*-B₁₈H₂₂ shows no measurable fluorescence, instead displaying much faster, picosecond nonradiative decay of excited singlet states. We showed that the determining factor for the dissimilar photophysics of *anti*- and *syn*-B₁₈H₂₂ is due to the significant differences in the geometrical rearrangements of their structures at their respective conical intersections between excited and ground energy states.

This work was published in *Inorg. Chem.*, 2012, **51**, 3, 1471-1479. The conception of the idea, all synthetic work and structural characterization, along with the majority of the UV-vis analyses, were conducted at the Boron Group IIC. Specialized UV-vis studies were made by Czech co-authors from other institutes, and high-level excited-state computational work was conducted by co-authors from Spain.

c) The first borane laser. Continuing from our work on delineating the photophysics of the highly fluorescent *anti*-B₁₈H₂₂, we subsequently established that this emission withstands the stringent conditions of high-energy pump excitation necessary for functioning as a laser material – the first boron hydride laser known. The work completed and accepted for publication in 2014 was published in the highly prestigious journal *Nature Communications*, 2015, **6**, 5958, and demonstrates that *anti*-B₁₈H₂₂ irradiates efficient and degradation-resistant laser emission in the blue, a spectral region of interest in applications such as spectroscopy or materials processing, among others. The new borane laser material shows a resistance against degradation that is superior to many of the commercially available state-of-the-art blue laser dyes. This high resistance against degradation means that the number of times the liquid medium has to be replaced is reduced, helping to solve issues with costs, occupational hazards and environmental impact due to the handling of solvents that are often toxic and flammable.

In this work scientists from the Department conceived the idea of useful emission from *anti*-B₁₈H₂₂, synthesized and characterized the laser material, and coordinated the publication process. Spanish co-authors designed and conducted the laser experiments.

d) Singlet-oxygen generation. We have also worked on the tuning of the photophysical properties of the highly fluorescent *anti*-B₁₈H₂₂, by straight-forward chemical substitution to produce 4,4'-(HS)₂-*anti*-B₁₈H₂₀, which facilitates intersystem crossing from excited singlet states to a triplet manifold. This subsequently enhances O₂(¹Δ_g) singlet oxygen production from a quantum yield of Φ_Δ ~ 0.008 in *anti*-B₁₈H₂₂ to 0.59 in 4,4'-(HS)₂-*anti*-B₁₈H₂₀, making the latter new compound a useful generator of singlet-oxygen. The work was published in *Inorg. Chem.* 2013, **52**, 9266-9274. This contribution describes the synthesis and full structural characterization of the new compound 4,4'-(HS)₂-*anti*-B₁₈H₂₀ and uses UV-vis spectroscopy coupled with DFT and *ab initio* computational studies to delineate and explain its photophysical properties. Here all conceptual, synthetic and structural characterization work (apart from X-ray crystallographic study) was carried out by the Department at the IIC. High-level excited-state computations were performed by our Spanish colleagues and co-authors.

e) Reversible small-molecule capture. We have been developing the capacity of the metallaborane system L₄M₂B₁₀H₁₀ (where M = Pt, Pd and L = phosphine or other ligand) to selectively and reversibly uptake various small molecules of gases (O₂, SO₂, CO, NO_x, acetylene, ethylene, etc.). There are numerous potential ways to tune the properties of this system according to requirement – e.g. choice of cluster metal, metal ligand, and substitution of the borane cluster. These alterations allow us to control the reversibility of small-molecule uptake, and the conditions by which molecule-release is affected; for example, reduction in pressure, heating, or irradiation with UV light. With the use of UV irradiation we also observed, in the case of the reversible uptake of O₂, that oxygen release from the L₄M₂B₁₀H₁₀ cluster also involves a transfer of energy to the oxygen molecule and its excitation from triplet to singlet states, and thus the evolution of highly reactive and bactericidal singlet-oxygen.

This system is presently undergoing an extensive experimental screening for potential applications such as low-concentration gas sensors, and bactericidal materials. Advanced catalytic processes are another of the potential applications of this system that we are probing, as well as immobilizations of these molecules on a solid support that can be used for heterogeneous performance.

This work has been published in, for example, *Inorg. Chem.*, 2011, **50**, 7511-7523 and *Inorg. Chem.*, 2012, **51**, 1685-1694. The conception of the idea, all synthetic work and structural characterization, along with the majority of the UV-vis analyses, were conducted at the Boron Group IIC. Specialized UV-vis studies were made by Czech co-authors from other institutes, and high-level excited-state computational work was conducted by co-authors from Spain.

4. Metal surface protection using carborane and borane thiols.

Carborane-thiol derivatives, functionalized inorganic cage molecules with the structure of nearly regular icosahedron, were introduced by our team as a new type of stable molecules for self-assembled monolayers (SAMs) and monolayer-protected colloids (MPCs). In this regard, we reported the first use of these molecules in 2005 and the new materials have since attracted a relatively broad attention for several reasons. The carborane-based SAMs have been proved to possess a number of unique features including lower concentration of defects, higher stability against heating, and anti-corrosive properties. These species have been proved to form densely packed and well-ordered 2D arrays on flat gold surfaces, and a special aspect addressed within our studies was the effect of their dipole moment orientation on work function changes of gold and silver surfaces. In the first part of this brief report, we show with some details our previous effort to systematically investigate these thiolated *closo*-carborane molecules as building blocks for SAMs on gold, silver and copper surfaces. In the second part, we comment on our recently developed synthetic strategies towards new molecules derived from this system with additional substituents, and in the third part, we present an *open*-cage system as an alternative to functional groups in providing reactive sites for further chemistry on surfaces.

Two positional isomers of *closo*-carborane-dithiols, 1,2-(HS)₂-1,2-C₂B₁₀H₁₀ (1) and 9,12-(HS)₂-1,2-C₂B₁₀H₁₀ (2), have been investigated as cluster building blocks for SAMs on gold, silver, and copper surfaces. These two isomers represent a convenient system in which the attachment of SH groups at different positions on the skeleton enables to attach them to a metal surface with opposite orientation of their molecular dipole. Both isomers were proved to exhibit the opposite orientation on metal surfaces. While the former isomer decreased the latter one increases the surface potential value of the modified metals. The relative changes of the surface potential correlate well with their dipole moments. Competitive chemisorption from mixtures of both isomers shows that the molecules of isomer 1 adsorbs faster on the surface than the molecules of isomer 2. These mixed SAMs also showed their potential use as a tool for adjusting the surface potential value according to requirement. The interaction between flat silver surfaces and these *closo*-carborane-dithiols was further studied as a molecular protection of silver surfaces against corrosion by hydrogen sulphide. A comparison of their protective qualities with several organic thiols was provided and all these derivatives were categorized according to their capacity to inhibit the interaction of silver with H₂S in the presence of water molecules in gas phase. We found that significantly better molecular protection for silver surfaces is afforded and isomer 2 proved to be particularly effective. The corrosion of silver by H₂S showed well-defined colour changes from lustrous silver, through yellow, violet, blue, and finally to grey. This was used in our report as a qualitative indicator of the extent of silver corrosion. As gold, silver and copper exhibit different chemistries, we have investigated the interaction of isomers 1 and 2 with a copper surface too. Isomer 1 exhibited etching of polycrystalline Cu films, and more detailed investigation of the experimental conditions showed that both the acidic character of SH groups and the presence of oxygen at the copper surface play crucial roles in how the surface reaction proceeds: whether toward a self-assembled monolayer or toward copper film etching. We found that each positional isomer requires completely different conditions for the deposition of a SAM on copper surfaces. Optimized conditions for the former isomer required the exposure of a freshly prepared Cu surface to vapor of 1 in vacuum, which avoided the presence of oxygen and moisture. Adsorption from a dichloromethane solution afforded a sparsely covered Cu(0) surface; isomer 1 effectively removes the surface copper(I) oxide, forming a soluble product, but apparently binds only weakly to the clean Cu(0) surface. In contrast, adsorption of the latter, less volatile

isomer proceeded better from a dichloromethane solution than from the vapor phase. Molecules of isomer 2 densely covered the copper surface cleaned up by the dichloromethane solution of 1. Both isomers exhibited high capacity to remove oxygen atoms from the surface copper(I) oxide that forms immediately after the exposure of freshly prepared copper films to ambient atmosphere. Isomer 2 showed suppression of Cu film oxidation.

Isomer 2 is also an interesting starting building block for the preparation of derivatives functionalized in the carbon positions one and two. We reported a convenient synthesis of 1,2-disubstituted 9,12-dimercapto-1,2-dicarba-*closo*-dodecaboranes (isomer 2 substituted in position one and two) starting from the 9,12-dimercapto-1,2-dicarba-*closo*-dodecaboranes with SH groups protected using methoxy-methyl (MOM) groups. This strategy enables different substituents to be attached directly to the cage molecules and use them in some further surface chemistry while using the above mentioned advantageous features *closo*-carborane-thiol self-assembled monolayers.

Alternative to reactive functional groups attached to the *closo*-carborane molecules represent open-face borane clusters which can act as a new class of reactive building blocks for the construction of novel and functional self-assembled monolayers. For this reason, we prepared three reactive *nido*-decaborane thiol cluster compounds, 1-HS-*nido*-B₁₀H₁₃ (1), 2-HS-*nido*-B₁₀H₁₃ (2), and 1,2-(HS)₂-*nido*-B₁₀H₁₂ (3) and characterized them as constituents of self-assembled monolayers (SAMs) with reactive open faces. Several experimental measurements indicated that the hydrophilic open face of the cluster is directed upward from the substrate surface, allowing the bridging hydrogen atoms to exhibit a similar reactivity to that of the bulk compound. The orientation of the clusters with their open faces pointing upward from the surface was as expected from the geometrical disposition of the open face relative to the position of the sulfur substituents. The presence of the reactive, hydridic, bridging hydrogen atoms on the surface was proved useful for providing reactive sites for further chemistry and this was shown by the reaction of a SAM prepared from 1-HS-B₁₀H₁₃ (1) with a solution of [PtMe₂(PMe₂Ph)₂], affording the addition of the metal moiety to the cluster.

5. Theoretical chemistry focused on polyhedral boron compounds.

In this domain of research pursued at the Department of Syntheses, we deal with the theoretical and computational treatises of the building blocks of boron cluster chemistry, for example with the 12-vertex *icosahedron*. With regards to the Group's interests in tricarbaboranes, we computationally predicted five possible tricarbaborane icosahedral cations together with their ¹¹B NMR spectra, thus supplementing the experimentalists with a means to correlate spectroscopic measurements with geometrical molecular positions. In this way, synthetic targets can be suggested by relatively quick computational practices, providing a more effective synthetic strategy.

Computational work was additionally conducted on a range of other fused polyhedra boranes, including, for example, the large boranes B₂₁H₁₈⁽⁻⁾ and B₂₀H₁₆ that contain four and three joint vertices respectively. Computational analysis of the structural dimensions of the former species, and comparison of this data with other known biologically-active borane species, led to the finding of B₂₁H₁₈⁽⁻⁾ to be a potent inhibitor of HIV protease.

Fused borane polyhedra via a metal vertex, as exemplified by (3-Fe(III)-(1,2-C₂B₉H₁₁)₂ and its Cr(III) analogue, were also studied. Both systems are paramagnetic. Our studies enabled full resolution of the ¹¹B NMR spectroscopic data collected for the iron compound in conjunction with high level DFT calculations, essential to its full structural characterisation. Other molecules studied by our theoretical methods include two diiodine icosahedral monocarbaboranes I₂-CB₁₁H₁₀⁽⁻⁾. These materials are very promising for conjoining multiple icosahedra. Additionally, our interests lay in sulfur-containing borane compounds that we found to exhibit a considerable interaction with two-dimensional aromatic benzene rings (in the form of phenylene group). This, we determined to be due to an as yet unknown chalcogen bonding phenomenon. This discovery belongs to one of the most important highlights of Dr. Drahomír Hnyk, especially within the context of the importance of sulfur in the human body when deactivating carcinogenic two-dimensional aromatic systems. In other work, we looked at the

ability of so-called *p*-carborane to transfer electronic effects. This carborane molecule was found to act more or less as a slight electron acceptor, which is comparable with other types of borane cluster molecules. Secondly, acidities of carboxylic acids based on its isomer, *o*-carborane, were established experimentally and were examined with computations, gas-phase acidities being measured in Madrid. *Aminoacids based on p-carborane are structurally related to p-aminobenzoic acid, which may evoke new comprehension of drug design.*

High-school students were also involved in the work in the area of metallocaboranes.

3. Research Plan of the team for 2015–2019

Maximum length of 3 pages.

Research Report of the team in the period 2010–2014

Institute	Institute of Inorganic Chemistry of the CAS, v. v. i.
Scientific team	Materials Chemistry Department

The Department of Materials Chemistry consisted of 8 scientists, 9 PhD students, 2 university master students, and 2 technicians (December 2014). A number of other students were working in the Department on their bachelor or master theses within the frame of ongoing cooperations with universities. There are 2 key scientists Kamil Lang and Václav Štengl; however, younger researchers Jan Demel, Kaplan Kirakci, Jiří Henych, Petra Ecorchard, Darina Schelonka, and Jiří Plocek have shown their potential in the area of material chemistry and have all presuppositions for growing their reputation.

There were 6 main research directions covering developing area of photoactive, low-dimensional, magnetic and thermoelectric materials, and reactive sorbents. We developed a number of synthetic routes for obtaining nanomaterials bearing specific functions and the methods of materials evaluation, established new cooperations, aimed at multifunctional materials and materials for practical applications with an added value thanks to intensive long-term research supported by grant projects of basic research. We focused on new perspective materials used for the fast removal and degradation of extremely toxic chemicals such as civil warfare agents or major environmental pollutants in waters, soil, and air. At the forefront of our interests were nanostructured materials based on transition metal oxides with detoxification ability requiring light (photocatalytic materials) or performing without light (reactive sorbents). We addressed the developing area of hybrid materials, polymer nanofibers, and nanocomposite films with an emphasis on their photophysical properties and potential use in constructing multifunctional platforms with photobactericidal, photovirucidal, and photooxidative properties. Graphene and graphene-like materials with interesting emissive, electrochemical and photocatalytical properties belong to the other group of investigated materials. We described new synthetic methods and achieved facile, reproducible, and scalable synthetic procedures with minimized environmental impact. We used the latest methods of analysis, the majority of which are located in the workplace and are operated by specialist personnel; other special methods were applied in cooperation with other research institutes and universities. The syntheses and properties of some advanced materials were new and the researchers from our Department were first to publish them (functional composites, degradation of chemical warfare agents, hydroxide nanosheets).

Our research topics were (and still are) funded by a number of national and international projects and are conducted with local and international partners from academic or commercial sectors.

1. Photocatalytic materials

The synthesis of photocatalytic materials was an important topic in the period 2010-2014. These materials were almost exclusively based on titanium dioxide (TiO_2), which was modified to improve its performance. The first preparation route, homogeneous hydrolysis, was based on the precipitation of aqueous solutions of metal salts by the addition of urea, which slowly decomposes at elevated temperatures leading to homogeneous precipitation of the metal oxide or hydroxide in the reaction volume. This process was easily scalable. The second procedure, thermal hydrolysis of titanium peroxo-complexes, utilized a readily prepared Ti precursor, which was transformed by refluxing at elevated temperature to TiO_2 nanoparticles. Both processes excluded problematic organometallic precursors, used water as the cheapest and ecological solvent, did not proceed at a temperature higher than 100 °C, and did not demand high pressures or autoclaving.

The introduction of low amounts of doping elements into the crystal lattice of titania can significantly improve the performance of the catalysts by modifying the electron band structure. The homogeneous hydrolysis was successfully applied to produce boron, tungsten, indium, selenium and tellurium, germanium, or gallium-doped titania with good photocatalytic performances predominantly under visible light irradiation. Doping affected the absorption spectra of the samples, particle sizes, morphology, surface area, and porosity which resulted in increased degradation rates of azo dye aqueous solutions. When possible, the ideal concentrations of the dopants were defined and the effects of high or insufficient doping levels were evaluated. Also, the intentionally prepared brookite-rutile photoactive mixtures and the mesoporous structured titania with a good photocatalytic performance prepared in the presence of cationic and anionic surfactants, were examined. High performance nanocomposite photocatalysts were also prepared by homogeneous hydrolysis. Graphene and graphene oxide, prepared by our original procedure, were used to improve the performance of TiO_2 by enhanced charge separation. The $\text{TiO}_2/\text{ZnS}/\text{CdS}$ nanocomposite was tested for azo dye degradation and photocatalytic hydrogen production. Titania nanoparticles were also successfully deposited onto a kaolin substrate or polymer nanofibres.

The method of thermal hydrolysis of peroxo-complexes can be employed for the preparation of TiO_2 catalysts doped by various elements that would not be possible if using the homogeneous hydrolysis method. The salts of the doping elements were dissolved in hydrogen peroxide and added to the reaction solution. By this method, the photocatalysts modified by molybdenum, niobium and tantalum, iodine, tin, and bismuth were prepared. All of the materials showed better catalytic performance. The fabrication of nanocomposites with graphene oxide can be also achieved by this method.

We designed the materials, performed the most of the synthetic work and characterization of the materials. Long-term cooperation has been maintained with the Institute of Plasma Physics of the CAS. The topics were plasma sprayed coatings based on TiO_2 and other materials such as titanates. Iron-doped coatings active under visible light or $\text{Cr}_2\text{O}_3\text{-TiO}_2$ mixtures were also prepared. Our group specialized in the measurement and evaluation of the photocatalytic behavior of these thin layers. We have also common interests with the Department of Engineering at Uppsala University in the characterization of the photocatalytic behavior of our samples. Surface chemical and photochemical properties of yttrium and zirconium co-doped titania prepared by homogeneous hydrolysis and bismuth-doped titania prepared *via* the peroxo-

complexes route were investigated by vibrational and other spectroscopic methods. We also characterized the structures of sorbed gaseous intermediates and their kinetics.

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2. Photofunctional materials

We are interested in delineating the photophysical parameters of certain photosensitizers (PSs) in complex environments and correlating these parameters to their photosensitizing efficacy. Understanding these relationships and, in particular, the interactions between PSs and their chemical environments, could help explain the differences in PS photophysical and photochemical properties of free PS molecules and corresponding materials. Our effort led to the syntheses of new PSs and photofunctional materials. The investigated topics were:

Development of novel PSs.

Synthesis and structure of hybrid materials. The materials studied by our team were composed of a PS, mostly of the porphyrinic type, and a host (inorganic or organic). The distribution of PSs is especially important in the case of porphyrinic molecules because, due to strong π - π interactions, the porphyrin molecules often form aggregates with reduced or no photochemical activity. Hence, *the hosts play an active role in controlling the photophysical and photochemical properties of introduced sensitizers.* The following materials were investigated:

- *Hybrid layered materials* prepared by intercalation of water-soluble porphyrins into layered double hydroxides (LDHs), layered simple hydroxides (Zn^{2+} , Eu^{3+} , Tb^{3+}), and clay minerals. The intercalation provides the arrangement of the guest molecules and eliminates the porphyrin aggregation.
- *Polymer nanofibers* with embedded porphyrins, phthalocyanines, and molybdenum clusters. The proper distribution of the embedded molecules, nanometric diameters of the fibers, and hydrophilicity of the fiber surfaces were found to be fundamental for the designed photofunction.

Properties of PSs. PSs were studied in solutions, dispersions, and embedded in photofunctional materials. Some of the studied PSs have excellent brightness, high yields of singlet oxygen ($^1\text{O}_2$) formation, and emission in the red region. Elementary processes occurring after excitation of PSs were investigated and correlated with the nature of the sensitizer environment. We summarized the structural aspects, absorption spectra, luminescence, and sensitizing properties of the photofunctional materials.

Functionality. Some of the investigated materials act as solid-state sensitizers that produce $^1\text{O}_2$, and as a result, they have bactericidal, virucidal, and photooxidation properties. The results from our research have laid the foundations for possible applications of these materials in the area of photoactive surfaces, catalysts, and oxygen sensors.

The main results were as follows:

Novel PSs. Our research was focused on the development of hexanuclear molybdenum cluster complexes as relevant alternatives to the PSs so far used. Our results showed that varying of the apical ligands allows for tuning of cluster redox and luminescence properties. Our discovery that $[\text{Mo}_6\text{I}_8(\text{CF}_3\text{COO})_6]^{2-}$ has quantum yields of luminescence and $^1\text{O}_2$ close to 1 and 0.85, respectively, made the preparation of cluster-based photofunctional materials possible (e.g., photoactive nanoparticles, nanofibers, nanogels). From our studies follow that the coordination of ligands to the $\{\text{Mo}_6\text{I}_8\}$ cluster core *via* carboxylic functions is a promising approach for obtaining hybrid cluster complexes with designed properties such as bright red emitters, luminescent (nano)particles, energy transfer acting molecules, and excellent $^1\text{O}_2$ producers.

The most of the original results were obtained by our team (it includes design, synthesis, characterization, photophysical and photochemical properties). Some measurements were obtained in cooperation with the Institute of Physics of the CAS (crystallography), J. Heyrovský Institute of Physical Chemistry of the CAS (some photochemical properties, electrochemistry), and University of South Bohemia (femtosecond spectroscopy).

In cooperation with the Department of Syntheses of IIC we investigated a new class of photoactive borane clusters (light-triggered gas release, luminescence, production of $^1\text{O}_2$). We also analyzed photophysical properties of novel azaphthalocyanines and, for the first time, we described intramolecular charge transfer states in this series of PSs, which has unprecedented importance in the design of sensors by the group at the Faculty of Pharmacy in Hradec Králové, Charles University. We also reported on the phototriggered release of oxygen (in the ground or singlet state) from dioxygen complexes.

Concept of photofunctional layered metal hydroxides. We investigated a new class of photofunctional hybrid materials whose photoactivity is based on intercalated porphyrin molecules located in the interlayer space of layered materials. Thus, these materials have properties of both inorganic (carrier, protection, and filler function) and porphyrin (photoactivity function) components. As inorganic components, we utilized LDHs and layered silicates; however, our research also extended to the use of layered metal hydroxide salts, i.e., layered hydroxides with the hydroxide layers composed of sole metal cation (Zn^{2+} , Eu^{3+} , Tb^{3+}). Layered hydroxides were found to act as hosts that allow the active porphyrin molecules to be organized in a two-dimensional and expandable interlayer space and separate porphyrin molecules from the surroundings. Further positive effects of the hydroxide matrix are enhanced thermal and chemical stability and reduction of photobleaching. Intercalation affects photophysical and photochemical properties; however, important features as luminescence and the quenching of the porphyrin triplet states by oxygen remain preserved. The quenching confirms that the porphyrin molecules are accessible to oxygen and can generate $^1\text{O}_2$.

In many cases, singlet oxygen lifetimes were quite short, even shorter than the lifetime of $^1\text{O}_2$ in water ($\sim 3.5 \mu\text{s}$).

In contrast to other researchers in the field, we succeeded in the synthesis of a well-crystalline LDH hybrid with almost perfect stacking of the hydroxide layers. Thus, we were able to analyze, in detail, the structure of the interlayer space: it is filled with nearly parallel porphyrin units that are inclined with respect to the hydroxide layers with an average angle of approximately 14° between the porphyrin plane and the layer normal.

We also performed the systematic experimental and theoretical investigation of the structural arrangements of dodecyl sulfate anions in the interlayer space of layered zinc hydroxide salts and of the structure of zinc hydroxide layers, with a detailed description of the zinc ions' coordination environment. We were first to report on an interstratification phenomenon in layered hydroxides intercalated with aliphatic molecules. Our results provided insight into the great variability of layered hydroxide structures controlled by external stimuli.

Many of the results on delamination, intercalation reactions of molecules, photophysical properties of the hybrids, fabrication of oriented layers were obtained by our team. Some results were new and were published for the first time by our team. To achieve these goals, funded by Czech Science Foundation (K. Lang as a PI) we collaborated with the Université Blaise Pascal, Clermont-Ferrand, France (structure of LDH hybrids; our PhD student was in this laboratory and performed the syntheses and some structural characterizations), Institute of Inorganic Chemistry of the SAV, Slovakia (synthetic layered silicates), Czech Technical University (some synthetic aspects), Charles University (molecular simulations), J. Heyrovský Institute of Physical Chemistry of the CAS (some photophysical aspects).

Composite materials. The ability of intercalated porphyrins to produce cytotoxic singlet oxygen upon irradiation with visible light led to an idea to utilize the nanocontainer and nanofiller aspects of LDHs for the preparation of LDH-porphyrin/polymer composites for bactericidal coatings. Their function can be derived from singlet oxygen produced within the interlayer space of LDHs. We studied polyurethane and poly(butylene succinate) composites. Both X-ray diffraction and transmission electron microscopy measurements indicated that the porphyrin-LDH fillers are well dispersed in the polymer matrices and that the porphyrin molecules remain intercalated within LDH layers. The amount of $^1\text{O}_2$ at the composite surface can be tuned by varying the filler loading and the amount of intercalated porphyrin in the filler. The photostability and photobactericidal properties of polyurethane composite films were studied in order to investigate their applicability as new photodynamic surfaces. In vitro antimicrobial tests showed that the *S. aureus* growth on the surface of the composite films is inhibited under white light irradiation and that the PS is not released from the composite. We also observed a total inhibition of *P. aeruginosa* growth indicating the efficacy against biofilm formation.

We formulated the concept and performed some structural characterization and most of the photophysical experiments.

Bactericidal and virucidal nanofiber materials. This topic is based on our observation published in 2007 that polymeric nanofibers are excellent hosts of photoactive compounds - the photosensitized production of singlet oxygen was accomplished by integrated porphyrin PSs with the nanofibers. There were two strategies leading to such materials: (a) pre-functionalization by mixing PSs with polymer solutions and

using these solutions directly for electrospinning or (b) post-processing, in which the PS is bound to the functionalized surface of the electrospun nanofibers *via* noncovalent or covalent bondings interactions. Polymeric nanofiber materials doped with porphyrins have bactericidal and virucidal surfaces upon visible light irradiation. Considering the industrial scale of the nanofabric production and the fact that bacteria cannot pass through a nanostructured material and are detained on its surface, the porphyrin-doped nanofabrics are prospective materials that would remain sterile while irradiated by visible light.

In our team, we contributed to the design of experiments, post-processing, and to the measurement and evaluation of photophysical and photochemical properties.

Photofunctional metal organic frameworks (MOF). The MOFs are assembled from distorted octahedral oxometalate clusters and these secondary building units are linked together by six distorted porphyrin units. The material has framework-dependent fluorescent properties. The ability of the MOF to produce long-lived $^1\text{O}_2$ motivates the design of novel MOFs with tuned photoresponses and porosity (see our research plans in 2015-2019).

Our team formulated the topic, performed the syntheses, characterization of respective phases, spectral, and most of the luminescence measurements.

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3. Reactive sorbents for chemical warfare agents (CWAs) and environmental pollutant degradations

One of the many ways to take advantage of the unique properties of nanostructured oxide materials is stoichiometric degradation of CWAs, volatile organic compounds (VOC) pollutants, or organophosphorus pesticides on their surfaces. If the size of the individual oxide particles decreases to tens or even individual units of nanometers, an increase in their specific reactivity is observed. The acceleration of the heterogeneous reactions on the surface of the nanocrystals is attributed mainly to an increase in the proportion of highly reactive sites such as edges and corners of crystals and in the number of dislocations and defects of shape. In recent years, we have developed methods suitable for the preparation of metal oxide powders with the tunable control of the primary particle size as well as the size of crystallite agglomerates. The investigation and development of new reactive sorbents has been in the scope of our research for more than 12 years.

Nanostructured metal oxides were prepared by the environmentally friendly method of homogeneous hydrolysis described in Section 1. This method provides products with a high surface area (above $300 \text{ m}^2 \text{ g}^{-1}$), mesoporous structure, and with a substantial number of dislocations, defects, and edges. Furthermore, this “wet” preparation method leads to the abundant occurrence of surface hydroxyl groups which can mediate and considerably affect degradation reactions. The prepared materials were used for degradation of sulfur mustard (yperite) and organophosphorus CWAs, such as soman and agent VX. Among many synthesized and tested sorbents, pure single component oxides, such as mesoporous manganese oxide, or mixed oxides of Ti-Fe, or Fe-Mn were used. Similarly to the photocatalytic materials, doped systems displayed better degradation ability. The introduction of other elements into the crystal structure of the parental oxide produces nonstoichiometric defects, improves mesoporosity, affects the particle size and morphology, and can consequently induce the formation of new active sites. Germanium doped titania exhibited both photocatalytic activity and reactivity towards CWAs. Zirconium showed to be the most promising doping element, affecting the morphology, surface area, and activity of Fe, Al and Zn oxides, or Ti-Fe mixed oxides. Zirconium doped titania functioned as an effective reactive sorbent for yperite contamination on sensitive electronics, such as a printed circuit board.

Recently, our efforts expanded to the use of sorbents in the civil sector. Some of the organophosphorus pesticides have similar structures to those of CWAs. They also pose high toxicity, can be allergenic, genotoxic, and are classified as persistent organic pollutants (POPs). Thus, these pesticides represent a serious threat to the environment. The behavior and degradation of a pesticides surrogate, trimethyl phosphate, on several nanostructured metal surfaces was described. Based on a long-term cooperation with the Faculty of the Environment of the J. E. Purkyně University in Ústí nad Labem (FE) we started exploring the degradation ability of our most perspective materials in detail. CeO_2 , synthesized by the FE group, showed very good degradation activity. We also proposed the mechanism of CeO_2 degradation ability.

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4. Low-dimensional materials

Graphene-based materials. Low dimensional materials have become a hot topic since the discovery of graphene and description of its extraordinary properties in 2003. The remarkable heat and electric conductivity, low weight, strength, and low toxicity of graphene predetermine its use in many areas including electronics, biological engineering, filtration, energy storage, photovoltaics, and materials engineering. However, its preparation in good quality and purity at a large scale is not trivial. Our team developed a relatively easy and low-cost synthesis using ultrasonic waves. We employed a high-intensity ultrasound device in a pressurized water-cooled reactor to

produce graphene flakes from natural or synthetic graphite by exfoliation. We also demonstrated an easy conversion of thus prepared highly hydrophobic graphene to graphene oxide, which can be dispersed in water. This conversion is based on a modification of Hummer's method with radical reduction of aggressive chemicals used in the process. Graphene oxide solutions were then readily available, for example, for the preparation of photocatalytic composites, as mentioned in Sections 1 and 3, or other applications. The stabilization of graphene in various solvents or exploitation of new or improved graphene properties was achieved by surface functionalization. We successfully coupled graphene oxide with carborane to produce a composite which can serve as a precursor for conductive self-assembled monolayers.

Graphene quantum dots (GQDs) are nanometer-sized fragments of graphene with unique optical, electronic, or other properties. Contrary to other inorganic materials (e.g., CdSe QDs), GQDs are non-toxic and relatively easy to prepare. We obtained GQDs dispersions by refluxing sonicated graphene in ethylene glycol or other solvents.

The same method used for graphite exfoliation, high-intensity ultrasound, was used for the preparation of MoS₂, WS₂, BN, and BCN nanosheets. These materials, called inorganic analogues of graphene, have unique properties for future applications. Similarly to graphene, these materials were fragmented to produce quantum dots. We investigated the synthesis of MXenes and sonically exfoliated MoS₂ monolayers having strong luminescence. MXenes were prepared by the exfoliation of the parent MAX phases.

Due to our experience with ultrasonic preparation of graphene, we also investigated other carbon-based nanomaterials. We cooperate with the Institute of Macromolecular chemistry of the CAS on graphene-ionic liquid interactions for the preparation of polymer composites. Recently, we achieved a multi-walled carbon nanotubes "unrolling" in ionic liquids, used as fillers in epoxy-based nanocomposites.

Metal hydroxide nanosheets with special properties. Layered metal hydroxides are materials composed of positively charged metal hydroxide layers separated by intercalated anions and water molecules. The possibility to incorporate a wide variety of anions and the controlled packing of inorganic and organic entities in the same material allow for the tuning of final properties.

We reported the preparation of layered cobalt hydroxide, layered nickel hydroxide, and layered nickel-cobalt hydroxide intercalated with lactate anions, and their spontaneous delamination in water to form corresponding hydroxide nanosheets. These hydroxide nanosheets form stable aqueous dispersions. The hydroxide nanosheets can be restacked to form transparent self-standing films with the original layered structure. The coverage of the surface with side-by-side stacks of nanosheets indicates two-dimensional agglomeration and suggests that these dispersions can be applied to prepare monolayers of nanosheets.

We found out that layered zinc hydroxide intercalated with dodecyl sulfate can be delaminated in butanol to zinc hydroxide nanosheets and solvothermally transformed into ZnO nanosheets flattened along the [001] direction. The procedure is a scalable one-pot reaction and produces ZnO nanosheet dispersions that are stable for over a month. The thicknesses of the prepared nanosheets are 0.6–0.7 nm and correspond to 2 or 3 stacked ZnO tetrahedral layers. Printing ZnO nanosheet dispersions ("ZnO ink") on suitable supports can provide a facile means for fabricating large area transparent films.

The assembled nanosheets form layers with an adjustable thickness and flexibility. We discussed the following functions: (i) *Electrochemically active ultrathin films with reproducible and stable charge-discharge properties in an alkaline electrolyte*. The nickel and cobalt hydroxide nanosheets show promise for use in nanocomposite materials for energy storage applications. (ii) *Photocatalytic activity of transparent ZnO films* –we attributed the high photocatalytic activity of the ZnO nanosheets compared to common morphologies to the fact that their {001} facets are predominantly exposed to the oxidized substrate.

We formulated the concept of delamination and performed syntheses, delaminations, structural characterizations of materials and nanosheets, and coordinated cooperations with external groups in the field of electrochemical and photocatalytical investigations.

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5. Magnetic and thermoelectric materials

We focused on the use of soft chemistry synthetic methods for the preparation of transition metal oxide materials with Fe(III) and Co(II) as main constituents.

Multiferroic hexagonal ferrites. Materials containing a coexistence of at least two ferroic orders continue to draw increasing interest because a magnetic field can tune the electric polarization of the material and an electric field can tune its magnetization. This is exciting because controlling magnetism by electric field can lead to smaller, more energy-efficient devices for magnetic technologies. In this context, we developed preparative procedures for epitaxial hexagonal ferrite thin films of M - and Y - type magnetic phases by means of a chemical solution deposition method using the seeded growth of a pre-crystallized seed layer. We performed chemical, structural, and microstructural characterizations and, based on complex orientation characterization, we developed a model of orientation growth of a bulk layer onto the seed layer.

Layered cobaltates $\text{Ln}(x)\text{CoO}_2$ with rare earths. The main idea to modify p-type thermoelectric material Na_xCoO_2 is to introduce a strong magnetism by insertion of rare earths ions and to stabilize the long-range magnetic ordering. This investigation may lead to new applications in the field of thermoelectric power generation technologies. We performed synthesis, structural, and magnetic characterization of novel rare-earth layered cobaltates $\text{Ln}(x)\text{CoO}_2$.

Multifunctional nanocomposites are materials which combine several functionalities in one material, wherein the individual component's dimensions are in the order of nanometers. We prepared several groups of materials: (i) $\text{CoFe}_2\text{O}_4/\text{CeO}_2$ - magnetic catalysts with a large specific surface. (ii) $\text{CoFe}_2\text{O}_4/\text{Al}_2\text{O}_3$, $\text{CoFe}_2\text{O}_4/\text{TiO}_2$, $\text{CoFe}_2\text{O}_4/\text{ZrO}_2$ - magnetic composites in non-usual high-k dielectric matrixes. New preparative methods were developed for the preparation of last two composites. (iii) Core-shell structures based on CoFe_2O_4 -diamond-silica or titania, combining magnetic and optical properties.

Selected papers

J. Buršík, R. Kužel, et al., *J. Solid State Chem.* 203 (2013) 100-105.

K. Knížek; Z. Jiráček, J. Buršík, et al., *J. Appl. Phys.* 111 (2012) 07D707.

S. Kubickova, J. Plocek, A. Mantlikova, J. Vejpravova, *RSC Adv.*, 4 (2014) 5113-5121.

6. Advanced inorganic materials for practice

One of the reasons why academic research institutes in the Czech Republic were in 2007/2008 transferred into public research institutions, was the legislative intent to offer research institutes the opportunity to better utilize and manage the results of their research activities. In 2010-2014, the team mainly dealt with the syntheses and applications of original inorganic materials in practice. In the area of qualified chemistry we were engaged in (a) technology of inorganic pigments based on natural aluminosilicates with a low content of Fe; (b) synthesis of TiO_2 and ZnO_2 nanosols for thin layers and combined optical materials; (c) development of inorganic matrices based on aluminosilicates matrices for the preparation of safety and environmental friendly materials with a shielding effect to neutron radiations for nuclear power plants, fire extinguishers; d) development of the technology for synthesis of photocatalytically active TiO_2 which functions in the UV and visible spectral regions for application in paints – the company ROKOSPOL a.s. produces the paint under the trade name DetoxColor (www.DetoxColor.cz); e) technology for the production of surface-colored kaolin and metakaolin with oxides of transient metals.

Selected licensed applications:

a) ČLUZ a.s., agreement to patent application PV 2012 -617, assigned 18.6. 2012. Title: New inorganic pigment based on natural aluminosilicates with low content of iron.

b) OPTAGLIO s.r.o., patent CZ 304031, assigned 28.12. 2011. Title: The way of preparation of homogenous nanosol of hydrated zinc peroxide- ZnO_2 with a low content of organic residuum and using of the nanosol and know-how of laboratory preparation of TiO_2 sol and sol modified by polymer additives.

c) Ankaba s.r.o., assigned 19.9. 2014. Title: Preparation of inorganic material destined for shielding of neutron radiation.

3. Research Plan of the team for 2015–2019

Maximum length of 3 pages.

Research Report of the team in the period 2010–2014

Institute	Institute of Inorganic Chemistry of the CAS, v. v. i.
Scientific team	Centre of Instrumental Techniques (CIT)

During the last five years, the members of the „Centre of Instrumental Techniques“ (CIT) participated on scientific studies in collaboration with many Czech and foreign (Slovakia, Spain, India, Ukraine, Russia, France, Japan, Germany, South Africa, etc.) scientific groups. The results were published in 119 publications, according to WOS. The most important results are following:

1. Synthesis and characterization of nanostructured materials for application in photocatalysis and energy conversion.

Materials for application in photocatalysis and energy conversion are among the leading topics in material science. The members of CIT are working together with domestic and international teams (Slovakia, Spain, India) dealing with problems associated with materials used for such purposes, concentrating on the control of particle size and shape during the synthesis, and the effect of nanoparticle aggregation on catalytic activity, etc. The CIT team contributes to these objectives by performing microscopic and crystallographic characterization of particular phases as well as, in some cases, also the synthesis of new materials.

More specifically, the following has been achieved:

Sulphur doped nanoparticles of titanium dioxide were prepared by the reaction of titanium butoxide and thiourea in methanol. X-ray powder diffraction (XRD) and high resolution transmission electron microscopy (HRTEM) were used to investigate the crystallinity of the prepared nanoparticles. Based on X-ray photoelectron spectroscopy measurements, sulphur in these materials is present in the S^{6+} form and substitutes Ti^{4+} in the titania lattice. The photocatalytic activity of these samples was determined by measurements of its influence on the degradation of 4-chlorophenol in aqueous suspensions under ultraviolet and visible irradiation. Electron paramagnetic resonance spectroscopy (EPR) confirmed the generation of $\bullet OH$ radicals from S doped TiO_2 under both visible and UV irradiation. The CIT team carried out the synthesis and characterization of these materials, and the interpretation of collected EPR spectra. Photoactivity measurements were carried out in cooperation with external scientists.

Nanocrystalline $PrFeO_3$ perovskite-type orthoferrite was synthesized at 700 °C by using three different synthetic methods, namely sol–gel, template and combustion method. The synthesized materials were structurally characterized and their photoactivity investigated. In an ethanol–water system, these photocatalysts give hydrogen generation of about 2847 $\mu mol \cdot g^{-1} \cdot h^{-1}$ under visible light irradiation. These materials appear to use a semiconductor-type mechanism for ethanol-assisted visible light photocatalytic water-splitting, and can also be interesting candidates for the development of hetero-junction type photocatalysts. The CIT team carried out the synthesis as well as structural and morphological characterization of the materials. Photoactivity measurements were carried out in cooperation with external scientists.

The phase transition of anatase nanoparticles into TiO_2 -II and rutile phases under grinding was also studied. The addition of ammonium carbamate to the reaction mixture inhibits the phase conversion and the cold welding of particles. The UV-visible absorption

spectrum showed a narrowing of the band gap width after grinding with an ammonium carbamate additive, resulting in a shift of the light absorption towards the visible region. By EPR, the formation of OH• radicals was observed under UV ($\lambda > 300$ nm) and visible ($\lambda > 435$ nm) irradiation. High photocatalytic activity of the ground sample under visible light irradiation was demonstrated by the measurement of the kinetics of the photocatalytic decomposition of 4-chlorophenol. The CIT team carried out structural and morphological characterization of materials as well as photoactivity measurements. The synthesis was carried out in cooperation with external scientists (Spain).

The growth of anatase particles during annealing up to 1000 °C of the dried precipitates prepared by neutralization of TiOSO_4 aqueous solutions with aqueous ammonia at desired pH at temperatures 0–80 °C was studied. The crystallinity of the precipitates depends significantly on the precipitation temperature; the precipitates prepared at low temperatures were tending to amorphousness whereas higher precipitation temperatures lead to more crystalline samples. Heating the sample results in crystallization of the amorphous part; treatment above ~400–500 °C produces a fully crystalline sample. The growth of anatase nanocrystals and the disappearance of a surface amorphous layer were observed at temperatures above 600 °C. All samples were highly photoactive. The fastest 4-chlorophenol decomposition, corresponding to the highest photocatalytic activity, was found for samples annealed at temperatures around 800–850 °C and having ~70nm in diameter. The CIT team carried out all described investigations.

Thick film titania photocatalysts coated on two types of soda glass supports, viz. beads and Rasching rings, were tested in vapour phase photodegradation of toluene, acetone, and ethanol in a batch recirculation photoreactor at 60–70 °C. The films were characterized by SEM and EDX (morphology, elemental composition, mapping). In addition, the effects of water vapour, shape and the packing arrangements of the glass supports on the photodegradation kinetics were examined. The thick TiO_2 films on both supports demonstrated high activity for the photodegradation of toluene, acetone, and ethanol according to first-order kinetics. The efficient photodegradation of higher concentrations of toluene, acetone, and ethanol was attributed to the better availability of active sites on the thick TiO_2 films for adsorption of VOCs, their photodegradation within a 'photoactive zone' constituting the outer surface layer of thick TiO_2 coating, and higher reactor temperature. The SEM and EDX data suggest that migration of sodium ions across the glass/ TiO_2 interface into a 'photoactive zone' of the thick TiO_2 layers did not occur. The Rasching rings support appears to show better efficiency because of their packing in the reactor that allows for better illumination of the catalyst surface. The CIT team carried out structural and morphological characterization of materials.

In addition to the new scientific knowledge attained, these results were also used in practical applications, such as the development of a TiO_2 – SiO_2 based photocatalytic composite coating, and as an air cleaner based on photocatalysis.

Selected papers

Bakardjieva, S. - Subrt, J. - Pulisova, P. - Marikova, M. - Szatmary, L.: Photoactivity of anatase-rutile TiO_2 nanocrystalline mixtures obtained by heat treatment of titanium peroxide gel. Materials Research Society Symposium Proceedings, Roč. 1352, č. (2012), s. 129-134.

Jirkovsky, J. - Lambrecht, M. - Peterka, F. - Subrt, J.: Photo-catalytic composition, useful in e.g. a photo-catalytic paint, varnish, tone support and cement additive, comprises nanoparticles of a photo-catalyst and an aqueous colloidal dispersion of silicon dioxide nanoparticles. CZ201000465-A3, (2011),

Neti, N. R. - Parmar, G. R. - Bakardjieva, S. - Subrt, J.: Thick film titania on glass supports for vapour phase photocatalytic degradation of toluene, acetone, and ethanol. Chemical Engineering Journal, Roč. 163, č. 3 (2010), s. 219-229.

Pulisova, P. - Bohacek, J. - Subrt, J. - Szatmary, L. - Bezdicka, P. - Murafa, N.: Anatase nanoparticles from hydrated titania gels. *Catalysis Today*, Roč. 161, č. 1 (2011), s. 84-90.

Subrt, J. - Criado, J. M. - Szatmary, L. - Dianez, M. J. - Murafa, N. - Perez-Maqueda, L. A. - Brezova, V.: Mechanochemical Synthesis of Visible Light Sensitive Titanium Dioxide Photocatalyst. *International Journal of Photoenergy*, Roč., č. (2011), s. 1-9.

Szatmary, L. - Bakardjieva, S. - Subrt, J. - Bezdicka, P. - Jirkovsky, J. - Bastl, Z. - Brezova, V. - Korenko, M.: Sulphur doped nanoparticles of TiO₂. *Catalysis Today*, Roč. 161, č. 1 (2011), s. 23-28.

Tijare, S. N. - Bakardjieva, S. - Subrt, J. - Joshi, M. V. - Rayalu, S. S. - Hishita, S. - Labhsetwar, Nitin. Synthesis and visible light photocatalytic activity of nanocrystalline PrFeO₃ perovskite for hydrogen generation in ethanol-water system. *Journal of Chemical Sciences*, Roč. 126, č. 2 (2014), s. 517-525.

2. Highly photoactive anatase foams prepared from lyophilized aqueous colloids of peroxo-polytitanic acid.

We have developed an original method for the synthesis of highly photoactive planar nanoparticle aggregates using lyophilisation of gels of peroxo-polytitanic acid and subsequent annealing. In addition to this synthetic work, we also described the structural, morphological and photocatalytic properties of all products. The study was carried out by the members of the CIT group.

The reaction of hydrogen peroxide with suspensions of thoroughly washed precipitates obtained by the neutralization of an aqueous solution of titanyl sulphate with aqueous ammonia, leads to transparent yellow liquids that are a two phase colloidal solution with a water phase and a liquid hydrated peroxo-polytitanic acid component. The freeze drying of this colloidal liquid provides a foamy material consisting of thin foils of peroxo-polytitanic acid containing a small but not negligible amount of chemically bound ammonia. These foams, annealed at temperature above 200 °C, lose water, ammonia and excess oxygen to give a foamy amorphous oxide. At higher temperatures above 280 °C the amorphous material crystallizes to anatase which transforms at temperatures >850 °C to rutile. The size and shape of the initial leaflets forming in the foam are preserved up to 900 °C. Subsequently, a slit-shaped porosity is formed during annealing. We observed that the annealed material is highly photoactive, probably owing to the highly anisotropic shape of anatase aggregates and their perfect crystallinity.

Peroxo-polytitanic acid foams, annealed at temperature above 500 °C, lose volatile components and excess oxygen, providing anatase in the form of thin leaves consisting of intergrown nanocrystalline anatase particles that transform at temperatures above 850 °C to rutile. The size and shape of the initial leaflets forming the foam is preserved up to ~900 °C. We observed that the annealed material is highly photoactive, owing to the highly anisotropic shape of the anatase aggregates and their perfect crystallinity. We observed outstanding photocatalytic activity of these materials as determined by measuring the kinetics of degradation of methylene blue and 4-chlorophenol as well as by measuring the formation of hydroxyl radical by EPR spectroscopy. All three methods demonstrated significantly higher activity in comparison with the commercially available Degussa P25 photocatalyst. Both methods used for photoactivity tests provided similar results; the activity increased with increasing annealing temperature in the order 500 °C < Degussa P25 < 600 °C < 850–950 °C. The •OH radical kinetic measurements by EPR also confirmed the unusually high activity of our materials. In comparison with Degussa P25, the sample annealed at 950 °C showed significantly higher production of •OH radicals.

TG-DTA, emanation thermal analysis, mass spectrometry detection and Fourier transform infrared and XRD were used to characterize the thermal behaviour of titanium

dioxide photocatalyst precursors prepared by precipitation at various conditions from peroxotitanic acid sols. HRTEM was used to characterize the surface microstructure. The sols contained TiO₂ anatase particles of approximately 10 nm in diameter. During heating of the air-dried samples, their chemical degradation took place producing anatase. At higher temperatures, the crystallization of anatase and the formation of a rutile phase was observed. To test the photocatalytic activity of the samples, the decomposition of 4-chlorophenol under ultraviolet and visible irradiation was monitored. We found that the photocatalytic activities of the samples are comparable to the Degussa P25 photocatalyst reference material.

Selected papers

Plizingrova, Eva - Volfova, Lenka - Svora, Petr - Labhsetwar, Nitin K. - Klementova, Mariana - Szatmary, Lorant - Subrt, Jan. Highly photoactive anatase foams prepared from lyophilized aqueous colloids of peroxo-polytitanic acid. Catalysis Today, Roč. 240, č. (2015), s. 107-113.

Pulisova, P. - Bohacek, J. - Subrt, J. - Szatmary, L. - Bezdicka, P. - Vecernikova, E. - Balek, V.: Thermal behaviour of titanium dioxide nanoparticles prepared by precipitation from aqueous solutions. Journal of Thermal Analysis and Calorimetry, Roč. 101, č. 2 (2010), s. 607-613.

Subrt, J. - Pulisova, P. - Bohacek, J. - Bezdicka, P. - Plizingrova, E. - Volfova, L. - Kupcik, J.: Highly photoactive 2D titanium dioxide nanostructures prepared from lyophilized aqueous colloids of peroxo-polytitanic acid. Materials Research Bulletin, Roč. 49, č. (2014), s. 405-412.

3. Corium preparation and properties.

The rigorous understanding of the nature of molten nuclear fuel – coolant interactions continues to be an important issue in safe nuclear energy. The members of CIT participate in an international team (Czech Republic, Russia, France) that deal with problems associated with severe nuclear accidents, the formation and properties of corium including characterization of particular phases present, the reaction of corium melts with concrete, etc. The CIT team performed microscopic and crystallographic characterizations of particular phases as well as emissions formed during formation of corium and interactions of corium melts with materials used in the construction of reactors. The members of CIT team also presented these results in several publications (S. Bakardjieva, V.Tyrpekl).

Following results were achieved:

The behaviour of melts, and the phase composition of crystallization products of six compositions in the uranium oxide–zirconium oxide–iron oxide system in air, have been investigated. It was revealed that crystallized samples containing 20–50 wt % uranium oxide and 25–80 wt. % iron oxide (the rest is zirconium oxide) consist of five crystalline phases and involve two types of eutectic structures. The possible factors responsible for this phenomenon have been considered.

The hydrogen release due to the chemical reaction of nuclear fuel and coolant during the molten fuel–coolant interaction and its impact on the steam explosion efficiency was described. The samples of debris from several fuel–coolant interaction tests have been characterized by solid-state analytical techniques. It was shown that the nonradioactive melts produce negligible amounts of hydrogen up to 3.6 g per kg of the melt. It was found that UO₂–ZrO₂ melt solidifies during fuel–coolant interaction into the face-centred (Fm3m) crystal cell forming a U_{1-x}Zr_xO_{2+y} solid solution. The oxygen over-stoichiometry of the solid solution is the evidence of fuel–coolant interaction and the release of hydrogen. A method combining chemical analysis by energy dispersive X-ray spectrometry (SEM/EDS) and XRD allowed the determination of the oxygen over-stoichiometry. Therefore, it has been indirectly estimated

how much hydrogen was formed during the chemical reaction between hot corium and water. It has been shown that up to 4.7 g of H₂ per kg of delivered corium melt can be formed by the reaction stoichiometric or suboxidized UO₂-ZrO₂ melts with water. The hydrogen formation during fuel-coolant interaction is primarily linked to the melt composition and secondary to the size of the fragmented melt droplets.

Selected papers

Bakardjieva, S. - Barrachin, M. - Bechta, S. - Bezdicka, P. - Bottomley, D. - Brissonneau, L. - Cheynet, B. - Dugne, O. - Fischer, E. - Fischer, M. - Gusarov, V. - Journeau, C. - Khabensky, V. - Kiselova, M. - Manara, D. - Piluso, P. - Sheindlin, M. - Tyrpekl, V. - Wiss, T.: Quality improvements of thermodynamic data applied to corium interactions for severe accident modelling in SARNET2. Annals of Nuclear Energy, Roč. 74, č. (2014), s. 110-124.

Petrov, Y. B. - Udalov, Y. P. - Subrt, J. - Bakardjieva, S. - Sazavsky, P. - Kiselova, M. - Selucky, P. - Bezdicka, P. - Journeau, C. - Piluso, P.: Experimental investigation and thermodynamic simulation of the uranium oxide-zirconium oxide-iron oxide system in air. Glass Physics and Chemistry, Roč. 37, č. 2 (2011), s. 212-229.

Tyrpekl, V. - Piluso, P. - Bakardjieva, S. - Dugne, O.: Material effect in the nuclear fuel - Coolant interaction: Analyses of prototypic melt fragmentation and solidification in the KROTOS facility. International Meeting on Severe Accident Assessment and Management 2012: Lessons Learned from Fukushima Dai-ichi, Roč., č. (2012), s. 130-135.

Tyrpekl, V. - Piluso, P. - Bakardjieva, S. - Dugne, O.: Material effect in the nuclear fuel-coolant interaction: Analyses of prototypic melt fragmentation and solidification in the KROTOS facility. Nuclear Technology, Roč. 186, č. 2 (2014), s. 229-240.

Tyrpekl, V. - Piluso, P. - Bakardjieva, S. - Nižňanský, D. - Rehspringer, J. L. - Bezdička, P. - Dugne, O.: Prototypic corium oxidation and hydrogen release during the Fuel-Coolant Interaction. Annals of Nuclear Energy, Roč. 75, č. (2014), s. 210-218.

Application of Mössbauer spectroscopy in characterization of nanostructured magnetic materials.

Mössbauer spectroscopy was used for characterization of various oxidic and metallic materials. In addition to Mössbauer spectra measurement and interpretation, the CIT team ensured thermoanalytical, microscopic and crystallographic characterization of particular phases.

The most important results achieved:

Synthesis of magnetic ϵ -Fe₂O₃ nanoparticles embedded in amorphous SiO₂ was performed. The structure and properties of the final product have been found to depend strongly on the initial conditions of preparation. Mossbauer spectroscopy analysis of the samples was complemented by XRD, magnetic measurements, and HRTEM. Thermal behaviour of highly crystalline ϵ -Fe₂O₃ nanoparticles of different apparent crystallite sizes was characterized using thermogravimetry, differential thermal analysis, and analysis of evolved gas by mass spectrometry. The phase composition of the samples was monitored *ex situ* by XRD. The results show that the thermal stability of this metastable iron oxide polymorph decreases with increasing particle size. For the particle diameter of 19 nm, the transformation temperature was equal to 794 °C, whereas for 28 nm only 755 °C. The surface of the nanoparticles contained adsorbed water and CO₂. The elimination of these species proceeds

in two steps: water is removed at temperatures below 200 °C and CO₂ in a temperature range between 200 and 450 °C.

The nanocrystallization kinetics of Fe₉₀Zr₇B₃ was investigated by *in situ* nuclear forward scattering of synchrotron radiation upon isothermal annealing. The nucleation and growth processes are accessed separately for the nanograins, their interfaces, and the residual amorphous matrix by monitoring the time evolution of the corresponding hyperfine parameters. This approach discloses the structural transformations taking place in this class of technologically important materials. In nanocrystalline Fe₉₀Zr₇B₃, hyperfine fields belonging to the amorphous residual matrix are distinguished from those of bcc-Fe nanograins by nuclear magnetic resonance spectroscopy on ⁵⁷Fe nuclei. With this technique, the nanograins located in magnetic domains can be distinguished from those positioned in domain walls. Structural features of core and surface regions of both types of nanograins are described. The presence of small (similar to 0.2%) inclusions of Zr was identified in the core of nanograins.

We have observed the temperature-dependent rotation of the uniaxial easy axis of magnetization and introduced the phenomenon of the superspin reorientation transition (SSRT) for the nanogranular thin films and multilayers. The effect is demonstrated on the nanogranular SiO-M_x-Si (1 1 1) multilayers, where M is the metal (Co, Fe or CoFe₂) of the nominal thickness $x = 3, 5$ and 10 nm, respectively. The morphology and layer thickness have been examined using TEM, X-ray reflectivity measurements and atomic force microscopy. Magnetic property measurements demonstrated that the orientation of the uniaxial in-plane easy axis of magnetization given by the film shape anisotropy was thickness-independent at temperatures above 200 K. Below 50 K, the film shape anisotropy has been overcome and the uniaxial easy axis was rotated into different directions for each sample series, forming angles from 40 up to 150° with respect to the film plane. Such an effect of the low temperature magnetization rotation has been attributed to the specific arrangement of the nanoparticles in the individual layers and has been assigned to the SSRT phenomena.

The magnetic properties of Mn_{0.5}Co_{0.5}Fe₂O₄ and Mn_{0.1}Mg_{0.2}Co_{0.7}Fe₂O₄ nanoferrites were studied. The compounds were synthesized by a glycol-thermal method with average particle sizes of about 13 nm and 8 nm, respectively. The Mössbauer measurements were performed at 300 K. The distribution of cations between tetrahedral (A) and octahedral (B) sites was investigated. The Mössbauer spectra indicate ferrimagnetic behaviour of the compound. Field cooled (FC) and zero field cooled magnetizations were performed by a superconducting quantum interference device magnetometer in the region of 4 to 380 K. The variation of the magnetizations with the applied fields up to 50 kOe was recorded at isothermal temperatures 4, 50, 100, 200 and 300 K. An increase in FC magnetization is observed with increasing applied field. This is explained based on superparamagnetic behaviour of the particles.

Selected papers

Abdallah, H. M. I. - Msomi, J. Z. - Moyo, T. - Lancok, A.: Mossbauer and Magnetic Studies of Co_{0.5}Mn_{0.5}Fe₂O₄ and Mn_{0.1}Mg_{0.2}Co_{0.7}Fe₂O₄ Nanoferrites. *Journal of Superconductivity and Novel Magnetism*, Roč. 25, č. 8 (2012), s. 2619-2623.

Bittova, Barbara Pacakova - Lancok, Jan - Klementova, Mariana - Vejpravova, Jana. Temperature dependent rotation of the uniaxial easy axis of magnetization in granular SiO₂-(CoFe/CoFe₂)-Si(111) multilayers. *Applied Surface Science*, Roč. 289, č. (2014), s. 257-265.

Lancok, Adriana - Miglierini, Marcel - Kohout, Jaroslav. Fe-57 Mossbauer spectroscopy of synthesized ε-Fe₂O₃ nanoparticles. *Physics of Metals and Metallography*, Roč. 109, č. 5 (2010), s. 524-533.

Miglierini, Marcel - Lancok, Adriana - Kohout, Jaroslav. Hyperfine fields in nanocrystalline Fe-Zr-B probed by Fe-57 nuclear magnetic resonance spectroscopy. *Applied Physics Letters*, Roč. 96, č. 21 (2010), s.

Msomi, J. Z. - Abdallah, H. M. I. - Moyo, T. - Lancok, A.: *Structural and magnetic properties of $Mn_xCo_{1-x}Fe_2O_4$ ferrite nanoparticles*. *Journal of Magnetism and Magnetic Materials*, Roč. 323, č. 5 (2011), s. 471-474.

4. Treatment of wastes.

Acid mine drainage and acid rock drainage are both strongly acidic waste waters rich in dissolved metals formed through complex extraction processes from pyrite and other sulphide minerals, such as pyrrholite, marcasite, chalkosite, covellite, arsenopyrite, chalcopyrite, etc. in the presence of both oxygen and water and as well as in the presence of chemolithotrophic bacteria and Archaea. These waste waters represent a significant danger to the environment. We have pioneered the use of a urea precipitation method for the treatment of these wastes. The method leads to nanocrystalline metal oxides which can be either safely deposited or used as sorbents. In addition, the synthesis of iron oxide - silica composite from acid-treated vermiculite was developed. The CIT team suggested use of the urea precipitation method for the treatment of waste waters and carried out microscopic and crystallographic characterization of particular phases.

The following results were achieved:

We found that AMD waters, containing sulphates of Fe^{+3} and Al^{+3} as dominant components, can be treated by homogenous thermal hydrolysis with urea. We identified four main phases in the hydrolysis products, namely: goethite, schwertmannite, ferrihydrite and jarosite. No crystalline phases of aluminium were detected. Depending on the precipitation conditions, the prepared samples consist of spherical aggregates of nanocrystals of various modifications of hydrated iron oxides. The specific surface area results show that with an increasing content of Al^{3+} , the specific surface area in the final product decreases. The results reveal that by using the homogenous hydrolysis of acid mine drainage with urea, it is possible to prepare easily filterable relatively pure oxide precipitates with a high degree of separation of Fe and Al.

TG-DTA, mass spectroscopy detections and XRD were used to characterize the thermal behaviour of iron precipitates from acid mine drainage prepared by precipitation with urea and natural iron precipitates sampled from the sludge bed. HRTEM and scanning electron microscopy (SEM) techniques were used to characterize the surface microstructure and shape of the synthesized and sampled iron precipitates. The SEM micrographs of the iron precipitates (natural and precipitated with urea) show that the samples had formed into agglomerates, probably due to attractive forces of quite large surface area. During heating of the all samples up to 200 °C, physically adsorbed water was removed. On further heating in the range from 250 to 350 °C in natural iron precipitates, the less stable forms (goethite, ferrihydrite and schwertmannite) transform to more stable forms like hematite. In case of synthetic samples, the transformation runs in two steps: first in the range from 250 to 350 °C, and second in the range from 600 to 750 °C.

We examined the annealing effect on the material obtained after acid treatment of ground vermiculite composed of amorphous silica and β -FeOOH. The XRD patterns of the starting sample, measured at temperatures from 30 to 1200 °C, showed that the crystalline phase was present up to a temperature of 300 °C, after which the sample became practically amorphous. At 850 °C the sample showed the first signs of a crystalline phase, which became fully developed at 1050 °C. The XRD, HRTEM and Mossbauer spectroscopy showed that after treatment at 1050 °C an emergence of a crystalline phase, consisting of quartz, cristobalite, α - Fe_2O_3 and ϵ - Fe_2O_3 . This effect showed that well-crystallized iron oxide nanoparticles embedded into the silica matrix are usually formed at relative high temperatures ~1000 °C in contrast to silica-free material. The element mapping of one particle of the composite obtained by annealing at the highest temperature showed well-separated Fe_2O_3 and SiO_2 particles. The

impurities of Al and Mg (from the original vermiculite) accompanied the silica components and TiO_2 associated with Fe_2O_3 grains was also detected.

Selected papers

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Michalkova, Eva - Schwarz, Marian - Pulisova, Petra - Masa, Branislav - Sudovsky, Peter. Metals Recovery from Acid Mine Drainage and Possibilities for their Utilization. Polish Journal of Environmental Studies, Roč. 22, č. 4 (2013), s. 1111-1118.

Perez-Rodriguez, J. L. - Maqueda, C. - Murafa, N. - Subrt, J. - Balek, V. - Pulisova, P. - Lancok, A.: Study of ground and unground leached vermiculite II. Thermal behaviour of ground acid-treated vermiculite. Applied Clay Science, Roč. 51, č. 3 (2011), s. 274-282.

Pulisova, P. - Masa, B. - Michalkova, E. - Vecernikova, E. - Marikova, M. - Bezdicka, P. - Murafa, N. - Subrt, J.: Thermal behaviour of natural and synthetic iron precipitates from mine drainage. Journal of Thermal Analysis and Calorimetry, Roč. 116, č. 2 (2014), s. 625-632.

Subrt, J. - Michalkova, E. - Bohacek, J. - Lukac, J. - Ganovska, Z. - Masa, B.: Uniform particles formed by hydrolysis of acid mine drainage with urea. Hydrometallurgy, Roč. 106, č. 1-2 (2011), s. 12-18.

3. Research Plan of the team for 2015–2019

Maximum length of 3 pages.

Research Report of the team in the period 2010–2014

Institute	Institute of Inorganic Chemistry of the CAS, v.v.i.
Scientific team	Laboratory of Environmental Geochemistry Analysis

Pollution chemostratigraphy in floodplains – the first case studies, novel methodologies, holistic approach

A series of case studies on Czech rivers (the Morava, Jizera and Ploučnice) has led to the development of a methodology for the sampling of sediment, its analysis (laboratory X-ray fluorescence spectroscopy, element analysis, cation exchange capacity determination), routines for selection of representative samples for external analyses (gammasspectrometric dating, ICP-MS element analysis, granulometry), data processing (identification of pristine sediments, optimal choice of geochemical background functions, local enrichment factors respecting grain-size affects and post-depositional migrations of pollutants), implementation methods of applied sedimentology, geographical information systems (GIS) and fluvial geomorphology. This broadly multidisciplinary approach is indispensable for the correct interpretation of element compositions (including risk elements) with respect to the internal structure of the floodplain architecture. The outputs of these studies were robust interpretations of floodplain sediments in a historical context of past fluvial development and pollution history. The methodology we developed enables the studying of floodplains that are considered weakly polluted (enhancement of risk element concentrations twice to three times above the local background). Recently, we have also implemented geophysical tools (electrical resistivity tomography, ERT) for deeper understanding of floodplain architecture. The most relevant results were:

- Determination of the mean aggradation rate of the Morava River floodplain at its lower reach, resulting in the finding of the surprisingly weak influence of the Medieval and modern agricultural practices, contrarily to what has been found for numerous smaller European river systems under different geographical and geological settings; pollution chemostratigraphy was indispensable as a dating tool.
- Demonstration of how geophysical and GIS tools help in the recognising of, and distinction between, different sedimentary environments of sediments (facies, former channel sediments versus overbank fines), which have a principal influence on the extent of pollution (the case study of the Jizera River). These principles are neglected in a vast majority of pollution studies published in environmental geochemistry and chemical analysis domains, that thus fail to reliably distinguish natural and anthropogenic contributions to risk element concentrations in sediments of variable lithology (grain size, the major part of composition variability of fluvial sediments).
- Identification of local pollution sources in the Ploučnice River system, in particular severe pollution by uranium mining in the Stráž p.R. area by underground chemical leaching; publication of the first evaluation of the impact of the mining on the floodplain sediments (the main risk elements ^{226}Ra , U and Zn) in the form of peer reviewed papers, implementation of modern approaches of applied fluvial sedimentology and environmental geochemistry.

The studies were started with the support of the Grant Agency of the AS CR (IAAX00130801, 2008-2011, J. Kadlec was PI), then Ministry of Education, Youth and Sports (December 2011-November 2014) and currently by the Czech Science Foundation (15-00340S, 2015-2017, T. Matys Grygar is PI). T. Matys Grygar is a leading researcher of this topic. Collaborations with research teams of J.E. Purkyně University in Ústí nad Labem and Palacký University in Olomouc have provided detailed GIS and geophysical services. Collaboration with Universities is essential as it allowed the involvement of a number of students.

Main publication outputs:

Grygar et al., 2010, CATENA 80, 106-121

Matys Grygar et al., 2011, CATENA 86, 192-207

Matys Grygar et al., 2012, Water Air & Soil Pollution 223, 739-753
Majerová et al., 2013, Water Air & Soil Pollution 224, art. No. 1688
Matys Grygar et al., 2013, Science of the Total Environment 452, 233-245
Matys Grygar et al., 2014, Applied Geochemistry 48, 1-15

Stratigraphy of the Miocene Most Basin fill

The strata of fine sediments, several hundred metres thick, mostly of lacustrine origin, were deposited during the latest Early Miocene. Their study using the conventional tools of sedimentology had been hindered because of their monotonous nature and lack of macrofossils. The dating was uncertain within a margin of error of several Ma (million years), whereas the absolute age is about 17 Ma. The only way to make progress in their study was to apply chemostratigraphy, cyclostratigraphy and magnetostratigraphy, i.e., the tools applied to such strata in the state-of-the-art analyses of the Cenozoic or younger sedimentary series of a sufficient length. Our approach was based on the analysis of element variability within each core (3-5 samples *per* m in 100-200 m long drill cores) and the correlation of depth profiles of different drill cores. We succeeded in the improvement of the local stratigraphy of the Most Basin fill, identified orbital cycles (Milankovitch cycles denoted P, O and short and long E) and dated the sediment (the basin wide lake with the total area >1000 km² existed in the late Burdigalian in 17.4-16.6 Ma). Orbitally driven changes in element composition clearly showed that the Most Basin fill recorded regional climate change just before the onset of the most important climate warming of the Neogene – the Miocene Climatic Optimum. The identification of geochemical/mineralogical changes and evolution of paleoflora allowed, for the first time, for the well-supported correlation of the evolution of the Most Basin with the Tertiary basins in North Germany, which were connected with the Most Basin by a joint trunk river from the late Oligocene to the Early Miocene.

The work was performed within the framework of a long-standing collaboration with the North Bohemian Mines, the largest coal-mining company in the Czech Republic, and a 3-year project of the Czech Science Foundation (P210/11/1357, 2011-2014, T. Matys Grygar was its PI). T. Matys Grygar has been the leading researcher, K. Mach (the main geologist of the North Bohemian Mines) was the most important collaborator.

Publication outputs:

Matys Grygar and Mach, 2013, Bulletin of Geosciences 88, 557-571
Matys Grygar et al., 2014, Geological Magazine 151, 1013-1033
Mach et al., 2014, Neues Jahrbuch für Geologie und Paläontologie-Abhandlungen 272, 13-45

Successful application of proxy analyses in sedimentary research

Element analyses and determination of the cation exchange capacity of the whole-rock sediments are two efficient tools that enable the stratigraphic correlation of sedimentary profiles. Element analyses can produce detailed depth profiles of element concentrations, or ratio of certain elements, which reflect past environmental conditions such as weathering intensity, hydrology regime in aeolian, fluvial, lacustrine and marine sedimentary domains. We have performed numerous analyses requested by principal investigators from other research institutions (GeoForschungsZentrum Potsdam, Germany, faculties of science of the Charles University in Prague and universities in Olomouc and Brno). The main funding was given by the Czech Science Foundation (P210/11/1891, 2011-2014, J. Kalvoda, Masaryk University, Brno was PI). Since 2014 similar works have been performed in the frame of CNC project by National Science Foundation (J. Michael Daniels, Denver University is PI in this project).

Main publication outputs:

Oberhänsli et al., 2011, Global and Planetary Change 76, 95-104
Bábek et al., 2011, Quaternary Science Reviews 30, 967-979
Lisá et al., 2014, Quaternary International 351, 25-37
Kumpan et al., 2014, Sedimentary Geology 311, 43-59

3. Research Plan of the team for 2015–2019

Maximum length of 3 pages.

Research Report of the team in the period 2010–2014

Institute	Institute of Inorganic Chemistry of the CAS, v. v. i.
Scientific team	Academic Materials Research Laboratory of Painted Artworks (ALMA)

Research of the team within a joint workplace with the Academy of Fine Arts in Prague (ALMA)

Academic Materials Research Laboratory of Painted Artworks (ALMA) is a joint scientific laboratory of the Institute (IIC) and the Academy of Fine Arts in Prague (AFA Prague) established by the Contract of Association in 2004. The professional structure of the joint team to 31st December 2014 was as follows: 3 scientists (one of them on the maternity leave) and 1 PhD student at IIC (defended 25th February, 2015), and 1 scientist, 1 technician, 1 PhD student and 2 conservators/restorers at the AFA Prague. The research in ALMA covers the interdisciplinary fields of conservation science, cultural heritage science and technical art history. Measured by the number of published scientific papers, impact factors and citations, ALMA can be considered as a national leader in the above given fields. Since 2011, ALMA has become an associate in the EU-funded international CHARISMA network focused on the development of **Cultural Heritage Advanced Research Infrastructures** and the promotion of **Synergies for a Multidisciplinary Approach** to conservation/restoration (programme terminated in 2013). Within the evaluated period, the research activities of the joint workplace were supported by one international project with Jagiellonian University in Krakow (funded by Czech Academy of Sciences) covering the period of 2009-2011, two projects of basic research (funded by Czech Science Foundation) covering the period of 2012-2016 and one project of applied research (funded by Czech Ministry of Culture) covering the period of 2012-2015.

The main focus of the team at IIC lies in the testing and implementation of non-invasive and non-destructive micro-analytical techniques and methodologies in the field of materials research of paintings. These methodologies, closely related to interdisciplinary research of historical painting techniques performed in AFA Prague, help in the evaluation of works of art in terms of their originality, age and provenance. Consequently, experimental research of painting pigments is focused not only on the materials' properties, but also on the historical methods of preparation and processes of degradation in the colour layer.

Based on the above given characteristics, the research outputs within the evaluated period of 2010-2014 can be categorised into results of (i) methodological studies, (ii) materials' studies and (iii) interdisciplinary (case) studies.

Methodological research

Within the methodological research, the main effort in the year 2010 was put on the finishing and summarisation of the results of a long-term evaluation of laboratory powder X-ray micro-diffraction (micro-XRD) in the fields of cultural heritage and forensic science. Although the micro-XRD is a very effective non-destructive technique for direct phase analysis of samples smaller than 1 mm containing crystalline constituents, it is much less frequently applied for the artworks' analysis than, e.g., Raman micro-spectroscopy (micro-Raman). When analysing heterogeneous fragments of paints or their polished cross-sections, it complements optical and electron microscopy with elemental micro-analysis, especially in cases when complicated mixtures containing phases with similar chemical composition are present. However, modification of X-ray diffraction to micro-scale together with its application on very heterogeneous micro-samples (as e.g. fragments of paints) leads to deviations from the standard procedure. Our team at IIC has evaluated basic limits of micro-XRD equipped with a mono-capillary with an exit diameter of 0.1 mm, for example the size of irradiated area, appropriate grain size, and detection limits allowing identification of given phases. We have tested the reliability and accuracy of quantitative phase analysis based on micro-XRD data in comparison with conventional XRD (reflection and transmission), demonstrated the wide use of micro-XRD for investigation of various types of micro-samples (contact traces, powder traps, colour layers) and showed the way to enhance data quality by proper choice of experimental geometry and conditions. The basic methodological research of micro-XRD with the key results published in *Anal Bioanal Chem* [1] has been followed by several comparative

analytical studies combining either micro-XRD with synchrotron-based micro-XRD (SR-XRD) or micro-XRD with micro-Raman. In both these cases the field of interest was the microanalysis of clay minerals and clay-based pigments, which have been systematically investigated by our team at IIC for many years (see materials' research below).

The comparison between laboratory micro-XRD and SR-XRD was performed through analysing a preparatory layer of the Gothic wall painting containing kaolinite. We showed that both techniques provided comparable information. However, the data obtained from SR-XRD, had better statistics, which was reflected in a smoother XRD pattern with sharper diffraction lines. XRD patterns from both techniques were used to determine kaolinite crystallinity indices, Hinckley and AGFI indices, which represented entirely novel information enabling the determination of the source locality of the material used for the painting. In a broader context, knowledge of the kaolinite crystal structure can contribute to the evaluation of the origin of other earthy (clay-based) pigments, because kaolinite is not only a component of kaolin (white earth), but it is also a frequent clay mineral in other natural pigments, such as ochres and/or red earths. [2]

The distinguishing of clay structures as a valuable tool for provenance studies of earth pigments still remains completely unexploited (particularly in the field of analysis of historical paintings) due to two reasons – (i) an almost absence of interdisciplinary approach in the analysis of fine art and (ii) unsuitable methodology of clay microanalysis that preferentially employs micro-Raman for the identification of mineral pigments in paints. We have found out that the detection of different clay minerals by micro-Raman is almost prevented if iron oxides (such as hematite) and/or titanium oxides (such as anatase) are admixed in the sample due to the high sensitivity of Raman spectroscopy to these types of minerals. Both of them represent common admixtures in natural earths. Therefore, the micro-Raman analysis of clay-based pigments of paintings should always be combined with micro-XRD measurements. Without taking into account the fact that only high Raman scatterers are preferably detected in natural clays, the interpretations of Raman spectra may easily lead to false conclusions (very common in many published case studies). [3]

In all the above-mentioned methodological studies, our IIC team played a key role in the whole investigation including both experimental and interpretational parts. Interpretation in the broader context of painting technique and technology has been complemented by AFA within the joint ALMA workplace. Synchrotron-based analyses were performed by Helmholtz-Zentrum Berlin, Germany, and Raman spectroscopy was carried out in cooperation with the Faculty of Science, Charles University in Prague. The corresponding author of the paper in JRS [3] is a Ph.D. candidate of Masaryk University in Brno who is supervised by our team.

Besides the non-destructive micro-analytical techniques performed on fragments of paints, the ALMA laboratory has been developing and testing the methodologies of non-invasive survey of works of art with the aim to combine the collection of visual and materials' information *in situ* with no need of transportation of the painting or its conservation and collection of samples. The non-invasive survey of paintings is a booming strategy in the last decades in the international cultural heritage research. ALMA has been involved very early - since 2005, when the team has organised a transnational access project with the Italian mobile laboratory MOLAB focused on non-invasive investigation of paintings of Viennese school of the 18th to the 19th century. It was one of the very first projects ever within a scope of the EU-ARTECH European programme focused on implementation of portable analytical methods on the investigation of cultural heritage and, of course, the first use of mobile instruments in the analysis of paintings in the Czech Republic. Within the evaluated period, the research in ALMA covered two fields.

The first one was devoted to a very detailed testing of hand-held analytical instruments (such as portable XRF, portable FTIR, and portable Raman) in comparison with laboratory techniques. This research is still running and the results are expected to be published soon in 2015. The first paper prepared for publication in the Journal of Raman Spectroscopy describes the analytical limits of use of different excitation lasers and compares the laboratory and portable Raman spectroscopy in the investigation of modern paints (František Kupka, Edvard Munch). Simultaneously, portable XRF has been applied in numerous case studies (see below).

The second field included testing and implementation of newly-developed pixel detectors for transmission X-ray radiography involving the collection of high-resolution and energy-resolved (materials-sensitive) X-ray images of painted areas, as well as X-ray induced fluorescence imaging (with no need of scanning). The conventional approach uses all energies from the source spectrum for the creation of an image, whereas the energy sensitive alternative creates images in given energy intervals, which enables the identification and discrimination of materials. Within a long-term collaboration, the

detectors are developed in the Institute of Experimental and Applied Physics of the Czech Technical University (IEAP), which is being part of the international consortium MEDIPIX, and tested in ALMA for the given purpose. The contribution of our team at IIC to already published results lies in the materials' and technological comparison of the data collected by novel and conventional approaches, respectively. [4, 5]

Materials research

The interpretation of materials' data obtained either by conventional or novel analytical approaches needs to be based on the contextual knowledge of historical painting technology and materials available that includes also the knowledge of their sources, technology of making as well as knowledge of their chemical degradation in painting layers. The contribution of the team at IIC to the systematically developed expertise of our joint workplace ALMA lies particularly in the experimental studies focused on the description of materials' properties, specific signs of their origin and pathways of degradation caused by internal or external agents, respectively. In numerous cases, the broader concept of our materials' research interrelates with other branches of materials' sciences and inorganic chemistry. With the aim to demonstrate its wider scope exceeding the cultural heritage application, we have selected two papers published in Applied Clay Science [6] and Crystal Research and Technology [7] to be peer-reviewed within our top five papers.

In the first paper [6], our team at IIC has performed the high-temperature X-ray powder diffraction (HT-XRD) experiments to describe in detail the thermal behaviour of expandable clay structures containing different interlayer ions. The changes of interplanar distances caused by either temperature or moisture alterations may in fact affect the mechanical stability of painting layers. Nevertheless, it turned out that the method can be used to characterise and differentiate various types of chemically modified (positively-charged) clays and (negatively charged) layered double hydroxides and to describe the thermal stability of their intercalates with, e.g., porphyrin. Within this research, other teams at the IIC were closely collaborating with our team, particularly in the fields of preparation and characterisation of intercalates with porphyrin, comparative tests with DTA and application outputs of the results. Preparation and characterisation of layered double hydroxides have been performed in cooperation with the Institute of Chemical Technology in Prague.

In the second paper [7], we have demonstrated an improved pathway of the synthesis of basic copper acetate followed by advanced characterisation of its structure. This research was originally motivated by the fact that crystal structures of numerous artificially prepared copper acetate-based historical pigments (the so-called "verdigris") have not been – so far – described and, therefore, they cannot be properly identified in the painting's micro-samples. This is the first time a single-crystal structure of basic copper acetate has been determined, thus providing the crucial information for the correct interpretation of the observed properties – with applications not only in the pigments and corrosion products, but also in hybrid multifunctional materials for tailor-made applications. The crystallographic data of the structure reported in this paper have been deposited in the Cambridge Crystallographic Centre, CCDC No. 818186. In our team at IIC, we have performed the synthesis, collected powder XRD, high-temperature XRD, DTA and FTIR data and summarised all the interpretations. Single-crystal measurements and interpretations have been carried out in cooperation with the Institute of Physics of the CAS, v.v.i., and crystallographic calculations also in cooperation with Jagiellonian University in Krakow within the frame of an international project.

In the subsequent step of investigation, materials' description of copper acetates has been followed by an extensive study focused on indisputable and non-destructive distinguishing of mineral-type and verdigris-type copper-based pigments in heterogeneous and minute samples of paint layers, which also included an experimental study of the loss of crystallinity of verdigris-type pigments in proteinaceous binding media and the effect of lead white and lead tin yellow as highly absorbing matrix on verdigris identification – both performed by our team at IIC. The new analytical protocol combining micro-FTIR and micro-XRD has been tested on more than twenty paintings (provided by AFA) containing copper pigments' mixtures and created in various historical periods. [8]

As it has been already described in the previous chapter, clay minerals are subjected to systematic research in our team at IIC, because they can play an important role in the provenance studies of earth pigments, which have been used in paintings since ancient times and are still in use. They are, in fact, sensitive indicators of physical-chemical conditions of the process of their formation and transformation in nature. To find characteristic signatures referring to these processes (as, e.g., the already-mentioned crystallinity of kaolinite) is not an easy task. The full scale analysis of clay samples usually include XRD of micronised randomly oriented samples, XRD of oriented samples after size fractionalisation and

subsequent solvation with organic molecules, chemical analysis, optical and electron microscopies (both scanning – SEM and high-resolution transmission – HRTEM) and infrared spectroscopy. All these methods and methodologies are available and applied at IIC, but most of the pre-treatments are destructive to the sample and thus cannot be used for fragments obtained from paintings (which usually should be archived due to their rarity). However, we have found and described a non-destructive way of distinguishing between green earths imported from the historical sites in northern Italy or Cyprus and the green earth of the Central European origin (from the deposit near Kadaň, Northern Bohemia). Although all of them are identified in the literature as celadonites (Mg, Fe- rich green micas), we have discovered admixtures of smectite (expandable clay) layers in the reference green earths from the historical production of Kadaň mine (collected in cooperation with the Technical University in Munich) that may not be present as a single phase, but more likely as an interstratified structure (mixed crystal) with celadonite. In the microanalysis of painting layers, smectite admixtures can be recognized using micro-FTIR. [9]

In the provenance/workshop/authorship assignments, rarely occurring pigments represent one of valuable fingerprints corresponding to either place of origin, period of artwork creation or author's preferences. For example, vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$), which is a rare blue mineral pigment, can be profitably used in authorship ascription or copy identification. However, its tendency to degrade complicates its proper identification in paint layers. Our team at IIC analysed reference vivianite mineralogical samples *via* X-ray diffraction and vibrational spectroscopies. The same methods, in their micro-configuration, were used on micro-samples of the paintings and their limits evaluated. A sedimentary origin of the pigment has been suggested due to characteristic admixtures and grain morphology. Then, vivianite was detected in various works made by Jean George de Hamilton (1672–1737) as a sign of author's preference indicating his artistic training in The Netherlands. [10] Regarding the fact that the identification of vivianite in paintings can be hampered by its degradation and related colour change to greyish, brownish or yellowish hues, which is highly undesirable, we have decided to experimentally determine the process and its causes. Temperature-related degradation of pure synthetic as well as partly oxidised natural vivianite has been studied by HT-XRD and Mössbauer spectroscopy. While temperatures around 70°C are already damaging to vivianite, exposition to 160 °C results in complete amorphisation of both the vivianite and its oxidation products. Furthermore, we proved (in cooperation with AFA Prague) that temperatures around 70°C can be easily achieved by, e.g., relining of canvas paintings in a traditional way using iron. The experimental research has been performed at IIC in 2014 and the results published at the beginning of 2015. [11]

Another rare mineral pigment is fluorite (CaF_2), which is documented in the Central European art of the period from ca. 1450 to ca. 1550. Its usage could correspond with the peak of production of silver in Bavaria, because silver mineralisation in a Bavarian mine was accompanied by an increased contents of dark violet variety of fluorite known as “antozonite”. Our research at IIC aimed to prove that only antozonite and no other varieties of fluorite have been used as a pigment in the studied artworks (e.g., late Gothic altarpieces in Kutná Hora) and to enrich the definition of antozonite, which still remains vague (antozonite = naturally irradiated fluorite). The X-ray diffraction study of antozonite confirmed that the structural disorder caused by natural irradiation may be expressed by the broadening of its diffraction lines. The higher is their full-width half-maximum, the lower is the sample's lightness. The Raman spectroscopic study showed that antozonites have a specific spectrum that can be used for its distinguishing in microanalysis and in provenance-related studies (as in the case of Kutná Hora altarpieces). The experimental research has been performed at IIC in 2014 and the results published at the beginning of 2015. [12]

Interdisciplinary research

Comprehensive case studies combining novel methodological approaches with the knowledge of experimental research and historical, archaeological, artistic and/or art-historic data were again widely represented in the evaluated period as a typical product of cooperation of IIC and AFA Prague. They dealt with the prestigious monuments of European cultural heritage located not only in the Czech Republic, but also abroad. The results have been published either in scientific journals focused on cultural heritage or in analytical journals. Regarding the fact that the conservation and cultural heritage sciences are still not earmarked as independent fields within the Web of Science journal categories (and ranked as Q3 journals in other disciplines), we have decided to organise interdisciplinary conferences with two-years periodicity (with contributions of sciences, arts and humanities) and to fill the gap by publishing interdisciplinary proceedings. These proceedings entitled *Acta Artis Academica* (AAA) have been included into the international ISI Proceedings database (Thompson Reuters) already in 2010. The most important examples of interdisciplinary research in ALMA are listed below.

Pre-Romanesque murals in Kostol'any pod Tribečom, Slovakia (one of the oldest wall paintings in the still standing construction in the region of Central Europe) have been investigated by portable X-ray fluorescence and by micro-analytical methods to identify painting materials (pigments and binders) and to explain the degradation of colours. Today-missing green and blue shades have been reconstructed according to residual concentrations of Cu, which correspond to copper chlorides - products of salt corrosion of copper carbonates azurite and/or malachite, which has been accelerated by micro-organisms. As it has been confirmed by powder X-ray micro-diffraction, original minium (Pb_3O_4) was transformed to brown-black plattnerite (PbO_2). Under increased humidity, even insoluble pigments are washing down from the walls and the intensity of colours further diminishes. [13]

Another unique mural paintings of exceptional quality, which can be discerned in spite of their extensive mechanical damage and colour fading, have been uncovered in the church of St. Gallus in Kuřivody, Northern Bohemia, dated to the second half of the 13th century. Materials' research provided by our team at IIC with particular use of portable X-ray fluorescence, Raman micro-spectroscopy and powder X-ray micro-diffraction revealed the presence of rare pigments. In Kuřivody, only a second identification of intentionally used yellow mineral crocoite (PbCrO_4) in the European art has been reported. In addition, light yellow mimetite ($\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$) has been never mentioned as intentionally used pigment in Europe. However, its finding in Kuřivody is related more likely to undesirable physical-chemical conditions causing its formation by alteration of orpiment (As_2S_3) and minium (Pb_3O_4). Regarding the materials, the almost forgotten paintings in Kuřivody can be seen as outstanding and rare example of ancient artistic tradition that has spread to Europe from Mediterranean in early Middle Ages. After all, mineral crocoite was already used by ancient Egyptians to paint sarcophagi and degraded orpiment decorates the walls of the Nefertari's tomb in Thebes. [14]

Further results of interdisciplinary studies have been published in AAA proceedings issued in 2010, 2012 and 2014, respectively. [15-17] They cover, for example, results of an extensive research of Late Gothic altarpieces in Transylvania, Romania, or the provenance studies of Gothic mural paintings in Lidzbark Warminski, Poland, dated to around 1400 and possibly attributed (through materials and technique) to Bohemian workshops coming from the Emperor Charles IV's court in Prague. Within the long-term cooperation with Moravian Gallery in Brno, we have also investigated a unique polychrome statue of Madonna dated by radiocarbon method to the interval between 990-1180, thus being the oldest piece of polychrome art in Czech collections.

Further, the prestigious publishing house Archetype Publications in cooperation with British Museum, National Gallery in London and a European network for the research of cultural heritage CHARISMA published a book composed of contributions presented on the interdisciplinary conference dedicated to the study of Renaissance art, which took place in London in May 2012. The members of ALMA team are the co-authors of the article which was created in international cooperation and deals with material and technological characteristics of early Renaissance altars in Transylvania. [18]

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Research collaborations of powder X-ray diffraction laboratory

The powder X-ray diffraction laboratory belongs, according to the Organization chart of IIC, to the ALMA laboratory; however, the second principal aim of the laboratory is to provide advanced expertise in methodologies of X-ray powder diffraction to researchers of IIC and other research groups in the country. Research collaborations include techniques of X-ray powder diffraction and especially micro-diffraction frequently not available elsewhere in the Czech Republic. Our research collaboration has numerous outcomes and selected papers are listed below. [19-23] It includes the collaboration with the Department of Materials Chemistry and Centre of Instrumental Techniques of IIC. From the external activities, long term collaborations were established among others with the University of Chemical Technology in Prague, Institute of Chemistry of the Faculty of Science of the Masaryk University in Brno, Institute of Chemical Process Fundamentals of the CAS, Faculty of Civil Engineering of the Czech Technical University in Prague, Faculty of Chemical Technology of the University in Pardubice, Nuclear Research Institute in Řež.

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3. Research Plan of the team for 2015–2019

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