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Proceedings of 4th Jožef Stefan International Postgraduate School Students Conference

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Part II

25. maj 2012, Ljubljana, Slovenija

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4TH JOŽEF STEFAN INTERNATIONAL POSTGRADUATE SCHOOL STUDENTS CONFERENCE

Zbornik - 2. del

Proceedings - part 2

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25. maj 2012, Ljubljana, Slovenija

Kazalo (Table of Contents)

Ekotehnologija (Ecotechnology)

The role of human activities on number concentration and size distribution of particles in indoor air

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Nanoparticles contribute importantly to the pollution of ambient air and thus to the resulting adverse effects on human health. There are number of various natural and anthropogenic sources of indoor particles from engineered nanoparticles used in cosmetology, industry and medicine to unintentionally produced nanoparticles by biomass burning and traffic emissions. Important indoor sources include cooking exhaust, cigarette smoke, candles and other sorts of flames, and solvents.

Smaller particles are chemically and biochemically more reactive and potentially more toxic than larger ones, due to large surface area. With dropping particle size, the probability of deposition in respiratory system is increasing. It has been now recognised that nanoparticles cause oxidation stress, pulmonary inflammation and cardiovascular events. Factors that influence nanoparticle toxicity include size, number, surface characteristics, shape, chemical composition, surface treatment and potential for aggregation/agglomeration. Currently, there are no legal thresholds for nanoparticle number concentrations in ambient air, nevertheless, it is acknowledged that mass based particle concentration limits do not effectively control smaller particles. Therefore, particle number concentrations are likely to be considered within future air quality regulation.

The aim of our research is to contribute to the improvement of knowledge on nanoparticles characteristics, sources, and transport by monitoring outdoor and indoor air and to evaluate its influence on human health. In this contribution, measurements of particle concentrations and size distributions during two human activities of generating particles, burning a candle and smoking a cigarette, are described. Characterisation of newly formed particles and their abundance in air afterwards are presented. Taking into account only number particle concentration and its size distribution, without chemical composition, burning a candle can be potentially more toxic than smoking a cigarette, because it produces significantly smaller particles and higher number concentration of particles. Furthermore longer retention time of particles formed during burning a candle in the air leads to longer exposure time.

MEDNARODNA PODIPLOMSKA ŠOLA JOŽEFA STEFANA

JOŽEF STEFAN INTERNATIONAL POSTGRADUATE SCHOOL

The role of candle burning and cigarette smoking on number concentration and size distribution of particles in indoor air

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Introduction

Nano aerosols are widely believed to cause adverse health effects. During breathing, particles are deposited on the walls of the respiratory tract, their deposition being stronger for smaller particles. Nano particles are chemically and biochemically more reactive and potentially more toxic than larger particles, due to their larger ratio of the surface versus bulk number of active atoms. In the indoor environment, nano particles are generated by human activities, such as cooking, cleaning, cigarette smoking, candle burning, and others.

Experimental

In the kitchen of a basement apartment, number concentration and size distribution of particles in the size range of 5–350 nm have been monitored during candle burning and cigarette smoking, using a Grimm Scanning Mobility Particle Sizer SMPS+C 5.400 instrument (Fig 1). Every four minutes, the instrument gives the total number concentration C(tot), number size distribution $dC(d)/d\ln d$ (with d as electrical mobility equivalent particle diameter), and geometric mean of diameters d_{GM}. We have been especially interested in the fractions of particles smaller than 10, 20 and 100 nm (x(<10), x(<20) and x(<100), respectively), as carriers for intake of radon decay products, a major cause of lung cancer, second only after smoking.

Fig 1: Scanning Mobility Particle Sizer + Counter

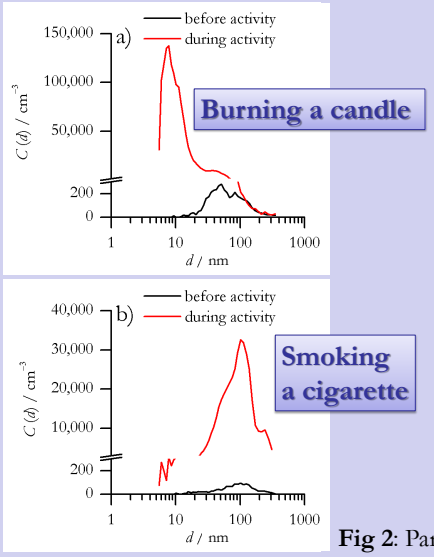

Fig 2: Particle size distribution during a) Burning a candle and b) Smoking a cigarette

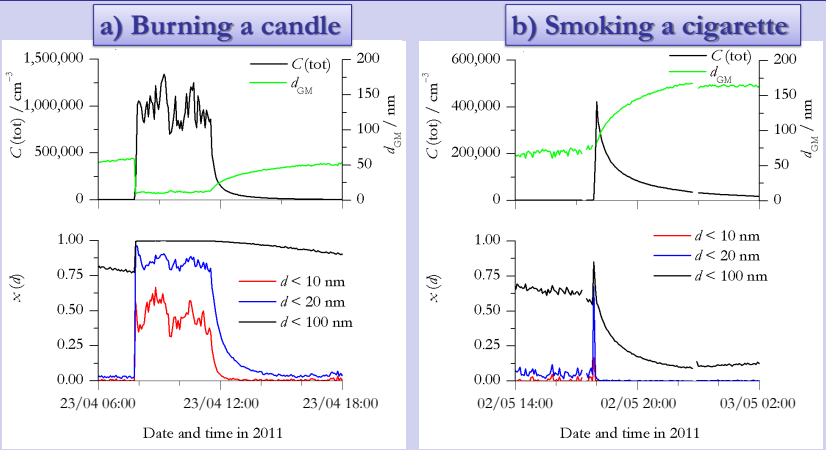

Fig 3: Time run of C(tot), d_{GM}, x(<10), x(<20) and x(<100) for a) Burning a candle and b) Smoking a cigarette

Results and discussion

During burning a candle (Fig 2a), high particle concentration in a narrow size range of 6–15 nm was observed, whereas during smoking a cigarette (Fig 2b), particle size ranged from 40 to 200 nm. During smoking, C(tot) values (Fig 3) were three times lower than during candle burning, in agreement with the reported emission rate of 1.91×10^{11} particles min^{-1} for the first and 5.52×10^{11} particles min^{-1} for the second activity [1]. The observed elevated x(<10), x(<20) and x(<100) values, lasting for more than six hours after the candle was extinguished, indicate longer retention time of particles released during this activity (Fig 3).

Conclusion

Considering solely the number concentration and size distribution of nano particles, without referring to their chemical composition, candle burning appears to be more harmful for our health than cigarette smoking, because it produces much higher number of particles with significantly smaller size. Furthermore, particles produced by candle burning showed much longer retention time in air, thus leading to longer exposures of residents.

Reference
[1] C. He, L. Morawska, J. Hitchins, and D. Gilbert, Contribution from indoor sources to particle number and mass concentrations in residential houses. *Atmos Environ*, 38(21): 3405–3415, 2004.

Cytostatics cyclophosphamide and ifosfamide – do they occur in Slovene wastewaters and surface waters?

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Pharmaceuticals contribute greatly to our wellbeing, but their residues are finding their way into the environment where they can have unintended consequences, often at very low concentrations. The aim of this study is to evaluate the presence of cytostatics, potent pharmaceuticals used in chemotherapy. Samples of wastewater from Institute of Oncology Ljubljana, Central Wastewater Treatment Plant Ljubljana and receiving surface water (Ljubljanica River) were analysed for the presence of two commonly prescribed cytostatics: cyclophosphamide and ifosfamide. By using gas chromatography-mass spectrometry, we found 12.1 μg L-1 of cyclophosphamide and 10.5 μg L-1 of ifosfamide in samples of wastewater from Institute of Oncology Ljubljana. The concentrations of both compounds in the influent and effluent of the Central Wastewater Treatment Plant Ljubljana and in the Ljubljanica River were under limits of detection (LOD(CF) = 11.2 ng L-1, LOD(IF) = 34.7 ng L-1) due to the dilution effect of the sewerage system, which collects wastewater from a wide region of Ljubljana and returns it after treatment to Ljubljanica River. In the future, a more sensitive analytical method will be developed that will allow us to detect the presence of cytostatics at lower concentrations (ng L-1). In addition, sampling will be repeated so that hourly, daily and weekly variations will be identified and the study of their occurrence will be extended to other waste and environmental waters.

CYTOSTATICS CYCLOPHOSPHAMIDE AND IFOSFAMIDE – DO THEY OCCUR IN SLOVENE WASTEWATERS AND SURFACE WATERS?

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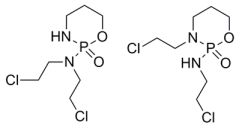

Figure 1: Structures of cyclophosphamide and ifosfamide.

Cyclophosphamide (CF) and ifosfamide (IF) are two commonly used cytostatics with the potential to cause adverse effects in the environment. The aim of our work is to **evaluate wastewaters** of hospitals, where CF and IF is used for chemotherapy, **influents and effluents of wastewater treatment plants** as well as **surface waters** in order to obtain quantitative data concerning their **occurrence in aqueous environment in Slovenia**.

(So far) we analyzed aqueous samples from:

Institute of Oncology Ljubljana (IO Ljubljana)

JP Vodovod-Kanalizacija, Central Wastewater Treatment Plant Ljubljana (CWTP Ljubljana)

Ljubljanica river - downstream from the WWTP discharge

… wastewater from IO Ljubljana flows towards CWTP Ljubljana, where it is treated and released in Ljubljanica river…

ANALYTICAL METHOD

Sampling
- grab samples of IO Ljubljana wastewater and Ljubljanica river
- time-proportional samples (24 hours) at JP Vodovod-Kanalizacija, CWTP Ljubljana
- samples were filtred and stored at -20 °C until analysis

Extraction
- HLB Oasis™ (3cc, 60 mg)
- elution: 3 mL ethyl acetate

Derivatization
- 100 µL trifluoroacetic anhydride
- conditions: 0.5 h at 60 °C

GC-MS analysis
- HP 6890 series (Hewlett-Packard) gas chromatograph with a single quadrupole mass selective detector
- column DB-5 MS 30 m × 0.25 mm × 0.25 µm (Agilent J&W)
- carrier gas: He
- 1 µL samples injected (splitless)
- The programme of GC oven: an initial T = 65 °C (2 min), 1st rate: 30 °C min^{-1} to 180 °C; 2nd rate: 15 °C min^{-1} to 280 °C; 3rd rate: 30 °C min^{-1} to 300 °C and held for 3 min

SAMPLE ANALYSIS

- estimation of concentration range of CF and IF in samples: extraction and analysis of different volumes (200 mL, 500 mL and 1000 mL)**
- Matrix-matched validation: synthetic wastewater free of CF and IF
- validation parameters: recovery (%), LODs and LOQs, linearity

RESULTS

Validation parameters	CF (± sd)	IF (± sd)
linear range	750 ngL^{-1} - 12500 ngL^{-1} (both)	
recovery (%) $_{(n = 3)}$	92.0 ± 2.3 %	99.6 ± 2.3 %
LOD $_{(n = 6)}$	11.2 ngL^{-1}	34.7 ngL^{-1}
LOQ $_{(n = 6)}$	37.2 ngL^{-1}	115.7 ngL^{-1}
r^2 values $_{(6 \text{ points}, n = 3)}$	0.984	0.997
RSD (%) $_{(3 \text{ conc. points}, n = 3)}$	2.1	5.7

Samples from IO Ljubljana contained detectable concentrations of CF and IF: 12.1 µg L^{-1} and 10.5 µg L^{-1}, respectively.

FURTHER GOALS

1. Optimization of analytical method for lower LODs and LOQs
2. Extraction of a higher number of samples and larger volumes with higher capacity cartridges (6cc, 150 mg)
3. Grab samples will be obtained (from IO Ljubjana and the Ljubljanica river) on an hourly basis to investigate hourly, daily and weekly variations
4. Samples will be collected from other wastewaters of Slovenian institutions, where CF and IF are administered and followed through WWTP to receiving surface water
5. Comparison of our data with other European countries, which are participating in the EU FP7 CytoThreat project
6. Analysis of the main metabolites of CF and IF in wastewaters and surface waters

Acknowledgements
This work was financially supported by the EU through the EU FP7 project CytoThreat (Fate and effects of cytostatic pharmaceuticals in the environment and the identification of biomarkers for and improved risk assessment on environmental exposure (grant agreement No.: 265264) and by the Slovenian Research Agency (Program Group P1-0143 and Young Researcher grant to M. Č.). We would also like to thank IO Ljubljana and and JP Vodovod-Kanalizacija d.o.o. Ljubljana for their collaboration.

Karakterizacija slovenskega oljčnega olja z uporabo stabilnih izotopov

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Potreba po spremljanju avtentičnosti in kakovosti prehrambnih izdelkov je povzročila, da se je pojavilo povpraševanje po metodah, s katerimi bi dokazali potvorjenost. Za odkrivanje ponarejanja živil se torej lahko poslužujemo tako imenovanega globalnega pristopa, pri katerem določamo oporečnost na osnovi fizikalno-kemijskih lastnostih vzorca. Te metode temeljijo na tako imenovanem izotopskem prstnem odtisu ali »fingerprintingu«. Z njimi ne določamo le stopnjo in način potvorjenosti, temveč tudi geografsko poreklo in celo leto proizvodnje izdelka. Poleg oljčnega olja smo v raziskave avtentičnosti prehrambnih izdelkov vključili tudi vina, med, sladkor, sadne sokove, ustekleničene vode in mleko ter mlečne izdelke. Omenjene analize prispevajo h kakovosti oziroma certificiranju določenih prehrambnih izdelkov in s tem k okrepitvi konkurenčne sposobnosti agro-živilske industrije.

MEDNARODNA PODIPLOMSKA ŠOLA JOŽEFA STEFANA

JOŽEF STEFAN INTERNATIONAL POSTGRADUATE SCHOOL

KARAKTERIZACIJA SLOVENSKEGA OLJČNEGA OLJA Z UPORABO STABILNIH IZOTOPOV

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Oljčno ali olivno olje je najstarejše poznano olje in hkrati eno najbolj zdravih:

- je lahko prebavljivo,
- pospešuje izločanje želodčnih sokov
- omogoča boljšo absorpcijo vitaminov (vitamin E).

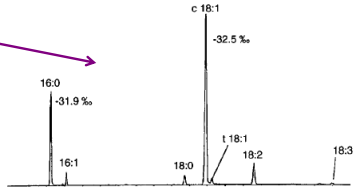
Glede na tehnologijo predelave in kakovost ločimo:

- oljčno olje, sestavljeno iz rafiniranih oljčnih olj in deviških oljčnih olj
- deviško oljčno olje
- ekstra deviško oljčno olje
- olje iz oljčnih tropin

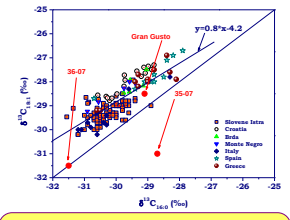
PRIPRAVA VZORCEV in ANALIZA

100 µl vzorca olja
↓ derivatiziramo
2 ml heksana
↓ in
200 µl KOH/MeOH
↓
stresamo in počakamo, da se plasti ločita
↓
zgornjo plast odlijemo in analiziramo metilne estre

Detekcija s plinskim kromatografom sklopljenim z masnim spektrometrom za stabilne izotope (GC-C-IRMS)

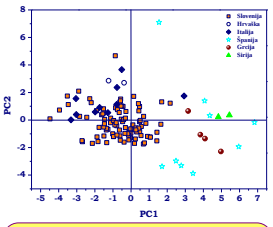


REZULTATI in DISKUSIJA



Slika 1: Odvisnost $\delta^{13}C_{18:1}$ od $\delta^{13}C_{16:1}$ v pristnih vzorcih iz leta 2006 in treh izbranih potvorjenih vzorcih oljčnega olja.

- Vrednost $\delta^{13}C$ v celokupnem oljčnem olju in posameznih maščobnih kislin (FA) se spreminja med **–31,6 ‰ in –29,1 ‰**.
- Potvorjenost oljčnega olja se določa z meritvami izotopske sestave ogljika v $C_{16:0}$ in $C_{18:1}$, pri čemer naj bi bile vrednosti $\delta^{13}C_{16:0}$:$\delta^{13}C_{18:1}$ v razmerju **1:1** (Slika 1).
- Koncentracije in izotopska sestava FA (Slika 2) dajeta zadovoljive rezultate pri ločljivosti oljčnih olj z različnih geografskih področij.
- Boljšo ločljivost med posameznimi področji bi lahko dosegli z uporabo meritev izotopske sestave O in H.



Slika 2: Projekcija oljčnih olj v ravnini, definirani z dvema glavnima osema PC1/PC2 po metodi glavnih osi (Principal Component Analysis – PCA).

ZAKLJUČEK

Z raziskavami smo:

- nadgradili bazo podatkov pristnih slovenskih oljčnih olj za leta 2006-2008 z rezultati o izotopski sestavi FA in opazili velike variabilnosti v $\delta^{13}C$ FA po posameznih letih;
- preverili uporabo stabilnih izotopov FA za določanje potvorjenosti oljčnih olj in izdelkov, ki vsebujejo oljčno olje (konzerve tun) in ugotovili, da določenih potvorb ne moremo določiti le na podlagi izotopske sestave FA;
- na podlagi $\delta^{18}O$ v oljčnem olju smo lahko določili potvorbo oljčnega olja z lešnikovim oljem;
- poleg oljčnega olja smo v raziskave avtentičnosti prehrambenih izdelkov vključili tudi vina, med, sladkor, sadne sokove, ustekleničene vode in mleko ter mlečne izdelke.

Jedkanje PET filmov v poznem porazelektritvenem delu kisikove plazme

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Na odseku za tehnologijo površin in optoelektroniko Instituta "Jožef Stefan" raziskovalci razvijajo metode za modifikacijo površin različnih materialov s termodinamsko zelo neravnovesno plinsko plazmo. Industrijski partnerji potrebujejo tovrstne tehnologije za izboljšanje kakovosti svojih izdelkov in nadomeščanje okolju neprijaznih tehnoloških postopkov. Za različne partnerje so razvili tehnološke postopke plazemskega čiščenja, selektivnega plazemskega jedkanja, površinske funkcionalizacije in hladnega upepeljevanja. V zadnjem času se predvsem ukvarjajo z modifikacijo površinskih lastnosti polimernih materialov, ki se uporabljajo v medicini. Originalne tehnološke postopke zaščitijo z mednarodnimi patenti, znanstvena odkritja pa objavljajo v vrhunskih specializiranih revijah.

Moja vloga v raziskovalni skupini, ki je izrazito interdisciplinarna, je razvoj postopkov za modifikacijo površine umetnih žil, s ciljem izboljšanja biokompatibilnosti. Umetne žile, ki se trenutno uporabljajo, imajo sicer odlične kemijske in mehanske lastnosti, žal pa prepogosto povzročajo različne po-operativne zaplete, kamor v prvi vrsti sodi tromboza. Preliminarne raziskave so pokazale, da je mogoče s primerno funkcionalizacijo notranje površine umetnih žil bistveno zmanjšati aktivacijo trombocitov in s tem nastajanje krvnih strdkov. Da bi inovativni tehnološki postopek uporabili v medicinski praksi, je potrebno opraviti obsežne temeljne raziskave, ki bi omogočile vpogled v izredno zahteven pojav kopičenja krvnih proteinov. V okviru svojega doktorskega izobraževanja je moja naloga natančno določiti vpliv različnih reaktivnih kisikovih delcev na funkcionalizacijo polimernih materialov za umetne žile, določiti intenzivnost interakcije izbranih reaktivnih delcev s krvnimi proteini in določiti morebitne poškodbe umetnih žil, ki so posledica interakcije obdelovancev z reaktivnimi delci.

Končni cilj mojih raziskav je optimizacija površinske modifikacije umetnih žil, ki bi omogočila minimalno depozicijo krvnih proteinov ob hkratni izboljšani biokompatibilnosti za pravilno vezavo endotelija na umetne žile.

Jedkanje PET filmov v poznem porazelektritvenem delu kisikove plazme

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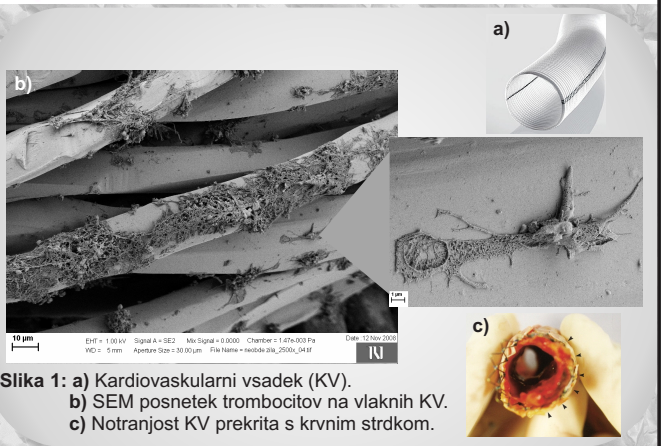
UVOD

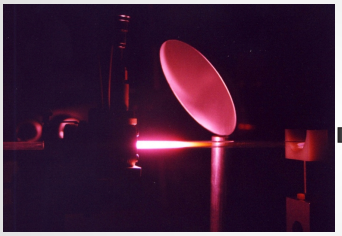
Praktična uporaba polimernih materialov v medicini je še vedno omejena s specifičnimi lastnostmi teh materialov. Pri uporabi polietilen tereftalata (PET) za umetne žile in katetre, se soočamo s problemom vezave bioloških substanc (proteini, trombociti) na površino polimernih materialov. Obdelava materialov z nizko-temperaturno plazmo velja za eno najbolj vsestranskih tehnik za pridobivanje edinstvenih lastnosti površin materialov, še posebej polimernih. Reaktivni plazemski delci reagirajo s površino polimera tako, da odstranijo sledove organskih nečistoč, obenem pa zmanjšajo vezavo proteinov.
Znano je, da se pri obdelavi polimerov s kisikovo plazmo na površini ustvarijo polarne funkcionalne skupine (povečana hidrofilnost) in da se površina materiala jedka. Slednje predstavlja ključno težavo za razvoj ustreznega industrijskega postopka, kjer je bistveno ohraniti določene mehanske lastnosti materiala.
Cilj raziskave je bil, da z uporabo zelo natančne metode kremenove mikrotehtnice z enoto merjenja dušenja nihanja (QCM-D) določimo vpliv nevtralnih kisikovih atomov na jedkanje PET-a v porazelektritvenem delu kisikove plazme.



Slika 1: a) Kardiovaskularni vsadek (KV).
b) SEM posnetek trombocitov na vlaknih KV.
c) Notranjost KV prekrita s krvnim strdkom.

METODE IN MATERIALI

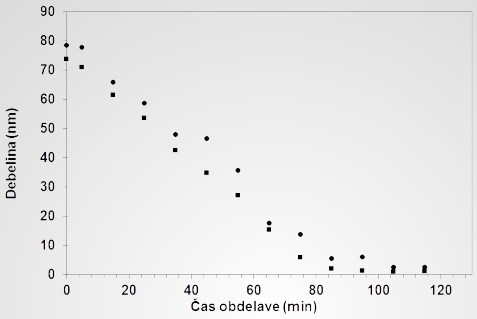
Modelne filme PET-a smo obdelali v porazelektritveni komori, prikazani na Sliki 1. Plazmo smo vzbujali z generatorjem mikrovalov, ki deluje na standardni frekvenci 2,45 GHz z nastavljivo močjo vse do 300 W.
Hitrost jedkanja smo določili tako, da smo najprej izmerili debelino prvotno nanesenega filma. Kristal smo izpostavili delovanju kisikovih atomov in ponovno izmerili debelino filma. Postopek smo ponavljali toliko časa, da je postala debelina filma nemerljivo tanka. Značilen rezultat je prikazan na Sliki 2.



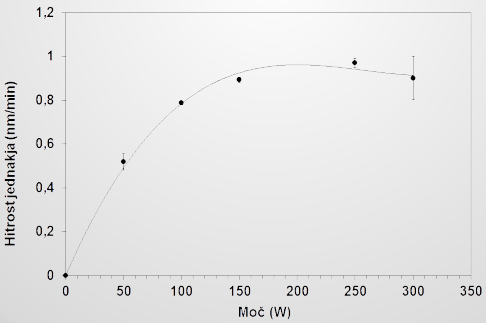
Slika 2: Mikrovalovna razelektritev kisikove plazme.

Slika 3: Shema eksperimentalnega vakuumskega sistema.

REZULTATI



Slika 4: Debelina PET filma v odvisnosti od časa obdelave pri moči 150 W.



Slika 5: Hitrost jedkanja v odvisnosti od moči.

ZAKLJUČEK

Rezultati naših meritev kažejo, da je izbrani polimerni material dobro odporen na jedkanje z nevtralnimi kisikovimi atomi. Za razliko od obdelave v plazmi, kjer smo opazili izredno agresivno jedkanje, je hitrost jedkanja v porazelektritvenem delu za dva velikostna reda manjša. Ker je hitrost jedkanja organskih nečistoč, ki se značilno nahajajo na površini katetrov, bistveno večja, lahko sklepamo, da je metoda obdelave v porazelektritvenem delu primerna za čiščenje katetrov po uporabi v medicinski praksi. Z atomi kisika lahko torej odstranimo nečistoče, ne da bi bistveno spremenili prvotne lastnosti katetra.

Entirely renewable and self-sufficient municipal energy system

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Climate change mitigation activities support usage of renewable resources due to their neutral impact on the environment. Various legislative acts stress the important role of municipalities in accomplishing the energy targets. This is why focus on municipality energy system and its development present a promising future orientation. Forming energy system on entirely renewable resources presents the new pathway, where the whole energy supply could be based on local supply facilities. In practice, the results could be applied for other municipalities, smaller local community, a district or a group of buildings. In addition, for concretizing the system more technical studies should be revealed.

The case study was presented for Podlehnik municipal energy system. Analyses of three different scenarios leading to entirely renewable energy system with mixes of biomass, solar and electricity confirmed on the sufficiency of renewable resources. The results confirmed the technical feasibility to develop an independent renewable municipal energy system. Demonstration of possibilities to develop energy systems on a 100% renewable and 100% local supply represents added value. In the future several research activities should be focused in providing detailed analysis of integration of renewable resources into energy supply chain from technical, environmental, economic and social aspect.

MEDNARODNA PODIPLOMSKA ŠOLA JOŽEFA STEFANA

JOŽEF STEFAN INTERNATIONAL POSTGRADUATE SCHOOL

Entirely renewable and self-sufficient municipal energy system

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Study program: Ecotechnology
International Postgraduate school Joseph Stefan
MENTOR: prof.dr. Leon Cizelj
Scientific Research Centre Bistra Ptuj, Slovenski trg 6, 2250 Ptuj

THEORETICAL part:



Problem statement

Objective: Decarbonization and decentralization of municipal energy system

Main challenges:
- to perform various scenarios of renewable energy system
- to demonstrate technical feasibility to constitute entirely renewable and self-sufficient municipal energy system

Results: Zero carbon emissions and local resources integration

Renewable scenarios for PODLEHNIK municipal energy system

Reference scenario for baseline year 2008

Scenario 1: BIOMASS

Individual heating:
Heat pumps: 10%
Solar thermal: 5%
Biomass boilers: 45%
District heating: biomass (40%)
Industry: total biomass
Electricity: 60% solar, 20% biomass, 20% biogas

Scenario 2: SOLAR

Individual heating:
Heat pumps: 10%
Solar thermal: 10%
Biomass boilers: 40%
District heating: biomass (40%)
Industry: total biomass
Electricity: 80% solar, 10% biomass, 10% biogas

Scenario 3: RES-MIX

Individual heating:
Heat pumps: 15%
Solar thermal: 5%
Biomass boilers: 40%
District heating: biomass (40%)
Industry: total biomass
Electricity: 70% solar, 15% biomass, 15% biogas

EXPERIMENTAL part:

Energy consumption in PODLEHNIK municipality

2008 – Present state

Structure of energy mix	Heat energy [MWh]	Electricity energy [MWh]	Share [%]
Conventional resources	4.145	3.224	50,85
RES	5.378	1.746	49,15

2050 – Future prospective

Structure of energy mix	Heat energy [MWh]	Electricity energy [MWh]	Share [%]
RES	5.647	5.949	100



OPTIONAL IMLEMENTATION:

Energy systems of municipalities, local community, districts, group of buildings.

CONCLUSION

- Technical feasibility of entirely renewable energy system was demonstrated
- Municipalities represent appropriate units for entirely renewable energy system implementation
- Integration of local resources have broader impacts on local economy
- Further work indicates economic, environmental and social analysis

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Selenium and its distribution in edible mussel *Mytilus galloprovincialis* collected from different locations

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Selenium (Se) is a complex, essential trace element for animal and human. It has numerous important biological functions that depend on the activity of certain Se-containing proteins. It is essential for the body because it forms seleno-enzymes that carry out redox reactions such as glutathione peroxidase (GPx), thioredoxin reductase, and thyroid hormone deiodinase families. However, Se is also considered to be a toxic element at high concentrations. Function and bioavailability of this element are strongly correlated with its chemical form, so it is necessary to control the selenium intake to avoid deficiency diseases and toxicity problems. Therefore it is important to determine the selenium species in foods, especially in seafood, because of its known accumulation capacity. Our aim in this work was to investigate selenium and its species with different analytical techniques in edible mussel Mytilus galloprovincialis collected from different locations (Slovenian coastline, Italy, Udine and NE Pacific). Furthermore we wanted to see if cooking of mussel has any effect on selenium concentration and its distribution. In this experiment we followed typical cooking procedure which is mostly used in Slovenia. To determine total concentration of Se, hydride generation atomic fluorescence spectroscopy (HG-AFS) was used. Total Se concentrations in mussels differ between the locations where mussels were bred. The lowest concentrations obtained were in mussel that comes from NE Pacific, but here we need to take into account that mussels were already cleaned and removed from shell when we bought them from the supermarket, while the mussels from Slovenia and Italy were cleaned in our laboratory. Selenium speciation was performed by a liquid chromatography as separation system and coupled to mass spectrometer as detector system (HPLC-ICP-MS). Two selenium species were determined, while future work will involve further species identification.

MEDNARODNA PODIPLOMSKA ŠOLA JOŽEFA STEFANA

JOŽEF STEFAN INTERNATIONAL POSTGRADUATE SCHOOL

Selenium and its distribution in edible mussel *Mytilus galloprovincialis* collected from different locations

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Study programme: Ecotechnology,
Jožef Stefan International Postgraduate School
MENTOR: prof. dr. VEKOSLAVA STIBILJ
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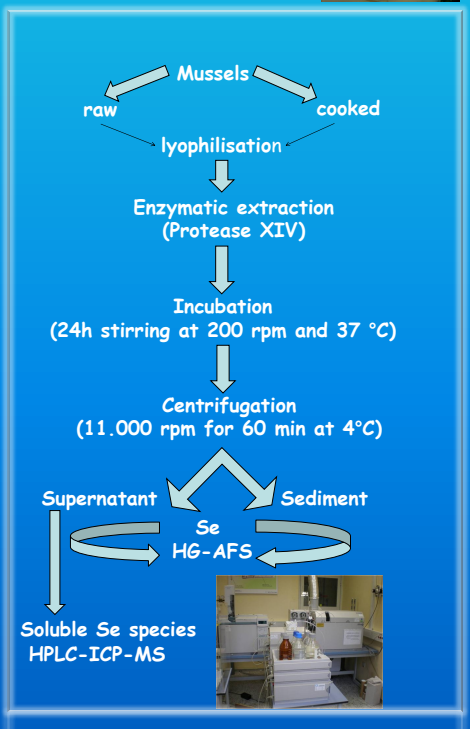
Why Selenium (Se) ?

- **essential element for animals and humans →** very narow range between essentiality and toxicity
- **the principal source of Se is diet** → **Seafood**, Plant food
- **bioavailability of Se depends on its chemical forms**

Samples and methods

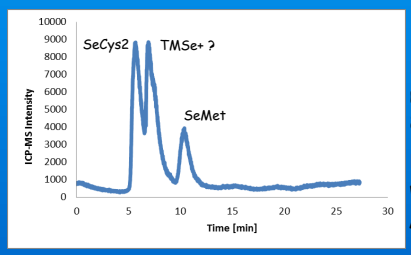
- **Mussel** *Mytilus galloprovincialis*
- **Three different locations**
  - Italy
  - Slovenia (Piranski zaliv)
  - NE Pacific (FAO87)



Results and discussion

		Mussel tissue DM a					
Sample (n)		Total Se µg g-1	Soluble Se µg g-1	Average solubility (%)	Selenium species identified		
					SeCys2 (µg Se/g)	SeMet (µg Se/g)	Se as $TMSe^+$
Mussel from Slovenian breeders (4)	raw	5.81 ± 0.33	4.32 ± 0.39	76.49	0.22 ± 0.03 (4.7)	0.09 ± 0.01 (1.9)	0.65 ± 0.08 (13.7)
	cooked	3.52 ± 0.21	2.70 ± 0.11	74.15	0.72 ± 0.09 (24.9)	0.27 ± 0.02 (9.8)	0.83 ± 0.04 (28.7)
Mussel from Italy (4)	raw	8.27 ± 0.34	5.58 ± 0.57	67.37	0.36 ± 0.03 (7.1)	0.33 ± 0.03 (6.5)	0.86 ± 0.06 (16.6)
	cooked	4.24 ± 0.20	2.64 ± 0.16	66.75	0.35 ± 0.09 (13.1)	0.37 ± 0.03 (14.1)	0.48 ± 0.14 (17.8)
Mussel FAO87 (5)	raw	3.15 ± 0.04	1.98 ± 0.15	62.77	0.45 ± 0.04 (22.8)	0.30 ± 0.02 (14.9)	0.47 ± 0.01 (23.4)
SRM 2976 (3)		1.74 ± 0.07	1.04 ± 0.07	58.4	0.15 ± 0.03 (14.8)	0.07 ± 0.01 (6.9)	0.13 ± 0.01 (15.1)

(n) Number of samples analysed
[a] Results are given as the average ± standard deviation on dry matter basis (DM)
[b] (% of identified soluble Se)



Conclusions

- Se concentration in raw mussels waried between 3.15 to 8.27 µg/g (DM)
- in cooked mussels Se amount was half lower: from 4.1 to 4.4 µg/g
- Se species identified were SeMet, SeCys2 (and $TMSe^+$ which was identified by comparison of retention time)

Results of in-situ measurements, laboratory experiments on lignite samples and numerical modelling of coal pillar, performing under research projects CoGasOUT and GHG2E

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In the last few years the importance of coal as an energy source is raising again, due to development of Clean Coal Technologies (CCT). However, coal combustion produces billions of tonnes of carbon dioxide each year and all of that is released to the atmosphere. Because of the problems with greenhouse gas emissions at Velenje Coal Mine we launched a research group on Clean Coal Technologies (at the end of year 2007). The task of the research group is to find new technologies for cleaner use of coal. Clean Coal Technologies research group also applied for two international projects. First is Development of Novel Technologies for Predicting and Combating Gas Outbursts and Uncontrolled Emissions in Thick Seam Coal Mining, which will improve coal excavation, safety and working conditions in the mine (CoGasOUT). The project is partially founded by Research Fund for Coal and Steel. The second project entitled Greenhouse Gas Recovery from Coal mines and Coalbeds for Conversion to Energy (GHG2E) is funded within the 7th framework programme. During both projects, "in-situ" monitoring is provided in the mine with the support of laboratory analysis, such as desorption and adsorption laboratory tests, coupled with numerical modelling of gas migration under the influence of stress change. Results will improve mines around the world with new technology to combat outbursts and high gas emissions.

RESULTS OF IN-SITU MEASUREMENTS, LABORATORY EXPERIMENTS ON LIGNITE SAMPLES AND NUMERICAL MODELING OF COAL PILLAR, PERFORMING UNDER RESEARCH PROJECTS COGASOUT AND GHG2E

Jerneja Lazar, Sergej Jamnikar, Simon Zavšek, Ludvik Golob, Janja Žula, Gregor Uranjek
Coal Mine Velenje, Partizanska 78, Velenje, Slovenija

INTRODUCTION

In the year 2007 Velenje Coal Mine launched a research group on Clean Coal Technologies (CCT). Clean Coal Technologies research group applied for two R&D international projects.

- *Development of Novel Technologies for Predicting and Combating Gas Outbursts and Uncontrolled Emissions in Thick Seam Coal Mining (CoGasOUT); Research Fund for Coal and Steel.*
- *Greenhouse Gas Recovery from Coal mines and Coalbeds for Conversion to Energy (GHG2E); 7th framework programme.*

During both projects, "in-situ" monitoring is provided in the mine, accompanied by laboratory analysis, such as desorption and adsorption laboratory tests and coupled numerical modelling of gas migration under the influence of stress change are performing.

Main objective of projects is prevention against gas and rock outbursts and high gas emissions in the mines.

EXPERIMENTAL WORK

Gas content determination experiments

Gas content in coal is determined by variations of desorption experiments amongst which US Bureau of Mines direct method and Australian Standard method [1] represent direct gas content determination method that uses physical principles of gas release from coal samples (Figure 1).

Sorption experiments

Sorption experiments are currently in preparatory stage where apparatus (autoclave) composition was re-designed and manufactured in 2011. Modification in apparatus will allow experiments both on solid coal core samples and on crushed coal samples.

Currently, test measurements are performed on different compositions of coal samples in order to test autoclave (Figure 2) and start with regular experiments with basis in existing knowledge [2].

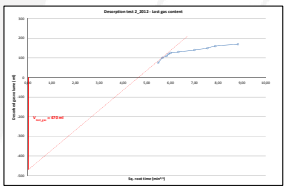

Figure 1: Lost gas determination from core coal sample (Jamnikar, 2012)

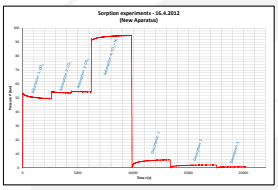

Figure 2: Sorption experiment on crushed coal sample (Razvojni Center Energija, 2012)

MINE MONITORING

Seam gas pressure monitoring

Seam gas pressure monitoring was established with purpose to correlate gas pressure behaviour in dependence of long-wall face approach with geotechnical monitoring, especially stress measurements.

Seam gas composition and isotopic analysis

Seam gas composition monitoring is performed at wells, drilled during development and preparatory work for long-wall faces. Samples of seam gas are taken and analysed for gas composition (gas concentrations) and isotopic composition of ^{13}C in carbon dioxide and methane [3].

Rock stress monitoring

Rock stress monitoring is an established methodology of long-wall face influence observations. Stress cells are built into bore-holes which are drilled with different orientations and inclinations. Rock stress monitoring design normally dictates bore-holes drilling into excavation pillars in order to detect influence of advancing long-wall face.

Amongst operating long-wall faces, K.-50 C (Mine Pesje) was chosen for multiple monitoring campaign (Figure 3).

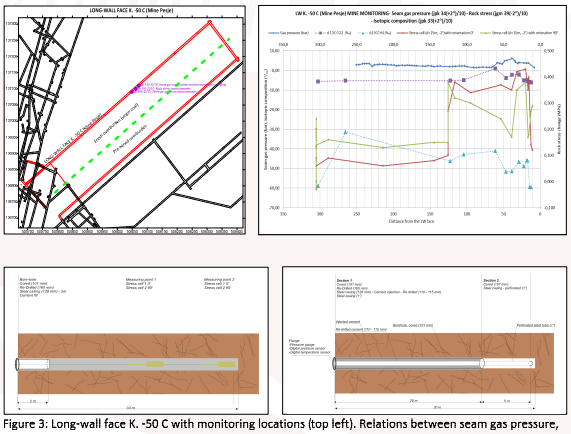

Figure 3: Long-wall face K. -50 C with monitoring locations (top left). Relations between seam gas pressure, gas isotopic composition and rock stress in dependence of distance to long-wall face (top right). (Jamnikar, Lazar, 2012)
Rock stress monitoring well (bottom left), Seam gas pressure monitoring well (bottom right).

COUPLED GEOMECHANICAL MODELLING OF LONGWALL FACE

Numerical modelling is widely used in coal mining for understanding the behaviour of coal under dynamic stresses. When the stress results are known then with stress-permeability correlation [4] permeability can be defined which is used for data in the coupled geomechanical program TOUGH2. The objective of the model analysis in Flac3D is to gather stress changes around the pressure borehole for monitoring gas pressure changing in dependence of advancing longwall face. The geometry of the longwall face Pesje K.-50/C was chosen.

The mining method is divided into coal face slicing in height of 4 m and top coal caving in average height of 11 m. The model was simplified and Mohr-Coulomb constitutive model was chosen (Figure 4).

Coupled geomechanical modelling with TOUGH2 will be performed. TOUGH2 is a general-purpose numerical simulator for multi-dimensional fluid and heat flows of multiphase, multicomponent fluid mixtures in porous and fractured media [5] (Figure 5).

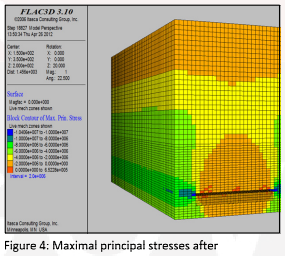

Figure 4: Maximal principal stresses after the excavation (Pa) (Lazar, 2012).

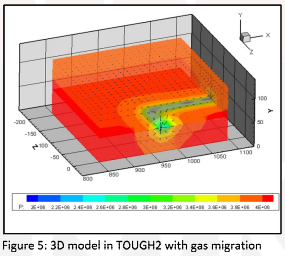

Figure 5: 3D model in TOUGH2 with gas migration around the LW face (Lazar, Si, Bacci, 2012).

REFERENCES

[1] W.P. Diamond, S. Schatzel. Measuring the gas content of coal: A review., 1986. *International Journal of Coal Geology 35 (1998), 311-331.* Paper.

[2] J. Žula, J. Pezdič, S. Zavšek, E. Burič. Adsorption capacity of the Velenje lignite: methodology and equipment, 2011, *RMZ – Materials and Geoenviroment, Vol. 58, No. 2, pp. 193-216, Paper.*

[3] T. Kanduč, J. Pezdič. Origin and distribution of coalbed gases from the Velenje basin, Slovenia, 2005. Geochemical Journal, Vol.39.

[4] S. Durucan, J. S. Edwards. The Effects of Stress and Fracturing on Permeability of Coal, 1986. *Mining Science and Technology, 3, 205-216.* Paper.

[5] K. Prues, C. Oldenburg, G. Moridis. TOUGH2 User`s Guide, Version 2.0, 1999. Ernest Orlando Lawrence Berkeley National Laboratory.

Use of monolithic chromatography for speciation of Pt based chemotherapeutic drugs

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Our work is based on monolithic chromatography which offers several advantages over standard (particle packed) chromatographic columns. Monolithic supports have high permeability and therefore allow thorough cleaning during regeneration after each separation run. This enables great robustness of such chromatographic columns which in turn enables higher throughput of samples. Monolithic supports are also cheaper and offer possibilities to be applied in numerous chromatographic separations of compounds in environmental and biological samples.

MEDNARODNA PODIPLOMSKA ŠOLA JOŽEFA STEFANA

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Use of monolithic chromatography for speciation of Pt based chemotherapeutic drugs

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INTRODUCTION

In order to understand pharmacokinetic of metal-based chemotherapeutic drugs, it is necessary to study their behavior and distribution in blood serum. For such speciation analysis hyphenation of inductively coupled plasma mass spectrometry (ICP-MS) with high performance liquid chromatography (HPLC) is the method of choice. Monolithic supports are progressively used for elemental speciation analysis as an alternative to conventional columns.
In the presented work, the analytical method based on convective interaction media (CIM) monolithic chromatography coupled to ICP-MS was developed to study the distribution of Pt in human blood serum samples after administration of Pt based drugs carboplati, oxaliplatin and cisplatin.

METHODS

Chromatographic separation on Agilent 1200 HPLC and elemental detection by Agilent 7700x ICP-MS

1.CIM -DEAE-1 mL column

- 0.05 M Tris HCl + 0.03 M $NaHCO_3$, pH 7.4 (buffer A)
- 0.05 M Tris HCl + 1 M NH_4Cl, pH 7.4 (buffer B)
- Sample volume: 100
- Flow 1 mL/min, gradient elution from 100 % A to 100 % B
- Analysis time: 10.5 min
- Column regeneration time: 9 min

Fig.1: CIM-DEAE-1 column

2.UV detection at 278 nm

3.ICP-MS

- RF power: 1550 W
- Carrier gas flow: 0.25 L/min, dilution gas flow: 0.92 L/min
- Integration time on m/z 195: 1 s
- Time resolved analysis: 622 s

Sample preparation

- Frozen serum was thawed, spiked, incubated 24 h at 37 °C and then diluted five times with buffer A.

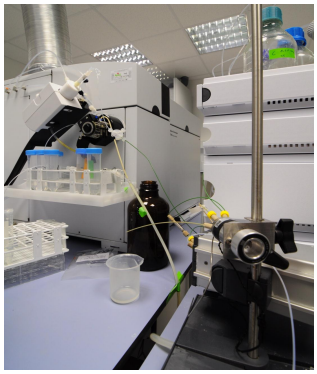
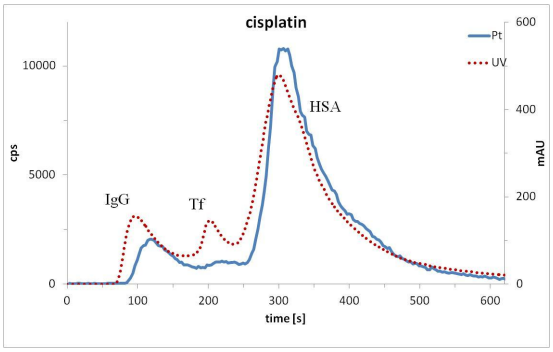
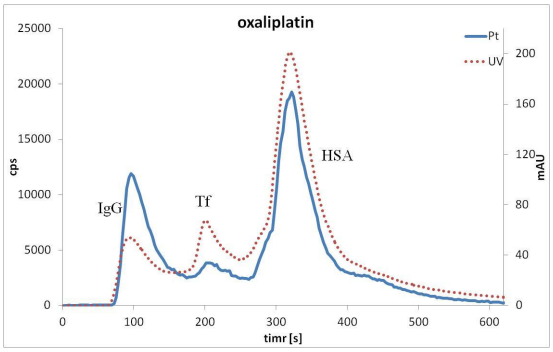


Fig.2: Instrument setup

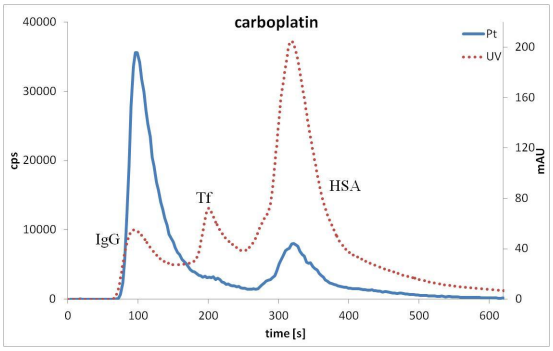
RESULTS AND DISSCUSSION



Chromatogram of cisplatin binding to human serum proteins: γ-Globulins (IgG); Transferrin (Tf); Albumin (HSA). Pt peak representing app. 14 % at the retention volume of IgG represents unbound cisplatin, app. 3 % of Pt is found under retention volume of Tf and 83 % under retention volume of HSA. Molar ratio of HSA/Tf is ~10/1 while Pt ratio between them is ~28/1. This demonstrates that HSA is the major cisplatin transporter because of its higher concentration and greater affinity.



Chromatogram of oxaliplatin binding to human serum proteins. Pt peak representing app. 27 % at the retention volume of IgG represents unbound cisplatin, app. 10 % of Pt is found under retention volume of Tf and 63 % under retention volume of HSA. Oxaliplatin is like cisplatin mostly bound to serum proteins, mainly HSA.



Chromatogram of carboplatin binding to human serum proteins. Pt peak representing app. 74.5 % at the retention volume of IgG represents unbound cisplatin, app. 7.5 % of Pt is found under retention volume of Tf and 18 % under retention volume of HSA. Carboplatin is found in serum mostly in unbound form.

CONCLUSIONS

In this work we further extend the applicability of our method for separating different Pt species in human blood. Method is based on monolithic chromatography which has several advantages over standard (particle packed) chromatographic columns. In our future work will further develop this method for speciation of Ru-based compounds.

Determnation of Cr(VI) in corrosion protection coatings by speciated isotope dilution ICP-MS

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Evropska unija je sprejela številne predpise s katerimi določa kritične meje Cr(VI) v protikorozijskih premazih, ki se uporabljajo v avtomobilski industriji (2000/53/EC) in elektronski opremi (2002/95/EC) ter v recikliranih izdelkih (2002/96/EC). Postopki, ki so trenutno v uporabi za analizo Cr(VI) vključujejo ekstrakcijo z vrelo vodo ali rahlo alkalno amonijevo raztopino, ter spektrofotometrično določitev Cr(VI) v ekstraktu oziroma določitev z ICP-MS. Ker omenjeni ekstrakcijski sredstvi nista dovolj učinkoviti, je bil naš cilj razviti novo analizno metodo, ki temelji na alkalni ekstrakciji. Pri razvoju ekstrakcijskega postopka smo uporabili stabilne izotope kroma (50Cr(VI) in 53Cr(III)) s katerimi smo sledili oksidaciji in redukciji kromovih zvrsti med samim ekstrakcijskih postopkom. Ugotovili smo, da alkalna ekstrakcija povzroči oksidacijo Cr(III) v vzorčku. Da bi preprečili oksidacijo kroma med ekstrakcijo, smo preverili v kakšni meri TRIS, EDTA in MgCl2 preprečijo oksidacijo Cr(III). Poskusi so pokazali, da TRIS ni sposoben preprečiti oksidacije in, da se pri dodatku EDTA pojavi redukcija Cr(VI). MgCl2 se je tako izkazal kot najustreznejši, saj pri 30 min ekstrakcije nismo zasledili oksidacije Cr(III) ali redukcije Cr(VI). Tako smo v vseh nadaljnjih poskusih za ekstrakcijo Cr(VI) uporabili ultrazvočno ekstrakcijo (30 min, 70 °C) in kot ekstrakcijsko sredstvo 2 % NaOH + 3 % Na2CO3 z dodatkom MgCl2. Omenjeni postopek ekstrakcije je zagotovil pogoje, pri katerih ni prišlo do pretvorb kromovih zvrsti, kar smo dodatno sledili med vsako ekstrakcijo z uporabo obogatenih stabilnih izotopov kroma 50Cr(VI) in 53Cr(III). Cr(VI) v ekstraktu smo določili z izredno občutljivo kvantitativno metodo izotopskega redčenja z ICP-MS. Ugotovili smo, da je bilo pri preučevanih vzorcih za ekstrakcijo celotnega Cr(VI) iz površine nanosa protikorozijskih prevlek potrebnih šest zaporednih ekstrakcij.

Determination of Cr(VI) in corrosion protection coatings by speciated isotope dilution ICP-MS

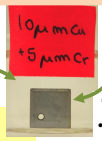
Authors:Breda Novotnik, **Jožef Stefan International Postgraduate school, Ecotechnology,** Tea Zuliani, Radmila Milačič, Janez Ščančar; Department of Environmental Sciences, Jožef Stefan Institute, Ljubljana, Slovenia; bnovotnik@ijs.si **Supervisor:** Assoc. prof. Radmila Milačič, **Co-supervisor:** Assoc. prof. Janez Ščančar

The European Union issued several directives limiting the amount of Cr(VI) in corrosion protection coatings and electrical equipment (the 2000/53/EC directive [1], RoHS no. 2002/95 [2], WEEE 2002/96/EC [3]). In a view of these demands, the aim of our work was to develop a selective, quantitative and sensitive analytical procedure for determination of Cr(VI) in corrosion protection coatings. A method based on alkaline extraction using 2 % NaOH + 3 % Na_2CO_3 and sonication at 70 °C was optimised. To prevent Cr(III) oxidation during extraction, addition of $MgCl_2$, EDTA and TRIS was tested. Samples were spiked with 20 ng mL^{-1} ^{53}Cr(III) and ^{50}Cr(VI) to follow species interconversion. Cr(VI) was quantified by speciated isotope dilution inductively coupled plasma mass spectrometry (SIDICP-MS).

Methods and results

Optimisation of extraction procedure

Metallic plate
10 µm Cu+5 µm HCr



Extracting solution
• 2 % NaOH+ 3 % Na_2CO_3

To prevent Cr(III) oxidation
• 0.1 M $MgCl_2$, 0.1M EDTA, 0.05 M Tris

Double spike
20 ng mL^{-1} ^{50}Cr(VI) + 20 ng mL^{-1} ^{53}Cr(III)

Sonication, 70 °C, 30-90 min

Chromatographic separation (anion-exchange FPLC):
• following oxidation/reduction
• extraction efficiency

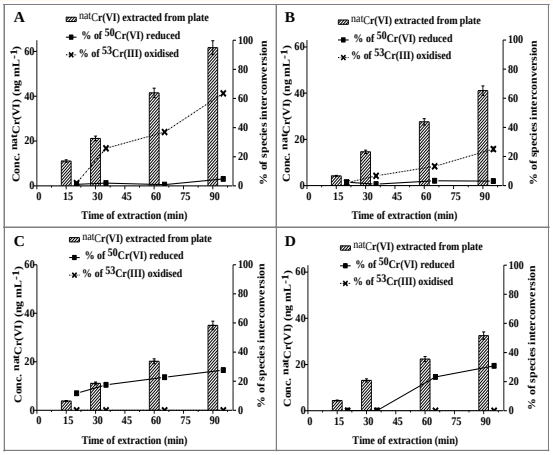


Figure 1: Extraction of Cr(VI) from 10 µm Cu+5 µm HCr, using (A) 2 % NaOH+3 % Na_2CO_3, (B) 2 % NaOH+3 % Na_2CO_3 + 0.05 M TRIS, (C) 2 % NaOH+3 % Na_2CO_3 + 0.1 M EDTA (D) 2 % NaOH+3 % Na_2CO_3 + 0.1 M $MgCl_2$. Samlpes were spiked with 20 ng mL^{-1} ^{50}Cr(VI) and 20 ng mL^{-1} and ultrasonic extraction applied at 70 °C over a time period of 90 min.

From Fig. 1A it is evident that oxidation of ^{53}Cr(III) occours after 15 min of extraction, when 2 % NaOH+3 % Na_2CO_3 is used. To prevent Cr(III) oxidation during extraciton the addition of Tris, EDTA and $MgCl_2$ was tested. Data of Fig. 1B indicate that Tris is not able to prevent Cr(III) oxidation. From Fig. 1C it is evident that the addition of EDTA causes reduction of ^{50}Cr(VI) after 15 min. $MgCl_2$ (Fig. 1D) prevents Cr(III) oxidation, but after 30 min of extraction reduction of Cr(VI) occurs. Therefore, 2 % NaOH +3 % Na_2CO_3 with addition of $MgCl_2$ and ultrasonic extraction (70 °C) for 30 min was applied in further experiments.

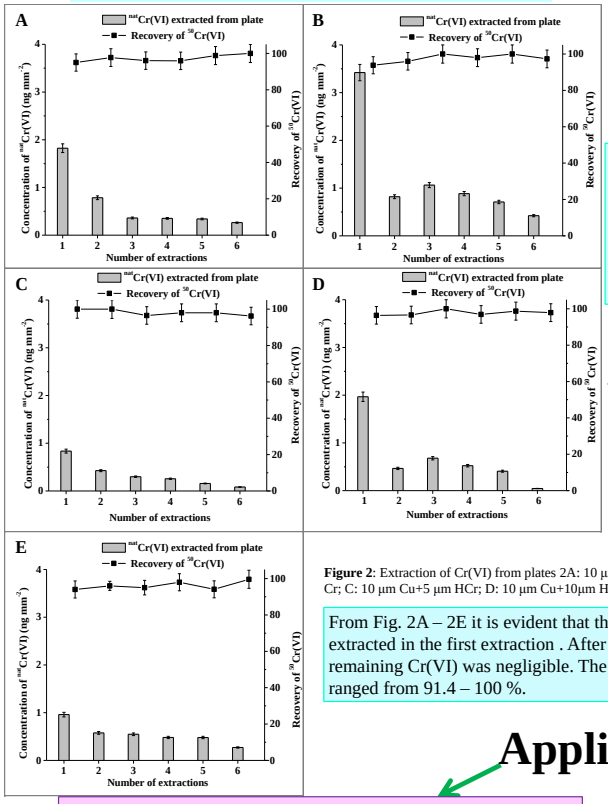


Figure 2: Extraction of Cr(VI) from plates 2A: 10 µm Cu+5 µm Cr; B: 10 µm Cu+10 µm Cr; C: 10 µm Cu+5 µm HCr; D: 10 µm Cu+10µm HCr; E: 10 µm Zn+5 µm Cr

From Fig. 2A – 2E it is evident that the majority of Cr(VI) is extracted in the first extraction . After the 7th extraction the remaining Cr(VI) was negligible. The recovery of ^{50}Cr(VI) ranged from 91.4 – 100 %.

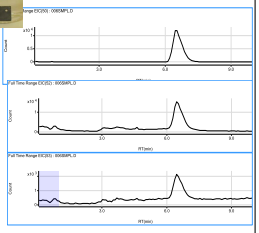
Metallic plates
A 10 µm Cu+5 µm Cr
B 10 µm Cu+10 µm Cr
C 10 µm Cu+5 µm HCr
D 10 µm Cu+10 µm HCr
E 10 µm Zn+5 µm Cr

0.1 M $MgCl_2$

Double spike
20 ng mL^{-1} ^{50}Cr(VI)+^{53}Cr(III)

Extracting solution
2 % NaOH + 3 % Na_2CO_3

Ultrasonic extraction, 70 °C, 30 min, several consecutive extractions



Chromatographic separation

SIDICP-MS
Ratio 50/52, Mass bias correction

Calculate the concentrations using equation:
$C_{pl}=N^{VI}{}_s \times ((R_{50/52} \times {}^{52}A_s - {}^{50}A_s)/({}^{50}A_x - R_{50/52} \times {}^{52}A_x) \times M_x$/plate surface (ng mm^{-2})

Application

Determination of Cr(VI) in vehicles
(European Directive 2000/53/EC on end-of life vehicles)

Determination of Cr(VI) in electronic and electrical equipment
(RoHS no. 2002/95 Directive)

Determining Cr(VI) for recycling and recovery of electrical goods
(WEEE 2002/96/EC Directive)

In conclusion, for efficient extraction of Cr(VI) and absence of species interconversions from corrosion preventing coatings, the use of 2 % NaOH + 3 % Na_2CO_3 with addition of $MgCl_2$ as extraction solution and ultrasonic extraction at 70 °C for 30 min is recommended. Several consecutive extractions are necessary to extract Cr(VI) from corrosion preventing coatings. With the addition of double spikes of enriched stable isotopes of ^{50}Cr(VI) and ^{53}Cr(III), species interconversion can be followed and the ratio $R^{VI}_{50/52}$ can be used to determine the concentration of extracted Cr(VI).

1. The Council of the European Union. European Directive 2000/53/EC on end-of life vehicles. *Official Journal of European Union*, 2000
2. The Council of the European Union. European Directive 2002/95/EC on the restriction of the use of certain hazardous substances in electrical and electronic equipment. *Official Journal of European Union*, 2002
3. The Council of the European Union. European Directive 2002/96/EC on waste electrical and electronic equipment (WEEE). *Official Journal of European Union*, 2002

Optimization of distillation separation procedure for methyl mercury in natural waters

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The aim of the research is to understand better the chemistry of mercury in aqueous media. Speciation of chemical species of mercury in water is of ultimate importance to understand its distribution, partitioning and fate in the environment.

The work presented is focused on the accurate determination of very low concentrations of a chemical form of mercury – monomethylmercury (MeHg), which is one of the most toxic compound that accumulates and biomagnifies in biosphere. Due to very low concentrations found in the environment, especially in water, the first step was to optimize the procedure and to improve the limit of detection, so that environmentally consistent data can be obtained. The method optimized has shown to be fit for purpose as demonstrated on real samples taken from the Mediterranean Sea. Concentrations in sea water are very low and are increasing with depth (from 1.4 to 72.5 pg/L). Because of low concentrations it is necessary to take all the precautions not to contaminate the samples and to use methods which are the most reliable. That is why the distillation is our method of choice.

Next steps will include further refinement of the distillation procedure form solid samples, such as sediments, where the proportion of inorganic mercury can interfere the analysis by artificial formation of MeHg.

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Optimizacija destilacije za izolacijo metil živega srebra v vodah

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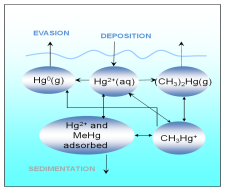
Uvod

Živo srebro (Hg) je strupena kovina, tako za ljudi, kot celoten ekosistem. Je naravni element, vendar je človek s svojo dejavnostjo njegovo vsebnost v globalni atmosferi v zadnjem stoletju potrojil [1,2]. Glavni antropogeni vir emisij živega srebra je izgorevanje premoga in ostalih fosilnih goriv. V okolju se Hg nahaja v različnih oblikah (elementarni Hg^0, anorganski Hg^{2+} in Hg_2^{2+}, organski Hg – npr. MeHg). Pretvorbe med različnimi oblikami Hg v naravnih pogojih tvorijo osnovo za lokalni, regionalni in globalni bio-geokemični cikel. Oceani igrajo pomembno vlogo pri globalnem kroženju Hg. V vodah in sedimentih se lahko Hg pretvori v metil-Hg (MeHg), ki spada med najbolj strupene spojine, ki se akumulira in biomagnificira v vodnih in kopenskih prehranjevalnih verigah. Pravilno merjenje Hg in njegovih spojin je zato izjemnega pomena pri oceni tveganja [3].

Kemijske oblike Hg v vodi (slika 1):

- Reaktivni Hg
- Celokupni /raztopljeni Hg
- Celokupni /raztopljeni MeHg
- Raztopljeni Hg(0)
- Dimetil Hg (DMM)



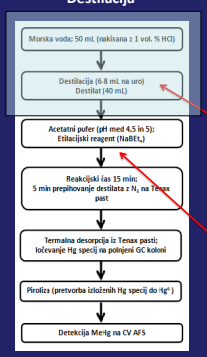
Slika 1: Glavne oblike Hg in njihove pretvorbe

Koncentracije Hg v naravnih vodah so nizke (od 0,2 do nekaj ng/L). V vodnih okoljih, še posebej v morskih vodah, se MeHg nahaja v zelo nizkih koncentracijah, t.j. običajno manj kot 10 % celokupnega Hg (THg) [3].

Kljub temu, da je destilacija v uporabi že vrsto let, je pri uvedbi metode ključno optimizirati parametre tako, da dosežemo mejo detekcije, ki je relevantna za okoljske študije, zlasti v morskem okolju. Namen dela je bil optimizirati naslednje stopnje postopka: temperaturo grelnega bloka, prepihovanje z dušikom med postopkom destilacije, dodajanje reagentov, čas destilacije, ter čiščenje reagentov in posodic.

Metode in materiali

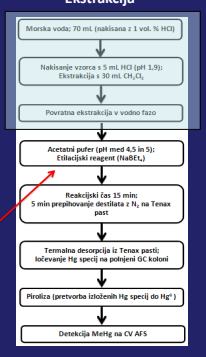
Destilacija



Slika 2: Destilacijska enota (Tekran, Kanada) (spodaj)

Slika 3: Avtomatski merilnik za MeHg, CV AFS z mejo detekcije 0,25 pg/L (Brooks Rand Labs, USA)

Ekstrakcija



Literatura

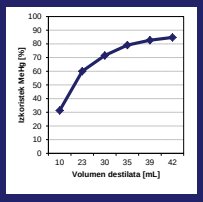
1.M. Horvat, L. Liang, N.S. Bloom. Comparison of distillation with other current isolation methods for the determination of methyl mercury compounds in low level environmental samples: Part II. Water. Analytical Chemical Acta, 282: 153-168, 1993.
2.J. Kotnik, M. Horvat, E. Tessier, N. Ogrinc, M. Monperrus, D. Amouroux, V. Fajon, D. Gibičar, S. Žižek, F. Sprovieri, N. Pirrone. Mercury speciation in surface and deep waters of the Mediterranean Sea. Marine Chemistry,107: 13-30, 2007.
3.UNEP Chemicals, Global mercury Assessment, Geneva, Switzerland, 2002.

Rezultati

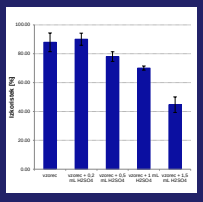
Da bi dosegli primerno hitrost destilacije (6,3 do 6,7 ml/h), smo temperaturo optimizirali na 122 °C. Izkoristki pri teh pogojih so bili med 80 in 85 %. Z višanjem temperature se hitrost destilacije poveča, vendar se to pokaže v nižjih izkoristkih MeHg.

Pomemben doprinos optimizacije destilacije je, da vzorcev med destilacijo ni potrebno prepihovati z dušikom. Med vzorci, ki so bili prepihovani in s tistimi, ki niso bili, ni bilo razlike. Izkoristek MeHg pri tistih, ki so bili prepihani je bil 81 ± 3 % in pri tistih, ki niso bili 79 ± 1 %. Na sliki 4 je prikazana krivulja za izkoristek MeHg iz 50 mL vzorca morske vode brez prepihovanja. Potrjuje, da je izkoristek v 40 mL destilata več kot 80 %.

Test, pri katerem smo pred destilacijo dodajali različne volumne 4M H_2SO_4 v vzorce, je pokazal, da dodatno nakisanje pred destilacijo ni potrebno. Z višanjem vsebnosti kisline v vzorcu se je zmanjšal pH, kar je motilo delovanje etilacijskega reagenta in povzročilo manjši izkoristek MeHg (slika 5). Rezultati pridobljeni s primerjavo med destilacijo in ekstrakcijo so pokazali, da sta metodi primerljivi (Tabela 1). Meja detekcije je pri destilaciji 0,42 pg/L, pri ekstrakciji pa 1,5 pg/L.



Slika 4: Destilacijska krivulja za izkoristek MeHg iz 50 mL vzorca morske vode

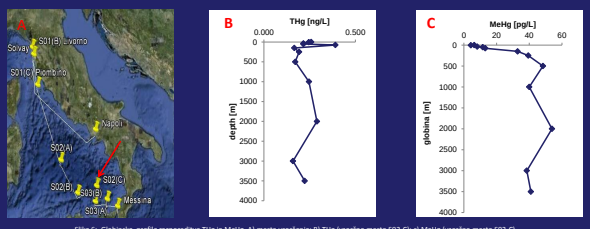


Slika 5: Primerjava med vzorci morske vode po dodatku različnih volumnov 4 M H_2SO_4.

Vzorci	Ekstrakcija [pg/L]	Povprečje	Destilacija [pg/L]	Povprečje
1	18,8	17,8	13,6	16,7
	16,9		19,7	
2	41,3	28,5	15,6	15,6
	15,6		15,6	
3	3,87	7,20	9,40	12,5
	10,5		15,7	
4	16,1	17,2	21,3	21,0
	18,4		20,7	
5	58,7	39,5	17,3	16,9
	20,3		16,4	
6	28,5	23,0	26,8	25,6
	17,5		24,5	

Tebela 1: Primerjava vzorcev med destilacijo in ekstrakcijo na različnih vzorcih morske vode.

Meritve MeHg smo izvedli tudi na realnih vzorcih iz Mediteranskega morja do globine 3500 m na raziskovalni ekspediciji FENICE v novembru 2011. Na sliki 6 so prikazana vzorčna mesta (A) ter globinska profila THg (B) in MeHg (C) na vzorčevalni točki S02-C. Z globinskim profilom smo opazovali razmerje THg in MeHg od morske gladine do globine 3500 m. Koncentracija THg (graf 6B) je na površini povišana in z globino pada, medtem ko graf 6C kaže trend naraščanja MeHg z globino.



Slika 6: Globinska profila razporeditve THg in MeHg. A) mesta vzorčenja; B) THg (vzorčno mesto S02-C); c) MeHg (vzorčno mesto S02-C)

Uporaba v praksi

Destilacija je v primerjavi z ekstrakcijo primernejša za vodne vzorce z nizko koncentracijo MeHg. Zaradi manjšega števila stopenj analize in manjše porabe reagentov je vrednost slepih vzorecv nižja. Prav zato pa je metoda destilacije tudi okoljsko in ekonomsko sprejemljivejša.

Photodegradation of Benzophenones

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The occurrence and fate of pharmaceuticals and personal care products (PPCPs) in the environment has become one of the emerging issues in environmental chemistry. This research was conducted to provide a better understanding of the fate of selected benzophenones in the aquatic environment under the influence of ultraviolet irradiation. The studied benzophenones include UV filters, a pharmaceutical (ketoprofen), its phototransformation products and others. Ketoprofen is a commonly used nonsteroidal anti-inflammatory drug with analgesic, antipyretic and anti-inflammatory activity. UV filters have the ability to absorb ultraviolet light and are therefore used in many cosmetic products such as sunscreen, moisturizer, hair spray, shampoo and lipstick.

As photodegradation of PPCPs caused by sunlight irradiation may be very important in the natural elimination process, we evaluated the photodegradation of the selected benzophenones. UV degradation was investigated in lab-scale experiments using mercury UV lamps. Whereas ketoprofen was prone to UV irradiation (it was completely degraded after 15 minutes of irradiation), other compounds were found highly resistant. Therefore the efficiency of the UV treatment was increased by combining UV irradiation and strong oxidant (hydrogen peroxide). As a result, the removal of benzophenones increased to up to 92 %.

The results of photodegradation treatment of the studied benzophenones will help us to get a better understanding of the cycling and fate of these compounds in the environment. They will also provide information whether UV irradiation has a potential for treatment of water, contaminated with benzophenones. In the future, our goal is to evaluate the presence and fate of benzophenones in different environmental compartments (aqueous environment, soils and sediments).

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PHOTODEGRADATION OF BENZOPHENONES

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Supervisor: Assoc. Prof. Dr. Ester Heath[1]
Co-authors: Dr. Tina Kosjek[1], Dr. Uroš Krajnc[2]

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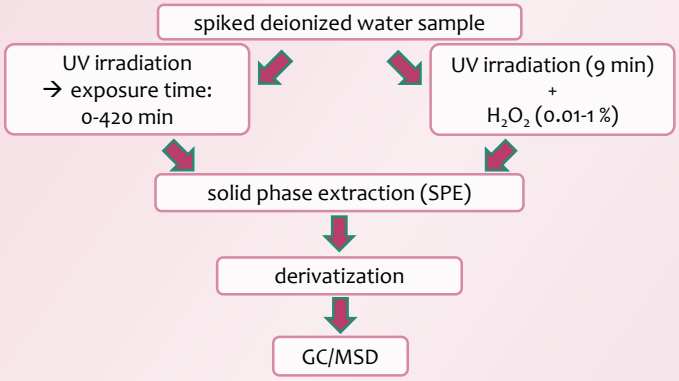
INTRODUCTION

In recent years there has been increasing concern regarding the presence and possible toxic effects of pharmaceuticals and personal care products (PPCPs) in the environment. The studied benzophenones include UV filters, a pharmaceutical, its phototransformation products and others.
The aim of this work was to gain greater knowledge of the fate of the selected benzophenones in the aquatic environment under the influence of ultraviolet irradiation.

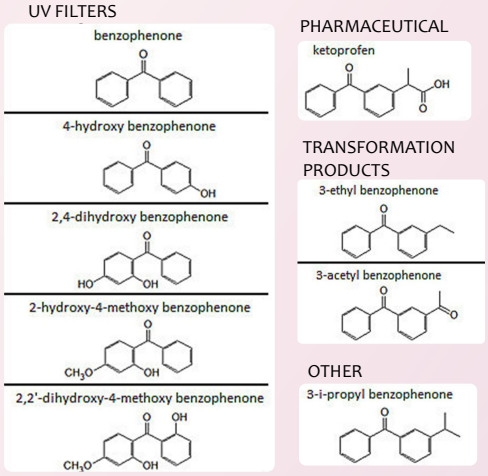
PRACTICAL APPLICATION

Photodegradation of PPCPs caused by sunlight irradiation may be of great significance in the natural elimination process. Therefore the results of photodegradation treatment of benzophenones will lead to a better understanding of their cycling and fate in the aquatic environment.
They will also provide information whether UV irradiation has a potential for treatment of water, contaminated with benzophenones.

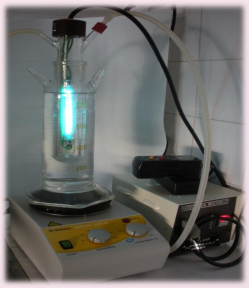
METHODS and MATERIALS



CHEMICAL STRUCTURES OF THE STUDIED BENZOPHENONES

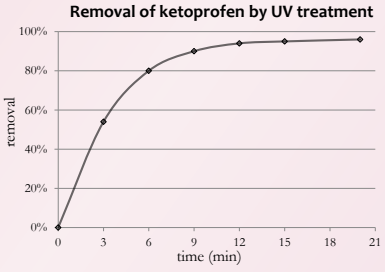


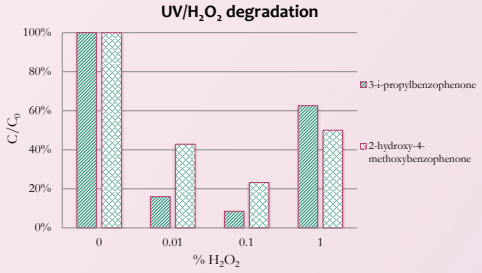
UV REACTOR



- Low pressure mercury lamp (254 nm)
- Medium pressure mercury lamp (> 290 nm)

RESULTS





- most benzophenones were resistant to UV irradiation with < 20 % removal after 420 min
- ketoprofen was almost completely (95 %) degraded after 15 min of irradiation (first order kinetics: k = 0.253 min^{-1}, $t_{1/2}$ = 2.74 min)
- efficiency of the UV treatment was increased by adding H_2O_2, reaching up to 77 % removal of 2-hydroxy-4-methoxybenzophenone and 92 % of 3-i-propylbenzophenone

FUTURE GOALS

- to determine the photodegradation kinetics of other benzophenones
- to evaluate their presence and fate in different environmental compartments (aqueous environment, soils and sediments)

Acknowledgements

We would like to thank Dr. Oliver Bajt, Marine Biology Station Piran, for his valuable suggestions and courtesy of UV lamps for our initial experiments.
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Poly[perfluorotitanate(IV)] Compounds of Alkali Metals, Unexpectedly Complicated Species in the Solid State

Igor Shlyapnikov[1,2], **Evgeny Goreshnik**[1], **Zoran Mazej**[1],

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Combining facts, that fluorine is the smallest and the most electronegative compound in the Periodic Table with the low bond energy in F2 molecule, its compounds show quite specific properties, which could be very different between various fluorides (i.e. from great chemical stability to high reactivity, from resistance to high-temperatures to low temperature decomposition with release of fluorine). Two typical examples are highly chemically inert polytetrafluoroethylene (Teflon®) and highly reactive fluorinating agent MnF4. Thus, fluorides could be successfully applied in various branches of science, technology and everyday life.

Much of the research is usually done due to economic benefits of industrial processes. But also contributions to fundamental science shouldn't be missed. They can't be precisely evaluated nowadays, but benefit in future. It's almost impossible to achieve highest possible results in any branch of human activities without strong theoretical explanations of processes. And that's what fundamental science does. Researches lead to various hypothesis and then to real operating theories and concepts. Also this work, which is devoted to poly[perfluorotitanate(IV)] compounds, mostly contributes to fundamental knowledge by collecting experimental material for understanding mechanisms of synthesis and opens new ways to selective synthesis of determined perfluorotitanates that then could be used as selective catalysts in different industrial productions.

MEDNARODNA PODIPLOMSKA ŠOLA JOŽEFA STEFANA

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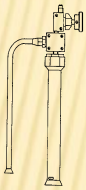
[1]*Department of Inorganic Chemistry and Technology (K1), Institute "Jožef Stefan"*

[2]*Jožef Stefan International Postgraduate School; Ecotechnology (doctoral degree program)*

Synthesis and crystal structure determination



$xAF + yTiF_4 \rightarrow$ „$A_xTi_yF_{4+x}\cdot nHF$“, A = Li, Na, K, Rb, Cs

- Loading calculated starting amounts of AF and TiF_4 (molar ratios $x : y$ = 2:1, 1:1, 1:2, 1:3) into reactor
- Condensing excess of anhydrous HF → warming to room temperature → mixing 1 day
- Decantation of solution to narrower arm → crystals growth → isolation → X-Ray diffraction analysis

$2AF + TiF_4 \rightarrow$ …

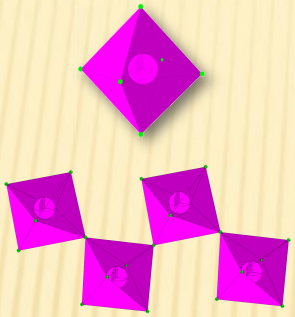
Well-known A_2TiF_6 salts

$AF + TiF_4 \rightarrow$ …

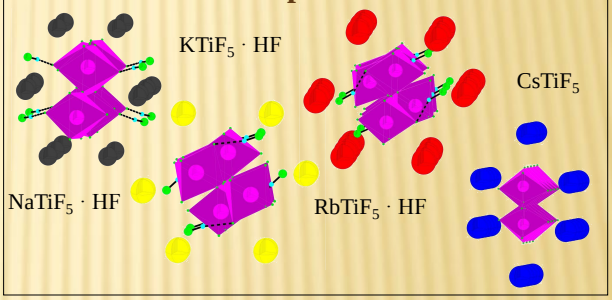
$CsTiF_5$ and $ATiF_5\cdot HF$ (A=Na, K, Rb)

$AF + 3TiF_4 \rightarrow$ …

Powdered matter



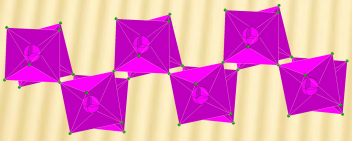
Differences in the structures of $ATiF_5$ compounds



$NaF + 2TiF_4 \rightarrow NaTi_2F_9 \cdot HF$

$CsF + 2TiF_4 \rightarrow CsTi_2F_9$

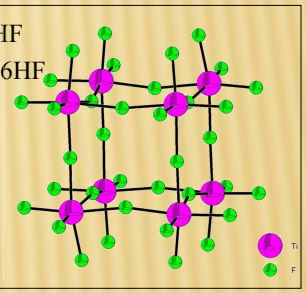
Anions – infinite double chains



$KF + 2TiF_4 \rightarrow K_4Ti_8F_{36} \cdot 8HF$

$RbF + 2TiF_4 \rightarrow Rb_4Ti_8F_{36} \cdot 6HF$

First example of octameric anion



Conclusions

1. Novel compounds in the system alkali metal fluoride – titanium tetrafluoride – hydrogen fluoride were synthesized
2. Unexpected octameric $[Ti_8F_{36}]^{4-}$ anion was described in $K_4Ti_8F_{36} \cdot 8HF$ and $Rb_4Ti_8F_{36} \cdot 6HF$ compounds

Vibrational spectra calculation of triphenylene: comparison of DFT and MP2 methods

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Computational methods in chemistry, or just "calculations" is a powerful instrument for revealing mechanisms of reactions, theoretical modeling of different processes and molecules. Modern supercomputers allow to model and even predict reactions even in such complicated tasks in biological systems as fermentative reactions, where geometry of an active center in molecule play fundamental role. This research is devoted to spectroscopy of aromatic hydrocarbons; we focused on two vibrational spectroscopy methods – Raman spectroscopy and infra-red spectroscopy (IR). Current work provides investigation of applicability of two calculation methods – density functional theory (DFT) and Moller-Plesset perturbation theory of second order (MP2). Applicability of methods was evaluated by comparison of calculated atomic coordinates and spectra with in literature available coordinates and experimentally obtained spectra. This investigation contributes to the building of the model for further calculations of more complicated structures, containing polycyclic aromatic hydrocarbons (PAH), e.g. complex compounds, which can include PAH molecules as a π- donor ligands or different PAH nitro-derivatives, which were proved to be mutagenic . Opportunity to predict and calculate spectra can help in understanding and detailed investigation of spectra of these compounds and, moreover, help to invent more precise methods for trace analysis of pollutants by sensitive spectroscopic methods.

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Vibrational spectra calculation of triphenylene: comparison of DFT and MP2 methods

Gleb Veryasov, univ. dipl. inž. kem.
Educational program: EKO3,
Jožef Stefan International postgraduate School
MENTOR: doc. dr. Adolf Jesih
Jožef Stefan institute, Jamova cesta 39, 1000 Ljubljana

The infrared (IR) and Raman spectra of triphenylene with intensities were calculated using both density functional theory (DFT, B3LYP method) and Moller-Plesset perturbation method of second order (MP2) with cc-pVDZ basis set. Spectra were compared with experimentally measured; the agreement between the observed and calculated spectra is good in case of IR spectroscopy, MP2 simulated spectra were found to have less vibrational band deviation from the real spectrum. In case of Raman spectroscopy, both methods gave good band position evaluation, however intensities are hardly correlated with experimental spectrum.

Triphenylene spectra calculation

Step 1. Geometry optimization → Step 2. Hessian calculation → Step 3. Spectra calculation

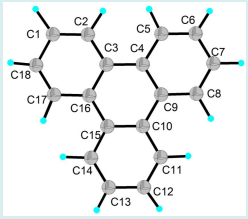

Figure 1. Triphenylene molecule

C-C bond lengths values in triphenylene molecule, shown in Fig. 1., experimental and calculated values (all values are given in Å)

Bond	Experimental	DFT	MP2
C1-C2	1,389	1,386	1,394
C2-C3	1,408	1,416	1,421
C3-C4	1,445	1,469	1,468
C4-C5	1,434	1,416	1,421
C5-C6	1,356	1,386	1,394
C6-C7	1,386	1,404	1,410
C7-C8	1,397	1,386	1,394
C8-C9	1,402	1,416	1,421
C9-C10	1,465	1,469	1,468
C10-C11	1,427	1,416	1,421
C11-C12	1,379	1,386	1,394
C12-C13	1,405	1,404	1,410
C13-C14	1,372	1,386	1,394
C14-C15	1,418	1,416	1,421
C15-C16	1,431	1,469	1,468
C16-C17	1,405	1,416	1,421
C17-C18	1,374	1,386	1,394
C18-C1	1,411	1,404	1,410
C16-C3	1,421	1,423	1,429
C9-C4	1,411	1,423	1,429
C15-C10	1,413	1,423	1,429

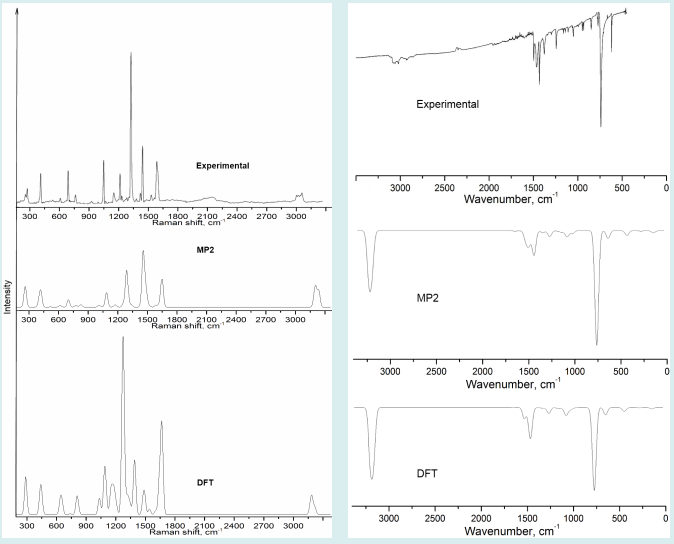

Figure 2. Calculated and experimental IR and Raman spectra of triphenylene

Calculated and experimental bands* and their intensities** (in brackets) in Raman and IR spectra of triphenylene

DFT						MP2				Experimental			
IR		Raman				IR		Raman				IR		Raman	
126	(0,02)	260	(0,32)	1379	(0,06)	118	(0,02)	257	(0,05)	1597	(0,04)	619	(0,33)	261	(0,08)
411	(0,01)	277	(0,01)	1461	(0,08)	404	(0,01)	260	(0,14)	1626	(0,02)	740	(1,00)	280	(0,12)
434	(0,04)	411	(0,14)	1476	(0,17)	410	(0,03)	393	(0,01)	1659	(0,26)	772	(0,11)	416	(0,22)
633	(0,04)	422	(0,16)	1528	(0,03)	617	(0,03)	404	(0,05)	3217	(0,07)	780	(0,04)	616	(0,06)
759	(1,00)	617	(0,13)	1590	(0,04)	743	(1,00)	420	(0,24)	3230	(0,04)	850	(0,10)	697	(0,24)
808	(0,01)	633	(0,10)	1629	(0,25)	1013	(0,01)	617	(0,02)	3234	(0,22)	936	(0,08)	772	(0,08)
1020	(0,01)	711	(0,01)	1654	(0,43)	1073	(0,03)	700	(0,13)	3247	(0,02)	951	(0,08)	1060	(0,30)
1069	(0,05)	787	(0,17)	1660	(0,28)	1131	(0,01)	708	(0,01)	3264	(0,02)	1051	(0,09)	1164	(0,09)
1135	(0,01)	806	(0,01)	3174	(0,02)	1266	(0,03)	778	(0,02)	3266	(0,24)	1109	(0,04)	1227	(0,21)
1259	(0,04)	1014	(0,12)	3175	(0,03)	1342	(0,01)	828	(0,02)			1142	(0,04)	1244	(0,07)
1461	(0,19)	1020	(0,02)	3189	(0,03)	1439	(0,11)	1013	(0,02)			1162	(0,04)	1297	(0,06)
1528	(0,07)	1069	(0,31)	3192	(0,12)	1496	(0,06)	1092	(0,26)			1244	(0,17)	1339	(1,00)
3175	(0,01)	1087	(0,08)	3204	(0,01)	1530	(0,04)	1177	(0,02)			1299	(0,03)	1392	(0,05)
3189	(0,29)	1135	(0,16)	3223	(0,05)	3217	(0,01)	1196	(0,01)			1340	(0,02)	1434	(0,09)
3207	(0,01)	1159	(0,20)	3225	(0,01)	3230	(0,16)	1266	(0,03)			1433	(0,44)	1457	(0,39)
3223	(0,30)	1177	(0,08)			3247	(0,01)	1298	(0,67)			1497	(0,23)	1546	(0,08)
		1192	(0,04)			3264	(0,19)	1342	(0,02)			2856	(0,02)	1580	(0,06)
		1256	(1,00)					1439	(0,01)			2926	(0,05)	1603	(0,30)
		1259	(0,39)					1468	(1,00)			3021	(0,08)	3031	(0,08)
		1300	(0,17)					1496	(0,12)			3057	(0,08)	3051	(0,07)
		1326	(0,11)					1505	(0,02)			3077	(0,08)	3070	(0,08)
		1374	(0,24)					1530	(0,01)			3107	(0,02)	3086	(0,09)

* - band positions are given in cm^{-1}. In table are given only bands with non-zero activity

** - intensities are given in relative units, normalized to the most intensive peak in spectrum

Conclusions

MP2 method give more precise evaluation of vibrational band positions; however, calculated intensities are hardly correlated with experimental values which can be explained as an influence of surrounding in crystal and alternating exciting field.

Hydrodynamic cavitation: a technique for augmentation of removal of persistent pharmaceuticals?

Mojca Zupanc[1,2], Tina Kosjek[1], Boris Kompare[3], Željko Blažeka[4], Uroš Ješe[5], Matevž Dular[5], Brane Širok[5], Ester Heath[1,2]

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To meet the ever growing demand for improved healthcare, pharmaceuticals are being produced in increasing amounts. As a consequence, pharmaceutical residues in the environment are becoming a concern. This is because many of these compounds have been proven to be resistant to conventional microbiological wastewater treatment. In response, new technologies are necessary to reach increasingly stringent regulation on water quality.

In this study we investigated hydrodynamic cavitation which is a potent advanced oxidation process (AOP) and is relatively cost-effective and easy for scale up. Caviation is the term given to the formation and subsequent implosion of bubbles that result when the partial local pressure in a fluid drops below vapour pressure. The collapse of the bubbles can generate a significant increase in local pressures and temperatures, called "hot spots". Such extreme conditions can result in the formation of free radicals, which are potent oxidising species capable of breaking down organic compounds. Our intention is to make use of these free radicals by deliberately cavitating the effluent flow from a wastewater plant. Additionally, our idea is to increase the amount of free radicals formed by adding hydrogen peroxide. Initial experiments have been carried out using a two reservoir system in which the fluid can be transferred from one to the other by varying the pressures in each. As the fluid passes from one reservoir to the other, it must pass through a constriction, which creates a pressure drop in the fluid resulting in cavitation. We tested the apparatus using six common pharmaceuticals: clofibric acid, ibuprofen, naproxen, ketoprofen, carbamazepine and diclofenac at various pressures 4, 5 and 6 bar. A pressure of six bars was optimum. In the case of carbamazepine and diclofenac, the results have been positive, improving the removal efficiency by 50% and 30 %, respectively, compared to conventional water treatment. In the case of clofibric acid, ibuprofen and ketoprofen the results are less conclusive. Further study will involve optimisation of cavitation process and its combination with biological water treatment in order to improve overall removal of resistant contaminants.

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[2] Jozef Stefan International Postgraduate School, Ecotechnology, Ljubljana, Slovenia
[3] Faculty of Civil and Geodetic Engineering, University of Ljubljana, Ljubljana, Slovenia
[4] Institute for ecological engineering (IEI) d.o.o., Maribor, Slovenia
[5] Faculty of Mechanic Engineering, University of Ljubljana, Ljubljana, Slovenia

INTRODUCTION

- occurrence of pharmaceuticals in different environmental compartments: ng L^{-1} to µg L^{-1} range.
- some pharmaceuticals not readily degradable by conventional treatment schemes: development of alternative methods (advanced oxidation processes)
- hydrodynamic cavitation:

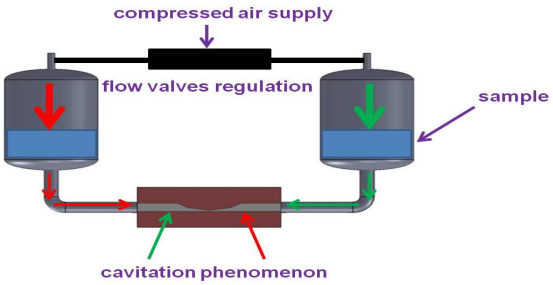
1.fluid passes through a constriction

2.increase of the fluid velocity and the decrease of static pressure

3.the inception and collapse of small bubbles and bubble clusters

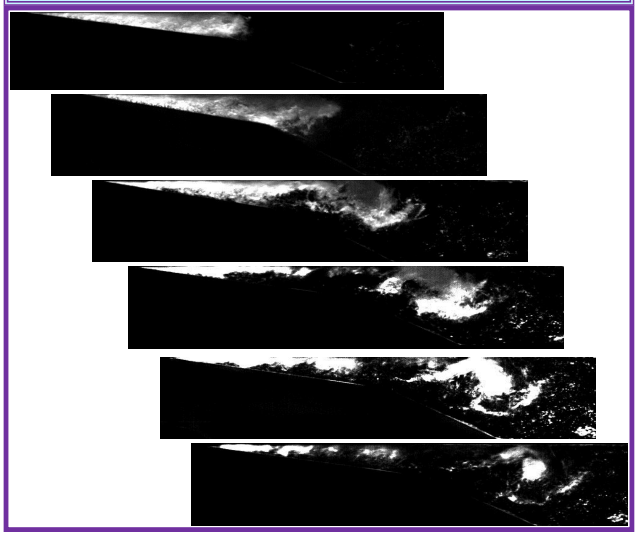
- aim of the study: investigate removal of selected pharmaceuticals with hydrodynamic cavitation under different operational conditions

EXPERIMENTAL SETUP

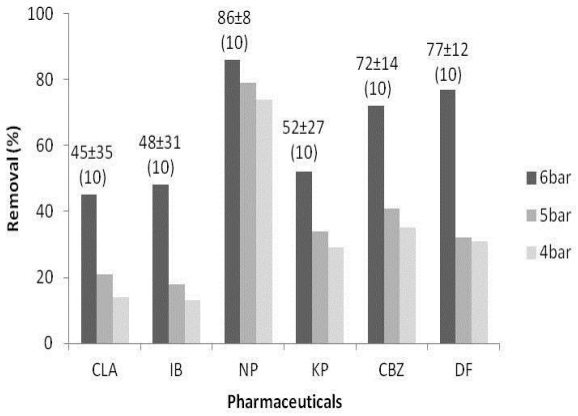


- sample volume: 1L
- different initial pressures: 6, 5 and 4 bar
- duration of cavitation: 30 minutes
- addition of 30 % H_2O_2: 20 mL
- pharmaceuticals concentration: 1 µg L^{-1}

HYDRODYNAMIC CAVITATION PHENOMENON



RESULTS



clofibric acid: CLA, ibuprofen: IB, naproxen: NP, ketoprofen: KP, carbamazepine: CBZ, diclofenac: DF

CONCLUSION

- previous study showed that carbamazepine and diclofenac are not readily removed during biological waste water treatment (21% and 48%): better removals acheived with cavitation
- results of cavitation : 45% removal of clofibric acid, 48% removal of ibuprofen, 86% removal of naproxen, 52% removal of ketoprofen, 72% removal of carbamazepine, 77% removal of diclofenac
- future work will combine hydrodynamic cavitation and Fenton process to achieve better removal of clofibric acid, ibuprofen and ketoprofen and further augment the removal of naproxen, carbamazepine and diclofenac
- transfer the technology to more complex matrices (effluents of biological wastewater treatment plants)

Informacijske in komunikacijske tehnologije (Information and Communication Technologies)

Reducing costs with computer power management

Lucas Benedičič[1], **Peter Korošec**[2]

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Many organizations are increasingly leaving their networked computers turned on 24 hours a day, 7 days a week, to allow for out-of-hours access by employees. Some administrators may say they want to do a backup, or the user may want to be able to remotely connect into her/his computer. But most of the time these personal computers (PCs) remain idle, wasting significant amounts of energy.

In this work, we present a software-based solution to automate the power control of desktop PCs. The deployment of the proposed system is simply done over the existing infrastructure (i.e. hardware) of the organization, thus minimizing the required investment. The controlling software, named Power Server, reads events from the personnel registration terminals. These events generate the power-state changes of the owner's PC, turning it on when arriving to office, and off when leaving home. Power Server also reacts to remote VPN connections in a similar way. The user may also modify the configuration and select, for example, to put the PC into a low-energy sleep or hibernation mode instead of turning it off.

The energy savings come from the fact that each PC is kept running strictly for the time it is being used, neither more nor less. Since even the latest low-power desktop PCs consume around 40 watts of power when idle, the potential savings of a Power Server installation are very promising: more than 52% of energy-consumption reduction, which means more than 10,000 EUR a year for an organization hosting just 300 desktop PCs.

There is other software that can be used to wake up sleeping PCs, such as Apple's Wake-on Demand and Microsoft's Sleep Proxy, but none of them provides the needed level of flexibility to maximize energy savings. Moreover, Power Server works without user's intervention, since the power-state changes are automatically performed, based on external events.

MEDNARODNA PODIPLOMSKA ŠOLA JOŽEFA STEFANA

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Reducing costs with computer power management

Lucas Benedičič, M.Sc.

Jožef Stefan International Postgraduate School,
Information and Communication Technologies

Advisor: **Assist. Prof. Peter Korošec**

Computer Systems Department, Jožef Stefan Institute

Objectives

Save power by automatically turning PCs off when they are not being used.

Operate without user's intervention.

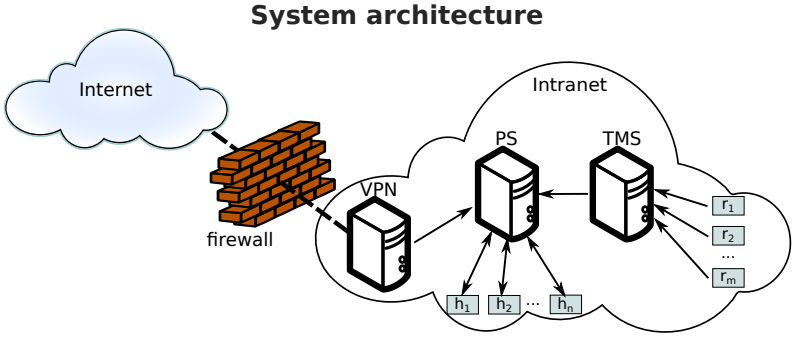
Take advantage of existing infrastructure (i.e. hardware) within an organization.

Main attributes

Minimal investment (*Power Server* is a software-only solution).

Gives the user the illusion the computer is always active.

System architecture



VPN Virtual Private Network server

PS *Power Server*

TMS Time Management System

$h_1,\ldots,h_n$ managed hosts

$r_1,\ldots,r_m$ personnel registration terminals

Implementation

Server side

Web application: administration and configuration tasks.

Activate host (WOL magic packet):

```
https://ps.example.si/[usr_id]/wakeup
```

Deactivate host (signal to host):

```
https://ps.example.si/[usr_id]/sleep
```

Host side

Win service / Un*x daemon: runs on every managed host ($h_1,\ldots,h_n$).

Avoids conflicts with user's tasks (e.g. backups, lengthy processes, updates, ...).

Access to user's personal configuration.

Consumption and cost analysis

Table 1: Power consumption measurements (W/h).

Equipment	Mode	Minimum	Maximum	Average	Std. Dev.
Computer	Active	35.73	127.91	78.39	31.27
Computer	Standby	1.32	2.63	1.69	0.74
Monitor	Active	16.10	128.22	42.48	25.45
Monitor	Standby	0.30	4.77	1.15	1.05

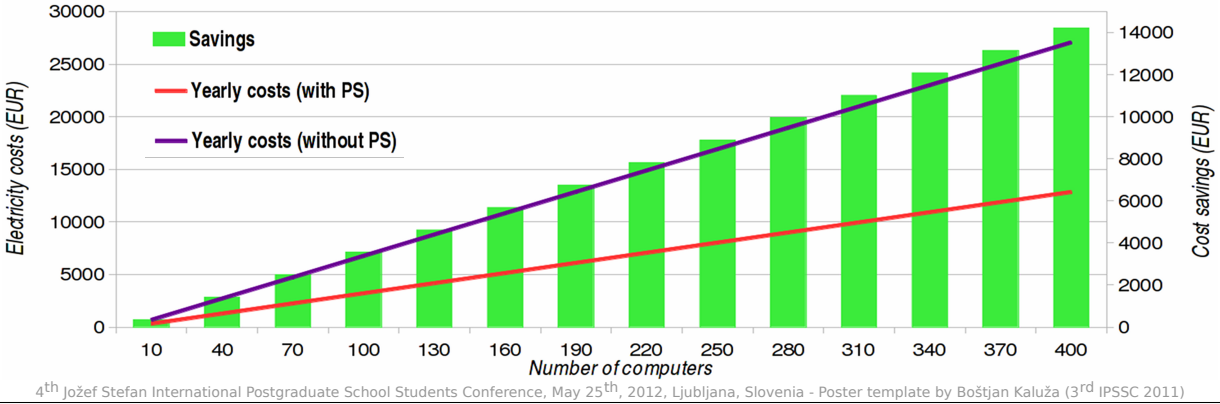
Table 2: Cost-saving estimation for one year (in EUR).

Equipment	Price (kWh)	2012 costs (no PS)	2012 costs (PS)	Savings
100 PCs	0.1109	6764.83	3210.02	3554.81
310 PCs	0.1109	20970.96	9951.06	11019.90

Results

Electricity-cost reduction of more than 52%.

Electricity-cost savings of more than 10,000 EUR for just 300 PCs.



Risk Assessment Using Local Outlier Factor Algorithm

Božidara Cvetković[1,2], **Mitja Luštrek**[1,2]
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The purpose of the medical expert systems is to disburden the workload of physicians and ease the detection of abnormal events. Research in this field is quite mature. However, modules that assemble the expert system are based on predefined rules created by the expert or models trained on the labelled data. For example, when a patient's health is normal, the parameters characterizing it usually follow some recurrent patterns. When the patient's health is not normal certain parameters move from the normal state and influence others. The rules and models created to detect the risk are highly correlated with the disease they were created for. This means that in case we would like to analyse a different disease, domain new rules have to be created and models trained. For that we would need relatively large amount of relevant labelled data.

There are four problems we are focused on in this research (i) can we use unlabelled data, (ii) is it possible to consider individuality of the patient regarding the pattern of vital signs and their influence to each other, (iii) can we detect the level of the abnormality and (iv) is it possible to detect how much do the analysed parameters contribute to the risk?

In this research we have adopted the Local Outlier Factor (LOF) algorithm, since it seems the most appropriate method to detect the abnormal events using unlabelled data and by that keep the individuality of the person. The algorithm was extended with the procedure for abnormality level detection per monitored parameter. The developed algorithm enables the doctor to see which of the monitored parameters contribute to the overall risk at most.

The disadvantage of LOF as a risk assessment method is that a new pattern is not necessarily a sign of increased risk. However, the advantage is that it can detect any kind of anomaly – there is no need for an expert to describe the possible anomalies and no need for examples of the anomalies (labelled data).

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Risk Assessment Using Local Outlier Factor Algorithm

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Study Programme: Information and Communication Technologies 3
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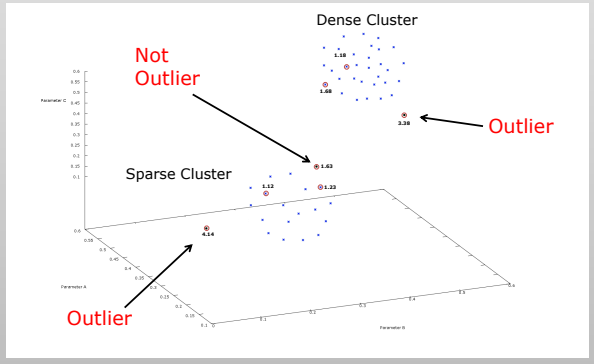
Supervisor: dr. Mitja Luštrek
Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana

Local Outlier Factor Algorithm

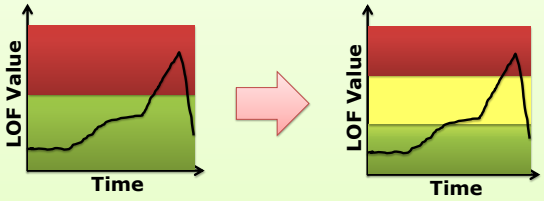
The key idea of LOF is comparing the local density of a point's neighbourhood with the local density of its neighbours.

Locality is given by k-nearest neighbours, whose distance is used to estimate the density.

Point in the graph is a n-tuple of chosen parameters.



GOAL: In addition to detect **normal** and **abnormal** events, we would like to **detect the level of risk**.



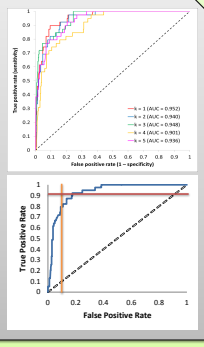
Method

I. Select n-tuple of monitored parameters

II. Nominal to numeric attribute conversion

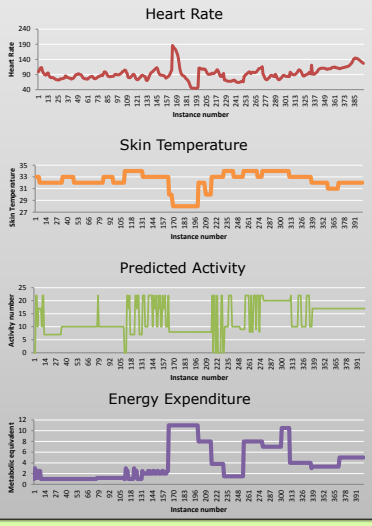
III. Select number of neighbours

IV. Set thresholds



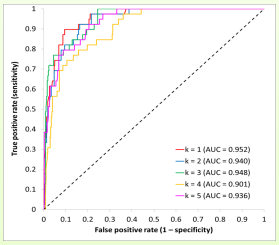
Experiment

Human activity monitoring (5 people)
- Use 4 parameters (HR,ST,PA,EE)

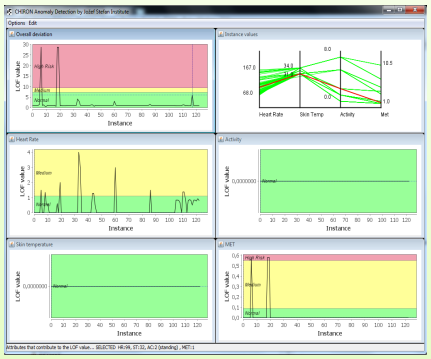


Nominal to numeric attribute conversion

	On all fours	Kneeling	Cycling	Lying	Running	Sitting	Standing	Transition	Walking
On all fours	0.00	2.12	3.64	2.51	6.42	3.09	2.78	2.80	4.42
Kneeling		0.00	3.08	2.30	6.06	2.0	2.16	2.67	3.69
Cycling			0.00	2.80	4.55	2.60	2.62	2.49	2.08
Lying				0.00	6.28	2.29	2.28	3.61	3.84
Running					0.00	6.10	6.05	4.78	4.03
Sitting						0.00	1.05	3.30	3.25
Standing							0.00	3.09	3.42
Transition								0.00	2.99
Walking									0.00



Set threshold



Monitor the user

Conclusion

In this paper we have shown that LOF can be used for health risk assessment. We have extended the general LOF to use nominal values in our case activity and to show the level of abnormality. The disadvantage of LOF as a risk assessment method is that a new pattern is not necessarily a sign of increased risk. However, the advantage is that it can detect any kind of anomaly – there is no need for an expert to describe the possible anomalies and no need for examples of the anomalies (labelled data).

Diagnostika sistemov z gorivnimi celicami in izboljšanje njihovega delovanja

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Gorivne celice so naprave, ki kemično energijo goriva (največkrat je to vodik) neposredno pretvarjajo v električno energijo. Energija se pretvarja s pomočjo elektrokemične reakcije, pri kateri se vodik spaja s kisikom, pri tem pa kot edini produkt nastaja voda. Zaradi tega so gorivne celice izredno čista tehnologija za pridobivanje električne energije.

Ob tem, da so gorivne celice okolju prijazne, jih odlikujejo tudi nekatere druge lastnosti: ne vsebujejo nobenih premičnih ali vrtečih se delov, tihost delovanja in visoki izkoristki. Te njihove dobre lastnosti jih delajo primerne za vgradnjo v raznorazne aplikacije, kjer lahko nadomestijo trenutne okolju neprijazne vire energije.

Pri aplikacijah, kjer so potrebni viri električne energije manjših moči, so se kot najprimernejše izkazale gorivne celice s protonsko prevodno membrano (ang. Proton Exchange Membrane – PEM). PEM gorivne celice, poleg že predstavljenih lastnosti, dodatno odlikujejo tudi nizka obratovalna temperatura in velika gostota moči. Področja, kjer so PEM gorivne celice primerne za uporabo, so: avtomobili in manjša prevozna sredstva za osebni prevoz, manjši delovni in transportni stroji, zasilni in brezprekinitveni napajalni sistemi, porazdeljeno sopridobivanje električne in toplotne energije ter vojaške aplikacije.

Še ne odpravljene težave, ki ovirajo prodor PEM gorivnih celic na širši trg, so povezane z zagotavljanjem zanesljivosti delovanja celic. Nezanesljivost je v največji meri posledica napak povezanih z nastalo vodo med delovanjem in njenim odvajanjem iz celic. Ti dve napaki sta tako imenovani poplavljanje celic in izsuševanje PEM membran. Napaki sta nemerljivi s standardnimi postopki, zato je za njihovo zaznavanje potrebno uporabiti diagnostične metode. Povečanje zanesljivosti delovanja pa se doseže tako, da se informacija, pridobljena z diagnostiko, uporabi v sklopu sistema vodenja, ki izvede ustrezno regulacijsko akcijo z namenom odpraviti napake.

V prispevku je predstavljena elektrokemična impedančna spektroskopija, ki je bila uporabljena za diagnosticiranje napak tekom delovanja. Hkrati pa je podan tudi koncept za implementacijo metode znotraj sistema vodenja gorivnih celic, ki poskrbi za odpravo napak in ustreznost delovanja.

MEDNARODNA PODIPLOMSKA ŠOLA JOŽEFA STEFANA

JOŽEF STEFAN INTERNATIONAL POSTGRADUATE SCHOOL

DIAGNOSTIKA SISTEMOV Z GORIVNIMI CELICAMI IN IZBOLJŠANJE NJIHOVEGA DELOVANJA

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Mentor: prof. dr. Đani Juričić
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PEM GORIVNE CELICE

- elektrokemične celice, ki omogočajo pridobivanje električne in toplotne energije neposredno iz vodika
- funkcijo elektrolita opravlja polimerna protonsko prevodna membrana
- voda je edini stranski produkt, zato ne onesnažujejo okolja
- nizke obratovalne temperaturah, tiho delovanje, velike gostote moči

OPIS PROBLEMA

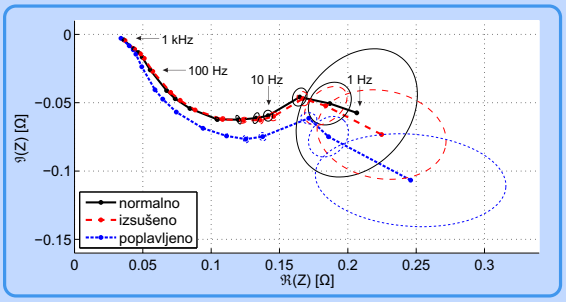
- tekom delovanja gorivne celice proizvajajo vodo, ki jo je potrebno učinkovito odvajati
- neustrezno odvajanje povzroči nastanek napak, ki negativno vplivajo na delovanje
- nezadostno odvajanje vode povzroči *poplavljanje* celic, preobsežno odvajanje pa *izsuševanje* PEM membran
- obe napaki se navzven kažeta kot padec izhodne napetosti in izkoristka gorivne celice

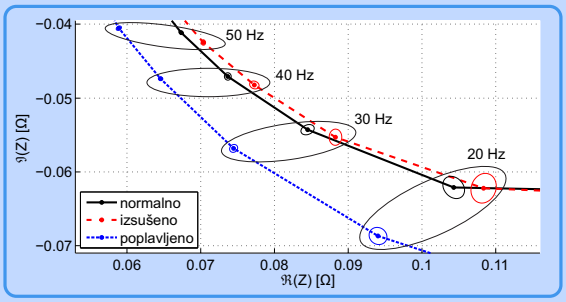
REŠITEV

- uporaba elektrokemične impedančne spektroskopije za diagnosticiranje poplavljanja in izsuševanja
- pridobljeno diagnostično informacijo uporabiti v sklopu celostnega vodenja z namenom odpraviti nastale napake in izboljšati zanesljivost delovanja PEM gorivnih celic

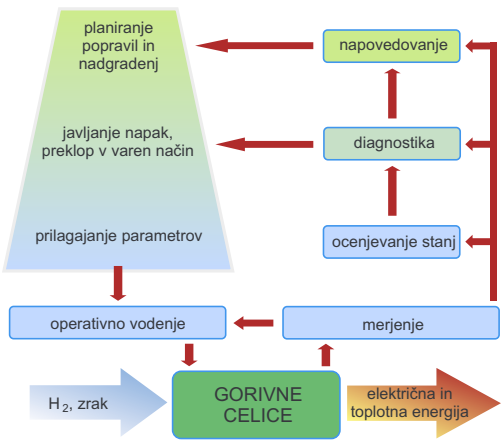
ELEKTROKEMIČNA IMPEDANČNA SPEKTROSKOPIJA

REZULTATI EKSPERIMENTALNE ŠTUDIJE





KONCEPTUALNA ZASNOVA CELOSTNEGA VODENJA



PRIMERI USPEŠNE UPORABE GORIVNIH CELIC

Vojaška mobilna enota – HyMIV

vgrajeni 7 kW sistem s PEM gorivnimi celicami zagotavlja napajanje naprav za elektronsko izvidništvo in protiletalsko bojevanje

Prednosti:
- tiho delovanje
- nizko temperaturni IR odtis
- večja avtonomnost
- hitra vzpostavitev delovanja

Bivalna kogeneracijska enota – GCCOGEN

PEM gorivne celice oskrbujejo bivalno kontejnersko enoto s potrebno električno in toplotno energijo

Prednosti:
- celovito zagotavljanje bivanjskih pogojev
- mobilnost
- visok izkoristek

Laboratori za vodikove tehnologije – TESTLAB

mobilni laboratorij za preizkušanje vodikovih tehnologij

Prednosti:
- omogoča preizkušanje vodikovih tehnologij na enem mestu pod nadzorovanimi pogoji

Partnerji:
IJS – Odsek za sisteme in vodenje, Domel d.d., INEA d.o.o., Ministrstvo za obrambo RS

Risk Assessment Model for Congestive Heart Failure

Hristijan Gjoreski[1,2]

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Congestive heart failure (CHF) is a common and chronic condition with an extremely poor prognosis. It is an issue when the heart cannot pump enough blood to the rest of the body. It is more common than most cancers, including breast, testicular, cervical and bowel cancers. Approximately 14 million people suffer from CHF in Europe.

In this paper we presented models that can predict the CHF risk of a patient. We were focused on predicting the long-term, static, risk that can be assessed upon patient's enrolment in the medical institution. The aim of the model was to predict the CHF risk, but also to provide additional explanation for the decision: the reason why the predicted risk is such as it is (low, medium or high).

To achieve this goal, we developed two types of hierarchical models: qualitative and quantitative. The first one is more user-friendly because it is using symbolic values for the data, e.g. low activity, high blood pressure, medium risk, etc. The other one is more mathematical and is using numbers instead of symbolic values.

We tested these models on a data created by a medical expert. First, the data is used as input to the models. Then, the models analyze the data and make the final decision (prognosis) for the risk. Additionally, both models have visualization mechanism, which shows the attributes that are extremes: the most and the least risky. Finally, the analysis techniques reveal healthy advices for the patient, such as: suggesting being more active, not to smoke and lose weight.

The results showed that the models successfully predict the correct risk factor, and also provide explanation mechanism which could assist the experts in their decision regarding the CHF risk factor.

MEDNARODNA PODIPLOMSKA ŠOLA JOŽEFA STEFANA

JOŽEF STEFAN INTERNATIONAL POSTGRADUATE SCHOOL

Long-term Risk Assessment Model for Congestive Heart Failure

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MENTOR: prof. dr. MATJAŽ GAMS
Research Supervisor: prof. dr. MARKO BOHANEC
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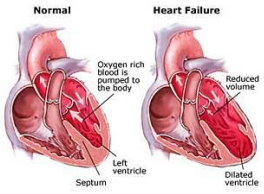
PROBLEM

Congestive Heart Failure

- The heart cannot pump enough blood to the rest of the body
- More common than most cancers
- Approximately 14 million people suffer from CHF in Europe



The CHIRON Project

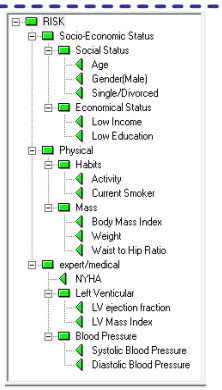
The CHF issue is addressed in the EU CHIRON project.

- **Goal**: development of reference architecture for personal elderly healthcare
- **Specifics**: creation of CHF Risk Assessment Model (RAM)
- **Requirements**: The RAM should additionally provide explanation mechanism of the assessed risk

SOLUTION

Long-term RAM

- Modeling of the static risk
- 15 out of 70 attributes were used
- 4 layer hierarchical structure
- Alternatives
  - Low-risk patient
  - Medium-risk patient
  - High-risk patient



Quantitative DEXi Model

- Symbolic attribute values, e.g. low activity, high blood pressure, medium risk etc.
- Utility Function (If-then rules)

	Age	Gender(Male	Single/Divor	Social Stat
1	50-60	no	no	low
2	50-60	no	yes	low
3	50-60	yes	no	low
4	50-60	yes	yes	**medium**
5	60-70	no	no	medium
6	60-70	no	yes	**medium**
7	60-70	yes	no	medium
8	60-70	yes	yes	**medium**
9	>70	no	no	**medium**
10	>70	no	yes	**high**
11	>70	yes	no	**medium**
12	>70	yes	yes	**high**

Quantitative Model

- Numerical attribute values
- Utility Function (Weighted sum of risks)

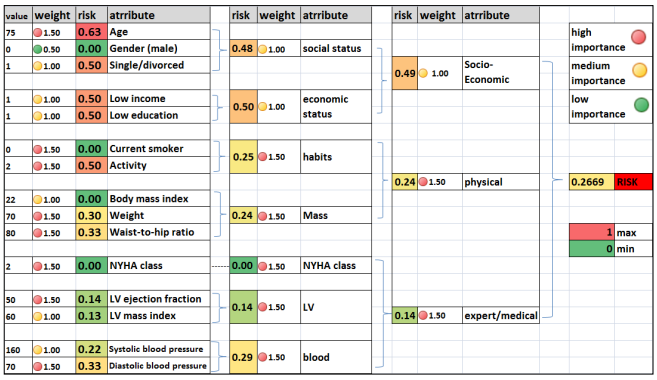
$$risk = \frac{1}{\sum_{i=1}^{N} w(p_i)} \sum_{i=1}^{N} w(p_i) risk(p_i)$$

EVALUATION & ANALYSIS

- **Both models** successfully evaluated the alternatives

Evaluation		Low Risk Patient	Medium Risk Patient	High Risk Patient
DEXi model		**Low Risk**	**Medium Risk**	**High Risk**
Quantitative model	0 - low; 1 - high	0.27	0.44	0.69

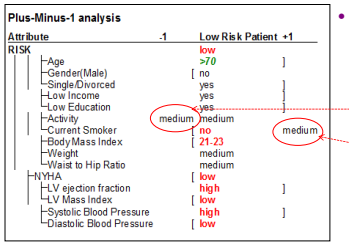
- Evaluation of the low-risk patient by the **quantitative model**



- **DEXi model** evaluation.

Attribute	Low Risk Patient	Medium Risk Patient	High Risk Patient
RISK	low	medium	*high*
Socio-Economic Status	*high*	*high*	medium
Social Status	*high*	*high*	medium
Age	*>70*	*>70*	*>70*
Gender(Male)	no	yes	yes
Single/Divorced	yes	yes	no
Economical Status	*high*	medium	*high*
Low Income	yes	no	yes
Low Education	yes	yes	yes
Physical	low	medium	medium
Habits	low	low	medium
Activity	medium	medium	*low*
Current Smoker	no	no	no
Mass	medium	*high*	*low*
Body Mass Index	21-23	>26	19-20
Weight	medium	*high*	low
Waist to Hip Ratio	medium	medium	low
expert/medical	low	medium	*high*
NYHA	low	medium	*high*
Left Venticular	low	medium	*high*
LV ejection fraction	*high*	medium	*low*
LV Mass Index	low	medium	*high*
Blood Pressure	low	low	*high*
Systolic Blood Pressure	high	medium	*low*
Diastolic Blood Pressure	low	low	*high*

Explanation is given by using **red** and **green** colors for the extreme attribute values.



- **DEXi analysis** for the low-risk patient
  - If the low-risk patient is **less active** or decides to **start smoking** in future, she will be classified as medium risk patient.

CONCLUSIONS

- The results showed that the models **successfully predict the risk factor**, and also **provide explanation mechanism** which could assist to **experts** in their decision regarding the CHF risk.
- The analysis techniques reveal **healthy advices** for the patient, such as: being more active, not to smoke and lose weight.

Prototip sistema za sprotni nadzor stanja industrijske opreme

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[2] Mednarodna podiplomska šola Jožefa Stefana, Ljubljana, Slovenija

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Sprotni avtomatiziran nadzor stanja opreme predstavlja pomemben trend v novih generacijah sistemov za avtomatsko vodenje procesov. Današnji postopki vzdrževanja procesne opreme so žal večinoma reaktivni (post-mortem), v najboljšem primeru pa preventivni. Napredno in ekonomsko bolj učinkovito prediktivno vzdrževanje pa se uporablja le v novejših in razmeroma kompleksnih aplikacijah. Prediktivno vzdrževanje temelji na naprednih postopkih diagnostike, prognostike in upravljanja vzdrževanja (angl. prognostics and health management, PHM), ki se nanašajo na napovedovanje preostale življenjske dobe komponent ter odločanje o vzdrževalnih posegih za zagotavljanje normalnega obratovanja naprav. Razlogi za majhno prisotnost prediktivnega vzdrževanja v industriji so predvsem visoka cena, zahtevna namestitev, pri tem pa so obstoječi nadzorni sistemi narejeni le za specifične aplikacije in jih ni možno enostavno prenesti na druge, podobne sisteme. Naš cilj je izdelati dovolj splošno platformo za sprotni nadzor stanja opreme s katero bi se izognili omenjenim slabostim.

MEDNARODNA PODIPLOMSKA ŠOLA JOŽEFA STEFANA

JOŽEF STEFAN INTERNATIONAL POSTGRADUATE SCHOOL

PROTOTIP SISTEMA ZA SPROTNI NADZOR STANJA INDUSTRIJSKE OPREME

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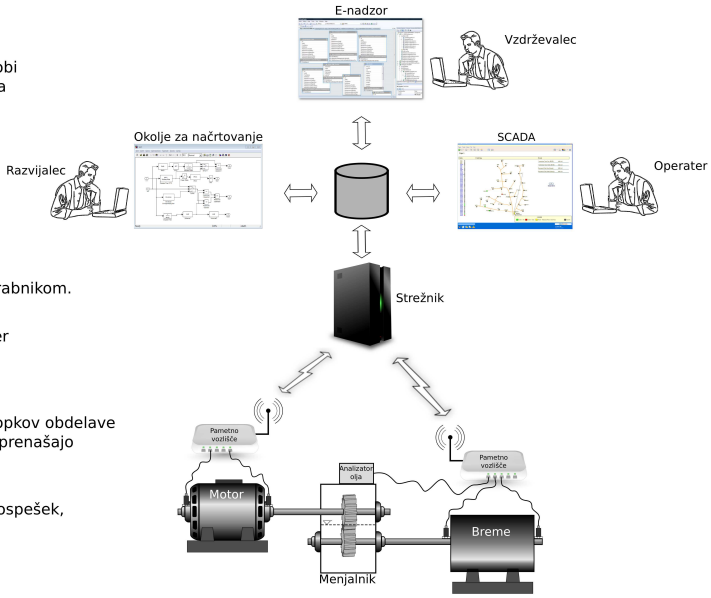
Mednarodna podiplomska šola Jožefa Stefana, Ljubljana, Slovenija

Mentor: prof. dr. Đani Juričić
Inštitut Jožef Stefan, Jamova cesta 39, 1000 Ljubljana

Koncept sistema za sprotni nadzor stanja

Nadzorni sistem je sestavljen iz več sklopov:

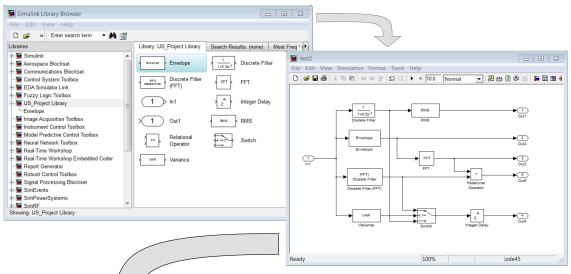
- uporabniški vmesnik:
  - E-nadzor
    informira vzdrževalce o trenutnem stanju ter predvideni življenski dobi nadzorovane opreme in omogoča planiranje vzdrževalnih posegov za zagotavljanje normalnega obratovanja naprav.
  - SCADA
    omogoča operaterjem spremljanje delovanja nadzornega sistema.
  - Okolje za načrtovanje
    služi načrtovanju naprednih postopkov obdelave signalov za pridobivanje informacij o stanju ter preostali življenski dobi opreme. Del postopkov poteka na pametnih vozliščih, del pa na strežniku.
- Podatkovna baza
  shranjuje podatke nadzornega sistema in je glavni vir informacij uporabnikom.
- Strežnik
  predstavlja podatkovni most med brezžičnim senzorskim omrežjem ter podatkovno bazo in uporabniki. Na njem se izvaja tudi zadnja faza obdelave podatkov iz pametnih vozlišč.
- Pametna vozlišča
  tvorijo brezžično senzorsko omrežje. Na njih se izvaja ključni del postopkov obdelave signalov, zajetih iz senzorjev. Rezultati se preko brezžičnega omrežja prenašajo na strežnik.
- Senzorji
  širok nabor senzorjev je možno priključiti na pametna vozlišča (npr. pospešek, hitrost, parametri olja, temperatura)



Okolje za načrtovanje

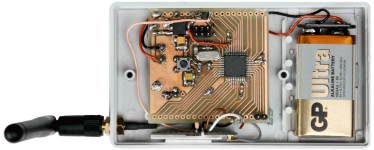
- podlaga je programski paket Matlab & Simulink
- izdelana posebna knjižnica blokov za načrtovanje postopkov obdelave signalov vibracij na vozlišču (filter, RMS, varianca, FFT, detekcija ovojnice itd.)
- m-funkcija za razčlenjevanje Simulink sheme ter izdelavo konfiguracijske datoteke za pametno vozlišče

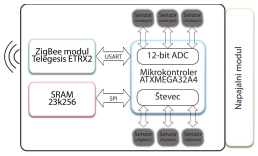
ANALIZA ⇨ NAČRTOVANJE ⇨ POŠILJANJE NA VOZLIŠČE



Prototip pametnega vozlišča

- majhna poraba energije
- nizka cena
- ZigBee brezžična komunikacija
- možnosti priklopa: 4 senzorji vibracij, 4 senzorji temperature, 4 senzorji hitrosti vrtenja, drugi analogni in digitalni signali
- hitrost vzorčenja do 10 kHz
- možnost brezžične konfiguracije postopkov obdelave signalov





4th Jožef Stefan International Postgraduate School Students Conference
May 25, 2012, Ljubljana, Slovenia

Integration of structured expert knowledge

Vladimir Kuzmanovski[1, 2], **Sašo Džeroski**[1, 2], **Marko Debeljak**[1, 2]

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Discovering knowledge in data or data mining becomes a very important discipline as part of information technologies. It helps people, companies and even whole businesses to use their own data in very practical way by finding interesting and sometimes scientifically approved patterns and knowledge. Basically, the value of information is always proportional to the scale of the problem it addresses.

Learning from the data and especially combine the learned patterns and knowledge in decision support system will significantly increase the reliability of decision maker and will produce a better support in decision making process.

The next generation of improvements of decision support systems will cover the expert knowledge integration. We proposed an approach of integration of expert knowledge with models inducted from data into final decision support system by integration of expert knowledge (expert system) with data mining algorithms.

MEDNARODNA PODIPLOMSKA ŠOLA JOŽEFA STEFANA

JOŽEF STEFAN INTERNATIONAL POSTGRADUATE SCHOOL

Integration of structured expert knowledge

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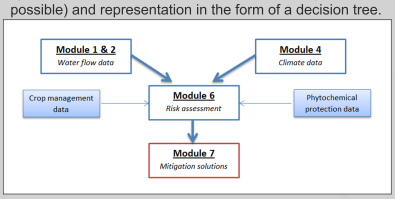
Mentor: Marko Debeljak
Co-mentor: Saso Dzeroski

Abstract

This poster presents an effective implementation of data pre-processing methodology and data mining referring to integrate decision rules as part of manually written expert system (expert knowledge) with models inducted from data. The methods we have used are standard methods for data pre-processing, including techniques for handling missing data, feature construction, transformation and aggregation, and J48 machine learning algorithm, implemented in WEKA data mining tool set for the process of integration of the manually created expert rules given in decision tables

Expert system

The first step in the integration should be optimization of the expert system.The given expert system is in the form of decision rules written in tables. The optimization of the expert system includes reduction of the decision rules (where it is possible) and representation in the form of a decision tree.



Data Pre-processing

Machine Learning (J48)

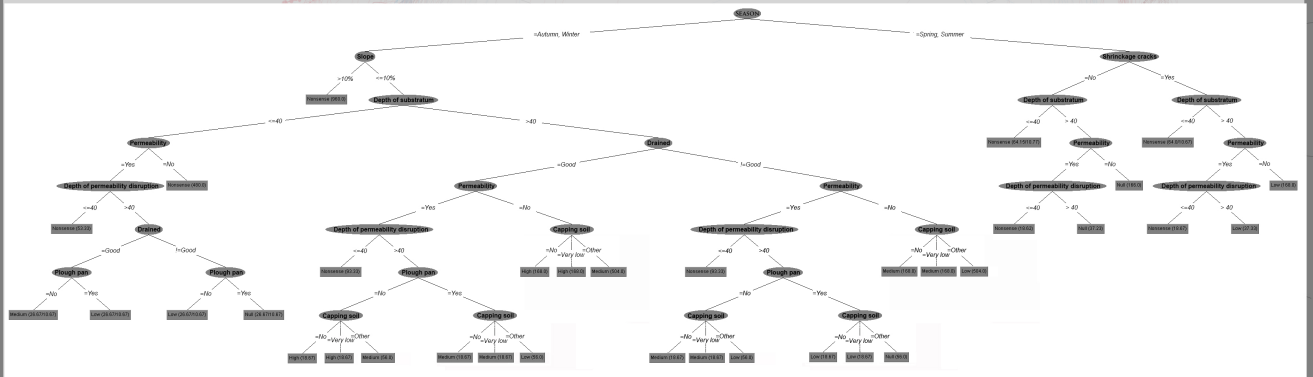
Data

For this particular poster we will keep the attention to tables from Module 1 & 2 only, which are about the diagnosis of water flows from the fields. Module 1 & 2 contains tables, divided in 3 parts depending on the weather season: autumn-winter, spring and summer. Beside tables, modules contains some additional information given in a text documents and describing additional information that will be targeted as inputs attribute. All of the attributes have nominal values.

	Module 1	Module 2
No. of tables	12	34
No. of input attributes	12	13
No. of target attributes	11	12
No. of instances	312	6816

Results & discussion

In the process of integration, the total 12 classification decision trees were built, one for each target attribute. Here we will describe the decision tree model for “transfer by drainage” which refers to the water transfer in drainage pipes which are buried under the fields.
The model has been built over dataset with 6818 instances, but 2402 of them were ignored because of the target attribute’s missing value, due to the chosen method for handling missing values. On the other hand, the correctly classified instances over training dataset are 100%.



The model that has been built can be used for validation of the expert system and discussion for the complexity of the existing expert knowledge. Furthermore, the described approach to integration of a given expert system and its further networking with the models induced from data collected during the regular data collection could result in a new generation of decision support systems which will significantly increase the reliability of decision maker.

Acknowledgment

ARVALIS Institut du végétal

We ackowledge ARVALIS for financial support of project EVADIFF (Evaluation et développement de modèles et outils d’aide à la décision utilisés pour la prévention des pollutions diffuses par les produits phytopharmaceutiques)

VESNA based platform for spectrum sensing in ISM bands

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All radio systems, including mobile phone network, Wi-Fi for computer networks, FM radio, satellite systems, use the same shared resource for communication: the radio spectrum. This spectrum is managed by regulatory agencies, which allocate frequency bands to various systems. A notable category of allocated frequency bands are the Industrial, Scientific and Medical (ISM) bands, which can be freely used for communication by any device. For example Wi-Fi and Bluetooth systems use this band. In order to develop new technologies that operate in different frequency bands, or to optimise existing systems, it is necessary to monitor the radio activity in a given band.

A low-cost spectrum sensing framework has been developed, which is able to monitor the signal power in the ISM frequency bands. This system is based on the VESNA wireless sensor platform. Wireless sensor networks are usually low-power networks of devices which collect information about their environment, such as temperature, humidity, pressure. In this case the wireless sensor node hardware has been used for collecting information about radio spectrum usage. This framework is being used for collecting experimental data about new, experimental radio systems, which will be more efficient. It is also planned to integrate the sensing capabilities of this framework with more advanced radio systems.

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VESNA based platform for spectrum sensing in ISM bands

ZOLTAN PADRAH[1,2], TOMAŽ ŠOLC[2]

Supervisor: doc. dr. MIHAEL MOHORČIČ

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Study program: Information and Communication Technologies

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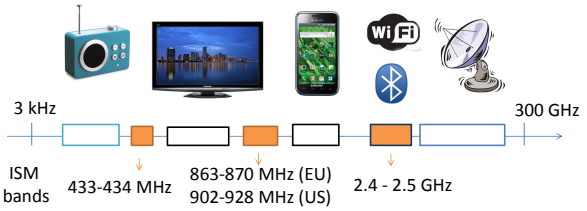
Radio spectrum and ISM bands

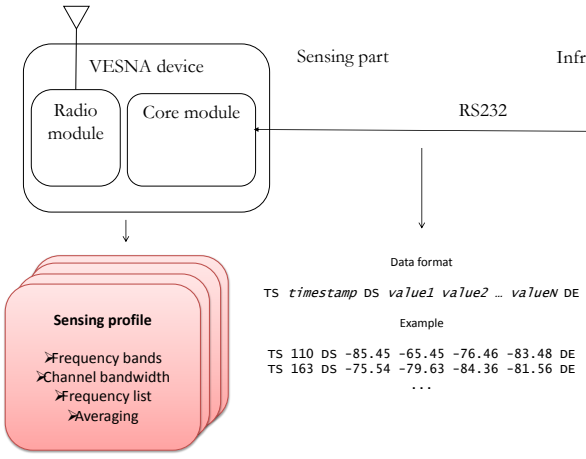
Frequency band allocation
Regulatory agencies

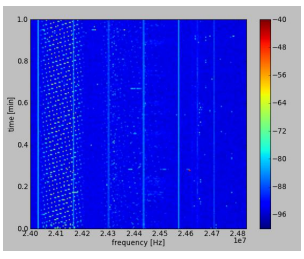


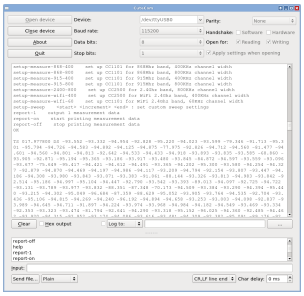
VESNA platform

- ST ARM Cortex-M3
- JTAG, USB, USART PC interface
- I2C, SPI, PWM, ADC, DAC, USART sensor and actuator interfaces
  - Code library: C/C++ (GCC)
- 300-900 MHz, 2.4 GHz radio interface (all ISM bands); TI CC1101, TI CC2500
- Software tools: Open Source
  - Eclipse IDE
  - Tool-chain: GNU Compiler Collection
  - Cygwin, Linux environment for Windows
  - JTAG server: OpenOCD
  - JTAG hardware interface: Olimex ARM-USB-OCD

Proposed framework

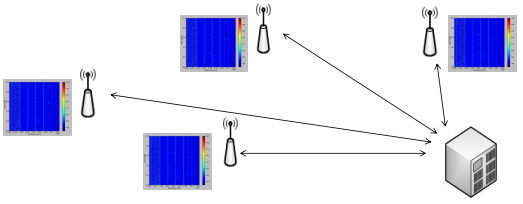






Applications and future work

- Optimization of radio networks
- Dynamic spectrum access
- Sensing for cognitive radio systems
- Integration of multiple sensing devices



Acknowledgements

The authors would like to thank SensorLab for its support.
sensorlab.ijs.si

The software on which the infrastructure part is based has been released as open-source:
http://www.tablix.org/~avian/blog/archives/2011/12/funcube_spectrum_analyzer/

Improving Performance of Wireless Mesh Networks with Network Coding

Erik Pertovt[1,2], **Kemal Alič**[1,2], **Aleš Švigelj**[1,2], **Mihael Mohorčič**[1,2]

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Wireless Mesh Networks (WMN):
- typical representatives of wireless access networks, where nodes, such as wireless routers, are highly connected to each other through multi-hop wireless links enabling various large-scale communications as e.g. Internet connection

Network Coding (NC):
- enables encoding multiple packets either from the same or from different traffic flows into one encoded packet for saving bandwidth and thus increasing the network throughput while maintaining the desired Quality of Service

Network simulation model for network coding:
- supports building WMN networks
- support for different NC and routing algorithms

Our work:
- studying, evaluating and comparing causes and consequences on the network performance of different NC approaches
- investigating several routing techniques for NC
- improving metrics based on the response of routing to the number of coding opportunities, packets queue lengths, etc.
- developing new NC and NC-aware routing algorithms and protocols for different environments

Results:
- NC significantly improves the performance of WMN; network throughput is increased and end-to-end packet delay is decreased

Our goal:
- further improvement of the capacity of WMN and similar networks through novel NC and routing techniques

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IMPROVING PERFORMANCE OF WIRELESS MESH NETWORKS WITH NETWORK CODING

Erik Pertovt, Kemal Alič, Aleš Švigelj, Mihael Mohorčič
Study program : Information and Communication Technologies
Jožef Stefan International Postgraduate School
ADVISOR: doc. dr. Mihael Mohorčič
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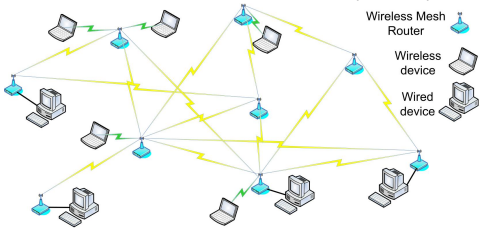
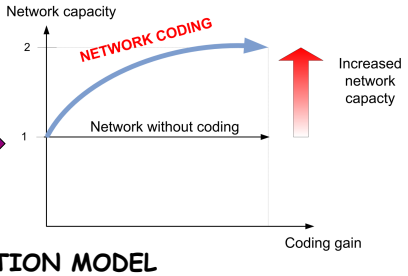
Wireless Mesh Network (WMN)

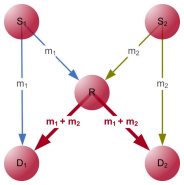


Increasing the network capacity through network coding for up to factor 2!



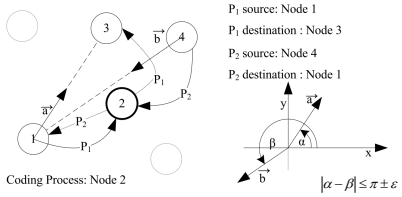
NETWORK CODING (NC)

- Enables encoding multiple packets either from the same or from different traffic flows into one encoded packet for saving bandwidth
  → **Increases the network throughput**



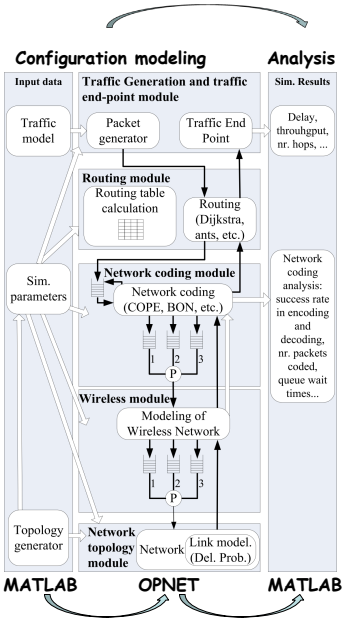
►BON: Bearing opportunistic NC algorithm

–An efficient and routing-independent algorithm
→ Requires no traffic information on which packets can be coded together, but selects packets to be encoded together based solely on position of nodes, thus bringing little additional overhead



DEVELOPED CODING SIMULATION MODEL

- **Network topology generator**:
  - Arbitrary number of nodes
  - Random positions
- **Network description program**:
  - Desired topology, nodes, links
  - Parameters of communication procedures (throughputs, number of packet restransmissions, loads, etc.)
- **OPNET Modeler simulation model**:
  - Traffic generator
  - Routing module
  - Network coding module
  - Wireless module
  - Network topology module



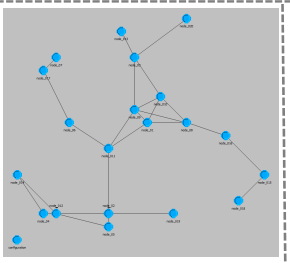
Objectives:

- Studying, evaluating and comparing causes and consequences of the performance of different network coding approaches
- Investigating routing techniques for network coding
- Improving metrics based on the response of routing to the number of coding opportunities, packets queue lengths, etc.
- Developing new NC and NC-aware routing algorithms and protocols

PERFORMANCE EVALUATION OF NETWORK CODING ALGORITHMS

Network:

- 20 same configured wireless nodes, as e.g. in homogeneous network
- Ideal symetric wireless links (1Mbit/1Mbit)

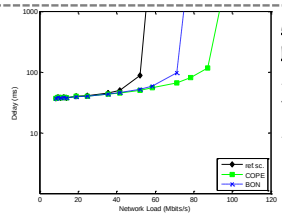


Parameters:

- Traffic load is generated on all nodes with the same intensity using exponential distribution of inter-arrival times and constant packet lengths (i.e. 10 Kbit)
- Traffic load is increased through simulation runs
- Every simulation run took 60 seconds and results were collected during 33 seconds of steady traffic conditions

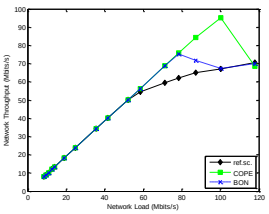
Quality of Service measurements:

- Delay in dependency of network load for BON, COPE and reference scenario without coding (ref.sc)



Quantity of Service measurements:

- Network throughput in dependency of network load for BON, COPE and ref.sc.



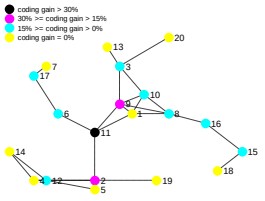
Measurements from the NC point of view:

- Nodes categorization based on their coding success
- Coding gain (G):

$$G = \frac{N_S}{N_C}$$

N_S → number of source packets (without coding)
N_C → number of packets required to send source packets with coding

- 4 groups of coding nodes



Mobile terminal as opportunistic sensor network device for research on cognitive radio networks

Marko Pesko[1,3], Luka Vidmar[1], Mitja Štular[1], Mihael Mohorčič[2,3]

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Wireless Sensor Networks (WSN):
- are wireless networks build of spatially distributed small and low-power autonomous devices called sensor nodes, equipped with heterogeneous sensors to measure various physical phenomena over specific area of interest.

Opportunistic sensor network devices:
- are devices which can be used as sensor nodes,
- can be mobile terminals which can opportunistically cooperate with WSNs in various scenarios.

Cognitive radio principles:
- include methods for more efficient spectrum usage,
- enable multiple users sharing the same frequency spectrum in a cooperative or competitive way,
- enable non-licensed secondary users to communicate on the same frequencies as licenced primary users if and only if they do not cause any harmful interference.

Hidden node problem:
- is a problem in cognitive networks where secondary users in some situations are not aware of the primary user's presence in the vicinity.

Our work:
- outlining mobile terminals' features which enable them becoming opportunistic sensor network devices,
- pointing out mobile network issues related to sensor measurements access on mobile terminals and their lack of WSN compatible communication interfaces,
- presenting solutions for these issues.

Future work:
- to test mobile terminals as opportunistic sensor network devices in real testbeds meant for spectrum sensing and efficient Radio Environment Maps building to support multiple issues in cognitive networks.

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Study program : Information and Communication Technologies

ADVISOR: doc. dr. MIHAEL MOHORČIČ

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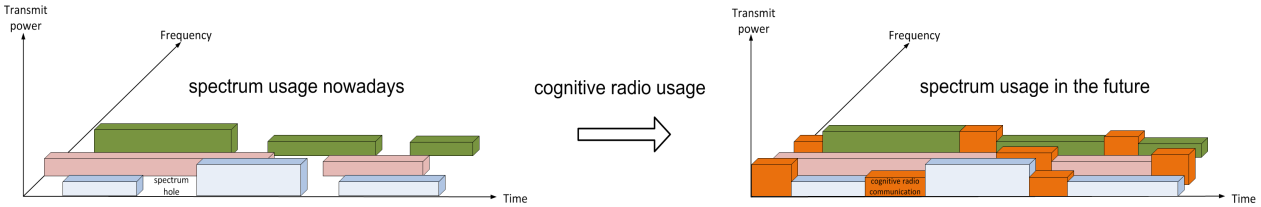


free spectrum – spectrum holes

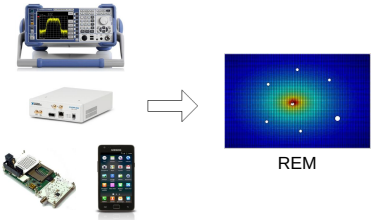
no free spectrum – used by cognitive radios

COGNITIVE RADIO (CR)

- CR enables communication in spectrum holes of licensed and unlicensed spectrum bands when these occur
- CR incorporates a cognition cycle:
  - **observation (spectrum sensing)**
  - orientation
  - planning
  - decision making
  - action making
  - learning on previous experiences
- CR principles research can be made by:
  - simulations
  - **tests in real environment**

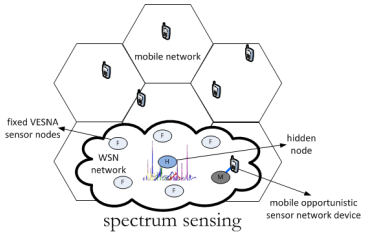
SPECTRUM SENSING

- Spectrum sensing is needed to provide the cognition cycle's inputs such as Radio Environment Map (REM)
- Spectrum can be sensed by:
  - **expensive** professional measurement equipment (spectrum analyzers)
  - **medium-cost** Universal Software Radio Peripherals (USRPs)
  - **low-cost** Wireless Sensor Networks (WSN) nodes + opportunistic sensor network devices



- A good compromise among price, number of devices, their computing, communication and sensing capabilities gives cooperation of sensor nodes and opportunistic sensor network devices such as mobile terminals

CONSIDERED SCENARIO



- The considered scenario consist of:
  - fixed VESNA sensor nodes (F)
  - mobile opportunistic sensor network device(s) (M)
  - hidden node or primary user transmitter (H)
  - mobile newtork support
- Real test scenario will sense spectrum over the specific area of interest and will be used to build REM

SENSOR MEASUREMENTS ACCESS OVER MOBILE NETWORK

Typical sensors on sensor nodes and opportunistic sensor network devices:

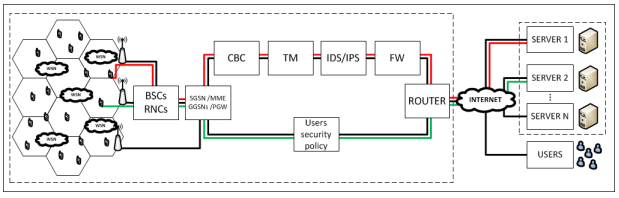
- Microphone, camera, touch screen, buttons, GPS, orientation, magnetic field, gravity, gyroscope, light, temperature, pressure, proximity, humidity, accelerometer, radio interfaces, and other sensors

Measurements access

- mobile operators block all session attempts from the direction of external networks
- Solutions:

— typical measurements transport route over mobile network where all communication sessions are initiated by sensor nodes, their gateways or opportunistic sensor network devices

— access from external networks possible only via private Access Point Name (APN) where security policy can be user defined



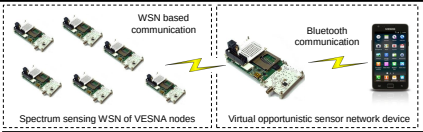
THE PROOF OF CONCEPT

Issues:

- communication among mobile terminals and VESNA sensor nodes (mobile terminals lack WSN communication)
- spectrum sensing with mobile terminal(s) without appropriate sensors for spectrum measuring

Tested solution:

- Bluetooth module was added to one VESNA node capable of spectrum sensing
- usage of private APN for cross mobile network communication



The authors would like to thank SensorLab for its support.

Inteligentni sistem za zaznavanje zdravstvenih težav pri starejših

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V razvitem svetu je vedno večji delež starejšega prebivalstva. Starejši navadno živijo izolirani od otrok, zato v primeru bolezni ali poškodbe težko dobijo pravočasno pomoč. Namen te študije je razviti tehnologije, ki bi olajšale samostojno življenje starejših. Članek predstavlja dva pristopa k razvoju sistema za detekcijo zdravstvenih težav pri starejših z namenom podaljševanja njihovega samostojnega življenja. Če je zaznana zdravstvena težava, sistem avtomatsko obvesti medicinsko službo. Gibanje starejših je zajeto s sistemom za zajem gibanja in celoten sistem je naučen, da prepoznava specifične zdravstvene težave. Semantični pristop uporablja semantične atribute, ki jih uporablja zdravstvena stroka, splošni pa za atribute uporablja vse izmerljive kote sklepov namesto specifičnih atributov za posamezne bolezni. Kljub temu dobro prepoznava zdravstvene težave, podobno kot semantični in pristopi iz literature.

Inteligentni sistem za zaznavanje zdravstvenih težav pri starejših

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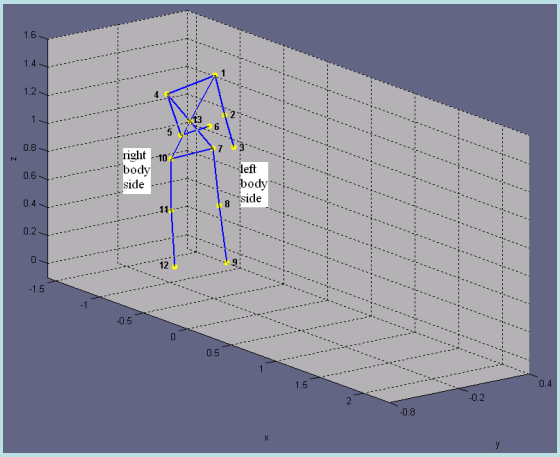
•Predlagamo pristop podatkovnega rudarjenja k inteligentnemu in vseprisotnemu sistemu nadzora zdravja.
•Cilj pristopa je prepoznati nekaj najpogostejših in najpomembnejših bolezni starejših, ki so lahko razpoznane z opazovanjem in analizo karakteristik njihovega gibanja.

Materiali in metode

Ciljne aktivnosti in zdravstvene težave za detekcijo. Vse situacije, ki jih prepoznavamo, je predlagal sodelujoči medicinski strokovnjak na osnovi pogostosti nad 65 let starosti, medicinske pomembnosti in možnosti razpoznavanja iz gibanja. Predlagan sistem uporablja dvostopenjski sistem za razpoznavo pomembnih situacij. V prvem koraku razpoznava med petimi aktivnostmi: padec zaradi nesreče, padec zaradi bolezni, hoja, vstajanje/sedanje, uleganje/vstajanje. V drugem koraku razpoznane hoje iz prvega koraka klasificira kot: Parkinsonovo bolezen, hemiplegijo, bolečine v hrbtu, bolečine v nogah ali normalno hojo. Oba koraka sta izvedena z metodo k-najbližjih sosedov in dinamičnim ukrivljanjem časa (dynamic time warping oz. DTW) za mero podobnosti.

Atributi za podatkovno rudarjenje:
•kot levega in desnega ramena glede na zgornji del trupa v trenutku *t*,
•kot levega in desnega kolka glede na spodnji del trupa,
•kot med spodnjim in zgornjim delom trupa,
•levi in desni komolčni ter levi in desni kolenski kot.



Dinamično ukrivljanje časa. Dinamično ukrivljanje časa (DTW) poravna 2 časovni vrsti na način, da minimizira neko mero. Optimalna poravnava je dobljena s preslikavo več zaporednih vrednosti ene časovne vrste v eno vrednost druge časovne vrste in tako je lahko DTW računan tudi na časovnih vrstah različnih dolžin. V nasprotju z Evklidsko razdaljo, DTW lahko najde podobnosti med vzorcema dveh časovnih vrst tudi če ta vzorca nista časovno poravnana ali pa sta vzorca različnih dolžin.

Eksperimenti in rezultati. Uporabili smo 256 meritev zdravih posameznikov in posameznikov z določenimi zdravstvenimi težavami, pri čemer je bil vsak posameznik 4-5 krat posnet z različnimi hitrostmi izvajanja aktivnosti.
Klasifikacijski proces upošteva eno vhodno testno časovno vrsto, ki jo primerja z vsemi ostalimi, da najde minimalno globalno razdaljo za vsako poravnavo in sklepa, da je vhodna meritev istega razreda kot učna meritev, ki ima najmanjšo razdaljo do te vhodne meritve. Metoda "izpusti enega" (leave one out) za 5-najbližjih sosedov da klasifikacijsko točnost 97.5 % za aktivnosti/padce in

97.6 % za zdravstvena stanja.

Zaključek. Članek predstavlja splošni pristop k detekciji zdravstvenih težav in padcev za namen podaljšanja samostojnega življenja starejših. Je splošen, ker ne uporablja specifičnih atributov, ampak splošen pristop iz kombinacije DTW in k-najbližjih sosedov. Dobimo klasifikacijsko točnost 97.5 % za aktivnosti/padce in 97.6 % za zdravstvena stanja. Kljub temu, da je metoda splošna in lahko razpozna tudi nove vrste gibanj, dosega visoke klasifikacijske točnosti, podobne pristopom s specifičnimi atributi iz literature.

Zahvala. Operacije, ki so pripeljale do tega članka, je delno sofinancirala Evropska Unija, Evropski socialni sklad. Avtor članka se zahvaljuje mentorju prof dr. Matjažu Gamsu za pomoč.

Sentiment analysis on tweets in a financial domain

Jasmina Smailović[1,2], **Miha Grčar**[1], **Martin Žnidaršič**[1]

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From psychological research it is known that emotions are essential to rational thinking. Also, it has been shown that the stock market is a direct reflection of the social mood. On the other hand, more and more people make their opinions available publicly online, making it available for analysis. Can we expect that the analysis of public mood can identify important events and predict the movement of stock market values? Our preliminary studies indicate that the answer is – yes. We analysed the Apple financial Twitter posts that were collected in a 10 months period. We identified days when people intensively talked about Apple and consequently identified important events for this company. Next, we performed statistical analysis for the period of specific 3 months, which is the period of the main changes in the stock price, to determine whether we can predict future movement of Apple`s closing price. The test showed that we are able to predict the rise or fall in closing price two days before it occurs. This kind of analysis can also be applied to other domains. For example, it can be used for the assessment of products, prediction of purchase decisions, earnings and other similar phenomena.

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SENTIMENT ANALYSIS ON TWEETS IN A FINANCIAL DOMAIN

JASMINA SMAILOVIĆ[1], MIHA GRČAR, MARTIN ŽNIDARŠIČ

[1]Study programme: Information and communication technologies,
[1]Jožef Stefan International Postgraduate School
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It is known that emotions are essential to rational thinking

The stock market is a direct measure of social mood

More and more people make their opinions available to the public via the Internet

Can analysis of public mood identify important events and predict movement of stock market values?

We investigate whether sentiment analysis of daily posts from Twitter can identify important events and predict a rise or fall in closing price before a change happens.

DATA PREPROCESSING SETTINGS FOR THE SVM CLASSIFIER

Machine learning approach

Training set: collection of 1,600,000 tweets

Testing set: manually labeled 177 negative and 182 positive tweets

Several parameters were changed and based on accuracy the best classifier was chosen.

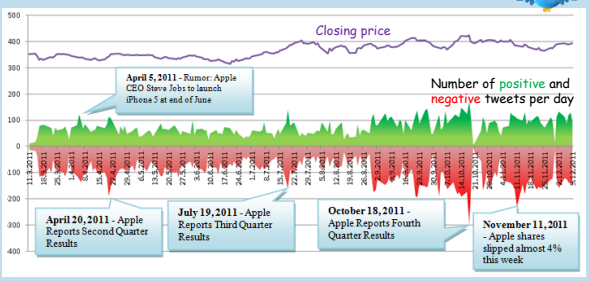
Maximum N gram length	Minimum word frequency	Replace usernames with a token	Replace web links with a token	Remove letter repetition	Accuracy	Precision/Recall
2	2	No	Yes	Yes	81.06%	81.32%/81.32%
2	2	No	No	Yes	78.83%	77.60%/81.87%
2	2	Yes	No	Yes	78.55%	75.86%/84.62%
2	2	Yes	Yes	Yes	78.27%	76.53%/82.42%
2	3	No	No	Yes	76.88%	77.97%/75.82%
1	2	No	No	Yes	76.32%	72.99%/84.62%

CLASSIFYING FINANCIAL TWEETS

We analyzed posts that discussed Apple stocks in the period from March 11 to December 9, 2011.

Number of positive and negative tweets for each day was counted.

Peaks in graph→ people intensively talk about Apple → important events.



Next, we applied The Granger causality test to check whether we can predict future movement of Apple closing price. The test indicates that positive sentiment probability could predict stock price movements, as we got a significant result in our dataset for a two day lag.

Lags	p-value
1	0.4855
2	0.0565
3	0.0872

Changes in values of positive sentiment probability with a delay of two days could predict a similar rise or fall in closing price.

Cross-lingual named entity extraction and disambiguation

Tadej Štajner[1,2], **Dunja Mladenić**[1,2]

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[2] Jožef Stefan International Postgraduate School, Ljubljana, Slovenia

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When attempting to understand text, one of the tasks that need to be solved is named entity disambiguation: for instance, Paris can refer to a city in France but it can also refer to a small city in Texas, USA or to a 1984 film directed by Wim Wenders having title Paris, Texas. Knowing the correct answer to that depends on the context. However, context is difficult to interpret if the input text is expressed in a different language than the knowledge base that these entities belong to.

This is a very common scenario in processing Slovene text. While using the Slovene Wikipedia for this purpose is easy, it does not contain many entities that we may be interested in. While the English one is over thirty times bigger, it introduces a language barrier. We overcome this by applying techniques from cross-lingual information retrieval to the problem of identifying proper names in text and linking them to concrete knowledge base concepts.

Another goal was to re-use language resources from languages with more resource in languages with less available resources. The work presented has resulted in a usable named entity extraction and disambiguation service that is able to work on Slovene text even while having a knowledge base in English.

The demonstration is available at http://enrycher.ijs.si

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Cross-lingual named entity extraction and disambiguation

Tadej Štajner[1,2], Dunja Mladenić[1,2]
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[2] Jožef Stefan International Postgraduate School
tadej.stajner@ijs.si

Goal

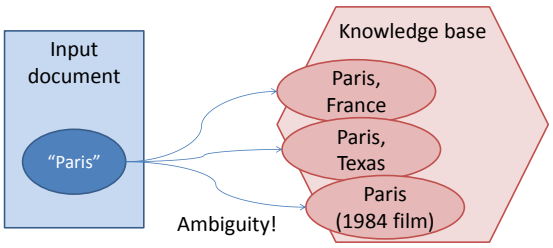
When attempting to understand text, one of the tasks that need to be solved is named entity disambiguation, connecting mentions within the text with entities in a knowledge base. For instance:

The phrase "Paris" can refer to a city in France but it can also refer to a small city in Texas, USA or to a 1984 film directed by Wim Wenders having title Paris, Texas.

Knowing the solution depends on the context. However, context is difficult to interpret if the input text is expressed **in a different language** than the knowledge base that these entities belong to. A knowledge base is a collection of entities, which have various properties, such as labels and textual descriptions.

This work focuses on solving the problem of **bridging the language barrier in text annotation**.

Basic problem



Having an input document with a mention phrase, select the correct entity that the text is referring to.

Current best practices

- Mention popularity – `P(entity|mention)`
  - "Kashmir" .. Kashmir_(song) = 0.05
  - "Kashmir" … Kashmir_(region) = 0.91

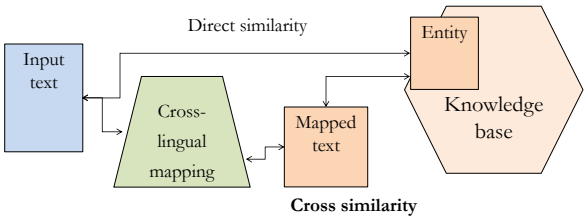
  Captures the most likely entity behind the mention
- Context similarity - `sim(ctx(mention), ctx(entity))`
  - Context of a mention: surrounding sentences
  - Context of an entity: the description of the entity

  Captures the entity that best fits the lexical context
- Coherence
  - Entities that appear together tend to be related to one another
  - Usually solved by a greedy graph pruning algorithm

  Collectively captures the entities that make sense appearing together

→ **How to compute similarity of context across a language barrier?**

Proposed solution



Instead of just directly computing similarity, map the input document into the target language via a mapping, and compute similarity in that space.

We train it via a parallel (or comparable) corpus:

- Not statistical Machine Translation – just providing a linear mapping from one language space to another, which is an easier problem to solve
- Statistical technique: Regression Canonical Correlation Analysis
- Our implementation trained on EuroParl

Related work

Directly calculate similarity using the available knowledge base, containing one or both languages

- Significantly better when containing both languages than using just the document language
- [A. Lommatzsch et al, Named Entity Disambiguation for German News Articles, WIR2010]

Cross-lingual dictionary

- A context-independent dictionary lookup
- Constructed from looking at anchor texts from non-English to English Wikipedia pages
- Very similar to just using the mention popularity feature, but with additional cross-lingual knowledge
- [Spitkovsky, V.I. and Chang, A.X., Strong baselines for cross-lingual entity linking, TAC 2011]

Using machine translation to translate input documents to English

- Requires a MT system to operate
- Achieves 94% performance of a monolingual baseline
- [P. McNamee et al.: Cross-Language Entity Linking, IJCNLP 2011]

Discussion

- Initial experiments show that using a cross-lingual context-similarity based measure helps compared to directly calculating similarity in the cases where the topic of the trained mapping strongly overlaps with the topic of the input text.
- Not yet certain whether it compares favourably to a machine translation based system.

Demonstration available at http://enrycher.ijs.si

Extending the Multi-Criteria Decision Making Method DEX

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The main purpose of this paper is to propose six new extensions to the DEX methodology. The methodology is a member of multi-attribute decision support techniques, which are used for supporting people at making better decisions. Usually such decisions are made in business environments, ecology, industry and also in personal decisions, e. g., choosing a family vehicle.
A DEX decision model is constructed as a hierarchy of attributes, which are connected in a logical sense. For example, when choosing a car, one would logically construct "maintenance price" from "buying price" and "consumption". The attributes used in the hierarchy are presented as qualitative (symbolic) values. The values are not presented as numerical (-1, 0.12, 18, …), but rather as "good", "medium" and "bad". This is particularly useful in decision situations where judgement prevails over exact formal treatment of criteria.

As written in the paper, the methodology was successfully used in many different applications, but still lacks some functionality for the decision maker. Three useful extensions were developed before, but there are still more functionalities needed from the system.

Our goal is to successfully design, investigate and finally implement six additional extensions to the DEX methodology in a new powerful decision support system. The presented extensions are related to the model structure (supporting full hierarchies), attribute representation (facilitating probabilistic and fuzzy computations, and numeric attributes), model representation (introducing modularization), aggregation functions (supporting general aggregation functions) and support for relational models.

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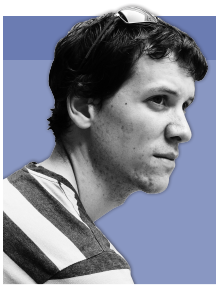
Extending the Multi-Criteria Decision Making Method DEX

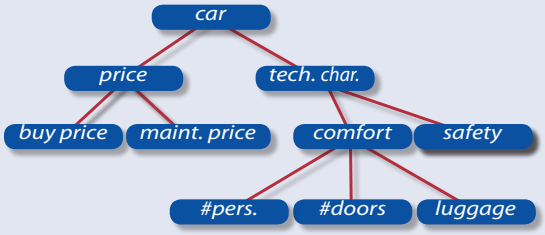


Nejc TRDIN [1,2] **Supervisor: prof. dr. Marko BOHANEC** [2]

[1] **Jožef Stefan International Postgraduate School**
Information and Communication Technologies (ICT3)

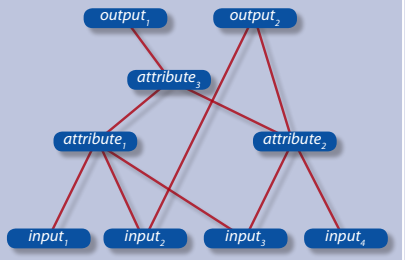
[2] **Jožef Stefan Institute**
Department of Knowledge Technologies

Qualitative Multi-Criteria Decision Making Method DEX

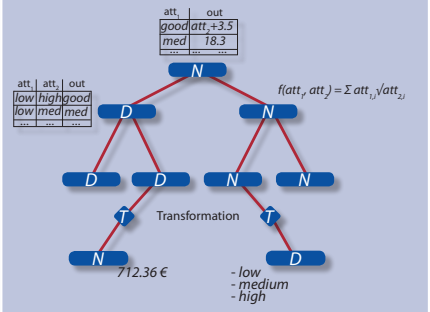


price	tech. char.	car
high	bad	unacc
high	acc	unacc
high	good	unacc
high	exc	unacc
medium	bad	unacc
medium	acc	acc
medium	good	good
medium	exc	exc
low	bad	unacc
low	acc	good
low	good	exc
low	exc	exc

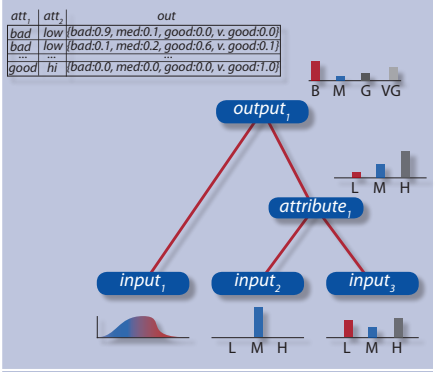
Full Hierarchies



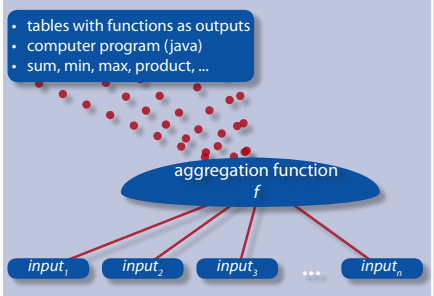
Numeric Attributes



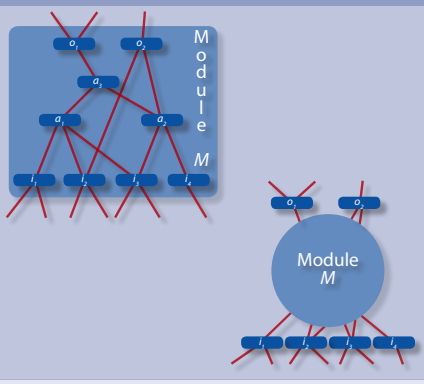
Probabilistic and Fuzzy Computations



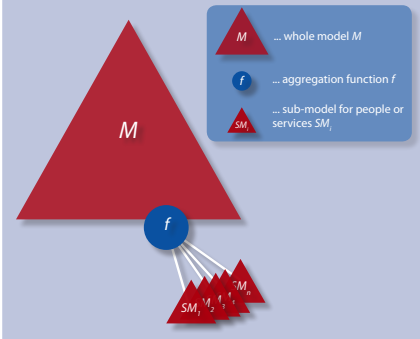
General Aggregation Functions



Modularization



Relational Models



The paper and this poster are the proposals of six new extensions, which will be further developed and included into a new software package. The proposed extensions and the DEX methodology will form a new decision modeling system with large capabilities.

Development of Discovery and Identification Protocol for Sensor Networks

Matevž Vučnik[1,2], **Zoltan Padrah**[1,2], **Carolina Fortuna**[1,2], **Mihael Mohorčič**[1,2]

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This paper describes a new protocol which is useful for collecting sensor measurements and metadata from sensor networks. The protocol is called Discovery and Identification Protocol (DIP).

Sensor networks are increasingly used to deliver sensor data from the world or real things and processes. Sensor data includes sensor measurements, which are samples typically in the form of a number (e.g. temperature), and the metadata, which is typically static information that gives meaning to the measurements (e.g. accuracy, calibration parameters, sensor settings etc.).

The DIP protocol was designed as a light-weight protocol to be used on sensor nodes which consume very little energy and can run on batteries. Sensor nodes are connected to the network through a wireless interface.

The paper is divided into two parts where the first part describes the design of the protocol and the second part describes the implementation of the protocol. In the conclusion we give a comparison of DIP and another more general protocol called Constrained Application Protocol (CoAP).

The protocols described enable the evolution of the current Web so as to include also the "Web of Things".

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Development of Discovery and Identification Protocol for Sensor Networks

Matevž Vučnik[1,2]

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[2]Jožef Stefan International Postgraduate School

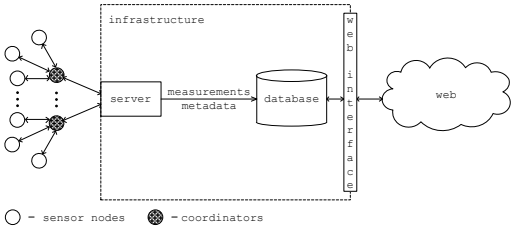
Study program: Information and Communication Technologies

Advisor: doc. dr. Mihael Mohorčič

Zoltan Padrah[1,2], Carolina Fortuna[1,2], Mihael Mohorčič[1,2]

System overview:
- Collection of large amounts of sensor data
- Accessibility of data through web interface

Use case:
- Realtime web based monitoring of consumed heath per apartment



Motivation:
- Automatic discovery of sensor nodes and data retrieval
- Simplify the management of deployed sensor networks

The application layer protocol DIP:
- Coordinator on one side communicates with sensor nodes and on the other with the infrastructure
- The infrastructure is included in the protocol to minimize the traffic in the sensor network by separating measurements and metadata

Implementation:
- VESNA sensor node platform
- and Contiki operating system with
- RIME communication stack

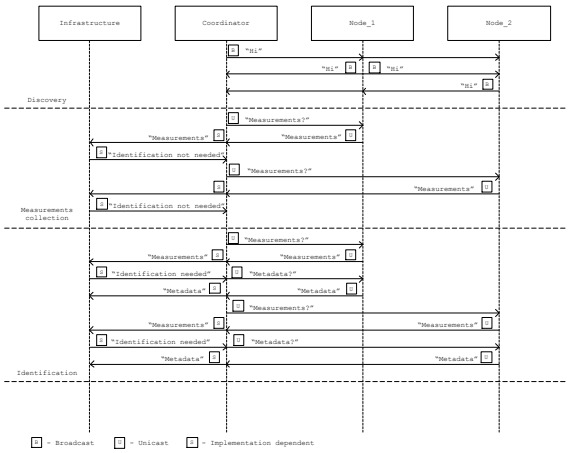
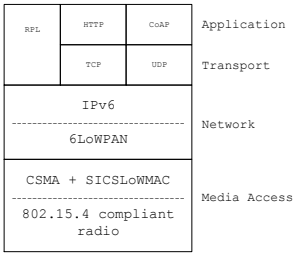


Table of known nodes:
- The discovered nodes are added to the table
- The coordinator iterates over the nodes and pulls the sensor data from them

coordinator table

index	node_address	TTL
0	141.155	10
1	146.132	10

Future Work:
- Internet protocol suite from physical layer to application layer on the sensor node
- New applications similar to the ones in the current web, only running on small low power devices and forming the "Web of Things"



The authors would like to thank SensorLab for its support.
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Nanoznanosti in nanotehnologije (Nanosciences and Nanotechnologies)

Spectroscopic THz imaging using organic DSTMS (4-N,N-dimethylamino-4'-N'-methyl-stilbazolium 2,4,6-trimethylbenzenesulfonate) crystals

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Terahertz (THz) region of the electromagnetic spectrum was not well explored until recently. This THz gap is located between infrared waves and microwaves at corresponding wavelengths between 3 mm and 30 micro meters. One of the most promising aspects of this new technology is its high sensitivity to interactions between molecules and some interesting characteristics in THz spectrum. Since THz waves are very sensitive to interactions between molecules this allows discrimination between different substances. Moreover, the THz waves penetrate barriers made of dielectric or non-conducting materials such as plastic, ceramic, paper, cardboard, wood, natural and synthetic fabrics. Thus, the THz technology presents an alternative method to X-ray or gamma ray imaging. The development and commercialization of the terahertz pulsed spectroscopy (TPS) and terahertz pulsed imaging (TPI) systems during the last decade put forward several ideas to use the THz systems for various industrial purposes.

One of the most promising features of a THz imaging system is its capability for spectroscopic discrimination. The acquired THz data contain rich information about the structure and composition of a sample. On the other hand, the characteristic spectral signatures of each individual substance can also be extracted from the THz data, and this can be used for substance identification. In this work we applied two concepts of the THz imaging in transmission geometry using organic DSTMS crystals as a THz generator and detector. We demonstrate that the time-domain THz imaging has the advantage of fast sample scanning at the expense of lower resolution. Therefore, it is appropriate only for the detection of some imperfections or impurities inside the investigated material and for thickness measurements, whereas for substance identification the multispectral imaging method is necessary. Fourier transform of the THz signal provides additional information about the investigated sample. Therefore, the frequency characteristics of each point can be viewed and the material properties, such as distribution of chemical compounds within the material, can be determined.

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Spectroscopic THz imaging using organic DSTMS (4-N,N-dimethylamino-4'-N'-methyl-stilbazolium 2,4,6-trimethylbenzenesulfonate) crystals

Study programme: Nanosciences and Nanotechnologies
Jožef Stefan International Postgraduate School

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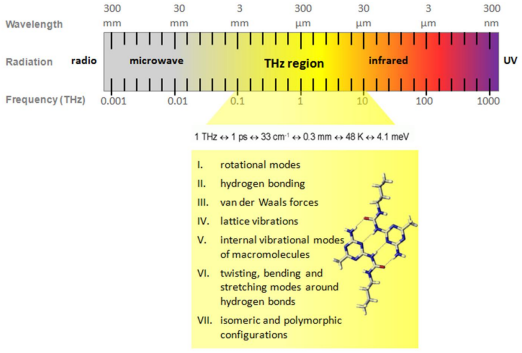
Introduction

❑ **THz gap** - between infrared waves and microwaves with corresponding wavelengths between 3 mm and 30 micro meters

❑ **promising aspects** - high sensitivity to interactions between molecules and some interesting characteristics in THz spectrum



THz imaging system in industrial applications:

❑ **pharmaceutical industry** (analysis of tablet coatings, 2D and 3D chemical imaging, chemical identity of the structure)

❑ **security** (scanning of packages, envelopes, etc.)

❑ **food industry** (quality inspection, contaminations detection)

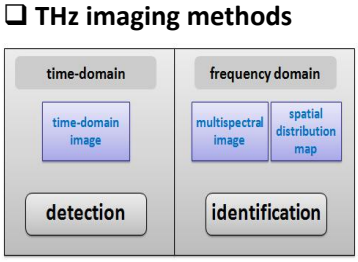
❑ **wood industry** (fibre structure inspection)

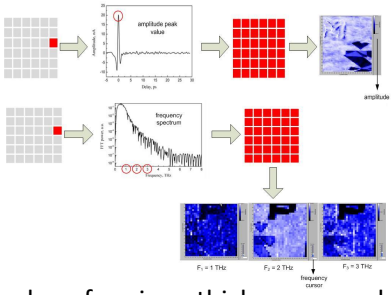
❑ ...

Experimental work and results

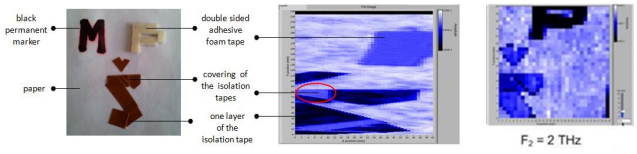
❑ **THz imaging system** in transmission mode using organic DSTMS crystals as a THz generator and detector with the spectral range from 0.3 THz to 11 THz

❑ **THz imaging methods**





❑ discrimination between samples of various thicknesses and material composition



Conclusions

❑ **time-domain imaging** for fast sample scanning appropriate for the detection of imperfections or impurities inside the investigated material and for thickness measurement

❑ **multispectral imaging** for classification and identification purposes

References

A. Zeitler, *et al*. Terahertz pulsed spectroscopy and imaging in the pharmaceutical setting - a review, *Journal of Pharmacy and Pharmacology,* 59(2): 209-223, 2007.

M. C. Kemp. Millimetre wave and terahertz technology for the detection of concealed threats: a review, In *Proccedings of Joint 32nd International Conference on Infrared and Millimeter Waves, 2007 and the 2007 15th International Conference on Terahertz Electronics. IRMMW-THz*, Cardiff, 2006.

C. Jansen, *et al*. Terahertz imaging: applications and perspectives, *Appl. Opt.*, 49(19): E48-E57, 2010.

Modelling of grain size distribution in spring steel microstructure

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Size distribution of grains is of considerable importance in understanding the microstructure of materials. It is necessary to evaluate the accuracy and precision of parameter estimation and to verify the possibility of expected grain size distribution testing on the basis of intersection size histogram. In order to review these questions a computer modeling technique was used to compare size distributions obtained experimentally with those possessed by model. According to the results it was concluded that new improvements in estimating and testing procedures enable grain size distributions to be more efficient.

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MODELLING OF GRAIN SIZE DISTRIBUTION IN SPRING STEEL MICROSTRUCTURE

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The average grain size and shape are the most important parameters for describing geometrical features of microstructure since the material properties are mainly influenced by them. There are various experimental methods for determining the grain size distribution on microstructure; however there is a little information on efficiency of grain size estimation from the measurements performed on metallographic planes. In order to determine the accuracy of methods for grain size distribution a modeling approach is presented. It was therefore concluded that the method presented in this study allows access on information not accessible experimentally and can be applied regardless of grain shape.

Intercept and Intersection Count Methods

The mean intercept length is a convenient and simple experimental method for determining the average grain size from metallographic sample. The test methods of determination of average grain size in metallic materials are primarily measuring procedures and because of their purely geometric basis are independent on the metal or alloy concerned.

For a single phase structure $N_L = P_L$ and either counting procedure can be used to determine G. The values of N_L and P_L are calculated by

Equation: $N_L = \frac{N}{\frac{L_T}{M}}$ And $P_L = \frac{P}{\frac{L_T}{M}}$

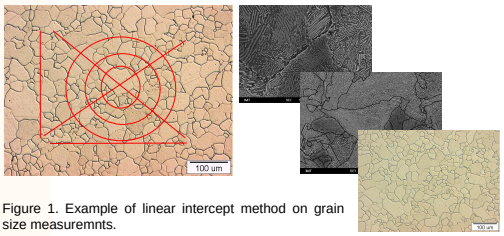


Figure 1. Example of linear intercept method on grain size measuremnts.

Jeffries Planimetric Method

The planimetric method is generally employed by drawing a circle 79.8 mm in diameter (500 mm) on a photomicrograph, then a count is made of the number of grains completely within the area n_1, and the number of grains intersecting the test circle n_2 according to

Equation: $N_A = f\left(n_1 + \frac{n_2}{2}\right)$ the value of f is $f = \frac{M^2}{5000}$

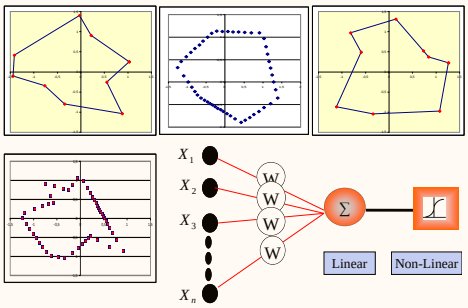
In planimetric method d is used to describe the grain size which might be inconvenient because the square root of the average grain area is calculated, which means that grains are square on the cross section but in reality they are not.

Conclusions

Quantitavie optimcal microscopy studies in spring steel microstructure revealed that the accuracy of grain size measurements is complicated by a number of factors which can lead to large erors in measurement. The objective of the present study is to establish a method that is efficient and has small and known maximum bias for estimation of grain size distribution in three imensions.

Discusion

Grain shape is extremly dificult property to measure, or even to define in a precise measure. It has been proven that no single measure can be unique to only one shape, therefore wide variety of grain shapes has been generated in our modelling aproach.



Each arbitrary shape is presented by an n-sided polygon. Each side of a polygon is a straight line. Curves and other smuther shapes were aproximated using neural network modelling. An arbitrary shape was represented by:

- A set of points $P = (P_0, P_{1,\ldots\ldots} P_n)$
- A set of lines $L = (L_0, L_{1,\ldots\ldots} L_n)$

The polygon could be of both convex and non-convex type. Modelling results show that the grain cross sections, produced by a random plane through crystals of varying size and shapes would have distribution of areas varying from maximum value to zero depending upon where the plane cuts each individual Fig 1. According to the results deviations in grain shape was another source of error in computations of spatial grain size from mean lineal intercept values.

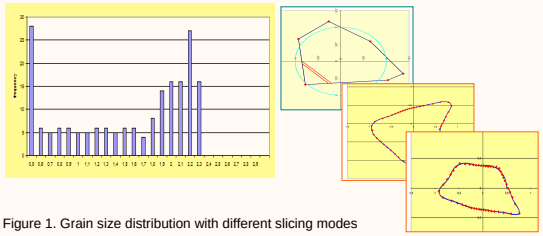


Figure 1. Grain size distribution with different slicing modes

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Influence of different stress concentration factors in mono-leaf spring on its final fatigue life

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One of the largest European producers of the spring steel material is Štore Steel Plant, which produces material for truck springs and the other springs for automotive applications. Generally, spring manufacturers produce springs from steel in the as-delivered condition. The springs are then heat-treated and tested. However, the fatigue testing of springs after manufacturing is a time-consuming and an expensive task. It is also too late to provide information to the steel producer, who needs in-time and appropriate information about the quality of the steel in the production from batch to batch. The aim of this research work is to develop a model which will enable the assessment of the fatigue life of mono and double leaf-spring based on information of material properties in the as-delivered condition. The idea is to model both mono and double-leaf spring and then run the simulations and determine the lifetime of the leaf springs. For our project, we use their spring steel in the as-delivered condition to perform dynamic tests on specimens, in order to obtain the material properties, which are the base for the leaf spring simulation. Since the spring steel manufacturer, as well as the spring producer, need fast data about the quality of their products, the idea is to use a faster testing machine for evaluating base material properties.

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INFLUENCE OF DIFFERENT STRESS CONCENTRATION FACTORS IN MONO-LEAF SPRING ON ITS FINAL FATIGUE LIFE

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Mentor: prof. dr. Leskovšek Vojteh
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Introduction:

The aim of this research work is to develop a model which will be able to assess the fatigue life of mono-leaf spring. We used FEM based software to simulate fatigue life of mono-leaf spring. This simulation is performed by means of S/N curves as input values for dynamic properties of the spring steel material 51CrV4.

Chemical composition of spring steel:

C	*Si*	*Mn*	*P*	*S*	*Cr*	*Mo*	*Ni*	*V*
0,52	0,35	0,96	0,011	0,004	0,94	0,05	0,13	0,12

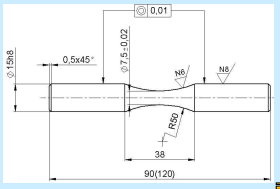
Static tensile test:

Static tensile tests are carried out using a 500kN Instron 1255 testing rig. Depending on the different specimen orientation and different tempering temperature of specimens next tensile properties of spring steel material are obtained:

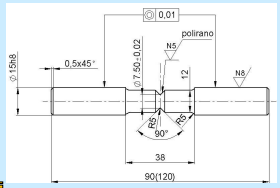
Orientation	Tempering temperature	Diameter [mm]	Yield strength [Mpa]	Tensile strength [Mpa]	Fracture elongation [%]	Fracture contraction [%]
Perpendicular (λ=90°)	475°C/1h	8	1373	1448	7,04	24,6
	425°C/1h	8	1502	1591	5,16	15,8
Longitudinal (λ=0°)	475°C/1h	8	1366	1442	10,6	41
	425°C/1h	8	1502	1606	9,9	42

Dynamic test on specimens:

Two types of specimens were prepared and tested: longitudinal and perpendicular relative to the rolling direction – segregation orientation. All specimens both for static tensile test and for fatigue test are cut off from base spring steel material in as-delivered condition (flat profile of dimensions 90x28 mm). After cutting and machining the specimens were heat-treated, quenched in nitrogen at 5 bars overpressure and then tempered at two different temperatures. The S/N curves are obtained by fatigue tests on notched as well as on smooth specimens using a compression-tension testing machine Instron 8802 of ±250 kN with the operating frequency of 30 Hz.

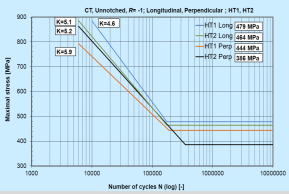


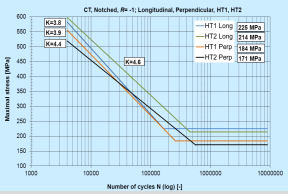
Unnotched specimen compression–tension loading kt = 1



Notched specimen compression–tension loading kt = 2

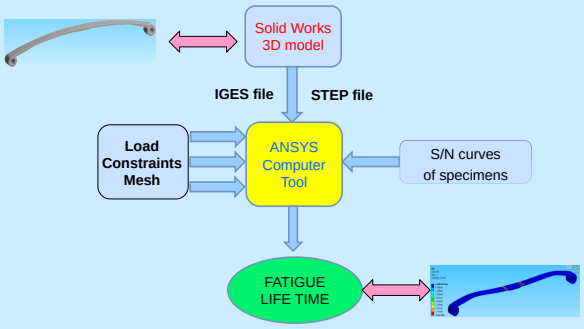
S/N curves



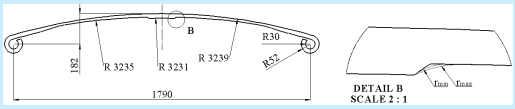


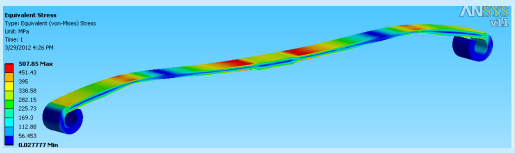
FEM based simulations:

The notch effect expressed by different stress concentration factor is examined by means of S/N curves as material input data. This is done performing dynamic simulation of mono-leaf spring using ANSYS software.



It is well known that sharp notches resulting with stress gradients act as stress raisers and present critical spots within the component. One way of improving the durability and safety of the mono-leaf spring is avoiding all sharp edge transitions at critical spots and replacing them with radiuses if structural and functional conditions allow such changes.





r, Radius [mm]	F, Force [N]	Stress von-Misses [MPa]	N, Fatigue life [-]
15	1690	539.65	71609
35	1690	503.32	80979
75	1690	489.57	84837
115	1690	476.82	5*10^7

Conclusion:

From the fatigue simulations it is clear that the longest fatigue life of mono-leaf spring is obtained using the largest radius of 115 mm. With this radius mono-leaf spring may be able to endure at least 5 Million cycles according to the S/N curve of unnotched longitudinal oriented specimens. Also, by using other S/N curves for perpendicular specimen orientation as well as for notched specimens, fatigue life is longer too. Regarding the dynamic properties of selected spring steel it is evident that the fatigue strength of perpendicular oriented specimens decreases for about 25% compared to longitudinal oriented specimens accompanied with lower tensile and yield strength. With reference to the different stress concentration factor of notched and smooth specimens, it is shown that fatigue strength of notched specimens is effectively lower as the stress concentration factor indicates.

Tailoring electrically-induced properties by stretching relaxor polymer films

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Dielectric spectroscopy investigates electrically-induced properties of a material as a function of frequency and/or temperature. Dielectric properties are related to polarizability and thus depend on the structure and molecular properties of a material. That is why dielectric spectroscopy is a useful tool for material characterization and it is used in pharmacy, biotechnology and material science.

The basic quantity in dielectric spectroscopy is complex dielectric constant ε*, which consists of the real, ε', and imaginary, ε", part. The real part is related to the stored energy within the medium, whereas the imaginary part describes the losses. That is why the dielectric constant is very important in devices for storing electrical energy (capacitors).

Besides storing electrical energy, there are also materials that are able to convert it into mechanical work (electromechanical effect) or into heat (electrocaloric effect) - note that electrical energy converted into heat in electrocalorics is not due to the electrical current running through them. Such properties of a material can be utilized in many devices such as actuators, sonars, integrated microelectromechanical systems or artificial muscles, which use the electromechanical effect, or in heating/cooling devices of new generation, which use the electrocaloric effect.
Example of materials that possess giant electromechanical and electrocaloric effect are relaxors and ferroelectrics. Our subject of study was special class of relaxors – relaxor polymers. Relaxor polymers in comparison to the other inorganic relaxors have some advantages: they have greater electromechanical response, exhibit fast response speeds and can also be prepared in a variety of shapes. Their disadvantage would be that they are stable only at relatively low temperatures (below 100 °C).

Dielectric constant is important for the electromechanical application of relaxor polymers, since the input electrical energy that can be converted into the strain energy, is directly proportional to the values of the dielectric constant of the material. Thus, in order to achieve better efficiency, systems with high values of the dielectric constant must be developed.

Tailoring electrically-induced properties by stretching relaxor polymer films

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Investigated material:
Relaxor poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene), P(VDF-TrFE-CFE), terpolymer.

Aim of research:
Stretching of polymer films strongly affects the conformation of polymer chains – for example, PVDF spontaneously crystallizes into a nonpolar trans-gauche chain conformation, which is transformed into a ferroelectric all-trans conformation only after uniaxial stretching. P(VDF-TrFE) spontaneously crystallizes into the all-trans polar structure (the overall microstructure of ferroelectric and relaxor polymers consists of the crystallites embedded in the amorphous matrix), however, stretching still might affect its properties. This is even more likely in relaxor P(VDF-TrFE)-based polymers, where the all-trans chain conformation in the crystallites is randomly interrupted by the gauche conformation, introduced by irradiation or chlorine atoms.

Investigation:
Dielectric, electromechanical and electrocaloric response was investigated and compared in the non-stretched and uniaxially stretched P(VDF-TrFE-CFE) terpolymer.

Interesting properties: →
- Giant electrostriction
- Large electrocaloric effect
- High electric energy density, fast response speeds

Applications:
- Actuators, Sonars, Artificial muscles
- Heating/Cooling devices of new generation
- Capacitors

Electrocaloric response

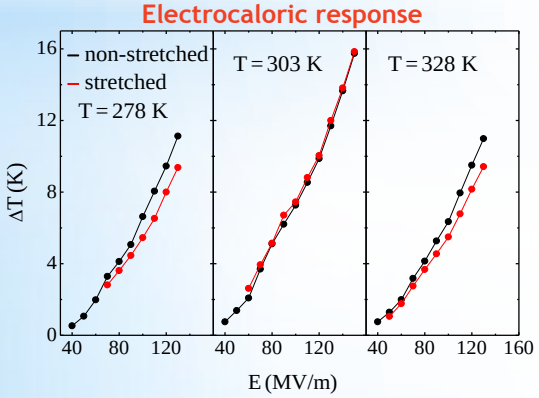

Figure 1: Comparison of the electrocaloric response as a function of the applied electric field, measured at three different temperatures: below, near, and above dispersive dielectric maximum.

Summary:
- Stronger decreasing of ε' in high E-fields (due to higher nonlinear contribution) in less oriented non-stretched films.
- Higher polarization in more-oriented stretched samples.
- Much higher electrostrictive ($S_3 \propto P^2$) response in the stretched terpolymer.
- Competition of disorder (higher in the non-stretched) and polarization (higher in the stretched films) in electrocaloric response.

Electrically-induced properties of relaxor polymer films can be tailored by controlling the preparation conditions which influence the trans-gauche and trans-trans polymer chain conformations.

Polarization & Electromechanical response

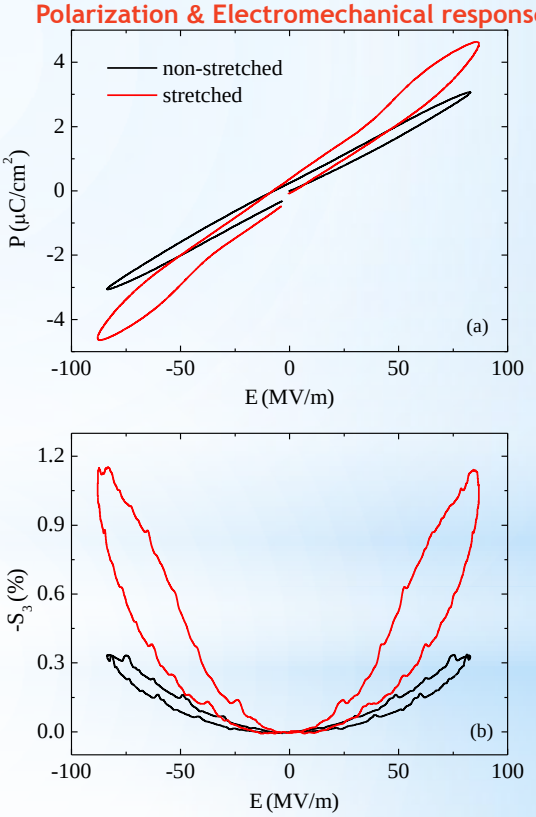

Figure 2: (a) Polarization hysteresis loops and (b) induced electrostrictive strain at 100 Hz in the stretched and non-stretched P(VDF-TrFE-CFE) samples.

Dielectric response

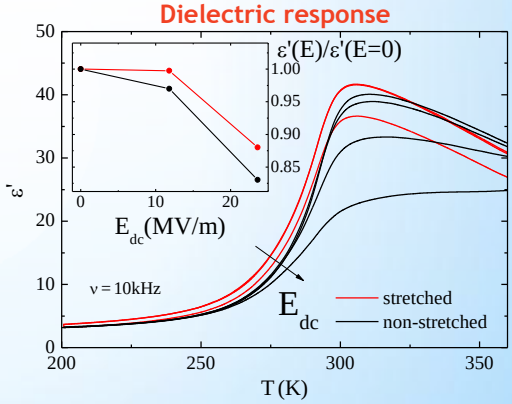

Figure 3: Temperature dependence of ε' at 10 kHz of stretched and non-stretched P(VDF-TrFE-CFE) samples in different dc bias electric fields (0, 11.8, 23.6, 47.2 MV/m). The inset shows normalized ε' peak values as a function of the dc bias electric field in both samples.

Terpolymer/copolymer blends on aluminum surface: Structural, caloric, and dielectric properties

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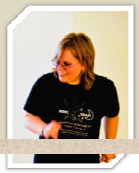
Relaxor polymers are very promising for a broad range of energy storage capacitor applications due to their unique physical properties. One of the advantages for use of polymers in such applications arises from the possibility of polymer film formation directly on a surface. Active metals such as aluminum can be used for substrates, as they are less expensive than noble metals and mechanically more stable than glassy carbon.

Investigations of relaxor poly(vinylidene fluoride–trifluoroethylene–chlorofluoroethylene) [P(VDF–TrFE–CFE)] terpolymer have revealed high values of dielectric constant at room temperature, fast response speeds, high strain levels and energy density, and large electrocaloric effect. Polymer blends exploit merits of both, base and additive polymer – due to interference effect, properties of base polymer can be tailored and improved. Recent studies show that polymer blends composed of P(VDF–TrFE–CFE) terpolymer as a base with a small amount of poly(vinylidene fluoride–chlorotrifluoroethylene) P(VDF–CTFE) copolymer (e.g. 5 or 10 mol %) as an additive have even higher polarization response, energy density, elastic module, and breakdown field than pure relaxor P(VDF–TrFE–CFE) system. We have thus decided to develop and investigate such polymer blend films on a metal surface.

We report structural, caloric, and dielectric properties of polymer blends of poly(vinylidenefluoride–trifluoroethylene–chlorofluoroethylene) terpolymer (a member of the relaxor polymers family that exhibits fast response speeds, giant electrostriction, high electric energy density, and large electrocaloric effect) and poly(vinylidenefluoride–chlorotrifluoroethylene) copolymer, developed on aluminum surface. Terpolymer films exhibit for a relaxor polymer material very high values of the dielectric constant of ≈80 around room temperature, which decreases in terpolymer/copolymer blends to ≈60. We show that addition of the copolymer enables us to govern the dielectric constant of the films without influencing the relaxor dielectric dynamics.



TERPOLYMER/COPOLYMER BLENDS ON ALUMINUM SURFACE

Structural, caloric, and dielectric properties

Andreja Erste[1,2,3], Vid Bobnar[1,2], Xian-Zhong Chen[4], Cheng-Liang Jia[4], Qun-Dong Shen[4]

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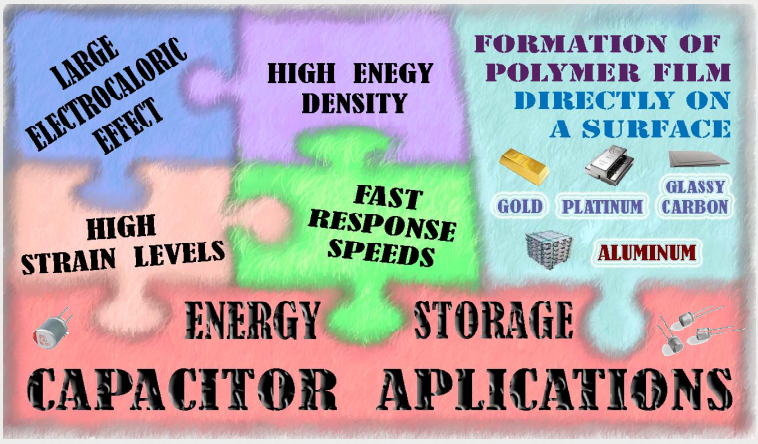
RELAXOR POLYMERS



MOTIVATION

Relaxor P(VDF–TrFE–CFE) terpolymer

- High ε' (≈60) at T_{ROOM}
- Fast response speeds
- High strain levels (3–4%)
- High energy density
- Large electrocaloric effect

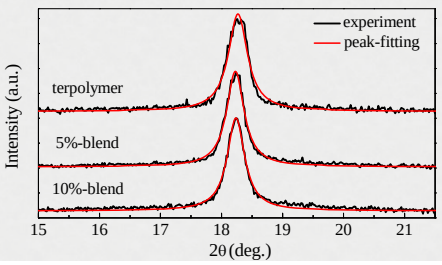
& P(VDF–CTFE) copolymer

- Higher polarization response
- Higher energy density
- Higher breakdown field
- Higher elastic module

& aluminum surface

STRUCTURAL

X – ray diffraction (XRD) studies



Increase of copolymer content:

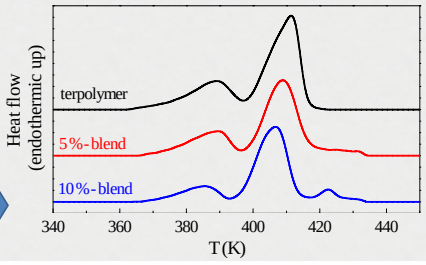
(i) lattice spacing is extended from 4.85 Å to 4.86 Å due to incorporation of CTFE units in the crystallites and
(ii) coherence length increases.

Confirmation of DSC results

Addition of copolymer introduces more defects and distorts crystalline ordering (increased mol % of copolymer => decreased crystallinity).

CALORIC

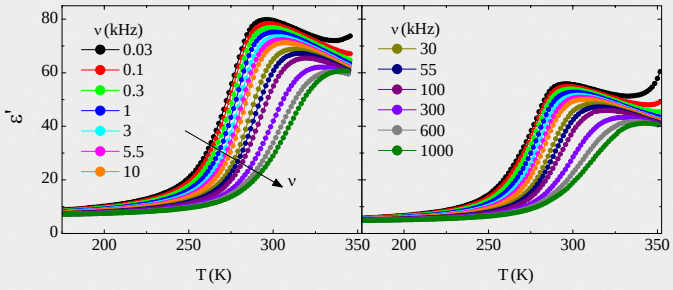
Differential scanning calorimerty (DSC)



DIELECTRIC

Dielectric spectroscopy

pure P(VDF-TrFE-CFE) terpolymer	blend with 10% of P(VDF-CTFE) copolymer



Relatively high values of the dielectric constant around room temperature of ≈80 in terpolymer decreases to ≈60 in terpolymer/copolymer blends.

Addition of copolymer:
(i) governs the value of the dielectric constant and
(ii) does not influence the relaxor dielectric dynamics.

Polymer blends exploit merits of both, base and additive polymer – due to the interference effect, properties of the base polymer can be tailored and improved.

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The adhesion of bacteria to austenitic stainless steel (AISI 316L) with different surface finishes

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V naravi mikroorganizmi na izpostavljenih površinah pogosto tvorijo skupke, ki jih imenujemo biofilmi. Adhezija bakterij na površino in tvorba biofilmov na nerjavnem jeklu predstavlja kronično vir kontaminacije z mikrobi v medicini in živilski industriji. Prisotnost bakterij povzroča tudi korozijo materiala ter zmanjšuje učinkovitost naprav, kot so toplotni izmenjevalci, hladilni stolpi in filtri. Adhezija bakterij na površino je kompleksen proces na katerega vplivajo lastnosti površine materiala (hrapavost, topografija, kemija), lastnosti bakterije in okoljski dejavniki.

Namen naše raziskave je preučiti vpliv hrapavosti in topografije nerjavnega jekla na adhezijo bakterij s pomočjo vrstičnega elektronskega mikroskopa (SEM) in mikroskopa na atomsko silo (AFM). Za namen naše raziskave smo iz nerjavnega jekla izdelali vzorce v obliki diskov s premerom 15 mm in debeline 1,5 mm. Površine vzorcev smo obdelali s pomočjo brusnega papirja različne granulacije (100-1200), da smo dobili različno topografijo in hrapavost naših vzorcev.

V raziskavi smo uporabili bakterijo Escherichia coli, ki smo jo čez noč gojili v Lauria-Bertani gojišču s stresanjem pri 37 oC. Nato smo bakterije centrifugirali 5 minut pri 10000 g in dobljeno bakterijsko usedlino resuspendirali v pufru (PBS). Pred pričetkom adhezijskih poskusov smo vzorce očistili z detergentom, ultrazvočno kopeljo v absolutnem etanolu in sterilizacijo. Vzorce smo vodoravno potopili v 10 ml bakterijske suspenzije v statičnih pogojih pri 37 °C za 2 h. Nepritrjene oziroma slabo pritrjene bakterije smo odstranili s tremi zaporednimi spiranji s PBS. Po adhezijskih poskusih smo vzorce z bakterijami pripravili za mikroskopiranje s SEM.

Do sedaj so bili narejeni poskusi le na vzorcih Aizv. Število in razporeditev bakterij je pri vseh vzorcih podobna. Bakterije se pritrjajo v neposredno bližino že pritrjenih bakterij in tvorijo skupke, redkeje je opaziti posamezne bakterije. Bakterije se pogosteje pritrjujejo v razpoke, praske in druge nepravilnosti na površini, saj jih ščitijo pred neugodnimi dejavniki okolja. V nadaljevanju naše raziskave bomo poleg hrapavosti preučevali tudi vpliv tankih plasti na nerjavnem jeklu na adhezijo bakterij.

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The adhesion of bacteria to austenitic stainless steel (AISI 316L) with different surface finishes

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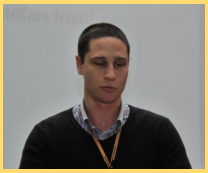
Study program: Nanosciences and Nanotechnologies,
Jožef Stefan International Postgraduate School
SUPERVISOR: prof. dr. Monika Jenko
Institute of Metals and Technology, Lepi pot 11, 1000 Ljubljana



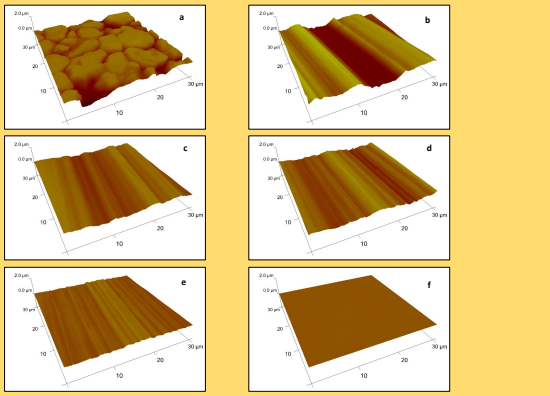
Introduction

The adhesion of bacteria to stainless steel presents a chronic source of the microbial contamination in food and medical industries. It also enhances the material corrosion, as well as decreases the performance of plants, heat exchangers and cooling towers. The aim of our research is to examine the effect of surface roughness and topography of austenitic stainless steel (AISI 316L) on the adhesion of bacteria.

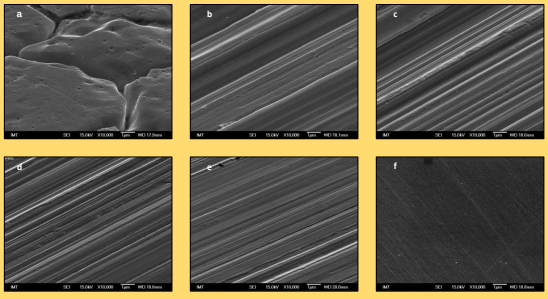
Factors influencing bacterial adhesion

- ENVIRONMENT
- BACTERIAL CHARACTERISTICS
- MATERIAL SURFACE

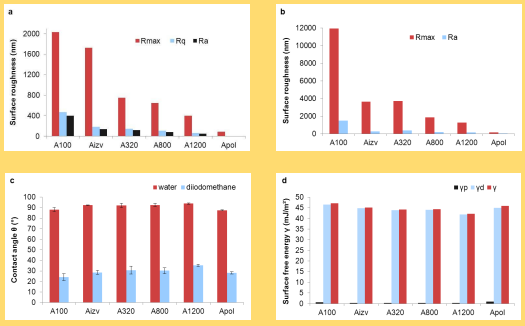
Surface characterization



AFM three-dimensional surface plots: a) Aizv, b) A100, c) A320, d) A800, e) A1200 and f) Apol.



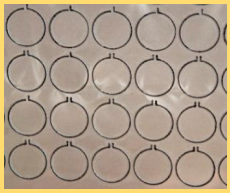
SEM surface images: a) Aizv, b) A100, c) A320, d) A800, e) A1200 and f) Apol.



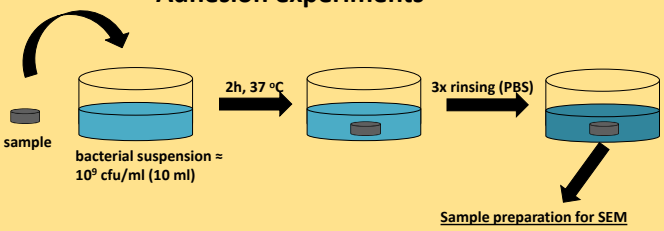
a) AFM surface roughness, b) profilometer surface roughness, c) contact angle and d) surface free energy.

SAMPLES: 316L stainless steel discs

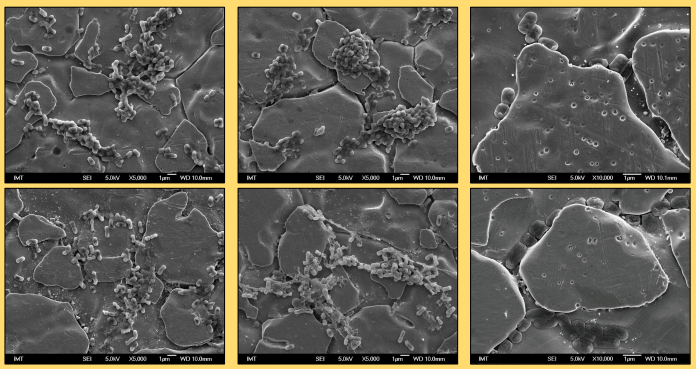
1. **Aizv** (as delivered, untreated)
2. **A100** (SiC paper P100)
3. **A320** (SiC paper P320)
4. **A800** (SiC paper P800)
5. **A1200** (SiC paper P1200)
6. **Apol** (1µm diamond paste)



Adhesion experiments



SEM images of bacterial adhesion



SEM images of attached *E. coli* to stainless steel sample Aizv: 5000x and 10000x magnification.

Conclusion

All samples had similar contact angles and consequently a similar surface energy. In our case, surface roughness has small influence on the surface energy. So far only the experiments on the Aizv samples were made. The number and the distribution of attached bacteria on different Aizv samples were similar. The bacteria usually attach to the immediate vicinity of the already attached bacteria, so that they form clusters. The bacteria prefer cracks, scratches and surface irregularities over the smoother surface. Individually attached bacteria are seen very rarely.

Influence of the suspension stability on the deposition of cobalt ferrite particles under an applied magnetic field

Petra Jenuš[1,2], Darja Lisjak[1] , Darko Makovec[1], Miha Drofenik[1,3]

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Magnetic nanoparticles (magnetic fluids, nanocomposites)

New methods for the controlled synthesis of iron oxide based nanoparticles are being developed. Additionally, we are focused on the functionalization of magnetic nanoparticles, primarily for biomedical applications. The surface properties of nanopowders, which determine their applicability, are tuned with inorganic coatings (i.e., a thin film of amorphous silica), with polymer coatings or with single-molecule layers. The coating prevents the agglomeration of nanoparticles, which further enables their dispersion in various liquids, i.e., magnetic fluids or the homogeneous incorporation of nanoparticles in various matrices.

Multifunctional materials

Nanocomposites combining the various properties of the constituent materials can be prepared by mastering the surface properties of nanoparticles. Examples of our studies include combinations of ferrimagnetics and dielectrics (magnetodielectrics) and ferrimagnetic and ferroelectric (composite multiferroics) materials. Current studies are also related to the development of new, magneto-optic materials for sensors and magneto-catalytic materials for environmental applications.

Magnetic materials for micro- and mm-waves

Magnetic materials suitable for the absorbers of electromagnetic waves and for the non-reciprocal ferrite devices are being developed. Ceramics and composites based on ferrites are studied for the microwave applications, and a new method for the preparation of magnetically oriented thick hexaferrite films for self-biased mm-wave applications has been developed.

Influence of the suspension stability on the deposition of cobalt ferrite particles under an applied magnetic field

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* Supervisor: prof. dr. Darko Makovec

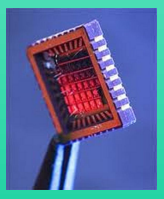
§ Introduction

$CoFe_2O_4$ (CoF) = spinel ferrite
- High magnetocrystalline anisotropy
- High coercivity
- Moderate saturation magnetization

magnetostrictive phase in *MAGNETO(DI)ELECTRIC COMPOSITES*

§ Applications

Spintronic devices



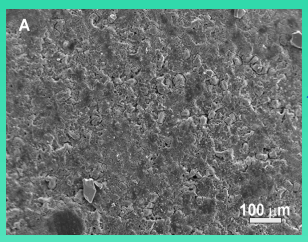
Sensors

Magnetic data storage

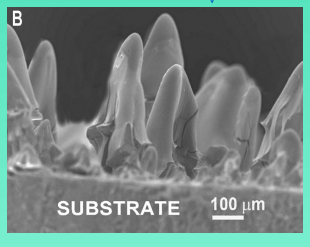
§ Experimental

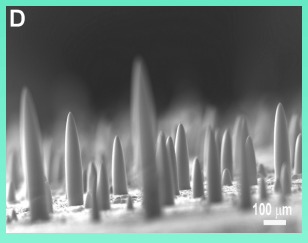
- Fe^{3+} and Co^{2+} aqueous solutions, NaOH, TMAH;
- Coprecipitation (CC) or Hydrothermal (HT) synthesis of $CoFe_2O_4$ nanoparticles;
- Particles were stabilized with citric acid in water;
- Deposits were applied under magnetic field (B=0,5T) on the Al_2O_3 substrate at room temperature and dried in air; — repeated 3 times
- Removal of the organic phase: 460°C for 2h.

§ Results



Sample	Synth. method	$T_{synthesis}$	Particle size (nm)	Ms - CoF powder (Am^2/kg)	c(g/L)	ζ-potential (mV)	$t_{sedimentation}$ (days)
Susp.A	CC	70°C	5-20	31	2	-58	> 200
Susp.B	HT	120°C	10-30	55	2	-47	>21
Susp.C	HT	150°C	15-40	61	10	-45	21
Susp.D	HT	200°C	15-50	68	10	-45	21





§ Conclusions

The deposits prepared from the stable suspension (A) were relatively homogenous. The suspensions prepared from the CoF nanoparticles with larger size had smaller zeta-potentials and were less stable. From these suspensions the deposits with columnar structures were formed. The morphology of the columnar structures depended on the suspension properties. Columnar structures with smooth surfaces and with dense and uniform distribution can be used in the magnetoelectric composites with the 1-3 structure type.

Acknowledgement: This work was financially supported by the Slovenian Research Agency.

Synthesis of cobalt ferrite nanoparticles using a combination of the co-precipitation and hydrothermal methods

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Because of its magnetic and electrical properties, cobalt ferrite is an interesting material. It has a moderate saturation magnetization, a large magnetic anisotropy, a remarkable chemical stability and a mechanical hardness. Because of these properties it can be used for recording media, spintronics, magnetic refrigeration, ferrofluids, magnetic resonance imaging, the delivery of drugs to specific areas of the body, etc. The presented results are part of the project aimed to improve the magnetic properties of cobalt ferrite particles along with the control of particle sizes and their stability, which would enhance the applicability of cobalt ferrite.

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Synthesis of cobalt ferrite nanoparticles using a combination of the co-precipitation and hydrothermal method

Sonja Jovanović[1,2], Mojca Otoničar [1,2]

1 Advanced Materials Department, Jožef Stefan Institute
2 Jožef Stefan International Postgraduate School

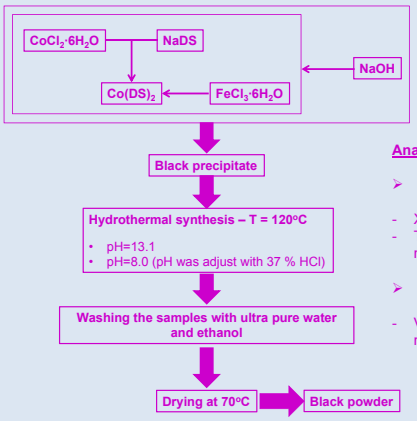
Supervisors: Prof. Dr. Danilo Suvorov[1], Dr. Matjaž Spreitzer[1]

Introduction

In recent years spinel ferrite nanoparticles have been actively investigated due to their magnetic and electrical properties. The spinel ferrites are large group of oxides which were first describe by Nishikawa (1915) and Bragg (1915). They have a structure of the natural spinel $MgAl_2O_4$ [1]. The general formula of spinel ferrites is MFe_2O_4, where M is divalent ion such as Co^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+}, etc. Cobalt ferrite is material which possesses an inverse spinel structure. It have a moderate saturation magnetization, a large magnetic anisotropy, remarkable chemical stability and a mechanical hardness and, due to these properties it can be used for recording media, spintronics, magnetic refrigeration, ferrofluids, magnetic resonance imiging, delivery of drugs to specific areas of the body, etc. [2-5].

In a recent study, Liu et al. examined the influence of synthesis time and concentration of metallic ions on the synthesis of $CoFe_2O_4$ nanoparticles [6]. They used sodium dodecyl sulfate (NaDS) during the synthesis, which enabled the control of the particles to a certain extent. However, they didn't investigate the influence of pH on morphology and magnetic properties, which is the main purpose of our work.

Experimental



Analysis

- **Crystal structure:**
  - X-ray diffraction (XRD)
  - Transmission electron microscopy (TEM)
- **Magnetic properties:**
  - Vibrating-sample magnetometer (VSM)

Results

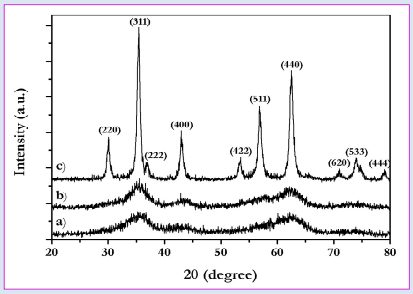


Figure 1. XRD patterns of the $CoFe_2O_4$ nanoparticles a) co-precipitation, b) pH=8.0 and c) pH=13.1

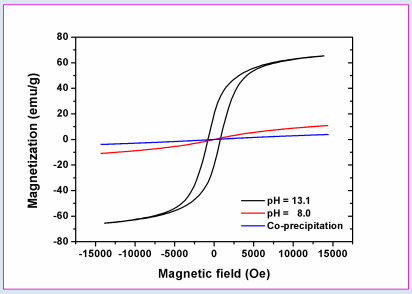


Figure 2. Hysteresis loops of the $CoFe_2O_4$ nanoparticles

Table 1: Magnetic properties of $CoFe_2O_4$ nanoparticles prepared at T=120 °C and pH = 8.0 and 13.1 and by co-precipitation

pH T=120 °C	Saturation magnetization M_S (emu/g)	Remanent magnetization M_r (emu/g)	Coercivity H_C (Oe)
Co-precip.	3.2	0.00	3.9
8.0	10.9	0.01	5.7
13.1	65.4	19.95	775.8

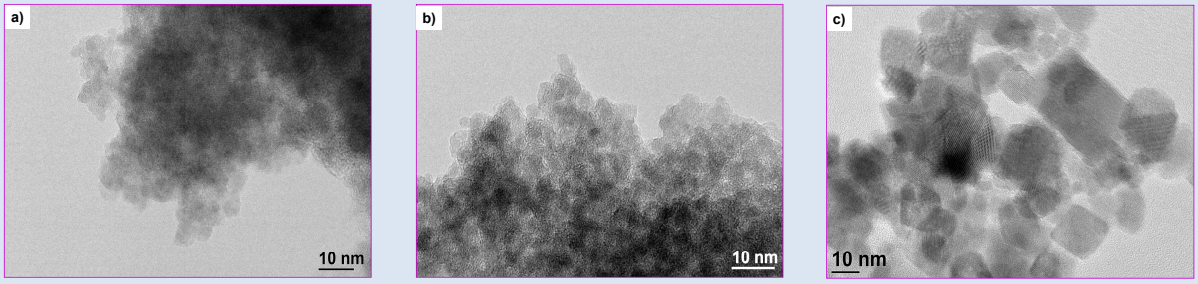


Figure 3. TEM images of $CoFe_2O_4$ nanoparticles a) co-precipitation, b) pH=8.0 and c) pH=13.1

Conclusion

The effect of pH on the structural and magnetic properties of $CoFe_2O_4$ nanoparticles prepared by a combination of the co-precipitation and hydrothermal methods was investigated. The results show that the crystallinity and average particle size increase with the increase of the pH. Also, the values of M_S, M_r and H_C follow this trend. The sample prepared at pH=13.1 has the highest values of M_S, M_r and H_C (65.4 emu/g, 19.95 emu/g and 775.8 Oe, respectively) and, according to the Scherrer's equation, the average crystallite size for the sample with pH=13.1 is 15 nm.

[1] Raul Valenzuela. *Magnetnic ceramics*. Cambridge University Press, 1994.
[2] E. S. Murdock, R. F. Simmons, R. Davidson. Roadmap for 10 Gbit/in² Media: Challenges. *IEEE Transactions on Magnetics*, 28 (5): 3078-3083, 1992.
[3] S. N. Okuno, S. Hashimoto, K. Inomata. Preferred crystal orientation of cobalt ferrite thin films induced by ion bombardment during deposition. *Journal of Applied Physics*, 71 (12): 5926-5929, 1992.
[4] P. C. Rajath Varma, R. S. Manna, D. Banerjee, M. Raama Varma, K. G. Suresh, A. K. Nigam. Magnetic properties of $CoFe_2O_4$ synthesized by solid state, citrate precursor and polymerized complex methods: A comparative study. *Journal of Alloys and Compounds*, 453(1-2): 298-303, 2008.
[5] M. Kishimoto, Y. Sakurai, T. Ajima. Magneto-optical properties of Ba-ferrite particulate media. *Journal of Applied Physics*, 76 (11): 7506-7509, 1994.
[6] Q. Liu, J. Sun, H. Long, X. Sun, X. Zhong, Z. Xu. Hydrothermal synthesis of $CoFe_2O_4$ nanoplatelets and nanoparticles. *Materials Chemistry and Physics*, 108 (2-3): 269-273, 2008.

Tempering Effects on the Microstructure, Mechanical Properties and Creep Rate of X20CrMoV121 and P91 Steels

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An increased efficiency of the fossil-fired power plants is obtained with higher operating temperatures and pressures of the steam that enters the turbine. The standard operating temperatures are 540-565 °C, but during the last 20 years large efforts have been made to reach the so-called ultra-supercritical (USC) conditions with the steam parameters up to 300 bars and 620 °C. These conditions require materials with the high creep-resistance, i.e., the ability to withstand a long-term loading at high temperatures. This requires a careful material selection and a periodical checking of its properties and remaining residual lifetime after the determined period of operation in power plants. The checking of the creep rate and creep strength is expensive and time-consuming. For this reason, simpler methods are being developed, which use less expensive and faster tests that enable the establishment of the state of the built-in steel. One among these methods is to check the room-temperature mechanical properties and microstructure after tempering, which simulates the changes in the microstructure and properties that occur after a longer operation in the power plant (in real conditions) by correlating the measured properties with the creep rate. The latter is measured using the standard creep test.

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Study program: Nanosciences and Nanotechnology

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INTRODUCTION

Creep resistance is the key property of materials that operate at high temperature and high pressure conditions in thermal power plants. Materials usually employed in these applications are the 9-12% Cr steels.

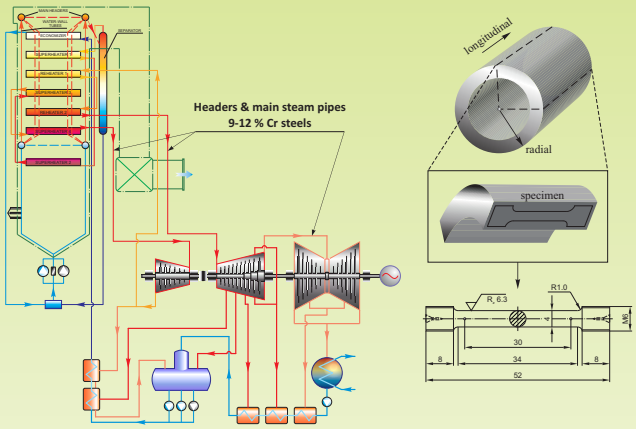
The aim of this investigation was to study the effects of tempering on the microstructure changes, particularly on the size and inter-particle spacing of carbide precipitates, and on the changes of room-temperature tensile properties of two creep resistant steels, X20CrMoV121 and P91. We also aimed to correlate the measured yield stress with the calculated creep rate.

EXPERIMENTAL

I. Heat treatment

Tempering for 2, 4320, and 8760 h (1 year) at 750 °C, and up to 17520 h (2 years) at 650 °C

II. Room-temperature tensile tests



III. SEM (Scanning Electron Microscopy) imaging and image analysis

The SEM specimens were prepared from the initial state of both steels, as well as after 2, 4320, and 8760 h of tempering at both 650 °C and 750 °C. Five images were acquired on each specimen at a magnification of 5000×.

JEOL JSM-6500F FE-SEM at IMT

IV. Analytical calculation

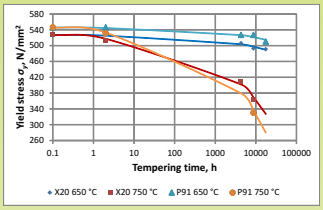
1. Using the R-software (http://www.R-project.org), the least square method was applied to estimate the parameter k_2 in $y(t) = k_1 - k_2 t^x$. The exponent x was appropriated to 1/3, whereas the k_1 to a specific initial value for each property.

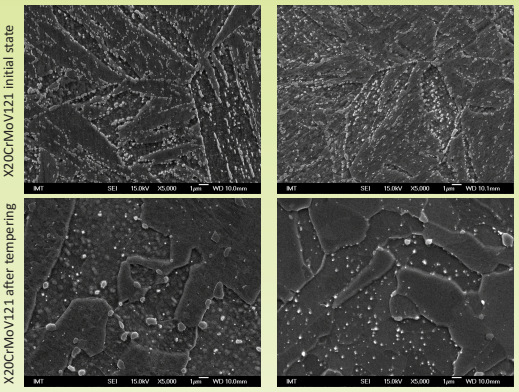
2. Dependence of the creep rate $d\varepsilon/dt$ on the inter-particle spacing λ is expressed through (Vodopivec et. al., Materiali in Tehnologije **38**, 2004):

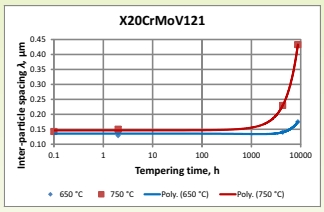
$$\varepsilon' = \frac{b^2 \cdot \lambda \cdot \rho \cdot \sigma^2 \cdot D}{k \cdot T \cdot G_{c,T}} = 3.69 \cdot 10^{-5} \cdot \lambda \;, \text{ where } \lambda \text{ is given by: } \quad \lambda = \frac{4d}{\pi \sqrt[3]{f}}$$

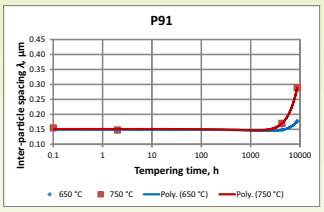
RESULTS

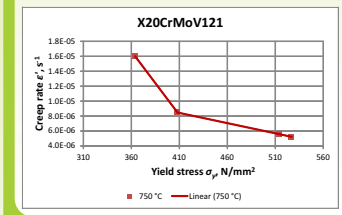
Parameters	X20CrMoV121		P91	
	650 °C	750 °C	650 °C	750 °C
k_1	527		546	
k_2	1.44	7.68	1.2	10.23

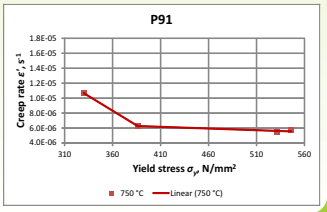












CONCLUSIONS

- Tempering at 650 °C causes relatively small changes of the microstructure and yield stress, unlike the tempering at 750 °C, where changes are more pronounced.
- Effect of tempering on the yield stress σ_y is quite similar for both steels; there is a mathematical expression, $y(t) = k_1 - k_2 t^x$ showing a good fit with experimental data.
- Microstructure changes are more pronounced after about 1000 h of tempering at 750 °C, expressed in terms of increase in particle size and inter-particle spacing.
- As the creep rate ε' increases, the yield stress σ_y decreases according to a dual-region linear function, with the change in slope after about 4320 h of tempering.

Phase transitions of the $NaNbO_3$ submicron-sized powder between room temperature and 700 °C

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The functional properties of ceramic materials directly depend on their crystal structure, which changes upon changing the temperature. Therefore the understanding of the crystal structure and the phase transitions is of great importance when the materials are to be used in devices for various applications.

In the present work we demonstrate the implementation of the two complementary analytical techniques for investigation of phase transitions and crystal structure of materials: the differential scanning calorimetry (DSC) and the X-Ray diffraction (XRD) combined with the Rietveld analysis. The first one was used to determine the transition temperatures, while the second one enabled the insight into the crystal structure of the material.

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Phase transitions of the $NaNbO_3$ submicron-sized powder between room temperature and 700 °C

INTRODUCTION

Functional properties of ceramics directly depend on their **crystal structure**, which changes upon changing the temperature. Therefore the understanding of the **crystal structure and the phase transitions** is of great importance when the materials are to be used in devices for various applications.

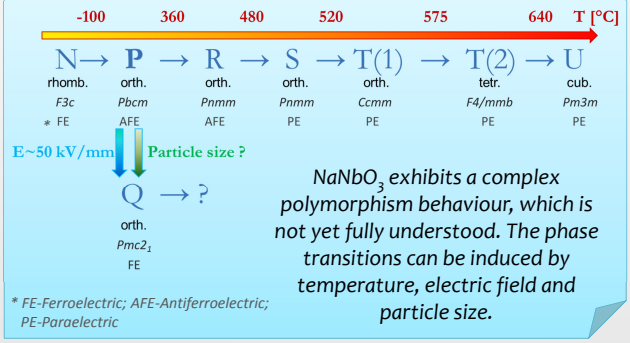
In the present work we demonstrate the implementation of two complementary analytical techniques for investigation of phase transitions: **differential scanning calorimetry** and **X-ray diffraction** combined with the **Rietveld analysis**. The first one was used to determine the transition temperatures, while the second one enabled us the insight into the crystal structure of the material.

GLOSSARY:

The term **polymorphism** describes the relations among different crystalline modifications (**polymorphs**) of the same chemical substance, which typically possess different physical properties. The transitions between different polymorphs are referred to as **phase transitions**.

WHY $NaNbO_3$?

FUNDAMENTAL RESEARCH

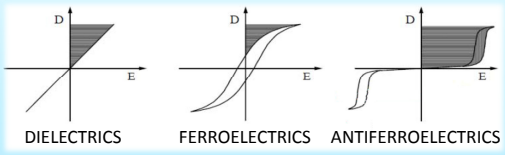


$NaNbO_3$ exhibits a complex polymorphism behaviour, which is not yet fully understood. The phase transitions can be induced by temperature, electric field and particle size.

* FE-Ferroelectric; AFE-Antiferroelectric; PE-Paraelectric

POTENTIAL APPLICATIONS

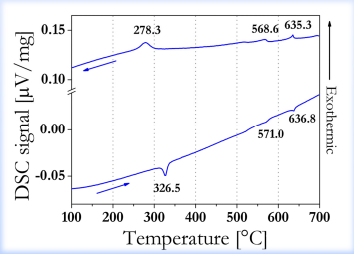
Antiferroelectric ceramics



The shaded area represents the amount of energy, which can be stored in different materials. This property makes the antiferroelectrics, such as $NaNbO_3$, interesting for high-performance capacitors.

EXPERIMENTAL WORK AND RESULTS

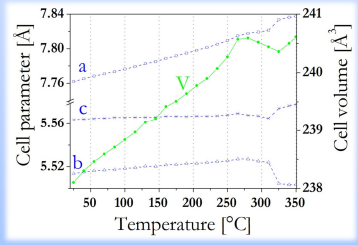
1. DETERMINATION OF THE PHASE TRANSITION TEMPERATURES



The phase transitions identified using differential scanning calorimetry (DSC) upon heating: *Q*→*R* (326.5°C), *T(1)*→*T(2)* (571°C), and *T(2)*→*U* (636.8°C).

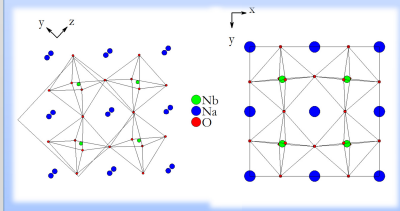
2. CALCULATION OF THE CELL-PARAMETERS

High-temperature X-Ray diffraction (XRD) was used to investigate the unit cell parameters (*a,b,c*) and the unit cell volume (*V*) upon heating. The change in the slope indicates the phase transition.



3. CALCULATION OF THE STRUCTURE

The structures at room temperature (a) and at 420 °C (b) were calculated by the Rietveld method. At 420 °C the *Na* cation is placed in the centre of the *x-y* plane and the cuboctahedral cavities become more regular (increase of the symmetry).



a) b)

CONCLUSIONS

Phase transition behaviour of submicron-sized $NaNbO_3$ powder was investigated using DSC and XRD. Three anomalies were found in the DSC curve upon heating: *Q*→*R* (326.5°C), *T(1)*→*T(2)* (571°C), and *T(2)*→*U* (636.8°C). The structural changes during the *Q*→*R* transition were investigated using XRD and the increased symmetrisation of the structure was related to the increased regularity of the cuboctahedral cavities and displacement of the *Na* cation.

This work was supported by the Slovenian Research Agency (contr. nr. 1000-08-310121; P2-0105).

The authors would like to thank to Jena Cilenšek (DSC), Edi Kranjc (XRD), and dr. Tadej Rojac.

Environmental Friendly Potassium Sodium Niobate Based Thin Films from Solutions

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Piezoelectric ceramic materials are used as sensors, actuators and micro-electro mechanical devices (MEMS). The continuous trend in miniaturization of micromechanic and microelectronic components has provided applications for thin films: the nanomaterials with thicknesses of less than 1 μm.

The properties of thin film-structures often differ from those of bulk ceramics and need to be understood in order to produce new devices. Thin films can be prepared by dry (physical) and wet (chemical) techniques. The former enable the preparation of high quality thin films but with an expensive equipment, while the latter are relatively quick, inexpensive and offer a good variety of possibilities for an easy modification of the composition for improvements in structure properties of functional thin films.

The basic steps of Chemical Solution Deposition (CSD) of thin films include the synthesis of the precursor solution, the deposition of the solution on the substrate, and the heat treatment of the deposited film. Among CSD, the alkoxide based sol-gel route enables the synthesis of different heterometallic solutions and gives the possibility to tailor the reactivity of the starting compounds. The detailed investigations of impacts of precursor solutions, nucleation and growth of the microstructure have led to increase the variety of materials systems that can be prepared and to tremendous improvements in the quality of the films.

The lead zirconate titanate based solid solutions (Pb(Zr,Ti)O3, PZT) are among the most widely studied materials for piezoelectric thin films. However, in the past years the research of lead-free ceramic materials intensified as a consequence of the increased awareness of the society towards the protection of the environment and human health from a hazardous substance, lead.

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Environmental Friendly Potassium Sodium Niobate Thin Films from Solutions

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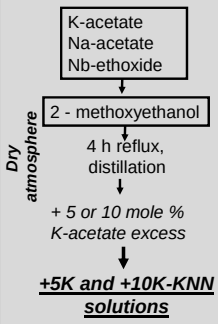
Mentor: prof. dr. Marija Kosec

INTRODUCTION **Increasing requirements for miniaturization of micromechanic and microelectronic components have increased the demand for thin film (thicknesses < 1 μm) processing. Chemical Solution Deposition or CSD is a relatively quick and inexpensive method for thin film deposition which offers a variety of possibilities for an easy modification of composition for improvements in structure properties of functional thin films. $(K_{0,5}Na_{0,5})NbO_3$ or KNN is a promising lead free ferroelectric material which could replace lead based perovskites. The major problem is volatilization of alkali compounds during processing, which hinders the control over the composition. In CSD, the losses can be compensated by adding alkali excess to the starting solution. In this work, we report CSD of KNN thin films from solutions with 5 or 10 mole % potassium excess.**

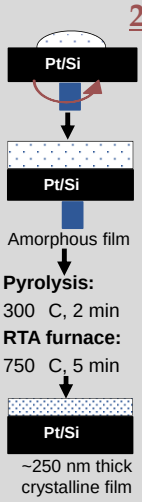
APPLICATIONS **of ferroelectric materials include *sensors, actuators, non-volatile memories, micro-electro mechanical devices (MEMS), etc..***

1. Solution synthesis



+5K and +10K-KNN solutions were prepared via alkoxide based sol-gel synthesis. Due to humidity sensitivity, the reagents were weighted and mixed in dry atmosphere. Potassium excess was added to solutions in order to compensate the expected losses.

2. Solution deposition

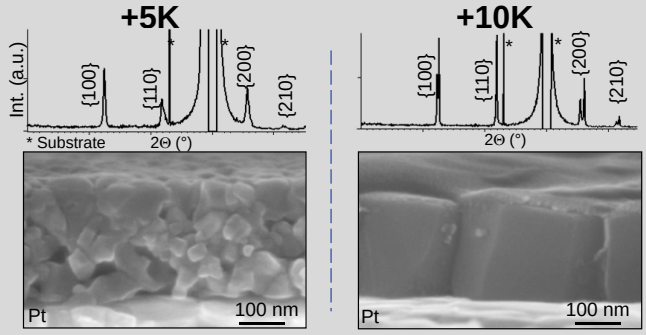


KNN solutions were deposited on the $Pt(111)/TiO_2/SiO_2/Si$ substrate and than the substrate was rotated. During spinning the solution spread across the whole sample by centrifugal force.

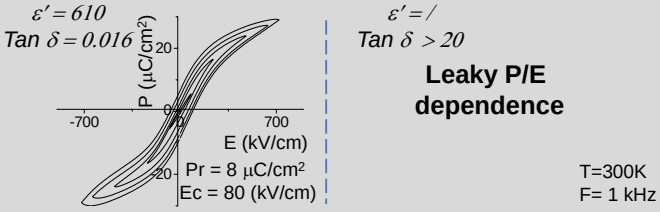
3. Heat treatment

Amorphous films were heated in order to remove water and trapped solvent, to decompose organic groups and finally, to induce a long range ordering, resulting in evolution of microstructure and crystallographic orientation.

• Phase composition and microstructure



• Dielectric and ferroelectric properties



Both KNN films crystallized in a preferentially {100} oriented pure perovskite phase. The +5K film had granular, while the +10K film had columnar microstructure. The room temperature dielectric permittivity and losses at 1 kHz of +5K- film were 610 and 0.016, respectively and the film exhibited ferroelectric behaviour, as evidenced by the P/E dependence. Only poor dielectric properties with high losses were measured in the +10K film, which we relate to the film microstructure. Namely, the grain boundaries, that could provide conduction pathways, are extending across the whole thickness of the film.

TO CONCLUDE, **materials and functional properties of the ~250 nm thick $K_{0.5}Na_{0.5}NbO_3$ films from solutions with 5 or 10 mole % potassium acetate excess were studied. Upon heating to 750 °C films crystallized in a pure perovskite phase with a {100} orientation. The amount of potassium excess in solutions contributed to the film's final properties. Depending on the amount of alkali excess in solutions, the films consisted of ~50 nm large equiaxed grains (5 mole %) or of ~200 nm large grains of cuboidal shape (10 mole %). In the film prepared from the solution with 10 mole % potassium excess the grain boundaries extended across the whole thickness of the film and could therefore provide the conduction pathway and contribute to poor dielectric properties. In contrast, the about 250 nm thick film prepared from 5 mole % potassium excess solution had the room temperature values of dielectric permittivity, dielectric losses, remnant polarization and coercive field at 1 kHz equal to 610, 0.015, 8 mC/cm² and 80 kV/cm, respectively**

The authors wish to acknowledge the support of Slovenian Research Agency (PR – 03099, P2 – 0105) and Centre of Excellence NAMASTE, Slovenia.

The Effect of the Firing Temperature on the Properties of LTCC

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The low-temperature co-fired ceramic (LTCC) is an important composite glass-ceramic material in the production of ceramic multilayer structures mainly for the telecommunications, automotive, and medical applications. In recent times the LTCCs were also recognized as useful materials for producing complex 3D structures with buried cavities and channels or so-called micro-electro-mechanical systems (MEMS). For MEMS structures are very important their chemical, thermal and mechanical properties, while in electronic circuits of the main importance are electrical properties.

The characteristics of the commercially available LTCC tapes processed under prescribed procedures are available in the datasheets and other open literature; however, the large and complex multilayer structures are usually fired for longer firing times and/or, higher firing temperatures, than the relatively thin LTCC tapes. The firing procedures determine the phase composition and the microstructure, which both influence the physical properties, such as the mechanical and thermal properties of the material.

Our research is focused on the study of the effects of the firing temperature and firing time on the phase composition, microstructure, mechanical properties and coefficient of thermal expansion of the material in order to understand the processes during the firing and their effect on the final properties of the material. In order to reach the desired final properties of devices, the mechanisms of the sintering and the crystallization of glass material and their influences on the physical properties must be known. With this knowledge the new material with designed properties can be developed.

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Background

Low-temperature cofired ceramics (LTCCs) technology is used for substrates for multilayer ceramic circuits, mainly for telecommunications, automotive, and medical applications. In recent times LTCCs were also recognized as useful materials for producing complex 3D structures with buried cavities and channels (or so-called) - micro-electro-mechanical systems (MEMS).

Most of LTCCs are glass-ceramics composites. These glass-ceramic composites are usually designed to yield a partial glass crystallization during the firing, which then minimizes the amount of glass phase in the composites and influences the mechanical and electrical properties of the glass-ceramic materials. Driven by the needs of the target application the interactions of different glasses with ceramic fillers during firing and the phases which crystallize from the glasses were extensively studied.

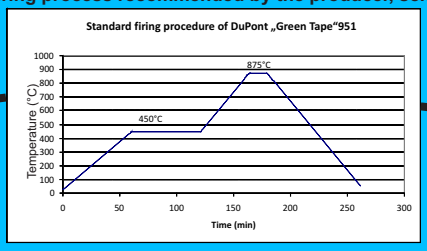
The main physical properties of commercially available LTCCs which are processed using the parameters specified by the producer are available in datasheets and other open literature. However, the production of large or complex 3D LTCC structures requires different, firing procedure.

Those unconventional firing processes affect the final functional properties of the LTCC material. To the best of our knowledge there is not much data available in the open literature about the influence of different firing conditions, such as firing temperature, on the microstructure, phase composition and consequently on the functional properties of the LTCC.

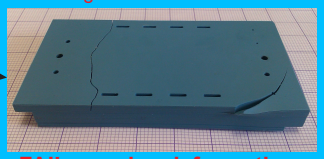
Firing process recommended by the producer, schematically.

Small and thin structure

OK - propertis of the material as specificate in the datasheets and in the other open literature.



Large and thick structure



FAIL - cracks, deformations NOT useful

When firing the large and complex structures the different firing conditions must be applied.

Different firing temperatures affect the phase composition and the microstructure which both influence to the properties of the material.

Experimental

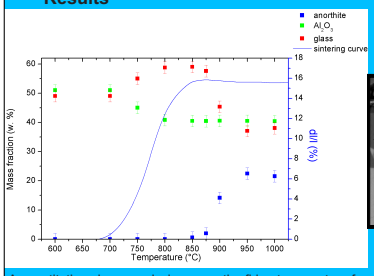
For the investigation the mostly used commercial Du Pont "Green tape" 951 LTCC tapes were used. The samples were fired for 1 hour at 450 °C in order to complete organic binder burn out, and at various maximum temperatures between 600 and 1000 °C for 15 minutes.

To determine the phase composition the fired samples were ground and analysed with a PANalytical X'Pert PRO MPD X-ray diffractometer (Almelo, Netherland). The XRD diffractometer was operated with a Cu Kα, configuration using a wavelength of 1.54060 Å in the angle 2θ range between 10 ° and 70 ° a step of 0.034 ° and an integration time of 100 s. A quantitative phase analysis of the ground, fired samples was performed using a Rietveld refinement. The 30 w. % of ZnO (Alfa Aeser, Puratronic, 99.9995 %, Alfa Aeser, Karlsruhe, Germany) was added as an internal standard. For the refinement the structures for Al_2O_3 (ICSD 73725), ZnO (ICSD 34477) and anorthite (ICSD 34667) were used.

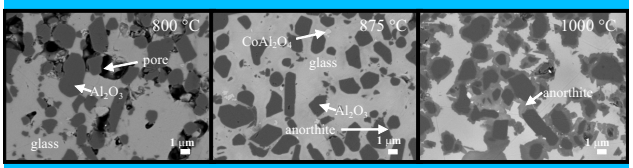
The microstructures of the samples were characterized using a Field-Emission Scanning Electron Microscope JSM-7600F (FEG-SEM).

The biaxial flexural strengths were measured on 10 replicas for each firing temperature on the circular samples with green thickness of 762μm and the diameter of 17 mm with the ball-on-three-balls (B3B) test using an Instron 1362 equipped with a 5 kN load cell and with a speed of 1 mm per minute.

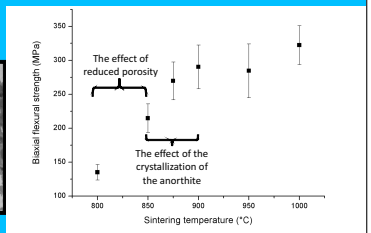
Results



A quantitative phase analysis versus the firing temperature for LTCC material, firing time 15 minutes. The sintering curve presented as a blue line is added in the same graph.



FEG-SEM microstructures of the samples fired at 800, 875 and 1000 °C for 15 minutes.



Biaxial flexural strengths of LTCC material fired for 15 minutes at different temperatures, showing the regions when strength is basically controlled by the porosity and anorthite, respectively.

Conclusions and applications

The influence of firing temperatures on the phase composition, microstructure and biaxial flexural strength of the LTCC was investigated. The investigated DuPont 951 LTCC is composed of Al_2O_3 particles and the glass phase. At 675 °C the LTCC starts to densify after the "liquid glass" is formed. Close to this temperature the particles of Al_2O_3 start dissolving and the amount of glassy phase increases up to 800 °C. From 675 °C to ~875 °C the sintering of the LTCC takes place and the material is fully sintered at 875 °C. The anorthite crystallizes on the surface of the Al_2O_3 particles. The amount of anorthite increases with the increasing firing temperature or time until it reaches the plateau value of around 22 w.% at 950 °C. The amount of glass is reduced accordingly. The biaxial flexural strength of the LTCC material fired at 800 °C is around 135 MPa and increases to ~ 220 MPa at 850 °C. The additional improvement of the biaxial flexural strength up to ~300 MPa was obtained between 850 and 900 °C when the anorthite crystalizes on the surface of the alumina particles. For the material fired at higher temperatures only small if any improvement of biaxial flexural strength can be observed.

Acknowledgement

The Slovenian Research Agency is acknowledged for its financial support of the projects "Ceramic materials for 3D structures and study of functional properties" (L2-2343), the Young Researcher project 100-009-310145. The financial support of the CoE NAMASTE is gratefully acknowledged.

Conformational preferences of alanine tripeptide in water, trifluoroethanol and dimethyl sulfoxide studied by vibrational spectroscopy

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Naše raziskovalno delo vključuje konformacijske analize kratkih peptidov, katerih namen je razumevanje vseh sil in interakcij znotraj peptida, ki bi pomagale razumeti začetno stopnjo proteinskega zvitja in vlogo konformacijskih preferenc aminokislin. Ramanska in infrardeča vibracijska spektroskopija ter vibracijski cirkularni dihroizem omogočajo natančno analizo konformacij posameznega proteina in peptida z razčlenitvijo posameznih konformacijsko odvisnih regij v spektru. Primerjali smo porazdelitev konformacij alanin dipeptida in alanin tripeptida v vodi. Alanin dipeptid je pretežno v PII konformaciji in delno v β konformaciji. Delež α_R konformacije je majhen. Alanin tripeptid pa poleg omenjenih konformacij vsebuje še znaten delež C_7 konformacije, ki je stabilizirana z intramolekularno vodikovo vezjo. Z zamenjavo topila smo pokazali, da se lahko ta vez prekine, pri čemer molekula zavzame bolj odprto, topilu dostopnejšo strukturo.

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JOŽEF STEFAN INTERNATIONAL POSTGRADUATE SCHOOL

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Mentor: Doc. Dr. Jože Grdadolnik

Conformational preferences of alanine tripeptide in water, TFE and DMSO studied by vibrational spectroscopy

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Introduction

To understand the basic physico-chemical principles which govern the protein folding process a detailed conformational characterization of the unfolded state is required. Short alanine peptides provide an attractive model system for testing the spectral structural parameters and for studying the structures with no elements of secondary structure in the absence of the denaturants. In the unfolded states of proteins alanine residue exhibits high polyproline II (P_{II}) propensity [1]. A recent conformational study of alanine dipeptide in water by vibrational spectroscopy indeed showed the three backbone conformations are 61% (P_{II}), 10% (α_R) and 29% (ß), respectively [2]. The aim of our study was to characterize conformational properties of blocked alanine tripeptide in water, DMSO and TFE and determine the population of each conformational state.

Methods

Infrared, Raman, Vibrational circular dichroism

All vibrational spectroscopy methods are sensitive to secondary structure of peptides and proteins. The conformational sensitive regions in spectrum are:

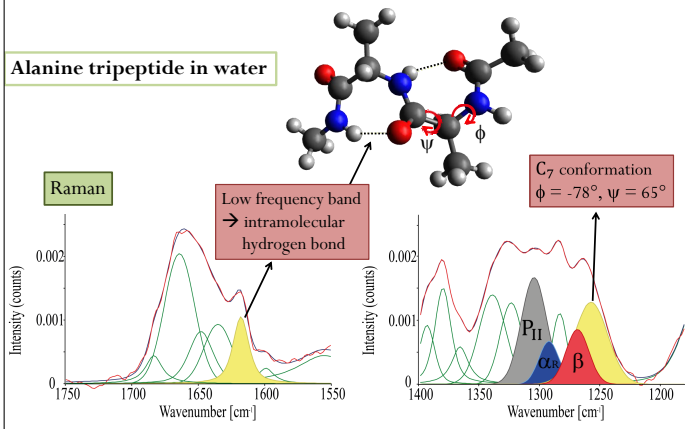
amide I (1610-1690 cm^{-1}): manly CO vibrational mode of peptide backbone gives information about secondary structure of peptide

amide II (1600-1500 cm^{-1}): less sensitive to various secondary structure elements, its frequency reflects the participation of backbone NH groups as proton donor in various types of hydrogen bonds (intra-/intermolecular)

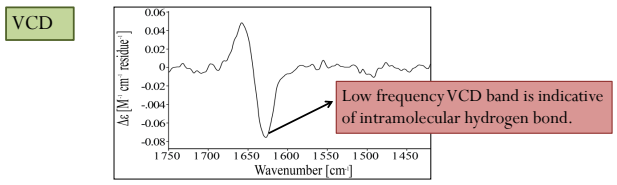
amide III (1200-1350 cm^{-1}): the most sensitive indicator for peptide conformations due to very localized frequencies

Results

INTRAMOLECULAR HYDROGEN BOND

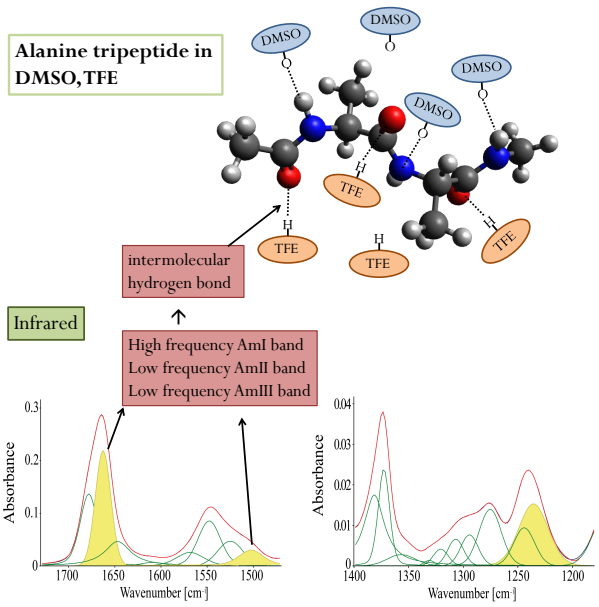


Fitted Raman spectrum in amide I (left) and amide III (right) region of Ac-Ala_2-NHMe in water at concentration 0.2 M at room temperature. The band colour represents particular conformation: grey P_{II}, red β, blue α_R, and yellow C_7.



VCD spectrum of Ac-Ala_2-NHMe in D_2O at concentration 0.2 M at room temperature.

INTERMOLECULAR HYDROGEN BOND



Infrared spectrum of Ac-Ala_2-NHMe in DMSO at concentration 0.2 M.

Conclusions

- We characterized different conformational population of alanine tripeptide in water, DMSO and TFE.
- In water alanine tripeptide possesses conformations P_{II}, ß, α_R and conformation that is stabilized with intramolecular hydrogen bond which is indicative of C_7 conformation.
- In DMSO (proton acceptor solvent) and TFE (proton donor solvent) alanine tripeptide mainly forms intermolecular hydrogen bonds with solvent.

References

[1] F. Avbelj, R. L. Baldwin. *Proc. Natl. Acad. Sci. U S A*, *100*:5742, 2003

[2] J. Grdadolnik, V. Mohaček-Grošev, L.R. Baldwin, F. Avbelj. *Proc. Natl. Acad. Sci. U.S.A.*, *108*:1794-1798, 2011

Basic study of relaxors: Materials for high technological devices

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Relaxor ferroelectric materials represent a subgroup of ferroelectrics. Pb(Mg1/3Nb2/3)O3 is one of the most famous and widely studied relaxor. Relaxor materials are known for their unusual properties which are useful for various applications in high technological devices. Relaxors exhibit high permittivity (used in capacitors), ferroelectric hysteresis (used in non-volatile memories), high piezoelectric effects (used in sensors, actuators and resonant wave devices such as the radio-frequency filters, scanning probe microscopy, ink jet printer, adaptive optics, micromotors, vibration sensors/attenuators, Hubble telescope correction), high pyroelectric coefficients (used in infra-red detectors), strong electro-optic effects (used in optical switches, segmented displays, modulators, image storage, holographic data storage) and anomalous temperature coefficients of the resistivity (used in electric-motor overload protection circuits). Our work is dedicated to understanding the ordering process in this material which is of a fundamental importance for the further application progress as well as engineering new materials with enhanced properties.

In this work we represent the study of the glass-ferroelectric phase transition that addresses also the long standing question about the ground state of relaxors in zero electric field. The isofield and isothermal measurements of the heat capacity reveal an excess of the heat capacity as well as released latent heat at the field induced ferroelectric transition. The detected latent heat confirms the existence of the real ferroelectric phase transition and support the physical picture of the dipolar glass like ground state of relaxors.

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BASIC STUDY OF RELAXORS: MATERIALS FOR HIGH TECHNOLOGICAL DEVICES

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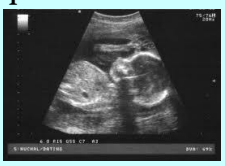
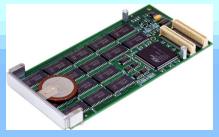
Abstract

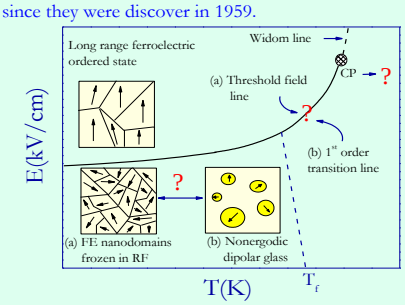
Relaxor ferroelectric materials represent a subgroup of ferroelectrics and are charcterized by extraordinery properties which are useful for various applications in high technological devices. Relaxors exhibit high permittivity, ferroelectric hysteresis, high piezoelectric effects, high pyroelectric coefficients, strong electro-optic effects and anomalous temperature coefficients of resistivity.

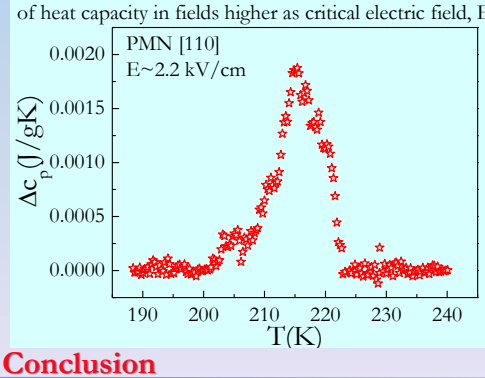



Our work is dedicated to understanding of ordering processes in these materials which is of a fundamental need for further application progress. Here, we address a long standing question about the nature of relaxor ground state in zero electric field. Over the years two possible relaxor ground state were presented as shown in electric field temperature diagram.

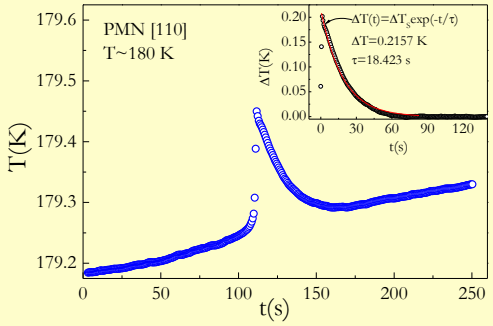
The nature of relaxors ground state is a matter of discussion since they were discover in 1959.



The isofield measurement obtained in ac mode show an excess of heat capacity in fields higher as critical electric field, E_C.



Anomaly of sample temperature observed in isothermal relaxation measurements is a consequence of the released latent heat at the ferroelectric transition.



Conclusion

[1] The ac and relaxation calorimetric measurements show an excess of the heat capacity as well as sharp increase of the sample temperature as a consequence of the released latent heat at the electric field induced ferroelectric transition.
[2] The detected excess heat capacity and latent heat confirm the existence of true thermodynamic first order phase transition in ferroelectric relaxor PMN [110] single crystal.
[3] Our findings firmly support the physical picture of dipolar glass like relaxor ground state for PMN relaxor.

Morfotropna fazna meja v $(Na_{1-x}K_x)_{0,5}Bi_{0,5}TiO_3$ piezoelektrični keramiki

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Mentor: doc. dr. Srečo D. Škapin

Novi piezoelektrični materiali brez vsebnosti svinca, ki v določenem območju sestav izkazujejo močno povišane vrednosti elektromehanske sklopitve, se raziskujejo zaradi njihove potencialne uporabe v elektroniki. Pri trdnih raztopinah s povišanimi piezoelektričnimi lastnostmi se namreč pojavi soobstoj dveh kristalnih struktur – območje imenujemo morfotropna fazna meja - zaradi česar se material enostavneje polarizira. Dejansko stanje kristalne strukture MPB je težko ovrednotiti, saj so metode ugotavljanja strukture posredne, povprečne ali invazivne, kar botruje številnim nesoglasjem stroke o realnem stanju strukture materiala. Naše raziskave so potekale na sistemu trdnih raztopin (Na1-xKx)0,5Bi0,5TiO3, za katere smo določili strukturne in električne lastnosti piezokeramik. Detajlne analize kristalne in domenske zgradbe so potekale s pomočjo presevne elektronske mikroskopije v kombinaciji z rentgensko praškovno difrakcijo.

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Morfotropna fazna meja v NBT-KBT piezoelektrični keramiki

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UVOD

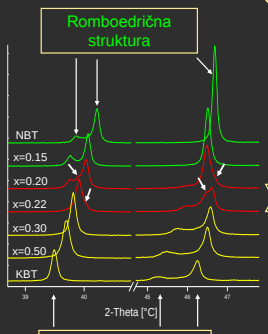
PIEZOELEKTRIKI brez Pb

→ morfotropna fazna meja (R + T struktura)

→ povišane vrednosti elektromehanskih lastnosti

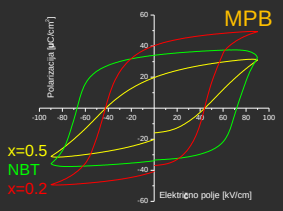
→ $(Na_{1-x}K_x)_{0,5}Bi_{0,5}TiO_3$ sistem (NBT-KBT)

RTG



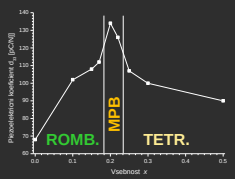
MORFOTROPNA FAZNA MEJA (MPB)

Soobstoj romboedrične in tetragonalne strukture



POLARIZACIJA

PIEZOELEKTRIČNOST

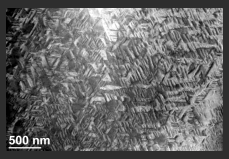


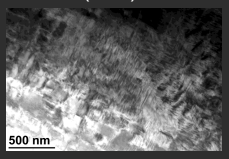
CILJ RAZISKAV

Določiti domensko in kristalno strukturo NBT-KBT keramike na morfotropni fazni meji s pomočjo presevne elektronske mikroskopije

TEM

NBT – romboedrična struktura (R3c)

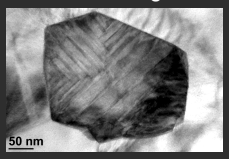


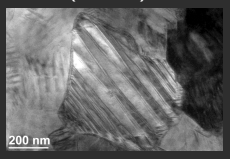


Igličaste ali lamelne domene - 'mrežasta domenska zgradba

71°/109° domene

KBT – tetragonalna struktura (P4mm)

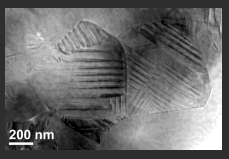


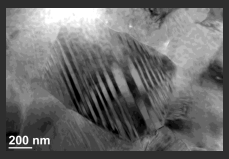


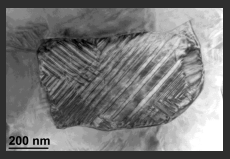
Lamelna domenska zgradba

90° domene

$Na_{0,4}K_{0,1}Bi_{0,5}TiO_3$ – MORFOTROPNA SESTAVA

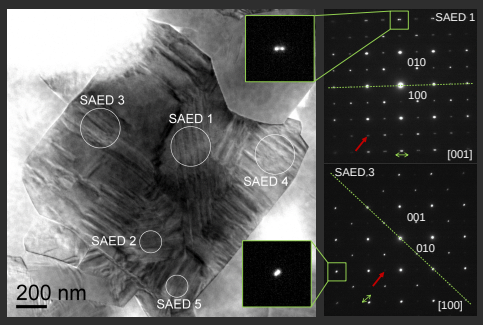






Lamelna domenska zgradba

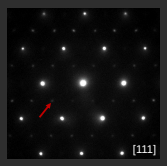
90° domene



cepitev uklonov vzdolž <110>

značilna tetragonalna cepitev uklonov

cepitev uklonov vzdolž <001>

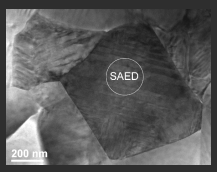


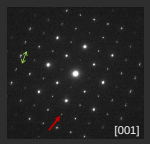
✓ Pojav ½(*ooe*) superstrukturnih uklonov v <100> in <111>

✓ Rotacija kisikovih oktaedrov vzdolž [100] / [010]

✓ $a^0a^0c^+$ tetragonalna struktura (P4bm)

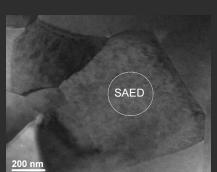
In-situ TEM segrevanje





Lamelna domenska zgradba pred segrevanjem

- značilna tetragonalna cepitev uklonov
- prisotni superstrukturni ukloni



Nanodomenska zgradba po segrevanju

- odsotnost cepitve uklonov
- prisotni superstrukturni ukloni

ZAKLJUČEK

$Na_{0,4}K_{0,1}Bi_{0,5}TiO_3$ → RTG: morfotropna sestava (R + T)

$Na_{0,4}K_{0,1}Bi_{0,5}TiO_3$ → TEM: tetragonalna struktura (P4bm)

Tetragonalna struktura sprožena z mehansko obdelavo vzorcev za TEM

Uporaba piezoelektrikov:

senzorji, aktuatorji, elektromehanski pretvorniki

The peak base as a characteristic feature of the Auger electron spectra

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The long term goal of our group is to automate the interpretation of spectra in Auger Electron Spectroscopy. To automate the interpretation of the quantitative and qualitative results obtained from the Auger spectra, in other words to enable the software to automatically tell us which elements are present in the surface of the sample and how much of each element is there, among other things, we must prepare the data by removing the background. The background interferes when we attempt to analyze how much of a specific element is presented in the sample. Even though the idea is straightforward, simply just to remove the background, the actual work of its removal is quite a challenge. Different researchers have taken different approaches to overcome the problem of how to define the background for its later proper removal. Our group has used neural networks for this purpose, modelling the background by feeding the neural network with the data that were obtained experimentally.

By visually inspecting the different approximated (modelled) parts of the background, a feature which we termed "the peak base" became apparent. We investigated further and found out that most of the researchers in the previous work on the topic of background definition and its later removal had treated this as an integral part of the feature that we termed "the primary background". But unlike the primary background, the peak base is actually formed from characteristic Auger electrons which normally would form the main peak, but are slowed down and lose slightly their characteristic energy since the electrons forming the peak base are generated deeper in the sample surface (the subsurface) and thus travel further and overcome additional obstacles on their way to the detector. Thus, the background that would normally be removed and hence its signal would be lost, actually carries information about our sample and can be used to detect elements when clear peaks are absent.

Through this work we attempt to bring the automation of Auger spectra interpretation one step closer. This on the one hand will make the analysis much easier for anyone involved in the study of metals and other materials through Auger spectroscopy, and on the other hand the proposed advanced treatment of the background part of Auger spectra will contribute to more reliable results about the elements present in the samples studied.

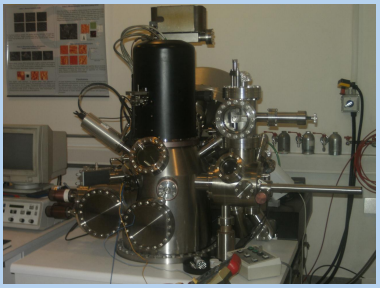
MEDNARODNA PODIPLOMSKA ŠOLA JOŽEFA STEFANA

JOŽEF STEFAN INTERNATIONAL POSTGRADUATE SCHOOL

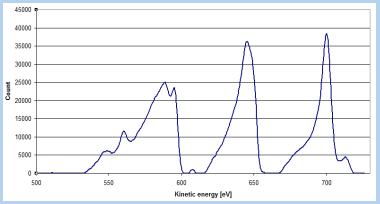
THE PEAK BASE AS A CHARACTERISTIC FEATURE OF THE AUGER ELECTRON SPECTRA

BESNIK PONIKU, mag. NiN
Study programme: Nanosciences and nanotechnologies,
Jozef Stefan International Postgraduate School
MENTOR: prof. dr. Monika Jenko
CO-MENTOR: doc. dr. Igor Belič
Institute of Metals and Technology, Lepi pot 11, 1000 Ljubljana

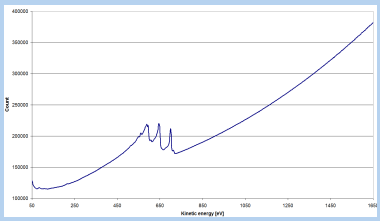
AUGER ELECTRON SPECTROSCOPY is used to detect elements on the surface of metallic samples and other solid materials in depths of the order of a few nanometers.



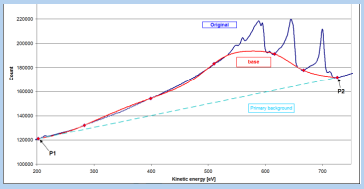
The Auger spectrum is not composed only of the characteristic Auger peaks through which the elements are detected,…



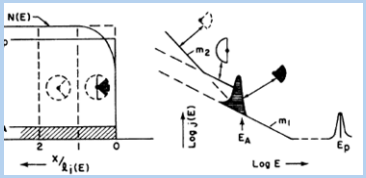
…but instead the characteristic peaks are situated on top of a background signal.



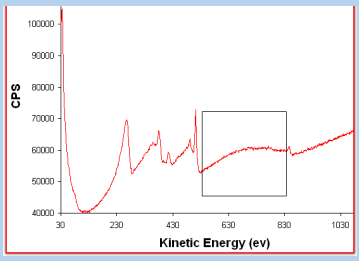
The background in Auger spectra interferes in quantitative analysis, and therefore should be removed. Our team used neural networks to define the background and observed three distinctive parts in the spectrum: the primary background, the peak base, and the main peaks.



Researching the literature we found out that the peak base originates from the Auger emission coming from the subsurface layers of the sample.



Spectra measured on a sample of TiNi alloy also confirm this claim.



The long term goal of our group is to automate the interpretation of spectra in Auger electron spectroscopy. Through this work we attempt to bring the automation of Auger spectra interpretation one step closer. Apart from making the analysis much easier for anyone who is involved in the study of metals and other materials through Auger electron spectroscopy, by clearly defining and dealing with obstacles like the background also the results obtained will be much more reliable.

From the case of the peak base presented above one other important factor should be kept in mind. The background contains information regarding the sample under investigation, and the peak base in particular could be used to detect the presence of an element when clear peaks are absent. Thus in the process of removing the background we should save that information for reference when necessary.

Underwater electromagnetic remote sensing

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The underwater remote sensing technology plays a key role in underwater investigation and unknown objects detection. Electromagnetic (EM) principles have long been recognized as a useful tool for the geophysical exploration and remote sensing. The technology that we selected includes an adapted version of the ground penetrating radar (GPR) and the continuous wave electromagnetic sensor (CWEMS), which are competing methods against the SONAR (sound navigation and ranging) and metal detector. The ground penetrating radar or GPR is a non-destructive geophysical method, which is based on the propagation of high frequency electromagnetic waves. The GPR method images structures in the ground that are related to changes in the dielectric properties. In addition, the CWEMS sensor has proven to be very effective in detecting both, ferromagnetic and nonmagnetic metallic targets, lying on the sea bottom or buried in the seabed. We measured the structure of the lake subsurface with a commercial GPR at frequencies of 50 MHz and 250 MHz, respectively. The used GPR system is capable to observe the subsurface below 10 m and through more than 3 m of the water layer with the 50 MHz antenna. However, a more detailed structure can be obtained with a higher frequency 250 MHz antenna at the expense of a lower penetration depth. The GPR method has several potential applications in the general exploration and security of the underwater environment as well as in the oil and gas industry. In addition, we measured and imaged several metal objects of different sizes and shapes with the CWEMS sensor. The discrimination between various metallic objects is possible, which makes the sensor appropriate for the underwater security imaging.

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JOŽEF STEFAN INTERNATIONAL POSTGRADUATE SCHOOL

Underwater electromagnetic remote sensing

Study programme: Nanosciences and Nanotechnologies
Jožef Stefan International Postgraduate School

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Introduction

Underwater remote sensing technology:
→investigation of the underwater environment and detection of unknown objects
→acoustic, **electromagnetic** and optical devices

EM propagation in water is very different from the propagation through air:

- ❑ high permittivity
- ❑ high electrical conductivity
- ❑ greater attenuation loss
- ❑ lower propagation velocity
- ❑ smaller wavelength

Applications of underwater remote sensing EM methods

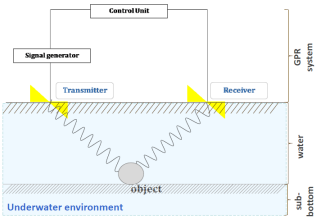
- ❑ mapping the location of objects buried under the bottom sediments or vegetation
- ❑ maritime security and safety
- ❑ harbour surveillance
- ❑ dams investigation
- ❑ oil and gas industry

Experimental work and results

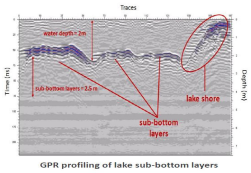
selected EM sensing methods

I. Ground penetrating radar (GPR)

- ❑ images structures in the ground that are related to changes in the dielectric properties

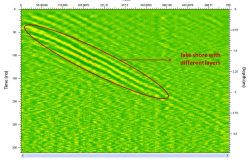


250 MHz antenna



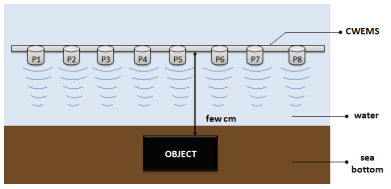
GPR profiling of lake sub-bottom layers

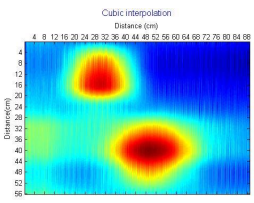
50 MHz antenna



II. Continuous wave electromagnetic sensor (CWEMS)

- ❑ The primary magnetic field produced by the transmitter is changed in such a way that a higher density of magnetic flux lines occurs due to the presence of metallic objects.





Conclusions

- ❑ GPR with the 50 MHz antenna is capable to observe the subsurface below 10 m and through more than 3 m of the water layer
- ❑ more detailed structure can be obtained with a higher frequency 250 MHz antenna
- ❑ CWEMS sensor is capable to image several metal objects of different sizes and shapes as well as different material composition

References

D. J. Daniels, Ground Penetrating Radar, 2nd ed., UK: The Institute of Electrical Engineers, 2004, pp. 1-352.

M. J. Harry, Ground Penetrating Radar: Theory and Applications, 1st ed., The Netherlands: Elsevier Science, 2009, pp. 1-176.

D. Margetis, Pulse propagation in sea water: the modulated pulse, Progress In Electromagnetics Research, vol. 26, pp. 89-110, 2000.

Annan, A. P. GPR Methods for Hydrogeological Studies, In: Hydrogeophysics, edited by. Y.Rubin and S.S. Hubbard, Springer, Netherlands, 2005, pp. 185-213.

Estimating the size of the maximum inclusion in a large sample area of steel

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The properties of steel and finished steel products are affected by non-metallic inclusions, formed during the steel production process. The detection and estimation of the size of the largest inclusions can be an important parameter in the quality control and lifetime estimation of steel and steel products. Statistical methods can be helpful, since they can provide an additional insight not necessarily apparent from the raw data. There are a few options that allow us to estimate the size of the largest inclusion to be expected. Unfortunately, there can be great discrepancies in the predictions from different models. Care should be taken when choosing a method and a model to investigate and analyse your product. Any of the models presented in this paper, on the other hand, can be used as a means of comparing different grades of steels or to define bounds, within which the quality of a given grade of steel is still acceptable.

ESTIMATING THE SIZE OF THE MAXIMUM INCLUSION IN A LARGE SAMPLE AREA OF STEEL

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Jožef Stefan International Postgraduate School
Study program: Nanosciences and Nanotechnologies

INTRODUCTION

Non-metallic inclusions, formed during steel production process, have a great impact on the properties of steel and finished steel products. The detection and estimation of the size of the largest inclusions is an important consideration in quality control and lifetime estimation of steel and steel products.

General extreme value (GEV) method can be used to estimate the maximum size of inclusions in a large amount of steel. Estimation of the sizes of extreme inclusions is affected by the presence of multiple types of inclusions in a single steel grade. The mixture and the competing risk models were suggested, where the diversity of the inclusions is taken into account statistically.

RESULTS AND DISCUSSION

To obtain the data, 544 sample areas, each of 0.27 mm^2, from a single steel slab were investigated. The area of each inclusion larger than 3 μm^2 was measured using automatic image analysis.

The fit of GEV model to the data gives the estimates for the parameters of the distribution. With the estimated parameters, the size of the largest inclusions can be calculated as a function of the number of sample areas S_0 to be investigated. Results are shown in Fig. 1.

Manually inspecting the samples, we see two types of inclusions contributing to the set of maximum inclusions. The fit of the mixture model nad competing risk model to data is shown in Fig. 2. Estimated inclusion sizes for the larger inclusions in each model are shown in Fig. 3.

Predictions of the three models show appreciable discrepancies. Competing risk model, which seems to best capture the underlying features and also gives a good fit to data, predicts the largest inclusions.

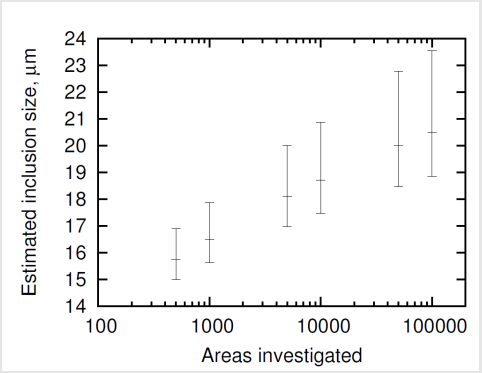

Fig. 1: Maximum inclusion size estimated from the parameters of the GEV model with 95% confidence intervals.

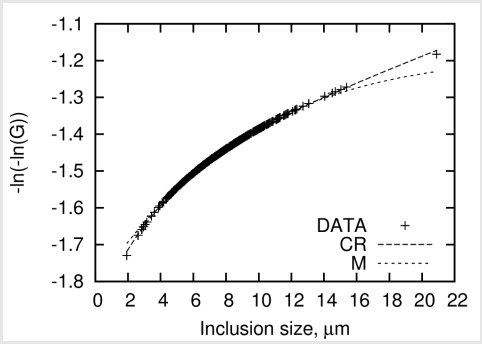

Fig. 2: The Gumbel probability plot with a comparisson of mixture model (M) and competing risk model (CR) fits to the data.

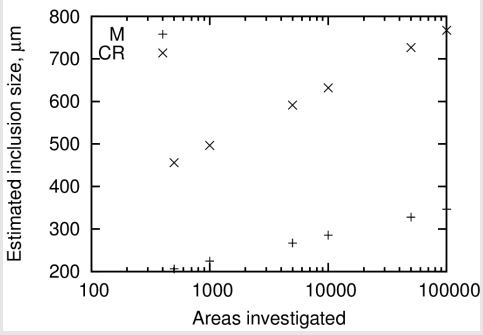

Fig. 3: Estimated inclusion size for the largest inclusions in mixture model (M) and competing risk model (CR).

Solvent capabilities of liquid and supercritical xenon

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The single crystal X-ray diffraction is a very powerful tool to get structural information on chemical compounds. Crystals are usually grown from solutions of these compounds and here the choice of a solvent plays a crucial role. Our research field involves syntheses and characterizations of new coordination compounds with binary fluorides as ligands (XeF2, XeF4, KrF2, AsF3, HF, etc.), as well as preparations of new binary and ternary fluorine compounds. Because of their high reactivity and/or low solubility in classical inorganic solvents, finding a suitable solvent and optimal crystallization conditions very often represents a difficult challenge. In addition, research on solvents and solutions has again become a topic of interest because many of the solvents commonly used in laboratories and in the chemical industry are considered as unsafe for reasons of the environmental protection, mainly because they are often used in huge amounts and because they are volatile liquids that are difficult to contain. An introduction of cleaner technologies has become a major concern throughout both the academia and industry. This includes the development of environmentally benign new solvents, sometimes called neoteric solvents (neoteric - recent, new, modern), constituting a class of novel solvents with desirable, less hazardous properties. This term covers supercritical fluids, ionic liquids, and also perfluorohydrocarbons. Despite its high price, liquid xenon's good solvating properties, optical transparency, very convenient critical properties, high density near critical conditions and inertness, makes it a promising solvent useful in the fundamental as well as applied research by opening a new possibility for high quality products.

MEDNARODNA PODIPLOMSKA ŠOLA JOŽEFA STEFANA

JOŽEF STEFAN INTERNATIONAL POSTGRADUATE SCHOOL

SOLVENT CAPABILITIES OF LIQUID AND SUPERCRITICAL XENON

Kristian Radan

Study programme: Nanosciences and Nanotechnologies

Jožef Stefan International Postgraduate School, Ljubljana, Slovenia

Mentor: **prof. dr. Boris Žemva**

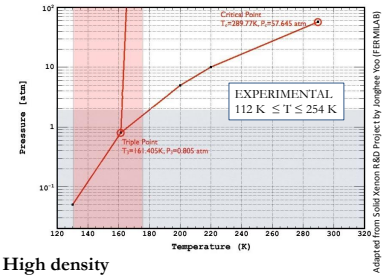
Department of Inorganic Chemistry and Technology, Jamova 39, Jožef Stefan Institute, Ljubljana, Slovenia

OBJECTIVES

- To investigate the solvent potential of liquid and near-supercritical xenon on the compound $XeF_2 \cdot 2SnF_4$
- To develope an experimental method and procedure for this purpose

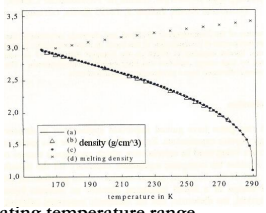
ADVANTAGES

- Convenient liquid and supercritical conditions

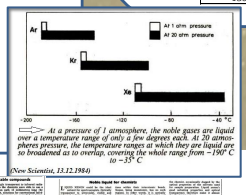


Adapted from Solid Xenon R&D Project by Jonghee Yoo (FERMILAB)

- High density



- Wide operating temperature range
- High polarizability
- Optical transparency (UV, visible, IR)
- Chemical inertness



At a pressure of 1 atmosphere, the noble gases are liquid over a temperature range of only a few degrees each. At 20 atmospheres pressure, the temperature ranges at which they are liquid are so broadened as to overlap, covering the whole range from −190° C to −35° C

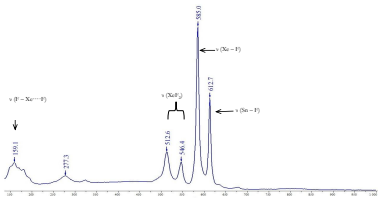
[New Scientist, 13.12.1984]

Articles from the 1980s (New Scientist) reporting the discovery of solvent properties of liquid and supercritical xenon.

EXPERIMENTAL

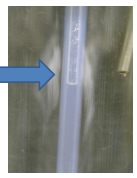
Solubility experiments and reaction vessels used for liquid (left) and near – supercritical (right) xenon.

RESULTS

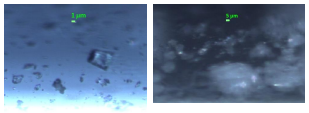


Raman spectrum and tentative assignments of an undefined crystalline product $aXeF_2 \cdot bSnF_4$, obtained from the reaction between SnF_4 and XeF_2 in liquid xenon. Table (below) shows the Raman study of known* xenon(II) fluorostannates(IV).

$XeF_2 \cdot 2SnF_4$	$3XeF_2 \cdot 4SnF_4$	Tentative Assignments
Raman Frequencies		
619(43)	619(38)	ν (Sn–F)
594(100)	594(66)	
580(25)	588(100)	ν (Xe–F)
	574(sh)	
	509(34)	ν (XeF_2)
	309(2)	
284(2)	283(2)	ν (Xe···F)
150(18)	160(12)	δ (F–Xe···F)



Crystals growing on the xenon liquid-gas interface.



Microscope magnifications of the crystalline adduct $aXeF_2 \cdot bSnF_4$ grown from liquid xenon.

* B. Družina, B. Žemva, J. Fluorine Chem. 34 (1986), 233 – 239.

CONCLUSION

- The solubility of the compound $XeF_2 \cdot 2SnF_4$ was investigated in liquid and near-supercritical xenon. An experimental procedure was developed and crystalline solids were obtained in both cases.
- Reaction between XeF_2 and SnF_4 occurred in liquid xenon at temperatures below –19 °C giving an undefined crystalline product $aXeF_2 \cdot bSnF_4$.
- More experiments are required to confirm the preliminary results and to obtain additional information on these systems.
- New possibilities for potential applications of liquid and supercritical xenon are opened.

A chemometric approach towards transmembrane region prediction of protein sequences

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Transmembrane proteins are membrane proteins spanning the whole biological membrane, acting both as barriers and communication channels between the intracellular and the extracellular spaces. They play crucial roles in the cell functioning acting as the transporters and receptors of various ligands, helping in the cell signalling etc. In addition, they are important as drug targets. However, the transmembrane proteins remain vastly unexplored due to experimental difficulties. Most of these proteins have unknown structures, and those with known structures often remain poorly annotated. Several interdisciplinary computational approaches along with experimental ones are therefore used to gain insights into the transmembrane proteins. Our lab expertizes: (i) the development and applications of standard and modern chemometrics techniques (clustering, classification, modelling, neural networks, genetic algorithms); (ii) handling of large amounts of multivariate data: transformations, projections, reductions, selection of variables and optimization of the data-representation for different modelling approaches; (iii) modelling using linear or non-linear methods – case studies in (Quantitative Structure-Activity Relationship)QSAR (modelling of biological properties), in analytical chemistry, determination of 3D molecular structures, calculation of descriptors and structure representations; validation of QSAR models. Our aim is to utilize this expertise for the characterization of transmembrane proteins using different chemometric methods for their structural elucidation. In the first step reported here, we have successfully developed a novel transmembrane region prediction algorithm. It is based on mathematical descriptors and neural networks. The prediction method, based on the sequence information, is independent of evolutionary data and physiochemical properties. The model is able to both predict successfully the transmembrane regions of unknown protein sequences and distinguish them from globular proteins. In the future, our aim is to utilize the data obtained from the inhibition studies applying chemometric tools, along with other computational and experimental methods, to study and predict the transport function of specific transmembrane proteins; and we are currently already working on these items. The chemometric methods along with other computational and experimental procedures, can be a very powerful aid to elucidate the structures and functional mechanisms of various transmembrane proteins.

MEDNARODNA PODIPLOMSKA ŠOLA JOŽEFA STEFANA

JOŽEF STEFAN INTERNATIONAL POSTGRADUATE SCHOOL

A chemometric approach towards transmembrane region prediction

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School : Jožef Stefan International Postgraduate School
Programme: Nanoscience and Nonatechnologies (old doctoral studies)

Supervisor : **dr. Marjana Novič**

Motivation

- Transmembrane proteins play important roles in maintaining normal cell functioning
- Important as drug targets
- Structures and functional mechanisms of very few transmembrane proteins are known
- Necessary to know the exact number and positions of the transmembrane regions present to further study a particular transmembrane protein
- **Using chemometric approach for transmembrane protein structure elucidation**

Problem Statement

AIM:

Predicting protein transmembrane regions using chemometric approach
Prediction based on only sequence information

Challenges:

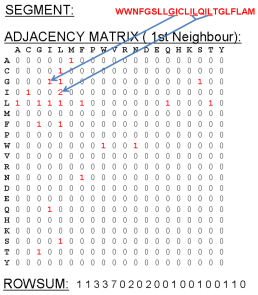
- Not all transmembrane proteins and their architectures are known
- Model using evolutionary data may not be sufficient for newly discovered transmembrane proteins (specially for those without known homologs)
- Different indices present for same physiochemical properties of amino acids

Transmembrane Region Prediction Algorithm

Features:

- Classification model is based on **mathematical descriptors**
- CPNN is used to built the model
- Classification model treats transmembrane and non-transmembrane regions of the dataset proteins separately
- Prediction algorithm uses sliding window approach

Mathematical Descriptors – Amino Acid Adjacency Matrix



- 20×20 amino acid adjacency matrix
- Each position represents number of times the corresponding amino acids occur adjacent to each other in the sequence
- 20-element rowsum vector acts as descriptors of the sequence

Advantages:

- Independent from **evolutionary data**
- Independent from **physiochemical properties**
- Efficient in predicting transmembrane regions of **proteins without homologs**

Results

Sensitivity : **86.40%** Positive predictive value : **90.97%**
Prediction accuracy : **90.75%**

Predicting Transmembrane Regions :

PDB ID	Experimental	Predicted	False Positive	False Negative
2npk	11	9	0	2
1bha	2	2	0	0
1otu	10	8	2	2
2bhw	3	3	0	0
2ahy	2	2	0	0
3c9m	7	7	0	0

Distinguishing from globular proteins:

PDB ID	Helices present	Predicted helices
3gak	14	0
3h9e	13	1 (106-117)
3b97	21	0
3cls	10	0
3h1v	19	0
2wu8	31	1 (318-333)
1i7y	9	0

Application

The developed algorithm is used to predict transmembrane regions of unknown proteins

Example – Bilitranslocase:

Bilitranslocase is a transmembrane protein with **only sequence information**
No homologs are reported

Predicted transmembrane regions : 24-48, 75-94, 220-238, 254-276
The predicted transmembrane regions are in accordance with hypothesis proposed from antibody studies

Comparison with other online available methods:

	Our Method	MAMSAT	HMMTOP	PHD	TMPRED	TOPPRED	SVMtm	waveTM	PHOBIUS	PHILIUS	CoPreThi	ConPred	igTM	HMMTM	Tmpro
TM regions predicted	4	3	3	5	4	4	2	5	2	3	3	2	2	2	4
TM 1	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
TM 2	Y	Y	N	Y	Y	Y	N	Y	N	Y	Y	N	N	N	Y
TM 3	Y	N	Y	Y	Y	Y	N	Y	N	N	N	N	N	N	Y
TM 4	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y

References:
[1] A. Roy Choudhury, M. Novič, SAR QSAR Environ. Res., 2009, 20, 741-754.
[2] S. Passamonti et. al., FEBS J., 2005, 272(13), 3282-3296.

Conclusion

- **Successful implementation of chemometric approach in transmembrane region prediction is shown**
- Model uses **mathematical descriptors**
- Independent from evolutionary data and physiochemical properties
- Successfully able to distinguish transmembrane proteins from globular ones

Acknowledgements: The project is supported by Slovenian Ministry of Higher Education, Science and Technology through the research grants P1-0017 and J1-2151-0104.

Vpliv legirnih elementov na lomno žilavost vzmetnega jekla 51CrV4

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V avtomobilski industriji se za izdelavo listnatih vzmeti uporablja predvsem vzmetno jeklo 51CrV4. Zaradi stalnega trenda po zmanjševanju mase komponent potrebujejo proizvajalci vzmeti jekla z izrednimi mehanskimi lastnostmi, med katerimi je zaradi želene dolge življenjske dobe vzmeti še posebej pomembna lomna žilavost.

Namen raziskovalne naloge je bil, da raziščemo vpliv vsebnosti različnih legirnih elementov na lomno žilavost vzmetnega jekla 51CrV, ki smo jo merili z nestandardnim postopkom preizkušanja lomne žilavosti s cilindričnim nateznim preizkušancem z zarezo po obodu in utrujenostno razpoko v dnu zareze preizkušanca, ki je bil vakuumsko toplotno obdelan.
Izdelano je bilo več vzmetnih jekel z različnimi dodatki Nb, Mo, C, Al in Ca.

Na osnovi meritev lomne žilavosti in izdelanega diagrama popuščanja smo ugotovili, da lahko izboljšamo lomno žilavost klasičnega vzmetnega jekla za 10% že z majhnimi spremembami vsebnosti legirnih elementov (dodatek 0,075 ut.% Nb ali zmanjšanje vsebnosti Al za 0,007 ut.% in Ca za 0,0013 ut.%).

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Vpliv legirnih elementov na lomno žilavost vzmetnega jekla 51CrV4

Bojan Senčič[1,2] ,Vojteh Leskovšek[3] (mentor)

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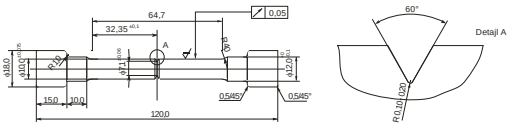
UVOD

V avtomobilski industriji se za izdelavo listnatih vzmeti uporablja predvsem vzmetno jeklo 51CrV4. Zaradi stalnega trenda po zmanjševanju mase vozil, tudi proizvajalci vzmeti težijo k zmanjševanju mase vzmeti, zato potrebujejo jekla z boljšimi mehanskimi lastnostmi, med katerimi pa je še posebej pomembna lomna žilavost K_{Ic}. Namen raziskovalne naloge je bil, da raziščemo vpliv dodatka različnih legirnih elementov na lomno žilavost, ki smo jo merili z nestandardnim postopkom preizkušanja lomne žilavosti s cilindričnim nateznim preizkušancem z zarezo po obodu in utrujenostno razpoko v dnu zareze preizkušanca, ki je bil vakuumsko toplotno obdelan.

MATERIALI IN METODE

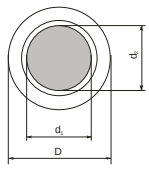
Izdelava valjancev iz vzmetnega jekla.

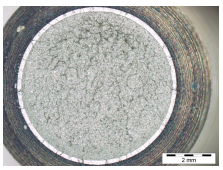
Izdelava K_{Ic} – preizkušancev



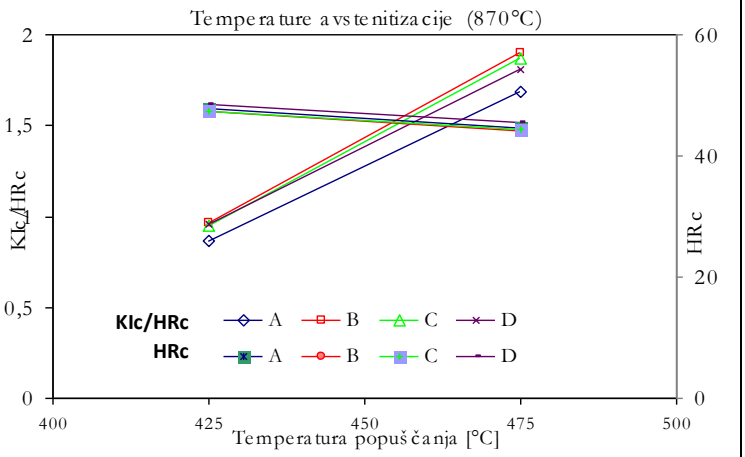
Vakuumska toplotna obdelava

Merjenje lomne žilavosti K_{Ic} in trdote HRc





REZULTATI



Digram popuščanja za 4 šarže vzmetnega jekla

UPORABNOST V PRAKSI

Z nestandardnim postopkom preizkušanja lomne žilavosti s cilindričnim nateznim preizkušancem z zarezo po obodu in utrujenostno razpoko v dnu zareze lahko uspešno merimo lomno žilavost vakuumsko toplotno obdelanega vzmetnega jekla.

S preliminarnimi raziskavami, smo ugotovili, da lahko pri enaki trdoti Rockwell-C povečamo lomno žilavost konvencionalnega vzmetnega jekla za 10%, in sicer z mikrolegiranjem elementov (Nb, Al, Ca, C in Mo).

Enaka ali večja duktilnost in lomna žilavost pri večji trdnosti pa proizvajalcu vzmeti omogoča zmanjšanje mase vzmeti in hkrati povečanje njihove vzdržljivosti v eksploataciji.

Dielectric and ferroelectric properties of sol-gel-derived $Na_{0.5}Bi_{0.5}TiO_3$ thin films

Tina Šetinc[1,2], Matjaž Spreitzer[1], Špela Kunej[1], Danilo Suvorov[1,2]

[1] Advanced Materials Department, Jožef Stefan Institute, Ljubljana, Slovenia

[2] Jožef Stefan International Postgraduate School, Ljubljana, Slovenia

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Perovskite materials have attracted a lot of attention over recent decades owing to their many interesting properties, especially from the application point of view. The uses of these materials are based on their intrinsic dielectric, ferroelectric, piezoelectric, and pyroelectric properties in the corresponding electronic devices, such as micro-electromechanical systems (MEMS), transducers, capacitors, actuators, high-k dielectrics, dynamic random-access memories, field-effect transistors, and logic circuitry. Furthermore, a considerable amount of interest in ferroelectric thin films has resulted from the possibility of integrating them with existing semiconductor technology, low operating voltages and high switching. Among the different film-deposition techniques, chemical solution deposition (CSD) methods (e.g., sol-gel, metallo-organic deposition) are low-cost techniques that provide high compositional control and uniform deposition, used in industry for the fabrication of commercial devices with a planar configuration.

The relaxor ferroelectric Na0.5Bi0.5TiO3 (abbreviated as NBT) has attracted increasing interest as a member of the dielectric perovskites with intriguing piezoelectric and ferroelectric properties. The distorted NBT structure exhibits good ferroelectric properties, with a large remanent polarization, Pr = 38 μC/cm3, and a relatively high temperature of the dielectric maximum, Tm = 320 °C, and was widely investigated as one of the key end-member compounds for lead-free piezoelectric ceramics. The main drawbacks of pure NBT are a large coercive field and a high conductivity, which causes problems in the process of poling. These phenomena are expected to be even more pronounced in the thin-film form due to the size effect and the lattice mismatch between the film and the substrate. Employing multilayered thin films or interposing a dielectric layer of a para-electric material between the ferroelectric layer and the bottom as well as top electrode offers a possibility to overcome these difficulties. However, in order to systematically investigate the dielectric and ferroelectric properties of multilayers some preliminary research on pure NBT thin films is required. Thus, the object of our research work was to fabricate the NBT thin films via the CSD method, and to investigate their morphological, dielectric and ferroelectric properties. The obtained results would be subsequently used for critically estimating the properties of multilayers in relation to pure NBT thin films.

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Tina Šetinc[1,2], Matjaž Spreitzer[1], Špela Kunej[1], Danilo Suvorov[1,2]
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[2] Jožef Stefan International Postgraduate School, Ljubljana, Slovenia
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INTRODUCTION

Ferroelectric thin films have been extensively investigated for their potential application in the microelectronic circuits due to low operating voltages, high switching speeds and possible integration with the existing semiconductor technology. Ferroelectric $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) is a complex perovskite with a relaxor-type behavior and an important end member of the binary and ternary compositions that exhibit promising ferroelectric and piezoelectric properties. Among various thin film deposition techniques, the sol-gel method is relatively low cost offering high chemical homogeneity and is thus often employed for preparation of thin films for microelectronic applications.

AIM

Fabrication of NBT thin films via 2-methoxyethanol route by chemical solution deposition onto $Pt/Ti/SiO_2/Si$ substrates. Investigation of the microstructural characterists, dielectric and ferroelectric properties of sol-gel derived NBT films.

EXPERIMENTAL PART

Sol synthesis

Titanium(IV) butoxide + Acetylacetone + 2-methoxyethanol + $Bi(OOCH_3)_3$ + $NaOOCCH_3$ + Acetic acid

Mixing at 80°C, 1h
Reflux & distillation
4 vol% formamide

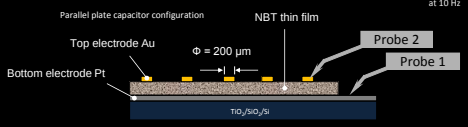
Preparation of thin films

NBT precursor sol: c = 0.3 M
Spin coating (3000 rpm, 20 s): $Pt/TiO_2/SiO_2/Si$ wafers
drying: 220°C – 3 min, pyrolysis: 460°C – 20 min
Thermal annealing: 600-700°C, 0.5 h
Characterization

Characterization of thin films

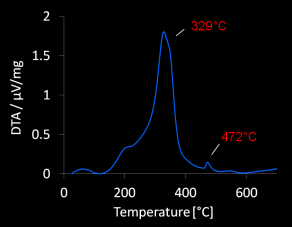
- Thermal analysis - TG/DTA (Jupiter 449 & 403C Aëoloss, Netzch)
- X-ray powder diffraction - XRD (ENDEAVOR, D4, Bruker, Axs)
- Scanning electron microscopy - SEM (JEOL 7600F)
- Atomic force microscopy - AFM (Veeco Dimension 3100)

Dielectric & ferroelectric measurements:
Probe station Cascade Summit 1200 AP
LCR meter – Agilent 4284A
Frequency range: 1 – 1000 kHz,
(*P-E*) hysteresis
Radiant precision workstation
at 10 Hz

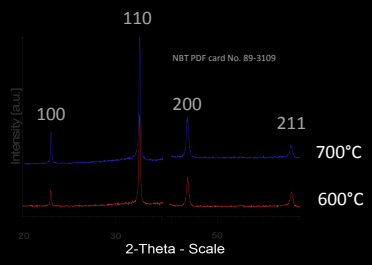


RESULTS

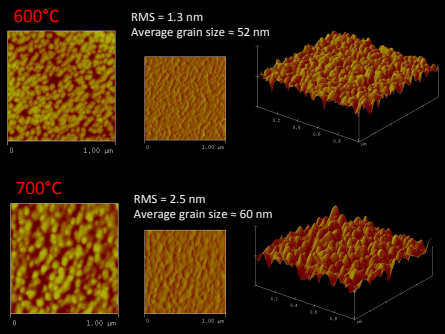
DTA



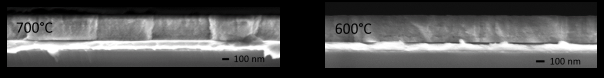
XRD



AFM

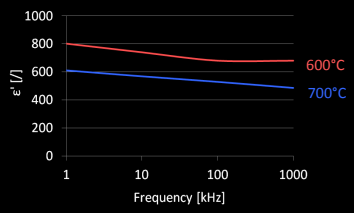


SEM

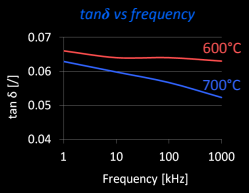


Dielectric properties

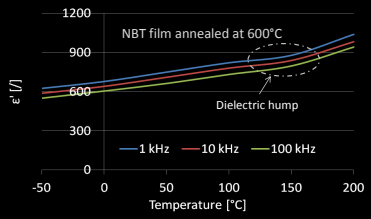
⇒ *ε' vs frequency*



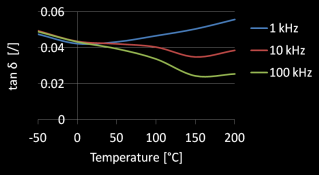
tanδ vs frequency



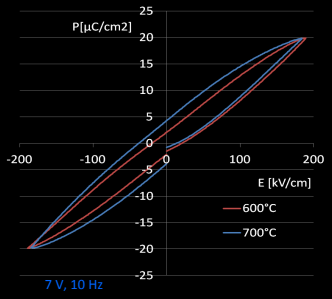
⇒ *ε' vs temperature*

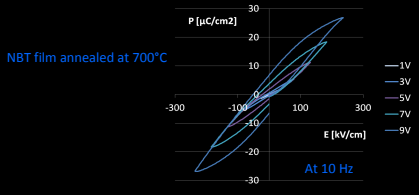


tanδ vs temperature



P - E hysteresis





SUMMARY

NBT thin films were single phase with polycrystalline structure. The measured dielectric constant at 100 kHz was 680 and 530 for thin films annealed at 600°C and 700°C with the corresponding dielectric losses of 0.065 and 0.06, respectively. In the temperature range from -50°C to 200°C dielectric permittivity at 100 kHz gradually increases from 550 to 940, whereas loss tanδ decreases from 0.05 to 0.025. Appearance of the dielectric hump is related to the frequency dispersion of the dielectric losses at the temperature ~150°C. Stronger ferroelectric properties exhibited films annealed at higher temperatures, i.e. 700°C, with the measured room temperature remanent polarization and coercive field of 6.7 μC/cm² and 50 kV/cm, respectively.
The dielectric properties of NBT thin films prepared by cost effective sol-gel method are intriguing even from the application point of view.

Synthesis and characterization of calcium phosphate coatings on ZrO_2 ceramics for bone implant applications

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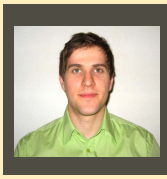
Naše raziskovalno delo obsega razvoj metod za pripravo bioaktivnih kalcijevih fosfatnih (Ca-P) prevlek na keramičnih kostnih implantatih, kot so npr. dentalni, kolčni in kolenski implantati. Intrinzična lastnost obstoječih implantoloških materialov je, da se slabo vežejo s kostjo, kar lahko posledično vodi do slabe fiksacije implantata v kosti, njegovega majanja in izpada. Ca-P imajo edinstveno lastnost, da v telesu reagirajo s kostjo in se z njo s kemijskimi vezmi čvrsto povežejo. Tako lahko z nanosom Ca-P prevleke na površino implantata izboljšamo njegovo fiksacijo v kosti in osteointegracijo. Naša raziskovalna skupina je razvila preprosto in poceni metodo za sintezo Ca-P prevlek na implantatih. Prevleke imajo dobre mehanske lastnosti, poleg tega pa nam metoda daje možnost, da kontroliramo sestavo in morfologijo prevlek. Dodatna prednost našega sinteznega postopka je, da lahko poteka pri milih pogojih, ki omogoča vključevanje zdravil v prevleke. Ker so post-operacijske infekcije pogost vzrok za neuspešnost implantacij, imajo prevleke z vključenimi antibiotiki potencial za izboljšanje uspešnosti kostnih implantatov.



Synthesis and characterization of calcium phosphate coatings on ZrO_2 ceramics for bone implant applications

MARTIN ŠTEFANIČ, univ. dipl. biokem.
Študijski program: Nanoznanosti in nanotehnologije,
Mednarodna podiplomska šola Jožefa Stefana
MENTOR: Prof. Dr. Tomaž Kosmač
SOMENTOR: doc. dr. Kristoffer Krnel

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Introduction

Calcium phosphate (Ca-P) coatings on zirconia bone implants have a great potential to improve the osseointegration of already-existing ceramic implants, owing to their bioactive and osteoconductive characteristics. A very promising approach for the preparation of Ca-P coatings is the so-called biomimetic method, which includes the immersion of the implant into a supersaturated Ca-P solution under physiological conditions. This method allows the synthesis of coatings with a good surface coverage on materials with complex shapes and good control over the coating composition. However, the drawbacks of the method are the relatively long time of the synthesis and, in particular, the poor adhesion of the coating to the substrate [1].

Objective

- To synthesize Ca-P coatings on zirconia ceramics by applying a simple biomimetic method that would allow a high deposition rate.
- To improve the attachement of the coating to the substrate by thermal and mechanical processing.

Experimental design

Materials

Polished Y-TZP discs

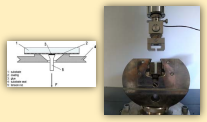
1. Deposition of coatings on ZrO_2 discs

2. Thermal processing of coatings
A) 600 °C, 1hour
B) 800 °C, 1 hour

*CIP - cold isostatic pressing

3. Bond strength evaluation

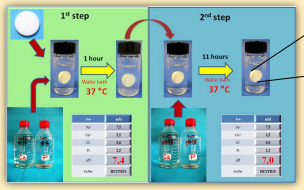
- ISO 4624
- Adhesive: HTK ULTRA BOND®

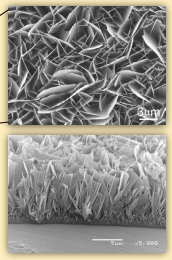


Results

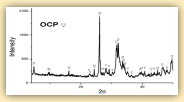
1.) Deposition of coatings

- Two-step synthesis:

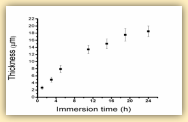




- XRD



- the coaitng is composed of octacalcium phosphate (OCP)



Coating thickness vs soaking time

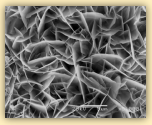
- Coating thickness was increasing with the time of immersion in the second solution (pH=7.0).

- Simple procedure
- mild synthesis conditions
- Rapid deposition

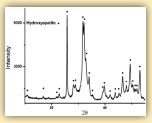
2.) Thermal processing of coatings

➢ 600 °C, 1h

- **Formation of hydroxyapatite (HAp).**



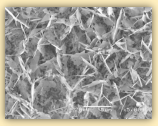
- Preserved lamelar morphology.



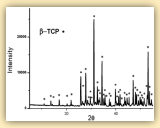
- OCP crstals transformed to hydroxyapatite (HAp) after firing at 600 C.

➢ 800 °C, 1h

- **Formation of β-tricalcium phosphate (β-TCP)**



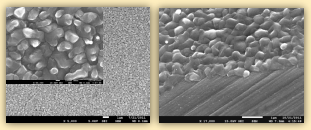
- the coating became porous



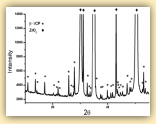
- The coating lost its integrity, such that by applying a small force, (e. g. sonification in a water bath) a majority of the coating could be easily removed, except for the thin β-TCP layer remaining on the zirconia surface.

Ultra-sound bath

t ≈ 5 min



- tilt angle = 35°



- Thin β-TCP coating remained on the ceramic surface after short ultrasonic treatment
- Coating thickness ≈ 500 nm

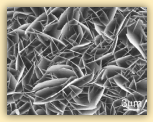
3.) Bond strength evaluation

Table: measured values of coatings bond strength

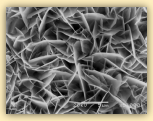
Sample	Bond strength (MPa)
As-deposited coating **(OCP)**	**1.8 ± 0.3**
600 °C, 1hour **(HAp)**	**3.2 ± 0.6**
800 °C, 1hour & sonification **(β-TCP)**	**29.3 ± 6.4**

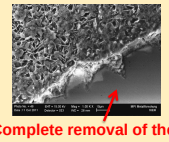
- 6 samples for each experimental group

A) As-deposited coating (OCP)

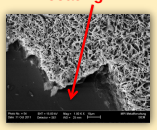


B) 600 C, 1h (HAp)



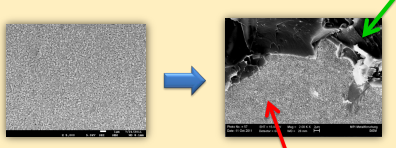


Complete removal of the coating



C) 800 C, 1h & sonification (β-TCP)

Adhesive



No detachement of the coating

Conclusions

- A two-step wet-chemical biomimetic method was employed for the rapid deposition of Ca-P coatings on ZrO_2 ceramics.
- The bond strength of the deposited coating is low (1.8 MPa), but can be significantly improved by thermal treatments.
- Thermal treatments at 600 C and 800 C caused conversion in the composition of the coating from the initial OCP to the Hap (600 C) and β-TCP (800 C) phase, respectively.
- Thin β-TCP coatings that were produced by firing the coated zirconia discs at 800 C and subsequent short sonification, reached high value of bond strength (29.3 MPa). The coatings could not be detached from the substrate with our tensile test.

References

[1] León B, Jansen J. Thin Calcium Phosphate Coatings for Medical Implants, ISBN: 978-0-387-77718-4; Springer, 2009.

[2] Bigi A, Boanini E, Bracci B, Facchini A, Panzavolta S, Segatti F, Sturba L. Nanocrystalline hydroxyapatite coatings on titanium: a new fast biomimetic method. Biomaterials 2005;26:4085-9.

Photocatalytic discoloration of the azo dye methylene blue in the presence of irradiated TiO_2/Pt nano-composite

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It is well know that TiO2 is characterized with photocatalytic properties by utilizing UV (ultraviolet) light. This phenomena is already been used for commercial applications such as self-cleaning concrete (Italcement Group) in building facades (Jubilee Church (also known as the Dives in Misericordia) in Rome) and pavements (Municipal District of Bergamo, Italy – Borgo Palazzo Street), self-cleaning windows (Pilkington), ect. Another field, in which the photocatalytic properties of TiO2 can be of advantage, is the water purification. Water contamination due to the industrial wastewaters which contain organic dyes has become a global problem. About 1-20% of organic dyes are lost during the industrial dyeing processes and released into the environment. The dyes itself and their degradation products represent toxic substances which cause diverse effects on animal and human health. Therefore, the purification and remediation of discharged waters generated from industrial processes is a necessity. Having in mind such problems, the idea of this work was to prepare TiO2 which could be used for azo dyes degradation in water. Since the UV light represents only a small part of the sunlight (only 2-3%) the goal of our work was to synthesize a TiO2 which exhibits improved photocatalytic properties under UV irradiation and also is active under Vis (visible) light irradiation. Since such TiO2 is able to degraded organic dyes utilizing solar energy (UV and Vis) it represents an economic and efficient method for water purification. We prepared such photocatalyst by forming a TiO2/Pt nano-composite which is able to effectively photocatalytically degraded the azo dye methylene blue under UV and Vis irradiation.

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[1]Advanced Materials Department, Jožef Stefan Institute

[2]Jožef Stefan International Postgraduate School

Supervisors: ***Prof. Dr. Danilo Suvorov[1], Assist. Prof. Srečo D. Škapin[1]***

Introduction

The largest group of pollutants that are released with the discharge water, generated form the textile and other industries processes are the organic dyes, including also the azo dyes. It is well known that some of the azo dye and their degradation products are high carcinogen. The most promising method for wastewater purification and remediation is the heterogeneous photocatalysis based on titanium dioxide (TiO_2). However, the most active TiO_2 crystal form, anatase, is useful only when irradiated with ultraviolet (UV) light. Since the sunlight contains only a small part of the UV irradiation (2-3%) the researches are focused towards the improvement of TiO_2 under UV irradiation or/and to the development of a visible (Vis) light active TiO_2.

Aim of the work

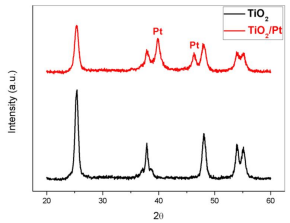
- The TiO_2 surface attachment with Pt particles should improve the TiO_2 charge carriers separation due to the electron storage function of the Pt particles. Therefore the formed TiO_2/Pt nano-composite should be an efficient photocatalytic material for the degradation of the azo dye methylene blue, as comparing to the bare TiO_2.
- The photosensitizing effect of the adsorbed dye methylene blue should induce the Vis light photocatalytic activity.

Experimental

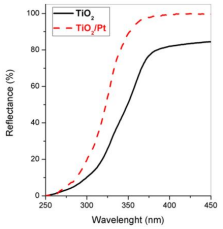
- **Materials:** Titanium n-butoksid ($TiO_4H_{36}C_{16}$, 98%), 1-Butanol (C_4H_9OH, 99%), Nitric acid (HNO_3, 65%), ultrapure water, Chloroplatinic acid hexahydrate ($H_2PtCl_6{\cdot}6H_2O$)
- **Synthesis:** Sonochemical synthesis of TiO_2 nano-powders and TiO_2/Pt nano-composites followed by thermal treatment in a reducing atmosphere (Ar/H_2=96/4) at 400°C for 3h.

Results

Phase composition (XRD analysis)



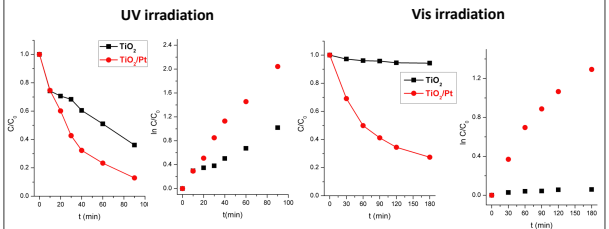
Optical properties (Diffuse reflectance spectroscopy)



Photocatalytic activity (UV-Vis spectroscopy)

Photocatalytic degradation kinetics of the azo dye methylene blue follows an apparent first-order reaction mechanism:

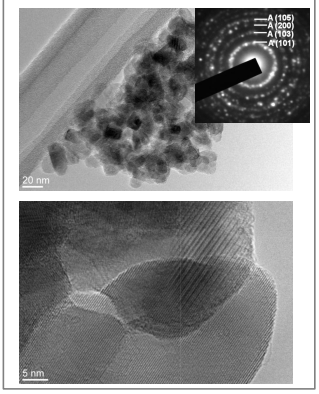
$$\ln C = \ln C_0 - k_{app} t$$



Sample	k_{app} UV (min-1) x 10^3	k_{app} Vis (min-1) x 10^3
TiO_2	10	0.3
TiO_2/Pt	23	7

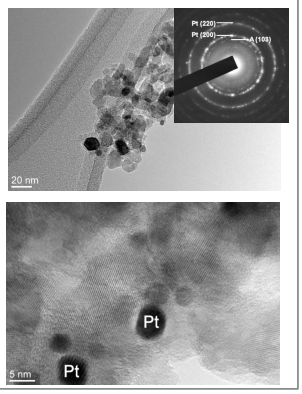
TiO_2

- TiO_2 crystal form anatase
- Average particle size d=7 nm
- Specific surface area 87 m^2/g



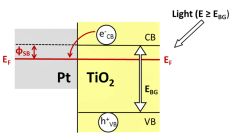
TiO_2/Pt

- TiO_2 crystal form anatase
- Average particle size d=10 nm
- Specific surface area 54 m^2/g



Conclusions

- Sonochemically synthesized TiO_2/Pt nano-composites consisted of Pt particles (up to 25 nm) and TiO_2 anatase particles (up to 10 nm).
- TiO_2/Pt nano-composites exhibited an enhanced photocatalytic activity for the methylene blue degradation when compared to the bare TiO_2.
- The UV enhancement is attributed to the attachment of TiO_2 particles with Pt particles, which acted as electron storage.
- The Vis light photocatalytic activity was induced with TiO_2 surface adsorbed methylene blue which acted as a photosensitizer.



Applications & Perspectives

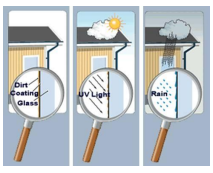
Self-cleaning concrete

Jubilee Church in Rome

Municipal District of Bergamo, Italy

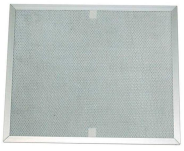
Self-cleaning windows

Pilkington windows



Air purification

Air Shield TiO_2 Photo-Catalysis Filter



Water purification

- No commercial product based on TiO_2 for water purification.
- TiO_2 for water purification still in research phase.

Life time assessment of real components exposed to high temperatures and pressures

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V proizvodnih industrijskih obratih je mnogo komponent pogosto izpostavljenih delu pri visokih temperaturah in delu pod tlakom. Visoka temperatura in povišan tlak pospešujeta poslabšanje mehanskih lastnosti jekla. Zaradi slabšanja mehanskih lastnosti jekla med obratovanjem lahko po določenem času pride do nepričakovane odpovedi kakšne od komponent. Poškodba komponente, ki deluje v okolju visokih temperatur in tlakov, pa je velikokrat podobna eksploziji bombe.

Zavedanje neprestanega slabšanja mehanskih lastnosti tako izpostavljenih komponent je iz ekonomskega in tehničnega vidika zelo pomembno. Odpoved takšne komponente povzroči ustavitev proizvodnje, nedoseganje zastavljenih ciljev in izpad dohodka, lahko pa tudi nevarnost ogrožanja življenja zaposlenih.

Stanje takšnih komponent lahko preverimo z različnimi metodami metalografske analize, kjer se pod mikroskopom preveri stanje mikrostrukture jekla. Metalografske preiskave lahko dopolnimo tudi z drugimi neporušitvenimi preiskavami, kot so ultrazvočne meritve, preiskave s tekočimi penetranti, meritve trdote, itd.

Na podlagi teh preiskav lahko ocenimo preostalo življenjsko dobo takšnih komponent in podamo mnenje o primernosti njihovega nadaljnjega varnega obratovanja.

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LIFE TIME ASSESSMENT OF REAL COMPONENTS EXPOSED TO HIGH TEMPERATURES AND PRESURES

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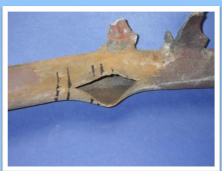
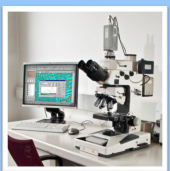
ABSTRACT

Components in industry are often exposed to elevated temperatures and high pressures. These conditions cause changes in microstructure and thermo-mechanical properties of steel components. With aim to determine the properties of steels after certain period of operation, thermo-mechanical investigations and microstructure characterization can be made and results used for remaining lifetime assessment of components. From economic and technological point of view this is very important information. Creep is one of the major mechanisms which cause deformation and degradation of steels at elevated temperatures. Creep can occur in local areas due to increased load or due to microstructural degradation during operation at elevated temperatures. Microstructure degradation of the steels can be defined by microstructural investigations on metallographic samples or replicas. Aim of this work is to present and compare methods for microstructure characterization, their applicability and limitations as well as microstructure degradation of steels used in Slovenian thermal power plants.

METHODS FOR MICROSTRUCTURE EVALUATION

▪Cut out the sample and examine it in the laboratory



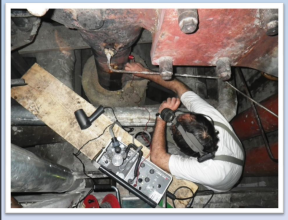


- Not allways possibile
- Destructive method
- Most accurate and reliable
- More test can be performed

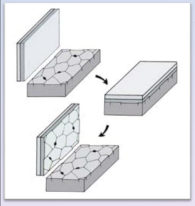
▪On field examination

- Non-destructive examination
- Portable microscope
- In situ metallographic analyse at 100X magnification
- Low accurracy

▪Taking metallurgical replica

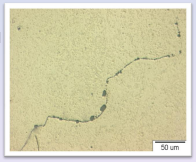


- Non-destructive examination
- Replicas can be taken on almost al components
- Hard to prepare good replica
- Gives information on microstructure state
- Metallographic replicas taken on field can be analysed with laboratory microscope



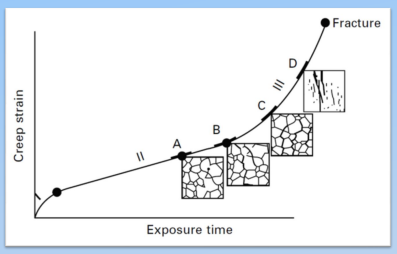
STEPS OF REPLICATION

- Appropriate surface preparation
- Pressing replica on surface
- Taking replica from surface, protect it and analysing in laboratory

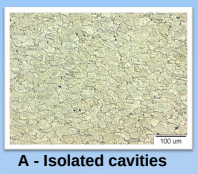


Microporosity linked to microcrack, found on replica

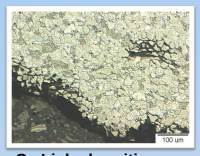
CREEP CURVE AND MICROSTRUCTURAL CHANGES



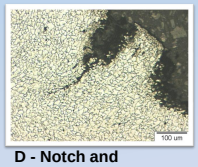
Level of degradation	Evolution of cavities	Actions
A	Isolated cavities	Planed examinations
B	Oriented cavities	Examination with replicas in planed intervals
C	Linked cavities (microcracks)	Limited operation until recondition
D	Macrocracks	Immediate recondition



A - Isolated cavities



C - Linked cavities - Microcracks



D - Notch and begining of crack

CONCLUSIONS

▪ From economic and technological point of view condition of steel components is very important.
▪ Good condition and awareness of degradation of crucial components is important for safety of employs and for the undisturbed production of factories. For instance for undisturbed electrical power supply of thermal power plants.
▪ Observation of microstructure change is the most sensitive method for monitoring the condition of steel components.
▪ There are few different possibilities for microstructure analyse, combinning all of them enable us to fully characterise stage of microstructure degradation.
  - ▪ Cut out the sample and examine it in the laboratory
  - ▪ On field examination
  - ▪ Taking metallurgical replica

Prispevki iz industrije (Contributions from Industry)

Razvoj in raziskava aluminija in aluminijevih zlitin

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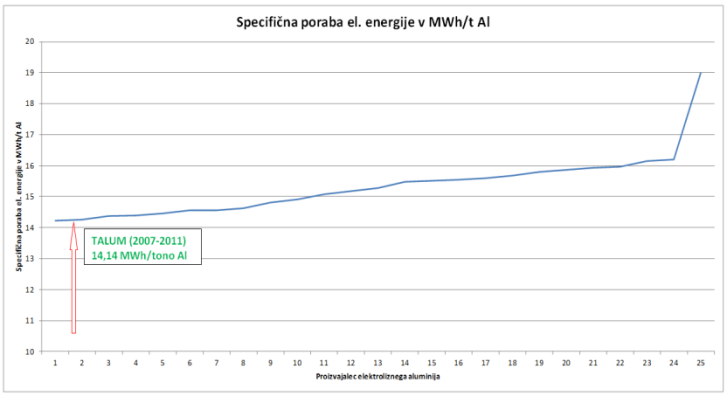
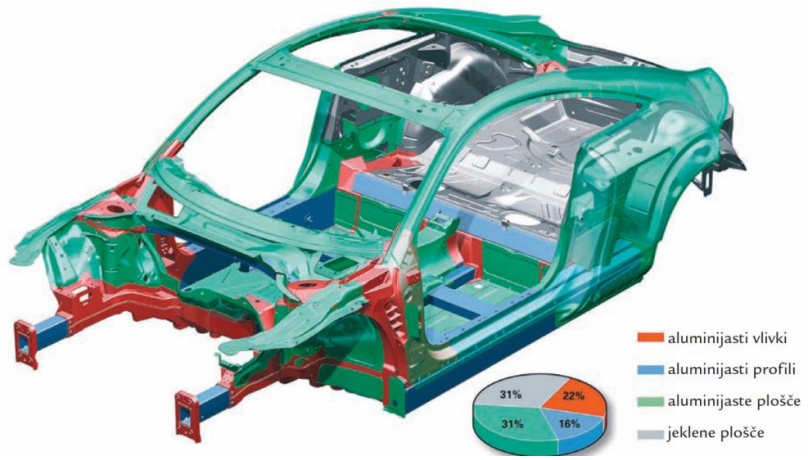
Usmerjenost in cilj skupine Talum d.d. je proizvodnja aluminijevih zlitin iz primarnega in sekundarnega aluminija ter proizvodnja izdelkov z visoko dodano vrednostjo. Širjenje spektra aluminija in aluminijevih zlitin ponuja velike priložnosti in možnosti za vstop na trg končnih proizvodov ter možnost novih specifičnih izdelkov v gradbeništvu, avtomobilski, letalski in sorodnih industrijah. Visoko dodano vrednost je moč doseči s proizvodnjo specifičnih izdelkov ali z oblikovanjem/preoblikovanjem izdelkov iz aluminijevih zlitin. Aluminijeve zlitine so lahke, trdne in oblikovalne/preoblikovalne s skoraj vsemi oblikovalno-preoblikovalnimi procesi.

Prvi pogoj za dobro aluminijevo zlitino je dobra osnova, tj. čisti aluminij. V Talumu proizvajamo elektrolizni aluminij, iz njega pa izdelujemo zlitine za preoblikovanje in livarsko industrijo. Proizvodnja aluminija spada med energetsko intenzivnejše industrije. Ponosni smo na to, da po porabi specifične energije na tono proizvedenega elektroliznega aluminija spadamo v sam svetovni vrh po energetski učinkovitosti in da bomo krojili »benchmark« pri določanju kompenzacije za indirektne emisije toplogrednih plinov.



Proizvodnja primarnega elektroliznega aluminija in primerjava specifične porabe električne energije na eno tono proizvedenega aluminija

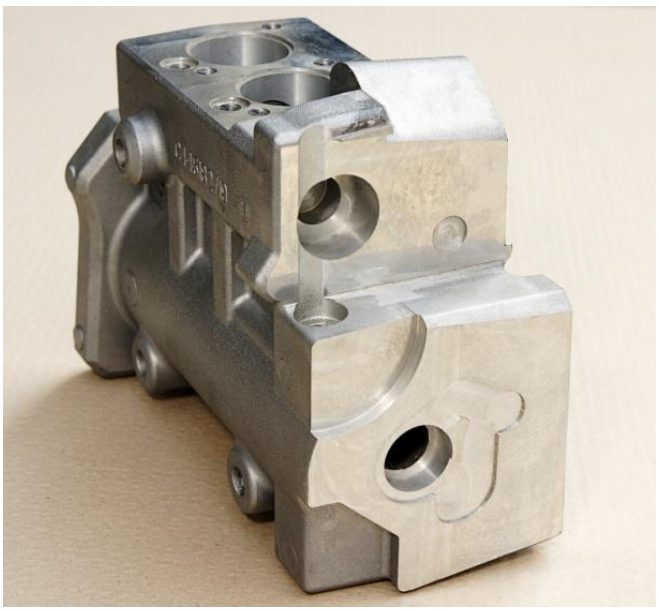
Trendi v avtomobilski in letalski industriji po zmanjšanju specifične teže so pripeljali k razvoju novih lahkih materialov. Na področju avtomobilske industrije se razvija in uporablja čedalje več novih materialov, ki prinašajo številne prednosti pa tudi velike izzive. Pridružujemo se besedam avtomobilskega koncerna Audi: *»Pravi material na pravem mestu za optimalno učinkovitost.«* Audi je s kombinacijo materialov naredil hibridno karoserijo, zmanjšal težo vozila, posledično pa prihranil pri porabi goriva. Delež aluminija se pri izdelavi avtomobilov povečuje iz dneva v dan.



Delež aluminija v avtomobilu Audi TT (vir: Mehanik in voznik, maj 2011)

»Shujševalne kure«, tj. zmanjšanje mase transportnih sredstev v transportni industriji, nas usmerjajo v razvoj novih materialov oz. aluminijevih zlitin. V Talumu želimo tako z razvojem aluminijevih kompozitov s pomočjo nanotehnologij razviti takšno zlitino, da bi z vmešavanjem nanodelcev oz. drugih primesi izboljšali mehanske lastnosti končnega izdelka. Tega razvoja in raziskav se lotevamo na ulitkih, ki so izpostavljeni visokim tlakom, kot so ohišja črpalk, in statično-dinamičnim obremenitvam, kamor spadajo vilice za motorno kolo. Vilice za motorno kolo so eden izmed najbolj obremenjenih konstrukcijskih delov motorja in so plod razvoja aluminijeve zlitine, tehnologije litja ter toplotne obdelave, izdelane pa so po strogo predpisanih metalurških postopkih, saj v materialu ni dovoljena niti najmanjša napaka.

Veliko podporo našim razvojno-raziskovalnim projektom nam daje naš akreditirani laboratorij, specializiran za raziskave aluminijevih zlitin, izdelkov iz aluminija in varstva okolja ter dejstvo, da je Talum vodilni partner v Razvojnem centru slovenskega gospodarstva za nove materiale in tehnologije RC Simit, d.o.o.. Ključni napravi v procesu raziskav in razvoja novih materialov, predvsem njihovih mehanskih lastnosti, sta ICP MS z lasersko ablacijo in trgalni stroj do 100 kN.



Ohišje črpalke, ki je izpostavljena visokim tlakom

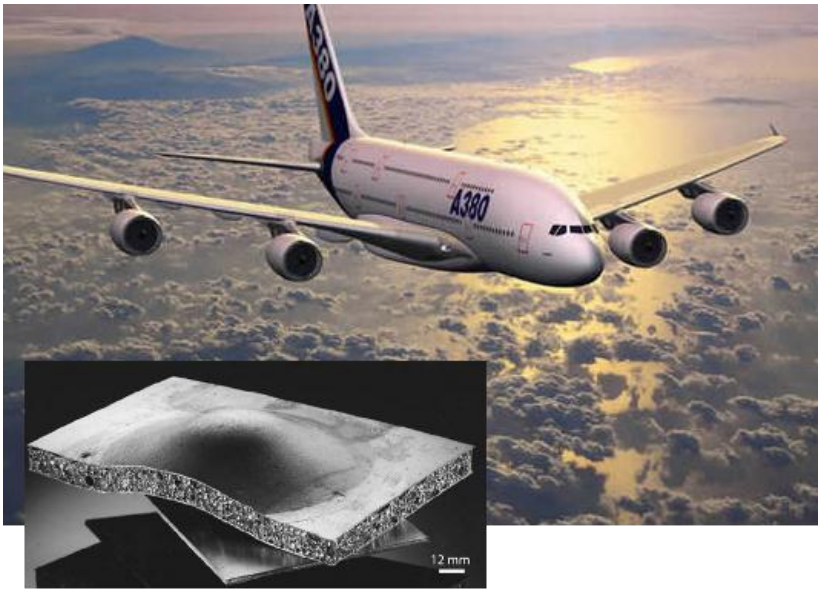
Vilice motornega kolesa

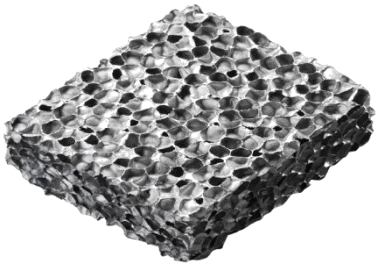
Izdelava standardnih zlitin in polizdelkov ne bo dovolj za preživetje. Na trgu moramo ponuditi nov material oz. nov končni izdelek z višjo dodano vrednostjo. Proučujemo možnosti za izdelavo aluminijevih profilov, novih tipov zlitin ter novih ulitkov. S Fakulteto za strojništvo Univerze v Mariboru, Inštitutom Jožef Stefan in podjetjem Unior Sinter iz Zreč sodelujemo pri projektu praškastih materialov. Usmerjeni smo v možnosti izdelave zlitin za prašno metalurgijo in ne nazadnje tudi v možnosti aplikacije sintranega aluminija. Prednost sintranja je izdelava takšnih oblik izdelkov, ki jih s konvencionalnimi postopki težje izdelamo oz. jih sploh ne moremo.

Izdelki, sintrani z aluminijevega prahu

Iz aluminijevega prahu je mogoče izdelovati tudi aluminijeve pene za uporabo v transportni industriji, gradbeništvu, toplotni tehniki … Prednosti, kot so nizka teža, odlične mehanske in toplotne lastnosti, bodo krojile razvoj varnostnih in nosilnih komponent predvsem v transportni industriji.

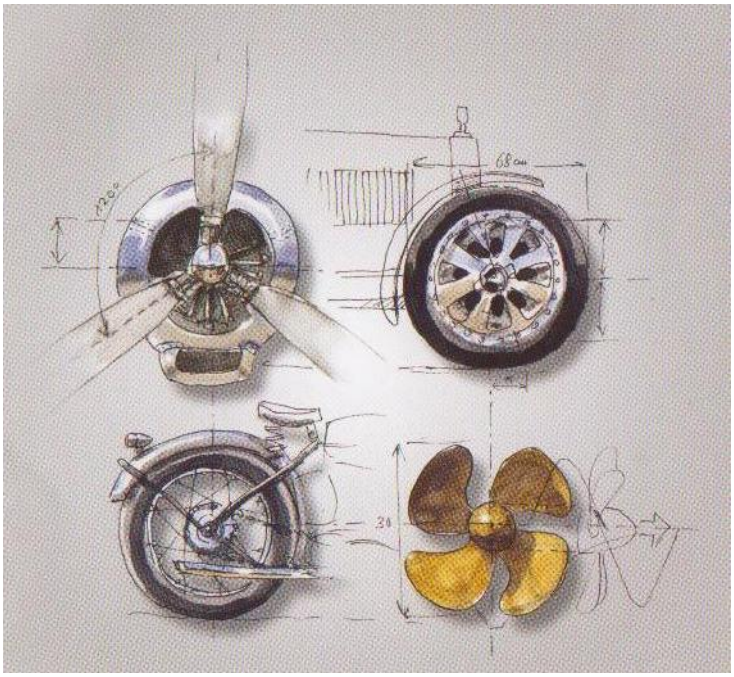
Talum se loteva projekta izdelave aluminijevih pen neposredno iz tekočega aluminija, kar predstavlja prednost pred klasičnimi sintranimi materiali tako v cenovnem oziru kakor tudi v kakovosti in ponovljivosti rezultatov.





Uporaba aluminijevih pen (vir: www.airbus.com)

Predvsem zaradi specifične teže aluminija, njegovih mehanskih in fizikalnih lastnosti ter obstojnosti so verjeli v ta material že pred več kot 100 leti. Aluminij je lahko rešitev za našo prihodnost tako z ekološkega kot uporabnega vidika. V Talumu verjamemo vanj in z njim soustvarjamo prihodnost.



Aluminij »kovina prihodnosti«

Organizator

V sodelovanju z

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Center odličnosti Napredni nekovinski
materiali s tehnologijami prihodnosti

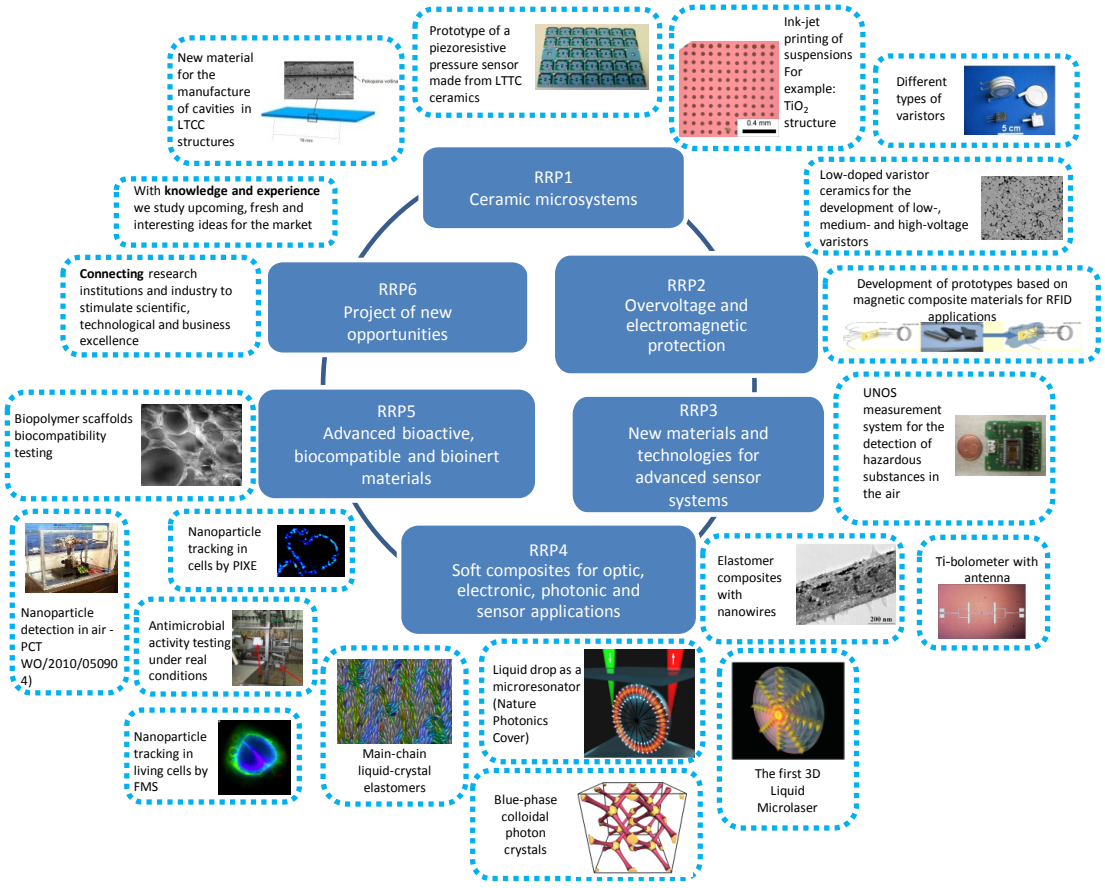
NAMASTE
Center odličnosti za integrirane pristope v
kemiji in biotehnologiji proteinov

"Materials are conquering the world"

CoE NAMASTE is a multi-disciplinary and trans-disciplinary consortium of research institutions and industry, who have decided to merge academic, technological and business expertise, skills and equipment in order to achieve major scientific and technological progress as well the transfer of results to industry. The working area is related mainly to inorganic, non-metallic materials as well as organics and composites and their implementation in electronics, opto-electronics, photonics and medicine. More specific topics are ceramic 2D and 3D structures; materials for overvoltage and EM protection; materials, micro- and nano-systems for sensors; soft composites for optical, electronic, photonic and sensor applications; and bioactive, biocompatible and bioinert materials, electrocaloric materials for a new generation of cooling devices and EM compatibility.

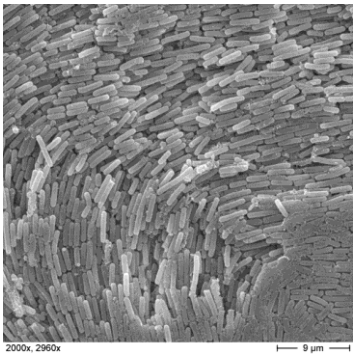
Strategic goals: continuity in research excellence, knowledge dissemination and technology transfer, and multi-disciplinary interconnections.

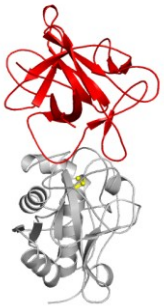
The consortium consists of three research institutions with eleven research groups, three non-profit organizations, and thirteen companies from different regions of Slovenia.

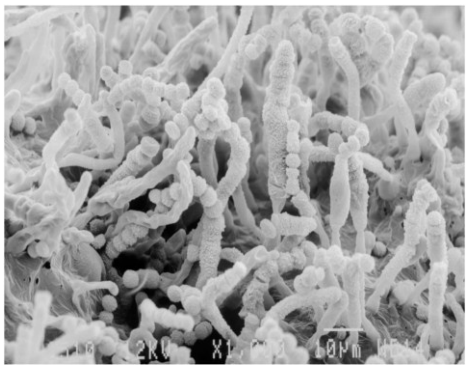


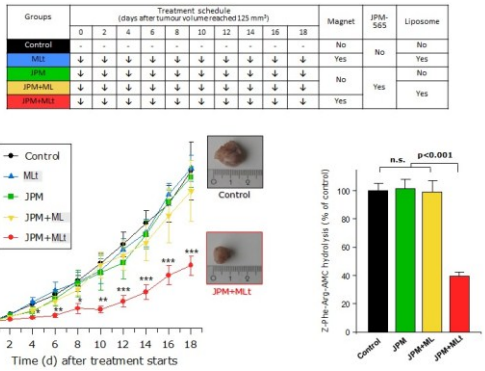
Center odličnosti za integrirane pristope v kemiji in biologiji proteinov

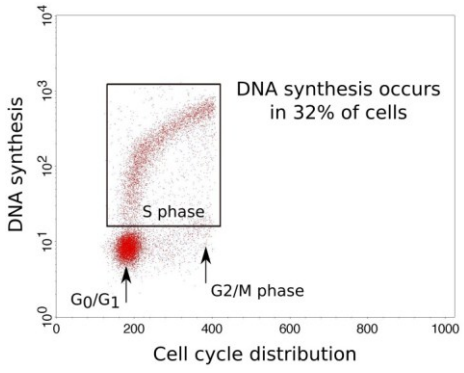
CIPKEBIP povezuje znanje, izkušnje in tehnologije vrhunskih slovenskih raziskovalnih skupin, ki se ukvarjajo z raziskavami proteinov. Izsledki in znanja iz raziskav bodo uporabljeni v razvoju tehnoloških procesov in pri skupnih nacionalnih in mednarodnih projektih z industrijskimi partnerji. Ustvarjeno znanje bo služilo za povečanje tekmovalnosti majhnih in večjih podjetij na biotehnološkem trgu. Skupni učinek centra odličnosti se bo pokazal tudi v izobraževanju mladih znanstvenikov, ki bodo lahko svojo poklicno kariero nadaljevali tako v industriji kot tudi v raziskovalnih ustanovah. Raziskovalno delo je organizirano v 4 sklopih raziskav, kjer sodelujejo javne institucije in podjetja (ustanovitelji CIPKEBIP): Mehanizmi in molekulske povezave v imunskem odzivu, Inter in intra celična komunikacija, Prilagoditveni mehanizmi ekstremofilov na okolje in Proteinska banka: Shranjevanje in proizvodnja proteinov.











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NANOCENTER PONUJA:

DOSTOP DO VRHUNSKE OPREME *univerzam, **inštitutom in industriji;***

TEHNOLOŠKO PLATFORMO *za zahtevno nanofakturo, nanoelektroniko in karakterizacijo nanostruktur vse do ravni posameznih molekul in atomov;*

RAZVOJ PODATKOVNIH BAZ *na področju nanoznanosti in nanotehnologije in protokole za metrologijo, sintezo in analizo.*

THE NANOCENTER OFFERS:

ACCESS TO SUPERIOR EQUIPMENT ***for universities, institutes and industry;***

TECHNOLOGICAL PLATFORM *for advanced nanofacturing techniques, nanoelectronics and characterization of nanomaterials down to the level of single molecules and atoms;*

DEVELOPING OF DATABASIS ***in the field of nanosciences** and nanotechnologies, protocols for metrology, synthesis and analysis.*

INFRASTRUKTURNI SEGMENTI:

SINTEZA NOVIH NANOMATERIALOV *je posebej pomembna za končno industrijsko uporabo in osnovne raziskave.*

PROCESIRANJE *oz. nanolitografske in samourejevalne procesne metode ter tehnologije vodijo v industrijske procese.*

KARAKTERIZACIJA *z metodami kot npr. elektronska in **optična mikroskopija, različne zahtevne spektroskopske metode, tunelska in tipalna mikroskopija, elektronske meritve nanometrskih vezij.***

MODELIRANJE *za načrtovanje molekularno-elektronskih naprav in lastnosti nanomaterialov.*

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SYNTHESIS OF NEW MATERIALS *especially important **for industrial application, as well as basic science.***

PROCESSING *nanolithographic and self-assembly processing methods and technologies, leading to industrial processes.*

CHARACTERIZATION ***electron and optical microscopy,** diverse advanced spectroscopic methods, tunnelling and scanning-probe microscopies, electron transport at nanoscale.*

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