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Zbornik - 2. del

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Barbara Bertoncelj[1,2], Katarina Vojisavljević[3], Janez Rihtaršič[1], Gregor Trefalt[4], Barbara Malič[3]

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Bulk Molding Compounds (BMCs) are a combination of polymer matrix, glass fibers and $CaCO_3$ mineral filler. Each constituent is having its own role that contributes to the final properties. The latter are dependent on chemical and physical properties of individual constituents, their relative amounts and spatial orientation and distribution of fibers.

BMCs are a preferred replacement for metals, such as steel and aluminum, because of their properties such as high strength and stiffness in combination with low density, low thermal expansion, corrosion resistance, etc. Moreover, the manufacturing process (injection molding) is energy efficient. Because the product is made in one piece there is no need for additional operations, such as machining and drilling.

The main use of BMCs is in mass production of components and products in automotive, electro and electronic industry. In such products, the mechanical response, for example, flexural strength, is important, but is sometimes hard to measure due to the complexity of the shape. Therefore, the microstructural analysis, i.e. Voronoi diagram analysis, can be applied to critical parts of BMCs products to obtain an insight about the mechanical response and to identify the causes for products failure or poor quality.

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MEDNARODNA PODIPLOMSKA ŠOLA JOŽEFA STEFANA

JOŽEF STEFAN INTERNATIONAL POSTGRADUATE SCHOOL

Microstructural analysis of Bulk Molding Compounds and correlation with the flexural strength

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Study program: Ecotechnology

Supervisor: prof. dr. Barbara Malič

Introduction

Bulk Molding Compounds (BMCs):

- multiphase materials consisting of polymer matrix, short glass fibers and mineral fillers
- properties depend on chemical and physical properties of individual constituents, their relative amounts and spatial orientation and distribution of fibers
- for production of components and products in automotive, electro and electronic industry
- preferred replacement for metals because of their properties such as high specific strength and stiffness, low thermal expansion, corrosion resistance, etc.

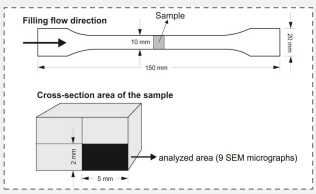
Orientation and spatial distribution of fibers depends on the molding process and the geometry of the mold.
Inhomogeneous fiber distribution can lead to poorer mechanical strength of composites.

Aim of the work

To study the influence of the glass fiber (GF) content on the microstructure and flexural strength of BMC composites.

Experimental

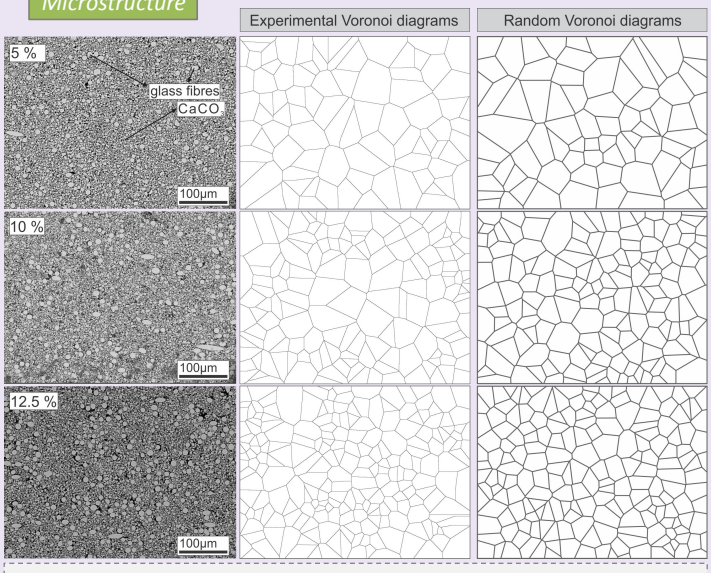
	Polymer matrix	Glass fibers	$CaCO_3$
	[wt%]		
1	21	5	74
2	21	10	69
3	21	12.5	66.5



Composition of BMC samples and scheme of the test specimen's dimensions, cutting position and the sampling scheme of the cross-sectional area for the morphological characterization.

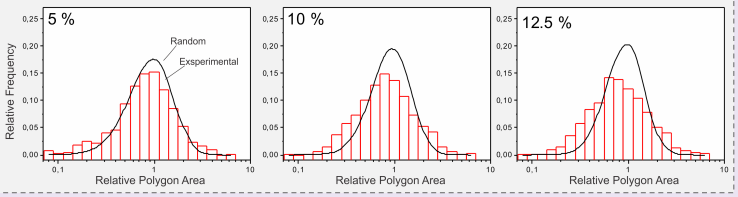
Results

Microstructure



Scanning electron micrographs were quantitatively characterized by Voronoi analysis in order to define the degree of the GF distribution homogeneity. As a reference, for each BMC composition a Voronoi diagram was generated from the modelled pattern of randomly distributed disks (right column).

Voronoi diagram analysis



Flexural strength

	Glass fibers [wt%]		
	5	10	12.5
σ_f [MPa]	61 ± 3	82 ± 5	76 ± 7

Conclusions

Voronoi analysis revealed that fiber distribution in the sample with 5 wt% of GF most closely approximates to the values of the random distribution. The divergence from the random distribution is more pronounced in the sample with 12.5 wt% of GF, which indicates fiber clustering. The flexural strength was the highest for the composite with 10 wt% of GF. A suitable combination of properties, i.e. a high level of fiber distribution homogeneity and high flexural strength can be achieved by tailoring the GF content in BMCs. The Voronoi diagram analysis can be applied to critical parts of BMCs. In this way the microstructure can be related to the mechanical response of the material which may be useful if mechanical testing cannot be performed, for example due to a non-standard shape of a selected part.

Metal-free azidation of alcohols catalysed by molecular iodine

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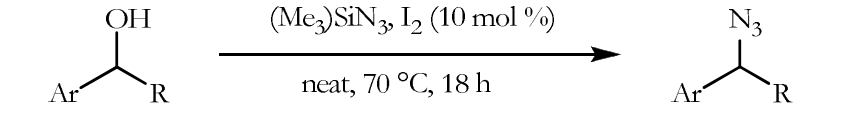
Since the preparation of the first organic azide, phenyl azide, by Peter Grieß in 1864, these energy-rich and flexible intermediates have enjoyed considerable interest. They have assumed an important position at the interface between chemistry, biology, medicine, and materials science. Industrial interest in organic azide compounds began with the use of azides for the synthesis of heterocycles such as triazoles and tetrazoles as well as with their use as blowing agents and as functional groups in pharmaceuticals. In more recent times in particular, completely new perspectives have been developed for their use in peptide chemistry, combinatorial chemistry, and heterocyclic synthesis. Thus, for example, azidonucleosides attract international interest in the treatment of AIDS.

Alcohols are cheap and readily available chemical resources. From economical and green-chemical point of view their direct efficient transformation to other useful synthons without the need for prefunctionalisation is a desired pathway, by which additional synthetic steps as well as additional solvent and reagent consumption can be avoided. Accordingly, a new method for direct transformation of alcohols to azides under solvent-free reaction conditions was developed, using iodine as a cheap metal-free catalyst. Untill now the reaction system has proved to be efficient on secondary benzyl alcohols, nevertheless, broader reaction scope is still being examined.



R = Alkyl, Phenyl, ArR[1]

Yield: 88 - 100 %

Metal-free azidation of alcohols catalysed by iodine

Klara Čebular[1,2], Monika Horvat[1], Stojan Stavber[1,2,3]

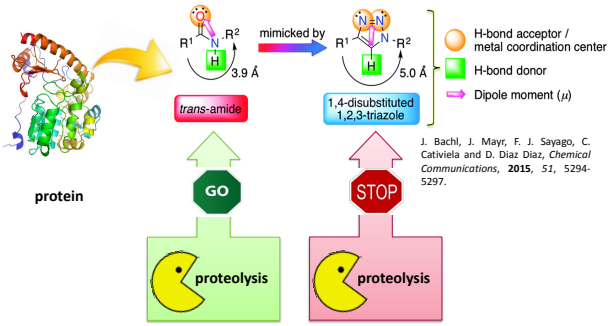
Study programme: **Ecotechnology**

[1] Jozef Stefan International Postgraduate School, Ljubljana, Slovenia; [2] Centre of Excellence for Integrated Approaches in Chemistry and Biology of Proteins, Ljubljana, Slovenia; [3] Laboratory for Organic and Bioorganic Chemistry, Department of Physical and Organic Chemistry, Jozef Stefan Institute, Ljubljana, Slovenia

Introduction

Application of azides

Azides are important compounds with significant application in organic chemistry in preparation of amines[1], nitrenes[2] and heterocyclic compounds, such as 1,2,3-triazoles. Their structural and electronic properties are similar to those of a peptide bond, which makes them pharmaceutically interesting molecules in peptidomimetic research,[3, 4] especially since general methods for their synthesis are available.

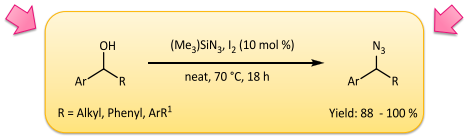


J. Bachl, J. Mayr, F. J. Sayago, C. Cativiela and D. Diaz Diaz, *Chemical Communications*, **2015**, *51*, 5294-5297.

A new method for azidation of alcohols

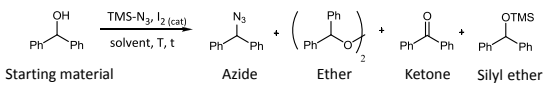
Although traditional methods for transformation of alcohols to azides are effective, they have several disadvantages:

- multi-step synthesis,
- demanding manipulation,
- use of metal catalysts (e.g. Bi(III), Cu(II), In(III), Fe(III), ...),
- toxic solvents,
- expensive reagents or
- long reaction times.

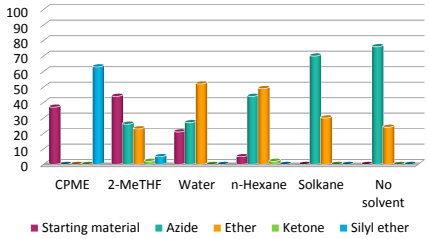


one-pot, metal-free, solvent-free

Results

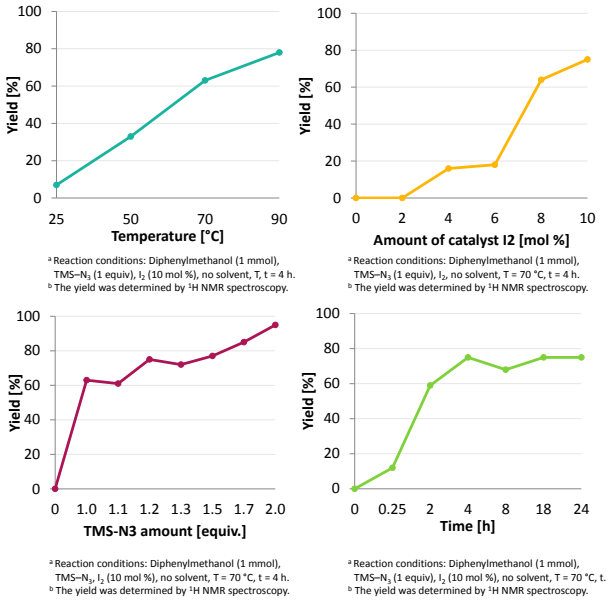


Effect of different solvents on distribution in the reaction mixture



[a] Reaction conditions: Diphenylmethanol (1 mmol), TMS-N_3 (1 equiv), I_2 (10 mol %), solvent, T = 70 °C, t = 4 h.
[b] Distribution of the substances in reaction mixtures was determined by ^{1}H NMR spectroscopy.
[c] We also checked solvents MeOH, EtOH, *i*-PrOH, Me_2CO, EtOAc, MeCN, CF_3CH_2OH, however, they all reacted with starting material.

Results



[a] Reaction conditions: Diphenylmethanol (1 mmol), TMS–N_3 (1 equiv), I_2, no solvent, T = 70 °C, t = 4 h.
[b] The yield was determined by ^{1}H NMR spectroscopy.

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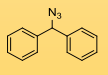
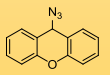
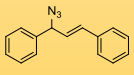
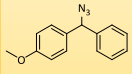
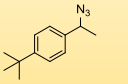
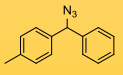
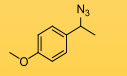
Figure 1: The effect of temperature, time, amount of catalyst and amount of TMS-N_3 reagent on azide yield.

Structures and yields [%][b] of synthesized azides

	100		88		100
	100		93		100
	100		100		95

[a] Reaction conditions: Alcohol (1 mmol), TMS–N_3 (1.2-2 equiv), I_2 (10 mol %), no solvent, T = 70 °C, t = 18 h.
[b] The yield was determined by ^{1}H NMR spectroscopy.

Conclusions

A new method for preparation of azides was developed, using iodine as a cheap metal-free Lewis acid catalyst under solvent-free reaction conditions. The reaction is assumed to proceed through carbocation intermediate, however, the mechanism of reaction is still under investigation. Up till now the reaction system has proved to be efficient on secondary benzyl alcohols, nevertheless, broader reaction scope is still being examined.

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Building composites from flay ash, cement and electric arc furnace dust: Environmental impacts

Ana Drinčić[1,2], Irena Nikolić[3], Tea Zuliani[1], Radmila Milačič[1,2], Janez Ščančar[1,2]

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Industrial waste materials may be re-used as substitute for natural raw materials in different building composites, if the final products possess appropriate mechanical properties and are environmentally acceptable. The main environmental impacts of building materials that contain waste by-products are estimated by applying different leachability tests. In the present study, the modified NEN 7375 test was applied for the evaluation of the long-term environmental impacts of the building composite, prepared in 99% from fly ash (80%) and cement (20%) and in the remaining 1% from EAF dust. Leachability of selected elements was followed in different time intervals over a period of sixteen days, using synthetic surface and synthetic sea water as leaching solutions. During the course of the experiment the leaching solutions were not replenished, enabling to follow diffusion and dissolution of contaminants. The data of the present investigation revealed, that leaching of Cr, Mo, V and As from the building composite investigated represent a limiting factor for its use due to negative environmental impacts.

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Building composites from flay ash, cement and electric arc furnace dust: Environmental impacts

Ana Drinčić[1,2], Irena Nikolić[3], Tea Zuliani[1], Radmila Milačič[1,2], Janez Ščančar[1,2]

[1]*Department of Environmental Sciences, Jožef Stefan Institute, Ljubljana, Slovenia*
[2]*Jožef Stefan International Postgraduate School, 1000 Ljubljana, Slovenia*
[3]*University of Montenegro, Faculty of Metallurgy and Technology, Podgorica, Montenegro*

1. INTRODUCTION

The potential use of recycled building materials composed in 99% from a mixture of fly ash (80%) and cement (20%) and addition of 1% of electric arc furnace (EAF) dust, was investigated regarding the environmental impacts. For this purpose, the modified NEN 7375 leachability test was applied using synthetic sea water and synthetic surface water as leaching solutions. To study the diffusion and dissolution of contaminants, leaching solutions were not replenished.

2. METHODS

Compact composite (7x5 cm)

Synthetic sea or surface water

Sampling after 0.25, 1, 1.5, 7, 9 and 16 days

ICP-MS operating parameters

Parameter	Type/Value	Helium mode	HECM mode	No gas mode
Sample introduction				
Nebuliser	Miramist			
Spray chamber	Scott			
Skimmer and sampler	Ni			
Plasma conditions				
Forward power	1550 W			
Plasma gas flow	15.0 L min^{-1}			
Carrier gas flow		1.05 L min^{-1}		0.75 L min^{-1}
Dilution gas flow		0.10 L min^{-1}		0.45 L min^{-1}
He gas flow		4.5 mL min^{-1}	10 mL min^{-1}	
Data acquisition parameters for total element concentrations				
Sample uptake rate	0.3 mL min^{-1}			
m/z of elements		^{51}V, ^{52}Cr, ^{55}Mn, ^{56}Fe, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{75}As, ^{78}Se, ^{95}Mo		^{111}Cd, ^{121}Sb, ^{137}Ba, ^{201}Hg, ^{208}Pb
m/z of internal standards		^{45}Sc, ^{72}Ge, ^{103}Rh, ^{115}In		^{45}Sc, ^{72}Ge, ^{103}Rh, ^{115}In

3. RESULTS

Table 1: Total element concentrations in fly ash, cement and EAF dust

Element	Fly ash (mg/kg)	Cement (mg/kg)	EAF dust (mg/kg)
As	30.0	15.0	178
Se	4.95	2.50	9.0
Ba	630	420	680
Fe	37000	14800	213450
Mn	278	750	18555
Co	27.0	15.0	30.0
Ni	150	90	385
Cu	90	135	3510
Zn	26.0	120	293330
Cd	65.4	74.5	980
Sb	2.65	2.45	302
Hg	<15	<15	<15
Pb	52.7	110	31860
Cr	160	91	4170
Mo	3.32	22.4	64.6
V	180	107	69.2

During the course of the experiment the concentrations of Ba, Fe, Mn, Co, Ni, Cu, Zn, Cd, Sb, Hg and Pb in all samples investigated remained in general, below the limits of detection of ICP-MS.

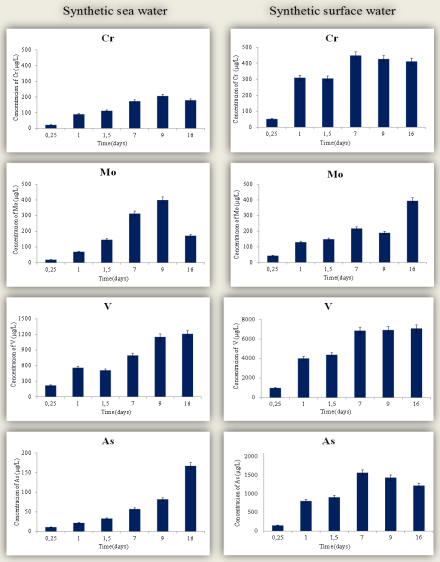

Figure 1: Leachability of Cr, Mo, V and As over time from composite investigated

4. CONCLUSIONS

- Data from the leachability test revealed that Cr, Mo, V and As, which were present predominantly in the form of highly soluble oxoanions, were leached from building composite (99% mixture of fly ash (80%) and cement (20%) and addition of 1% of EAF dust) with synthetic sea and surface water in high concentrations that were not environmentally acceptable.
- The leachability of Cr, Mo and As from the building composite investigated arose mainly from EAF dust, while of V from EAF dust, cement and fly ash.
- The use of EAF dust, which was incorporated as additive to composites from fly ash and cement, should be omitted.

HPGe gamma detector effective solid angle calculation

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k_0 instrumental neutron activation analysis (k_0-INAA) is a powerful multi-elemental analytical method, based on irradiating a sample with neutrons, and measuring the gamma spectrum of the resulting radioactive products. The high penetrability of neutrons and gamma rays in matter makes k_0-INAA almost, but not completely, matrix insensitive, and it is able to achieve combined standard uncertainties of 3.5 % or better.

We identified and corrected a source of systematic error, however, it turned out to be negligible for the chosen sample. We also improved the flexibility of a computational step, enabling us to perform the method on samples of arbitrary shapes, which resulted in a 4%-18% correction over the previous approximation for the case of a wire-shaped sample.

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HPGe gamma detector effective solid angle calculation

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Study program: Ecotechnology

k_0-INAA:

Advantages:
- Multielemental
- Accurate (~3.5%)
- Large range
- Almost matrix-insensitive
- Almost non-destructive

Requirements:
- Irradiation facility
- Calibrated gamma detector

Detection efficiency must be adjusted to include sample self-absorption and different sample shape.
Adjustment done using *efficiency transfer*:

$$\varepsilon_p^{geo} = \varepsilon_p^{ref} \cdot \frac{\overline{\Omega}^{geo}}{\overline{\Omega}^{ref}}$$

$$\overline{\Omega} = \iint_{source,detector} F_{eff} F_{att} \, d\Omega$$

Improved efficiency transfer:
- More sample geometries possible:
  -Before: Cylinder with same axis of symmetry as detector
  -After: Box and cylinder, may be vertical or horizontal, may be offset from center
- Inclusion of activation inhomogeneity (assumed linear between sample top and bottom)

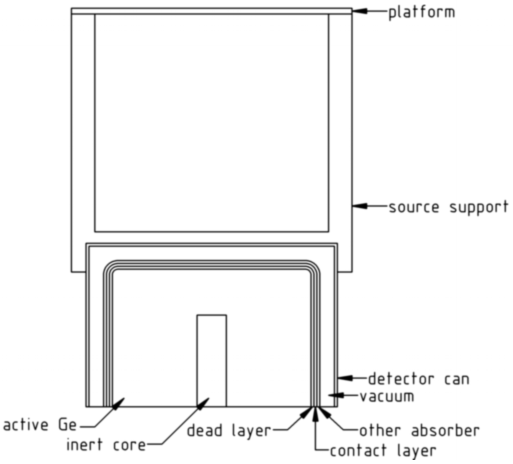
↓

- Improved accuracy & traceability
- Increased flexibility

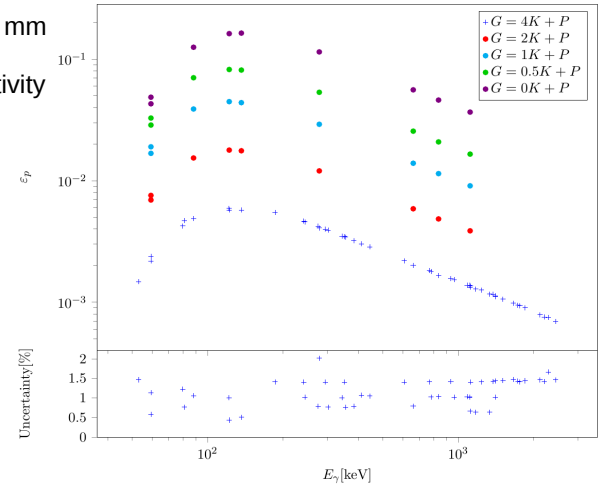
Basics of k_0-INAA (Instrumental Neutron Activation Analysis):
- Sample and monitor coirradiated
- Both separately measured on gamma detector
- Gamma peak ratios between sample and monitor tell us sample elemental composition

$$\rho_a[mg/kg] = \frac{\left(\frac{N_p/t_m}{SDCW}\right)_a}{\left(\frac{N_p/t_m}{SDCw}\right)_{Au}} \cdot \frac{10^{-6} k_{0,Au}(Au)}{k_{0,Au}(a)} \cdot \frac{G_{th,Au} f + G_{e,Au} Q_{0,Au}(\alpha)}{G_{th,a} f + G_{e,a} Q_{0,a}(\alpha)} \cdot \frac{\varepsilon_{p,Au}}{\varepsilon_{p,a}}$$

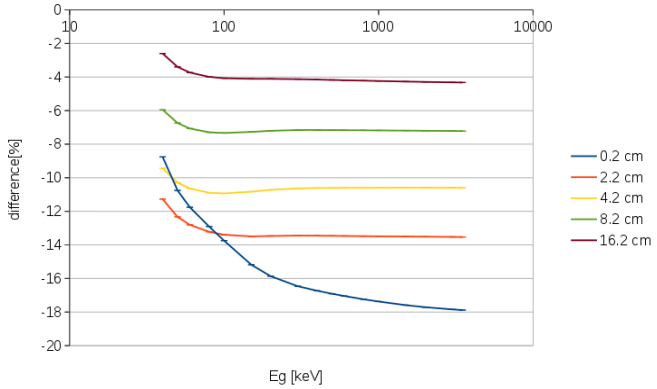
Typical HPGe gamma detector:



Point reference source calibration points at different source-detector distances (G):



Results:
Samples: wire: horizontal cylinder, length: 10 mm, radius: 0.5 mm
vertical cylinder: height: 0.1 mm, radius: 5 mm
1) Homogeneously activated wire vs. wire with 0.5 ratio of activity at end-points: less than 0.01% difference in efficiency.
2) Homogeneously activated wire vs. vertical cylinder:



Implementing molecularly imprinted polymer (MIP) in the analytical method for determining sertraline residues in aqueous environment

Tjaša Gornik[1,2], **Anja Krajnc**[1], **Amadeja Koler**[3], **Marko Turnšek**[3], **Ester Heath**[1,2], **Jernej Iskra**[3,4], **Peter Krajnc**[3], **Karel Jerabek**[5], **Tina Kosjek**[1,2]

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Molecularly imprinted polymers or MIPs are materials with high selectivity towards a target molecule, because it is used as a template during polymerization. Based on their selectivity, different applications including sensors, capillary electrochromatography, enantiomeric separation, catalysis and solid phase extraction, have been proposed. The focus of our research is the antidepressant sertraline, a highly prescribed pharmaceutical that poses a threat to the environment due to its toxic effects on aquatic organisms. Our aim is to develop an analytical method using a MIP as a solid-phase extraction sorbent highly selective for sertraline, its metabolites and transformation products. First results showed that the assessment of the MIP effect for sertraline, the template and concurrently the target molecule, is hindered due to its continuous leaching from the MIPs. The MIP effect was proven for the metabolite norsertraline. In the future we would like to use MIPs to selectively isolate structurally related sertraline compounds from environmental aqueous samples and adapt the method for bioanalytical and forensic applications.

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Tjaša Gornik, Anja Krajnc, Amadeja Koler, Marko Turnšek, Ester Heath, Jernej Iskra, Peter Krajnc, Karel Jerabek, Tina Kosjek

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(programme Ecotechnology)
Supervisor: Asist. Prof. Dr. Tina Kosjek, co-supervisor: Prof. Dr. Ester Heath
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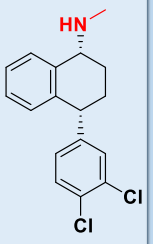
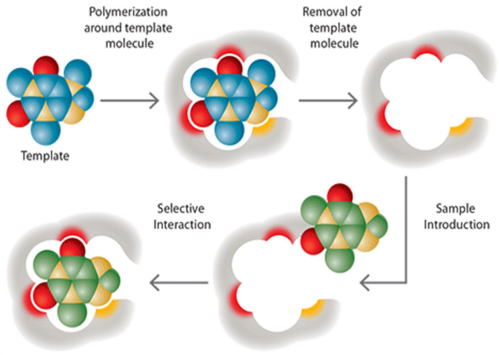
Introduction:

- **Sertraline as a pharmaceutical:** antidepressant, SSRI, metabolite norsertraline
- **Sertraline in the environment:** at ng/L concentrations in surface and wastewaters and at ng/g concentrations in sediment, soil and aquatic organisms
- **Molecularly Imprinted Polymers (MIPs):** synthetic polymeric materials with high selectivity for their target molecule (the target molecule is used as a template, forming either covalent or non-covalent interactions with the polymer)
- **MIP effect:** selectivity fot target analyte(s): their adsorption of to MIP is larger than the adsorption to unspecific polymers
- **Objective:** to develop a highly selective method for environmental and biological samples using molecularly imprinted solid phase extraction (MISPE) for identifying and quantifying sertraline, its metabolites and environmental transformation products in aqueous samples
- **Tested polymers:** MT86, MT87, MT88 (quantity of temaplate added: 1.5 g, 0.82 g, 0.43 g)





Materials and Methods:

The SPE Oasis HLB method was based on one previously developed in the Group for organic analysis at the Department of Environmental Sciences, JSI. The method was further optimized for determination of norsertraline.

SPE Oasis HLB method	
Internal standards	sertraline-D_3 norsertraline-$^{13}C_6$
Conditioning	3 mL EtAc
	3 mL MeOH
Equilibration	3 mL MilliQ H_2O
Sample load flow	1-2 ml/min
Drying	30 min vacuum
Elution	3 x 0,6 mL 2 % triethylamine in MeOH
Derivatization	15 µL Ac_2O + 5 µL pyridine, 15 min

Instrumental Analysis	GC-MS
Polymerisation	divinylbenzen + acrylic acid + sertraline + THF/H2O + 1 % AIBN
Removal of the template from MIP	washing (EtAc, DCM, MeOH) + Soxhlet extraction (acetone, DCM, EtAc)
Extraction from MIP	12 mL of EtAc/DCM/MeOH = 1/1/1

Abbrevations
EtAc – ethyl acetate; DCM - dichloromethan; MeOH - methanol; THF - tetrahydrofuran; AIBN - azobisisobutyronitrile; GC-MS – gas chromatograph coupled with mass spectrometer; EI – electron ionisation

Acknowledgments
The authors acknowledge the financial support of the Slovenian Research Agency (J1-6744: "Razvoj polimerov z molekularnimi odtisi in njihova uporaba na področju okoljske in bio-analitike" and P1-0143: "Kroženje snovi v okolju, snovna bilanca in modeliranje okoljskih procesov ter ocena tveganja").

Results and Discussion:

SPE Oasis HLB method optimisation:
- 2 % of triethylamine in methanol was used for elution
- recovery: 65.2 ± 5.9 % (sertraline); 50.2 ± 1.6 % (norsertraline)
- derivatization time was shortened from 1 hour to 15 minutes

GC-MS analysis:
- SIM method: retention times of sertraline and norsertraline were 13.5 minutes and 12.7 minutes; chosen *m/z* in the table, quantification ions in bold

SIM method	***m/z***
sertraline	**347**
	349
sertraline-D_6	350
	352
norsertraline	**274**
	333
norsertraline-$^{13}C_6$	**280**
	282

GC-MS analysis	
Instrument	7890B/5977A Agilent Technologies, USA
Oven temperature programme	100°C held for 2 min, then 25°C/min to 300°C and held for 6 min
Column type	HP-5ms Ultra Inert (30 m x 0.25 mm x 0.25 µm)
Carrier gas	helium
Carrier gas flow	1 mL/min
Injection type	splitless
Injection volume	1 µL
Injector temperature	270 °C
Ionisation mode	EI

MIP effect results:
- countinued leaching of sertraline from 40 to 160 µg/mL/g of MIP → impossible to the evaluate the MIP effect for sertraline in concentrations of up to 25 µg/mL
- MIP effect shown for norsertraline (MIP/control polymer ration for MIP MT88 110 % and MT87 160 %)
- based on the presented results, MT87 was selected for further testing

Future work:
- further optimization of „classical" analytical method;
- development of selective and sensitive reference analytical method for determination of sertraline, its metabolites and transformation products;
- Determination of sertraline residues in aqueous environment

Maternal blood levels of selected elements and birth weight of mother-child pairs living in Slovenia

Marta Jagodic[1,2*], Janja Snoj Tratnik[1,2], Darja Mazej[1], Anja Stajnko[1,2], Majda Pavlin[1,2], Mladen Krsnik[3], Alfred B. Kobal[4], Lijana Kononenko[5], Milena Horvat[1,2]

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The aim of our study was to access the influence of selected elements in maternal blood samples (manganese (Mn), copper (Cu), zinc (Zn), arsenic (As), selenium (Se), cadmium (Cd), lead (Pb) and mercury (Hg)) on birth weight. In the evaluation of these associations we took into account the mother's and baby's social-demographic characteristics and the mother's dietary and lifestyle habits. Maternal blood was sampled 4-6 weeks after delivery.

The concentrations of selected elements did not represent any health risk for the mother-child pairs. Statistical analyses showed that the gender of the baby, gestational age, maternal age and pre-pregnancy body mass index were the main predictors for birth weight, and that the concentration of Mn in maternal blood was significantly and positively associated with birth weight.

This work was supported by the National Human Biomonitoring program financed by the Chemicals Office of the Republic of the Republic of Slovenia and the Slovenian Research Agency and the EU founded CROME-LIFE+ program (Cross-Mediterranean Environment and Health Network program).

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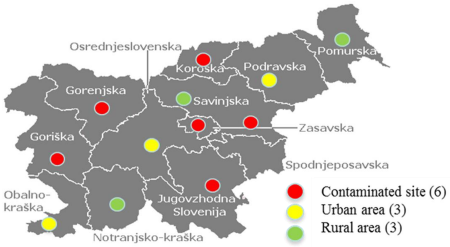

Correlations with baby birth weight (kg)			
Variable	r_s	*p-value*	*N*
Residential location*	0.000	0.994	448
Age of mother (years) - groups	-0.043	0.346	493
Pre-pregnancy body mass index - groups	**0.092**	**0.042**	**483**
Education - groups	-0.033	0.469	470
Estimated gestational age (week)	**0.325**	**0.000**	**473**
Gender of baby	**-0.096**	**0.033**	**494**
Variable	r_p	*p-value*	*N*
Log10 Mn (ng/mL)	**0.178**	**0.001**	**370**
Log10 Cu (ng/mL)	-0.074	0.102	494
Log10 Zn (ng/mL)	0.004	0.938	494
Log10 As (ng/mL)	0.018	0.689	494
Log10 Se (ng/mL)	-0.042	0.347	494
Log10 Cd (ng/mL)	0.053	0.239	493
Log10 Pb (ng/mL)	0.076	0.091	494
Log10 Hg (ng/mL)	-0.040	0.376	493
Baby length (cm)	**0.717**	**0.000**	**493**

* Potentially contaminated, rural, and urban areas. N=sample number, r_s-Spearman correlation coefficient, r_p-Pearson correlation coefficient.

RESULTS AND CONCLUSIONS

The levels of exposure to selected toxic elements were generally low and the levels of essential elements were consistent with other studies, indicating that these factors do not represent any health risk for the mother-child pairs.

The multiple regression model showed that the gender of the baby, gestational age, maternal age, and pre-pregnancy body mass index were the main predictors for birth weight, and that Mn in maternal blood was significantly and positively associated with newborn weight.

Dietary habits showed insignificant correlations with a baby's birth weight, with the following food items being tested: vegetable, fruits, nuts, milk, eggs, poultry, game, other meat, freshwater fish, and fresh, tinned and frozen sea food.

The positive association observed between birth weight and Mn in maternal blood could be explained by the essential role of Mn in fetal development as an important cofactor in enzymatic reactions in bone formation and metabolic regulation of amino acids, lipids, proteins, and carbohydrates [5, 6].

This work was supported by the National Human Biomonitoring program financed by the Chemicals Office of the Republic of Slovenia and the Slovenian Research Agency and the EU founded CROME LIFE+ program (Cross-Mediterranean Environment and Health Network program).

INTRODUCTION

The objective of the present study was to evaluate the impact of maternal blood levels of selected toxic and potentially toxic elements (manganese (Mn), copper (Cu), zinc (Zn), arsenic (As), selenium (Se), cadmium (Cd), lead (Pb) and mercury (Hg)) on the birth weight of their babies, taking into account the socio-demographic characteristics and dietary and lifestyle habits of the mother. The literature suggests that a mother's exposure to even trace levels of certain toxic elements and the adequacy of her intake of essential elements may influence the infant's birth weight [1, 2].

METHODS

Recruitment:

535 pregnant women (19-39 years) from 12 regions across Slovenia were selected as part of the National Human biomonitoring study in Slovenia (2007-2015).

Sampling procedure:

Maternal blood was collected approximately 4-6 weeks after delivery.

Mothers also completed a questionnaire to report their age, prior areas of residence, familial background, social factors, education, weight before and through pregnancy, height and weight post-partum, parity, detailed reproductive, medical and occupational history, life style, relevant paternal/pregnancy related information, information about the newborn child, and dietary information.




Sample preparation and chemical analysis:

Levels of selected toxic and potentially toxic elements were analysed using a Direct Mercury Analyser (DMA 80) for Hg [3] and Inductively-coupled plasma mass spectrometry (ICP-MS) for As, Cd, Cu, Mn, Pb, Se and Zn [4].

Statistical analyses:

Associations between birth weight and a) predictors obtained through the questionnaires and b) levels of selected elements in the mother's blood samples were tested using univariate and multiple linear regression analysis.

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Iodine and selenium content in buckwheat seeds after foliar spraying of plants with I and Se solution

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Iodine and selenium are essential elements that are necessary for thyroid hormones synthesis. They both come into the body by food consumption. Deficiency problems caused by insufficient intake mainly results from the low content of the two elements in soils. Consequently, the transfer of both elements to the food chain, where plants are the first level, is low. To avoid health problems caused by iodine and/or selenium deficiency, other food sources of the elements should be found.

Our aim was to enrich buckwheat seeds with iodine and selenium. Plants were foliar sprayed with different forms of iodine and/or selenium. The results showed increased concentrations of both elements. According to World Health Organizations, recommended daily intakes (RDI) are 150 μg I/day and 30–70 μg Se/day. By one portion (100 g) of untreated buckwheat seeds a person would intake approx. 2 % of RDI for iodine and 4–10 % of RDI for selenium (on the supposition that all of iodine and selenium present in seeds are absorbed). By consuming a portion of treated buckwheat seeds from the present study, 20–40 % of iodine RDI and 13–220 % of selenium RDI would be ingested. Therefore some further optimizations regarding the concentrations used for foliar spraying are still needed, but this is a promising approach to provide sufficient iodine and selenium intake for humans.

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Study programme: Ecotechnology

Supervisor: prof. dr. Vekoslava Stibilj

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Did you know ...

... that iodine and selenium are essential elements for humans, important for thyroid hormones synthesis?

... that we have to consume them with food?

... that soils are often low in concentrations of iodine and selenium and consequently the transfer to the food chain, where plants are the first level, is low?

... that we need new sources to avoid health problems caused by iodine and/or selenium deficiency?

... that it is possible to enrich plants with iodine and selenium?

... that buckwheat has high nutritional value since it is rich in content of vitamins B1 and B2, lysine and antioxidants?

... that buckwheat seeds contain less than 50 ng/g of iodine and selenium?

Aims

The aims of study where to investigate:

- if buckwheat can be iodine and/or selenium enriched by foliar spraying
- which form of each element is better for spraying
- if there are any interactions when both elements are applied simultaneously

Methods

Foliar spraying of buckwheat just before blooming with the following solutions:

- water (control)
- I(–I)
- I(V)
- Se(IV)
- Se(VI)
- I(–I) + Se(IV)
- I(–I) + Se(VI)
- I(V) + Se(IV)
- I(V) + Se(VI)

Concentrations: 1000 mg I/L and 10 mg Se/L

⇩

Sampling in mature phase, drying at 40 °C, milling

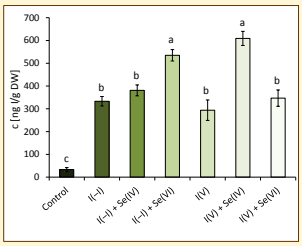
⇙ ⇘

Alkaline extraction ⇩ Iodine determination (ICP-MS)

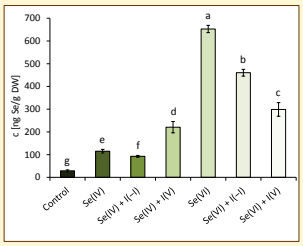
Acid digestion ⇩ Selenium determination (ICP-QQQ)

Results

Iodine content



Selenium content



- Iodine concentrations in seeds from treated plants approx. 10-fold higher than in control seeds regardless to the form of iodine applied
- Foliar spraying with I(V) + Se(VI) elevated iodine content compared to I(V) treatment
- Foliar spraying with I(–I) + Se(VI) increased amount of iodine in comparison with I(–I) treatment

- Selenium concentrations were dependent on form used for treatment – compared to control, in Se(IV) treated seeds, concentrations were approx. 4-fold higher while concentrations were more than 20-fold higher when Se(VI) was applied
- Presence of iodine in both forms decreased selenium content
- Compared to Se(IV) treatment alone, Se(IV) + I(–I) slightly decreased Se concentrations while Se (IV) + I(V) elevated it

Conclusions

- Foliar spraying of plants before blooming had no influence on plant growth since no differences were observed in height or dry seed mass between control and treated plants
- No differences in iodine content were found when using different forms (I(–I) or I(V))
- When applying Se(VI) higher selenium contents were found in buckwheat seeds compared to Se(IV) treatment
- There were some interactions between iodine and selenium observed when both elements were applied together
- Foliar spraying approach might be used for production of functional food

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Evidence of cave ventilation and its contribution to soil CO_2 flux

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Studying and understanding carbon cycle is important due to increased concern regarding concentrations of "greenhouse" gasses in the atmosphere. Special attention in last decades is given to its natural sinks and sources and possible artificial storage of CO_2 "captured" from industrial sources. One of the important natural CO_2 sink /source are also soils. Different soils and environments dictate different carbon dynamics. Soils developed on karstic areas are globally widely distributed. Beside carbon originating (in different forms) from plants and plant material, the presence of carbonate rocks affects soil carbon dynamics with its dissolution and precipitation processes. Furthermore, below soils there can be a presence of subterranean caves and cavities, which can act as temporal reservoirs for CO_2. This "captured" CO_2 can migrate back to the soil and to atmosphere when favorable conditions are present. Different pathways and sources of soil CO_2 can be studied using stable isotope techniques. In present study natural abundance stable isotopes of carbon were used to detect and quantify the influence of subterranean cave to soil CO_2 and soil CO_2 fluxes. Soil CO_2 fluxes were measured with special chambers and a rough estimation for contribution of cave air to the CO_2 flux was made. Although present research is of great importance for understanding soil carbon dynamics in such areas, it has a potential applicability also in detection of carbon leakage from artificial subterranean storing of carbon captured from industrial sources.

Evidence of cave ventilation and its contribution to soil CO_2 flux

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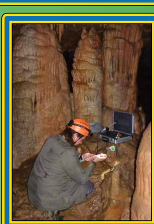
1 INTRODUCTION: Measurements of soil CO_2 fluxes are important for understanding the mechanisms that are affecting the soil CO_2 efflux and for determining whether the ecosystem under investigation acts as a sink or source of CO_2. Soil CO_2 flux measurement provides only the information of the bulk CO_2 fluxes originating from different sources. To gain deeper understanding of soil carbon dynamic it is important to distinguish and study those sources. Karstic area is specific due to its CO_2 contribution originating from abiotic sources, such as from carbonate rock dissolution/precipitation processes and subterranean caves. Soil CO_2 fluxes were measured from soils above subterranean cave, while stable isotope composition of soil and cave CO_2 was used to determine possible influence of cave air to soil CO_2. **AIM: The aim of this study is to evaluate the ventilation as the main source of soil CO_2 flux on annual basis.**

2 STUDY AREA: Velika Jeršanova doline (45°47' N, 14°12' E) is a collapse doline located in the forest near Postojna, Slovenia (**Figure 1**). Two sampling sites were selected: a) Test site, above the cave (AC) located directly above the last hall of Pisani rov and b) the control site, at the bottom of the doline where no cave (NC) influence is expected (**Figure 7**).

Figure 1: Location of the study area.



3 SAMPLING AND MEASUREMENTS: Soil CO_2 fluxes were measured with automatic soil respiration system "Ukulele" which is a system of closed dynamic chambers developed at the Laboratory for Electronic Devices at the Slovenian Forestry Institute [2]. The system measures the increment of CO_2 concentration in a closed space above soil surface using infrared gas analyser (IRGA) LI-840 (LI-COR, USA). Three flux chambers were installed at each site. Each chamber has integrated thermocouples and FDR sensors for measuring soil temperature (TS) and soil water content (SWC), respectively.

4 RESULTS AND DISCUSSION:

- Distinct soil CO_2 flux trends at AC and NC during the year

- AC: maximum average fluxes in autumn 2014 (1.62 ± 0.73 μmol m^{-2} s^{-1}); minimum average fluxes during cave ventilation period (1.18 ± 0.37 μmol m^{-2} s^{-1}) **(Figure 4c)**

-NC: maximum average fluxes in spring 2015 (2.33 ± 0.90 μmol m^{-2} s^{-1}); minimum average fluxes in summer 2014 (0.50 ± 0.4 μmol m^{-2} s^{-1}) **(Figure 4d)**.

- Period when $\delta^{13}C_{light}$ **(Figure 4a)** values rise, exactly coincidences with the period when $\delta^{13}C_{cave}$ values rises (orange line). Rising of $\delta^{13}C_{cave}$ together with lower cave atmosphere CO_2 concentrations were consequences of cave ventilation **(Figure 3)**.
- Cave ventilation does have effect on soil CO_2 and was roughly estimated that cave can contribute up to 80% of soil CO_2
- Cave CO_2 contribution of 22% to annual soil CO_2 fluxes was estimated.

5 APPLICATIONS:

- Contribution to one of the major scientific challenges in achieving societal goals of the 21st century: "the categorization and quantification of major surface types as sources or sinks of CO_2".
- Understanding of the various sinks and sources of carbon in the Karstic environment in relation to the land use in the hinterland as an important priority in the EU policy and could also be applied in the IPCC revision of CO_2 emissions to the atmosphere.
- Soil gas flux monitoring system above "geological storage" of CO_2 captured at industrial sources.

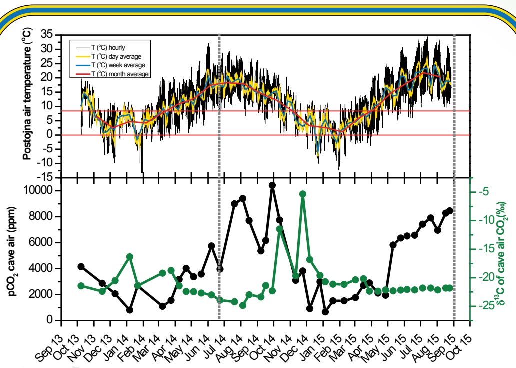


Figure 2: Time series of soil and cave air CO_2 concentrations and its ^{13}C isotope composition, ^{222}Rn concentration in cave air and Postojna air temperatures with marked lines of cave temperature of 8.4 °C and 0°C

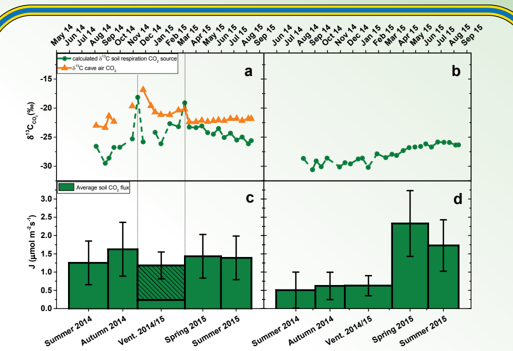


Figure 3: Time series of calculated isotopic composition of the isotopically light end-member from samples gathered at AC and NC site (a and b). Bar-plots of average fluxes for particular season and cave ventilation period (b and c). Hatchet part of the bar-plot is the estimated contribution of cave air. Dotted lines represent the ventilation period at AC site.

6 REFERENCES:

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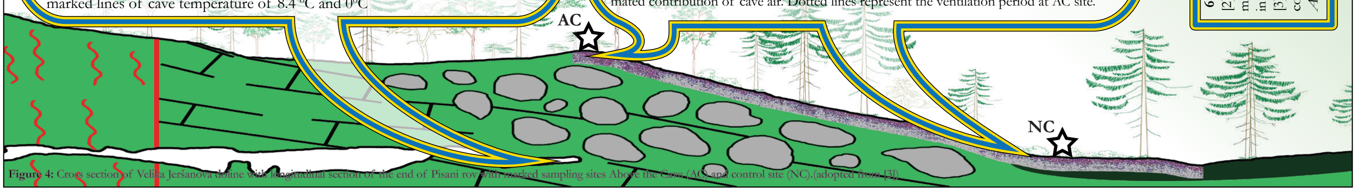

Figure 4: Cross section of Velika Jeršanova doline with longitudinal section of the end of Pisani rov with marked sampling sites Above the Cave (AC) and control site (NC).(adopted from [3])

Does iodine affect selenium content in buckwheat sprouts?

Ana Kroflič[1,2], Ana Jerše[1,2], Nina Kacjan Maršić[3], Mateja Germ[3], Helena Šircelj[3], Vekoslava Stibilj[1]

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Selenium and iodine are essential trace elements for human and animals health. Two-third of the whole human population is suffering from selenium and iodine deficiency. Supplementation of the diet with selenium and iodine is promising approach to improve human nutrition with both elements. Cereals, meats and fish are main source for Se, while iodine is uptaken mainly with salt iodination.

Buckwheat is considered as a functional food with high nutritional value, rich in vitamin B_1, B_2, lysine and potential antioxidants, such as tocopherols and phenolic substances. Buckwheat is consumed also as buckwheat sprouts.

The aim of present work was to research (1) how treatment with Se and I influence on germination, height and mass of buckwheat sprouts, (2) the impact of different forms of Se and I on Se content in sprouts and (3) use of treated buckwheat sprouts for Se fortified food.

In our research we found out, that Se and I treatment have minor effect on agricultural parameters (germination, height and mass of sprouts). Se content were enhanced in all treatments. Se and I enhanced buckwheat sprouts can potentially be used for functional food to increase amount of consumed Se from food.

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Does iodine affect selenium content in buckwheat sprouts?

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Study programme: Ecotechnology
Supervision: prof. dr. Vekoslava Stibilj
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INTRODUCTION

- Selenium and iodine are essential trace elements for humans and animals
- Two-third of the whole human population is suffering from their deficiency
- Selenium and iodine fortification is promising approach for enrichment of Se and I in food
- Buckwheat → high nutritional value → vitamin B_1, B_2, lysine and potential antioxidants, such as tocopherols and phenolic substances (3-flavanols, rutin, phenolic acids)

The aims of present work were to found out:

1. how treatment with Se and I influence on germination, height and mass of buckwheat sprouts
2. effect of different forms of Se and I on Se content in sprouts and
3. use of treated buckwheat sprouts for Se fortified food.

METHODS

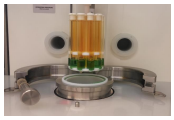
Buckwheat seeds soaked in Se (10 mg/L) and/or I (1000 or 1500 mg/L) solution (in 3 replicates)

↓

10 days of germination

↓

Sampling and lyophilisation



↓

Acid digestion

↓

Se determination (ICP-QQQ)

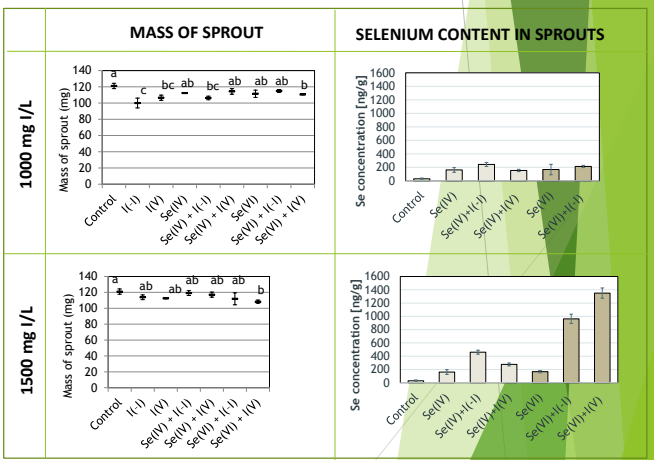
RESULTS

1. INFLUENCE OF IODINE ON GERMINATION, HEIGHT AND MASS OF SPROUTS

- Germinations in all treatments were similar (71-83 %), with exception of sprouts treated with Se(IV) and I(V)
- Height of sprouts varied from 63 to 83 mm
- Se and/or I treatments have minor effect on mass of sprouts

2. INFLUENCE OF IODINE ON SELENIUM CONTENT IN SPROUTS

- Se content was enhanced in all treatments (high standard deviations due to various Se uptake between replicates)
- Se content was similar, regardless to Se forms in soaking solutions
- I presence in soaking solution enhanced amount of Se
- Soaking in Se and 1000 mg I(V)/L has minimal impact on Se content
- Se content was the highest when treated with Se(VI) and 1500 mg I/L in both forms



CONCLUSIONS

- Se content in buckwheat sprouts was similar, regardless to Se forms
- There were minimal differences in agricultural data between soaking in 1000 and 1500 mg I/L
- According to control plants, Se content was increased in all treatments
- I presence in soaking solution enhanced amount of Se
- The highest Se content was measured in Se(VI) and 1500 mg I/L treated sprouts
- Se and I treated buckwheat sprouts can potentially be used for functional food to increase amount of consumed Se from food

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Mimicking nature – iron catalysed oxidation of alcohols

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We have developed new method for selective aerobic oxidation of secondary alcohols. By mimicking nature we were able to obtain ketones in excellent yields. Nitric acid and $FeCl_3$ worked as catalyst in 1,1,1,3,3,3-hexafluoro-propan-2-ol solvent which is essential for reaction to proceed. Reaction was selective for secondary alcohols and no reaction occurred on primary alcohol group. This makes method very useful in synthesis of complex molecules where protection of primary alcohol is needed to avoid undesired reaction. Our method reduces number of steps in synthesis and material used.

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Mimicking nature – iron catalysed oxidation of alcohols

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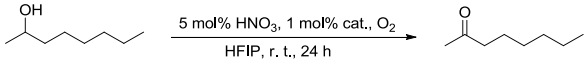
Introduction

Oxidation of alcohol is a fundamental reaction in organic chemistry. Thus obtained ketones are common precursors in synthesis of complex molecules in pharmaceutical and fine chemistry industry. In the past, toxic and environmentally hazardous stoichiometric reagents were used. Following 12 principles of green chemistry O_2 and H_2O_2 are point of interest as clean oxidant.[1] Although O_2 is powerful oxidant its low reactivity prevents its direct application. By using catalyst in oxygen-transfer chain chemists were able to mimic aerobic respiratory chain in the nature. Most often TEMPO[2] and noble metals are used as catalysts[3].

Over the years there has been extensive research done with fluorinated alcohols which showed their unique properties.[4] The most commonly used fluorinated alcohols are 2,2,2-trifluoroethanol (TFE) and 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) which are commercially available. Fluorinated solvents work as template catalyst similar like enzymes. They stabilize transition state by providing complementary charge to a reagent which consequently decreases energy barrier.[5]

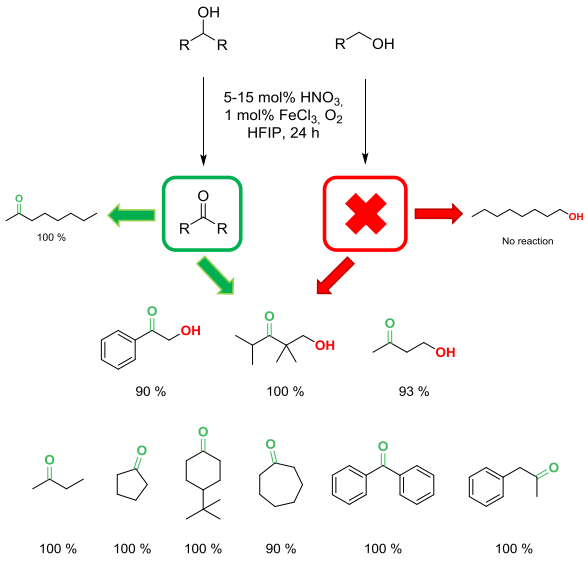
Our goal was to use fluorinated solvents to activate nitric acid in aerobic chain of oxidation of alcohols. We investigated use of nitric acid in cohesion with iron based metal catalyst as a green and cheap metal catalyst. Molecular oxygen was terminal oxidant.

Inorganic co-catalyst



Catalyst	$FeCl_3$	$FeCl_2$	CuI	$AlCl_3$	HCl	$K_3[Fe(CN)_6]$	$Fe(NO_3)_3$	NaCl
Conversion [%]	100	57	7	1	100	2	8	1

Selective oxidation of aliphatic alcohols



Conclusion

We developed simple and practical method for aerobic oxidation of alcohols by nitric acid as catalyst. Reactions proceeded with high selectivity and excellent yield. It is worth mentioning no reaction occurred on primary alcohol group. This makes this method very useful for selective oxidation of alcohols into ketones on big and complex substrates with no need for protection of primary alcohols which is usually done to avoid undesired products.

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Determination of polybrominated diphenyl ethers in sewage sludge with GC-ICP-MS

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Polybrominated diphenyl ethers (PBDEs) belong to the group of brominated flame retardants. They are persistent organic pollutants that are via food chain bioaccumulated or biomagnified in living organisms. Increasing concentrations of PBDEs in humans have caused health concerns due to their toxicity. In municipal wastewater treatment plants, up to 90 % of the PBDEs from wastewater end up in sewage sludge. The analysis of sewage sludge for PBDEs provides valuable information about the risks associated with the re-use of sewage sludge as biosolids for land application. Thus, reliable analytical methods are needed in order to evaluate the contribution of contaminated sewage sludge to the PBDEs' pollution of the environment. The newly developed method is simple, reliable and sensitive. To demonstrate the applicability of the procedure, PBDEs were determined in sewage sludge samples from WWTP Domžale-Kamnik.

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Determination of PBDEs in sewage sludge by GC-ICP-MS

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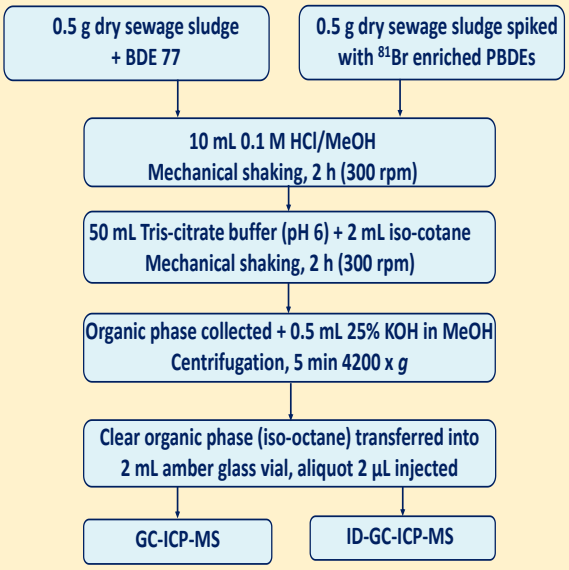
ABSTRACT: Polybrominated diphenyl ethers (PBDEs) are flame retardants, which due to their widespread use are present as pollutants in the environment. Because of their low aqueous solubility and resistance to biodegradation, PBDEs preferentially partition into the sludge during wastewater treatment. Sewage sludge is mostly disposed in landfills or applied to the land. The determination of PBDEs in sewage sludge is a useful strategy for assessing the environmental fate of PBDEs present in wastewaters. The aim of this study was to develop a reliable analytical procedure with minimal sample preparation for a determination of six PBDEs in sewage sludge samples by GC-ICP-MS.

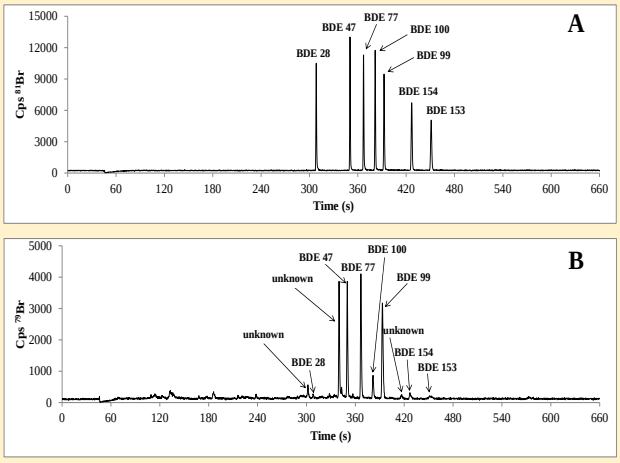
ANALITYCAL PROCEDURE



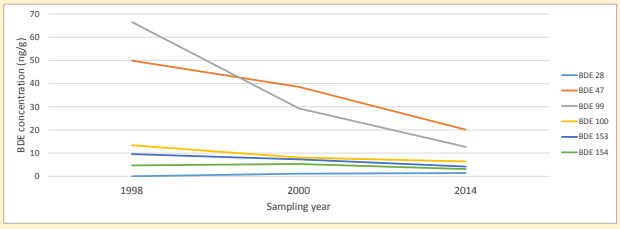
APPLICATION

- The procedure for determining PBDEs in sewage sludge is reliable and sensitive with minimal sample preparation
- Analysing a sewage sludge is important in accordance to safety disposal in landfills or use of sewage sludge as fertilizer

RESULTS



Chromatograms of (A) the six PBDEs and internal standard BDE 77 in isooctane (20 ng mL^{-1} each) and (B) sewage sludge (WTTP Domžale-Kamnik, sampling year 2000) spiked with internal standard BDE 77.



Concentrations of PBDEs found in sewage sludge samples from WWTP Domžale-Kamnik over a period of 16 years.

Razvoj metod za pripravo aciloksialkilnih predzdravil fosfatov ter uporaba topil, primernih za farmacevtsko industrijo

Jerca Pahor,[1,2] **Ajda Podgoršek Berke,**[2,3] **Alen Čusak,**[3,4] **Gregor Kosec,**[3] **Hrvoje Petković,**[3] **Stojan Stavber,**[1,2,5]

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Za uspešno pripravo zdravil je ključna učinkovitost kemijskih metod, ki omogočajo sintezo učinkovin. V primeru aktivnih učinkovin, ki vsebujejo fosfatno skupino, je potrebno te dodatno modificirati, da lahko dosežemo želeno delovanje, t.j. pripraviti »predzdravilo«, ki omogoči učinkovito delovanje zdravila. Ker metod na tem področju primanjkuje, smo tekom naših raziskav razvili novo metodo, ki omogoča uspešno pripravo enega izmed tovrstnih predzdravil. Pri tem smo uporabili ekonomične reakcijske pogoje, s čimer je mogoče zmanjšati stroške sinteze tovrstnih učinkovin in topila, ki so manj škodljiva od topil, ki se jih običajno uporabljajo v sintezni kemiji in so primerna tudi za sintezo v farmacevtski industriji.

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Razvoj metod za pripravo aciloksialkilnih predzdravil fosfatov ter uporaba topil, primernih za farmacevtsko industrijo

Jerca Pahor,[1,2] Ajda Podgoršek Berke,[2,3] Alen Čusak,[3,4] Gregor Kosec,[3] Hrvoje Petković,[3] Stojan Stavber[1,2,5]

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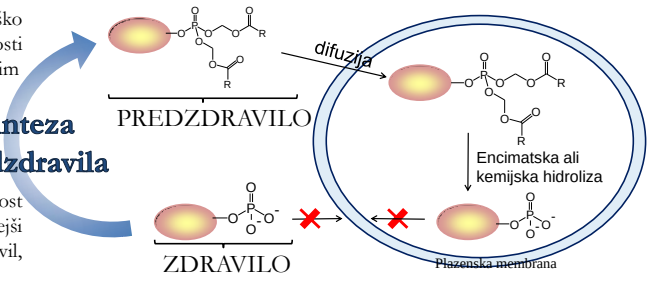
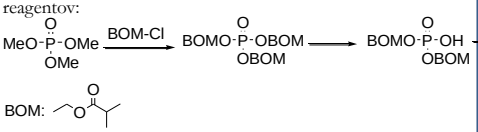
Uvod

Fosfatna skupina je pogost strukturen element v različnih spojinah z biološko aktivnostjo [1,2]. Pri razvoju tovrstnih učinkovin je potrebno precej pozornosti posvetiti omejeni biološki dostopnosti, povezani s slabo permeabilnostjo. Tovrstnim problemom se lahko izognemo s pripravo predzdravila [1,3,4]. Najpogosteje uporabljen tip predzdravila za fosfate so aciloksialkilni estri [1]. Večina objavljenih procedur je vezanih na pripravo POM estrov ter vključuje več-stopenjske reakcije in nizke izkoristke. Še manj obetavni so sintezni postopki za pripravo drugih aciloksialkilnih estrov. Ker kemijska stabilnost teh skupin močno variira, je razvoj metod za učinkovito pripravo najrazličnejši aciloksialkilnih predzdravilnih oblik zato ključen za optimalen razvoj novih zdravil, ki vsebujejo fosfatno skupino.



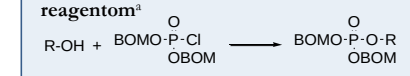
Rezultati

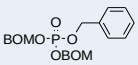
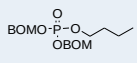
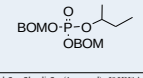
Po naših izkušnjah [6] je za pripravo aciloksialkilnih predzdravil najučinkovitejša uporaba klorofosfatnih reagentov:



Bis(BOM) klorofosfat nov reagent, sintetiziran s pomočjo metode [5].

Fosforiliranje različnih alkoholov z novim reagentom[a]



Alkohol	Produkt	Izkor. [%][b]
BnOH		72
1-BuOH		77
2-BuOH		39

[a]Reakcijski pogoji: alkohol 2a, 2b ali 2c (1 mmol), DIPEA (1,5 ekv.) in DMAP (0,1 ekv.) so bili raztopljeni v DCM (10 ml). Bis(BOM) klorofosfat 1c (1,5 equiv.) je bil dodan kot raztopina v 5 ml DCM pod Ar pri 0°C. Reakcijsko zmes smo pri sobni temperaturi mešali še dodatnih 12 h. [b]Izkoristek izoliranega in očiščenega produkta..

Sinteza BOM predzdravil

Ekonomični reakcijski pogoji:

Uporabljeni:
- **1.5 ekv. reagenta**
- **1.5 ekv. baze**

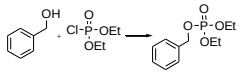
Pogoji uporabljeni za soroden reagent v literaturi [5]:
- **5 ekv. reagenta**
- **7 ekv. baze**

Uporabnost za industrijo

Cenovno ugodnejši proces

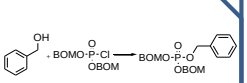
Uporaba manj strupenih topil, primernih za farmacevtsko industrijo

Fosforiliranje v manj strupenih topilih:



V.	Topilo	Izkor. [%][b]
1	DCM	94
2	heptane	31
3	t-BuOMe	50
4	EtOAc	74
5	2-Me-THF	82

[a]Rekcijski pogoji: benzil alkohol 2a (0,5 mmol), DIPEA (1,5 ekv.) in DMAP (0,1 ekv.) so bili raztopljeni v DCM (2,5 ml), dietil klorofosfat 3 je bil dodan po kapljicah pod Ar, rakcijsko zmes pa smo mešali pri sobni temperature še dodatni dve uri. [b]Konverzijo v 3a smo določili z ^{1}H NMR spektroskopijo surove reakcijske zmesi.



V.	Topilo	Izkor. [%][d]
1	DCM	72
2	2-Me-THF	30

[a]Reakcijski pogoji: benzil alkohol 2a(1 mmol), DIPEA (1,5 ekv.) in DMAP (0,1 ekv.) so bili raztopljeni v DCM (10 ml). Bis(BOM) klorofosfat 1c (1,5 equiv.) je bil dodan kot raztopina v 5 ml DCM pod Ar pri 0°C. Reakcijsko zmes smo pri sobni temperaturi mešali še dodatnih 12 h. [d]Izkoristek izoliranega in očiščenega produkta.

Zaključki

- **Sinteza novega klorofosfatnega reagenta, ki omogoča pripravo predzdravil, maskiranih z BOM skupino.**
- **Bis(BOM) klorofosfatni reagent je primeren za fosforiliranje različnih tipov alkoholov.**
- **Mili in ekonomični pogoji fosforiliranja.**
- **Uporaba topil, primernih za farmacevtsko industrijo.**

Zahvala

Avtorji se zahvaljujemo za finančno pomoč Javni agenciji za raziskovalno dejavnost Republike Slovenije (PR-05021 and PR-0134). Delo je bilo financirano tudi s Sedmim okvirnim programom Evropske Komisije (št. FP7/2007-2013, HEALTH-F2-2011, št. sporazuma 277984, TIRCON podjetju Acies Bio d.o.o.). Za pomoč pri NMR analizah se zahvaljujemo Slovenskemu NMR centru Kemijskega inštituta ter Centru za masno spektroskopijo Instituta »Jožef Stefan« za meritve na visokoločljivostnem masnem spektrometru. Za pomoč ter souporabo laboratorijev se zahvaljujemo raziskovalcem podjetja Acies Bio.

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[1] Hecker, S. J.; Erion, M. D. *Journal of Medicinal Chemistry*, 51, 2328-2345, 2008. [2] Srinivasan, B.; Baratashvili, M.; van der Zwaag, M.; Kanon, B.; Colombelli, C.; Lambrechts, R. A.; Schaap, O.; Nollen, E. A.; Podgorsek, A.; Kosec, G.; Petkovic, H.; Hayflick, S.; Tiranti, V.; Reijngoud, D.-J.; Grzeschik, N. A.; Sibon, O. C. M. *Nature Chemical Biology*, 11, 784-792, 2015. [3] Schultz, C. *Bioorganic & Medicinal Chemistry*, 11, 885-898, 2003. [4] Krise, J. P.; Stella, V. J. *Advanced Drug Delivery Reviews*, 19, 287-310, 1996. [5] Hwang, Y.; Cole, P. A. *Organic Letters*, 6, 1555-1556, 2004. [6] Jenko, B.; Kosec., G.; Petkovic, H.; Podgorsek Berke, A.; Pahor, J.; Cusak, A.; Sibon, O. C. M.; Srinivasan, B. Patent, 2015; Vol. WO2015063177.

A study of the thermal release of mercury compounds in FGD gypsum from the Šoštanj Thermal Power Plant using mass spectrometry

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The Šoštanj Thermal Power Plant (ŠTPP) is the biggest power plant in Slovenia and is important in generating the electricity and district heating energy. Flue gas desulphurization (FGD) gypsum ($CaSO4 \cdot 2H_2O$) is a useful by-product of FGD, which is produced by reacting sulphur dioxide (contained in the flue gas) with a $CaCO_3$-water suspension. FGD gypsum is used in many application including new construction materials (e.g., wallboard), agriculture, etc. The burning of coal is also major emission source of mercury, a major global pollutant and mercury compounds are present in wet FGD gypsum as well as other waste product from the power station (fly-ash). These compounds, that are unstable over a long period can decompose and/or released into the environment. Different Hg compounds have different decomposition temperatures and knowledge about the stability of the compounds is important.
A heating furnace coupled with cold vapour atomic absorption spectrometer is the normal method used to measure mercury solid samples. FGD gypsum, however, contains very low concentration of mercury and determining/observing mercury compounds at higher temperatures is almost impossible using this method. To overcome this limitation we have developed a new method based on mass spectrometry. The advantage of the mass spectrometer is its better sensitivity and that it allows us to observe different ions simultaneously. Our work has shown have shown that particle size is an important factor for retaining of Hg in gypsum where much higher concentration of mercury is present in finer compared to coarser fraction. This is important information in the production of new material where low amounts of Hg and other toxic metals might be present.

Temperature stability of Hg compounds in gypsum samples studied by mass spectrometry

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Aim of this study

- To optimize method for temperature fractionation of mercury compounds by using mass spectrometer
- To assess and better understand stability of mercury compounds present in solid by-products from Šoštanj Thermal Power Plant (ŠTPP) particularly in gypsum samples;
- To emphasize the importance of particle size (finer vs. coarse fraction of gypsum);
- Try to interpret mercury reactions following by thermal decomposition of mercury and other compounds related;
- To identify mercury compounds present in gypsum samples;
- To evaluate gypsum as a raw material for further production or disposing to the landfills.

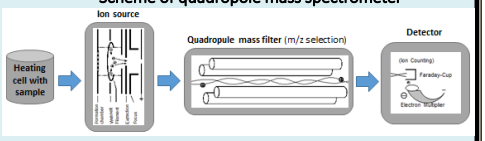
Methodology

TEMPERATURE FRACTIONATION OF GYPSUM SAMPLES:

Quadrupole mass spectrometer (MS):

- Mass of the sample: 1-10 mg;
- Better sensitivity compared to CV AAS but background and interferences problem
- Temperature range: room T – 650 °C;
- Heating rate: 10 °C min^{-1};
- High vacuum: better than $1e^{-6}$ mbar.

Scheme of quadropole mass spectrometer



PARTICLE SIZE DETERMINATION:

Microtrac PSA FRA 9200 based on Fraunhofer laser diffraction

- Gypsum samples from block 6 (ŠTPP);
- 3 finer and 2 coarser fractions.

MULTIELEMENTAL ANALYSES:

k_0-INAA neutron activation analyses:

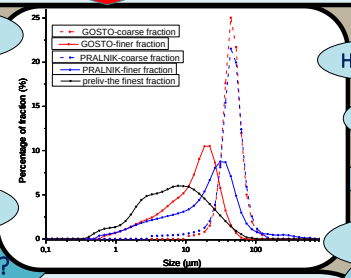
- Analyses of 44 elements was done by k_0-INAA determination;
- Bottom ash, fly ash and gypsum samples were analysed in order to see the distribution of Hg and other trace elements in by-products.

HgSe ?

Hg(0), Hg-comp.(ads.) Al, Fe?

$HgSO_4$?

? ? ?



Hg_2SO_4 ?

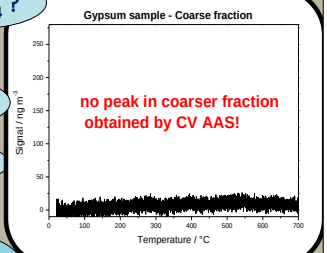
$HgBr_2$?

HgS ?

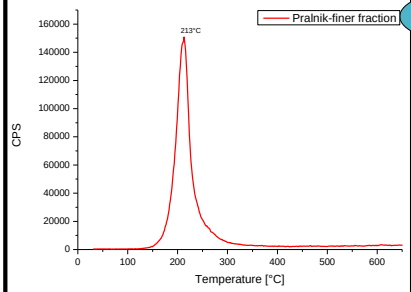
Hg_2Cl_2 ?

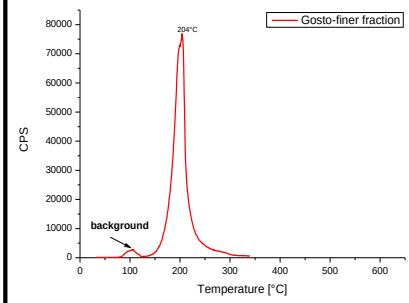
HgO ?

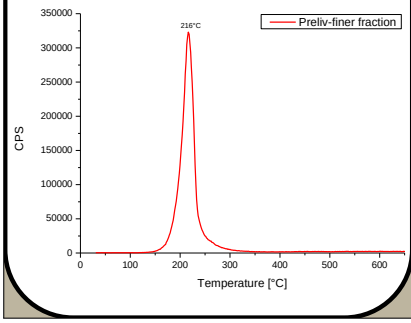
$HgCl_2$?



MS: finer fractions







Results: gypsum samples

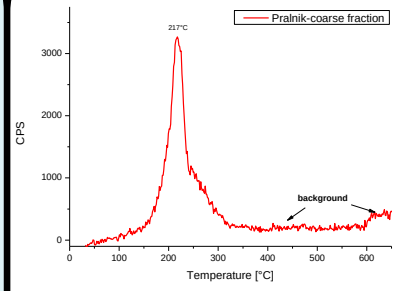
- Fly and bottom ash contains small amount of Hg
- The concentration of Hg in gypsum samples not separated into coarser and finer fraction is ~1 mg kg^{-1}
- Separation into finer and coarser fraction:

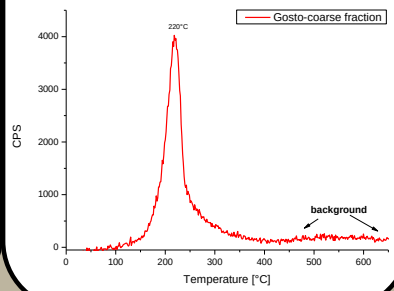
Sample 1 (PRALNIK): finer fraction **8.9 mg kg^{-1}**, coarse fraction **0.3 mg kg^{-1};**
Sample 2 (GOSTO): finer fraction **12.5 mg kg^{-1}**, coarse fraction **0.2 mg kg^{-1}**;
Sample 3 (PRELIV-the finest fraction): only finer fraction **20.6 mg kg^{-1}**

Higher Hg content in finer fraction, but temperature of released peaks are almost the same in finer and coarser fraction → the same Hg-compounds in both fractions

- Knowledge about interaction between Hg, ligands, metals, particles present in FGD slurry is IMPORTANT!
- Hg-compounds have different chemical and physical properties → **different releasing temperature!**

MS: coarser fractions





Conclusions

- Partitioning of Hg in wet FGD system is influenced by particle size;
- Temperature fractionation is useful for determination of temperature stability → important for further production (e.g. wallboard from gypsum) or landfill disposing;
- Identification of Hg-compounds in gypsum is difficult → none of Hg-standard fits exactly with the peak maximum of the real samples ;
- MS is more sensitive than CV AAS and appropriate method for understanding desorption/decomposition processes → observation of more ions at the same time.

Stable isotope composition and elemental profile as a tool for determination of cheese species and geographical origin

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Consumer awareness about importance of nutrition in today's lifestyle is leading to increasing demands for safety and quality control of foodstuff. Adulteration of food, due to large economic profits motivation, is nowadays in various consumer sectors commonly practiced. In recent years the demand for authentic dairy product (especially sheep and goat cheese) is steadily increasing, thus the proof of provenance is becoming a vital issue in food and consumer protection. For verification of correct declared geographical origin and distinguishing cheeses according to animal species, the use of stable isotope composition of light elements in a combination with elemental profile is becoming the industry standard. Obtained researched data can serve to support and protect existence of PDO status of Bovški and Kraški sheep cheese and Tolminc cow cheese, and consequently also for promoting local products and contributing to the local economy.

ISO Fd Food ERA Chair Safety Quality Traceability

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MEDNARODNA PODIPLOMSKA ŠOLA JOŽEFA STEFANA
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STABLE ISOTOPE COMPOSITION AND ELEMENTAL PROFILE AS A TOOL FOR DETERMINATION OF CHEESE SPECIES AND GEOGRAPHICAL ORIGIN

Doris Potočnik[1,2], Marijan Nečemer[3], Nives Ogrinc[1,2]

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Increasing consumer awareness and quality expectations resulted in an increasing interest in demand for high quality dairy products with clear geographical origin, such as product with a Protected Denomination of Origin (PDO) or protect geographical indication (PGI). The Protected Designation of Origin (PDO) trademark has been assigned to numerous local products based strictly on their area of origin, while PGI covering dairy products has at least one said stage that takes place in a certain area. Proof of provenance thus become one of the main topics in food science.

Our study includes a combination of elemental and stable isotope analysis of cow, goat and sheep cheese provided from several farms from different regions of Slovenia to identify the patterns that allow us to distinguish among cow, goat and sheep cheese and to discriminate according to their region of production.

SAMPLING

- 17 samples of sheep cheese
- 6 samples of goat cheese
- 9 samples of cow cheese
- 5 samples with mixed origin; sheep-goat-cow (1 sample), sheep-goat (1 sample), goat-cow (2 samples) and sheep-cow (1 sample)

Two types of cheese have EU PDO status: Bovški sheep cheese (Bovški ovčji sir) and cow cheese (Tolminc) and one local PDO status Kraški sheep cheese (Kraški ovčji sir).

ANALYTICAL METHOD

Stable isotope analysis

- determination of $\delta^{13}C$, $\delta^{15}N$, in casein with IsoPrime 100 – Vario PYRO Cube (OH/CNS)

Elemental analysis

- determination of macro- and micro-elements (P, S, Cl, K, Ca, Zn, Br, Rb, Sr) on a freeze-dried samples by X-ray fluorescence spectrometry (XRF)

Statistical analysis

- calculations and multivariate analysis were carried out using the XLSTAT software package (Addinsoft, New York, USA).

Table 1: Classification of mixted cheese samples: Sheep (S), cow (C), goat (G)

Sample description mixture	Predicted group
S+C+G	S
S+G	S
G+C	G
S+C	S

Mixes samples with added cow milk are identified as pure sheep or goat cheese, due to low content of cows' milk and prevailing sheep or goat milk in the sample. The most influent parameters that distinguish cheese type were K, $\delta^{15}N$, Br, Ca and Zn, S, P and Ca.

CONCLUSIONS

Sheep, cow and goat cheeses produced in close Slovenian regions, at a distance of 10 to 150 km, are characterized using stable isotope ration of C and N and elemental contents of P, S, Cl, K, Ca, Zn, Br, Rb, Sr. Linear discriminant analysis classification is a useful parameter in distinguishing cheeses according to animal species and differentiating geographical origin of sheep's cheese in close regions of productions. This preliminary study can contribute to supporting and protecting existence of PDO status of Bovški and Kraški sheep cheese and Tolminc cow cheese and guarantee to the consumer on its authenticity, which can in turn promote local products and contribute to the local economy.

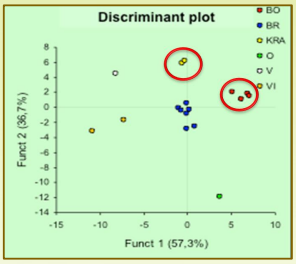

Figure 1: Distribution of sheeps' cheeses according to the location of production: BO-Bovec, BR-Brkini, KRA-Karst, O-Central Slovenia, VI-Vipava, V-South region. The main discriminating variables were K, $\delta^{13}C$, Mn, S, Cl, and P.

Acknowledgements

The work was performed within the project V4-1108 entitled "The use of specific methods for determination and prevention of adulteration of milk and dairy products" financially supported by Slovenian Research Agency and Ministry of Agriculture and the Environment. The research represents a part of the ERA Chair ISO-FOOD project. We thank Mlekarna Planika for supply cow cheese Tolminc and Kmetijski gozdarski zavod Nova Gorica and all local producers of goat and sheep milk and cheese for providing the samples.

Cadmium exposure biomarkers and their associations with renal function biomarkers at low level of exposure

Anja Stajnko[1,2], Janja Snoj Tratnik[1], Darja Mazej[1], Marta Jagodic[1,2], Mladen Krsnik[3], Lijana Kononenko[4], Milena Horvat[1,2], Ingrid Falnoga[1]

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Cadmium (Cd) is a non-essential metal to which general population is mostly life-long exposed through diet, drinking water and/or tobacco smoke. Cd accumulates mostly in kidneys, which are also the major target of its toxicity. To estimate the exposure of population to Cd its levels in urine and blood are measured. To evaluate its possible kidney effects, association between urine Cd levels and levels of urine proteins, which are indicators of kidney function, are studied. Cd levels in urine at elevated exposure (occupational; >4 μg/g Crea) are well established as a biomarker, but its use at low environmental exposure (< 1 μg/g Crea) has recently been questioned.

The aim of present study was to estimate the appropriateness and reliability of U-Cd and blood Cd (B-Cd) as biomarker(s) of choice at low level of exposure (< 0.5 μg/g Crea).

Our results confirmed recent observations that urine Cd at low levels of exposure is not a reliable biomarker. Such low levels are significantly influenced by variations observed in normal physiology (kidney function) or pathology related to unidentified cardiovascular diseases and uncertainties introduced by data normalization for diuresis (by creatinine or SG). For that matter Cd in blood seemed to be much better biomarker for Cd exposure at very low levels.

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Cadmium exposure biomarkers and their associations with renal function biomarkers at low level of exposure

Anja Stajnko[1,2], Janja Snoj Tratnik[1,2], Darja Mazej[1], Marta Jagodic[1,2], Mladen Krsnik[3], Alfred B. Kobal[2], Lijana Kononenko[4], Milena Horvat[1,2], Ingrid Falnoga[1]

Supervisor: doc. dr Ingrid Falnoga

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STUDY BACKGROUND

General Cd health risk assessment relies on association between urine Cd and biomarkers of renal function. U-Cd is a well established biomarker at elevated levels of exposure (>4 µgCd/g Crea), but its use and associations at low levels of exposure (<1.0 µgCd/g Crea) has recently been questioned. As Cd in plasma is mainly bound to metal protective proteins, metallothioneins (MTs), and in this form it uses the transport pathways of renal function biomarkers, Cd positive associations with these biomarkers may be due to co-excretion and not due to Cd renal effects. Moreover, low levels of U-Cd are significantly affected by (pato)physiological variations, accumulated Cd in kidney, recent exposure (due to smoking), and methodological issues (discrepancies in relation with corrections for diuresis).

Aim of present study was to assess the associations between various biomarkers of exposure or/and renal function and to evaluate the appropriateness and reliability of U-Cd or/and B-Cd as biomarker(s) of choice at low level of exposure.

METHODS

❖ **STUDY POPULATION:**

Participants of Slovenian HBM Survey (2007-2015): 1081 healthy occupationally unexposed individuals aged 18-49 years (533 primiparous post-partum females and 548 males)

❖ **DATA:**

questionnaire data: personal, soci-demographic, nutritional, life style;
blood (B) levels : Cd, Pb, Hg, As, Se
urine (U) levels: Cd ;creatinine (Crea); specific gravity (SG); renal function proteins: albumin (Alb), α_1-microglobulin (A1M), N-acetyl-β-glucosaminidase (NAG) and immunoglobulin G (IgG)

❖ **STATISTICAL ANALYSIS:**

differences between groups by ANOVA; correlations between selected biomarkers performed by Pearson's correlation and multiple linear regression (adjusted for diuresis, age, smoking, BMI, B-Pb, B-As, B-Hg, B-Se);

FUTURE WORK

❖ MTs; low molecular proteins involved in essential metal homeostasis (Cu, Zn) and Cd immobilization with detoxification

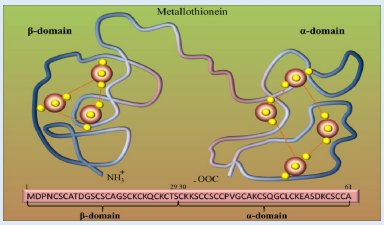

Figure 1: structure of MT (*Ruttkay-Nedecky et al., 2013)*

❖ various subisoforms of MT proteins → polymorphisms in their genes → individual genetic variability → more/less susceptible individuals; Objective: to determine whether there is an interaction between the selected MT polymorphisms and Cd levels and other elements

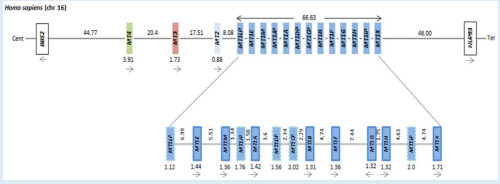

Figure 2: genes of MT subisoforms (Moleirinho et al, 2011)

❖ **EXAMPLES FROM LITERATURE:**

GENE polymorphism	STUDY
MT1a	*higher B-Cd at high exposure (Lei et al.2012)
MT2a	*higher B-Cd, B-Pb & lower B-Zn (Kayaalti et al., 2011)
MT4	*higher Hg in hair (Gundacker et al., 2009)

* minor allele carriers

RESULTS

❖ **LEVELS:**

- GM of blood and urine Cd was bellow 0.5 ng/g (ng/ml) **(Table 1)**
- GMs of renal function biomarkers were far below critical levels **(Table1)**

Table 1: Geometrical means and range of Cd and renal function biomarkers expressed in corrected and uncorrected forms , stratified by gender

BIOMARKER	MALE	FEMALE	p-value
B-Cd (ng/g)	0.22 (0.10 – 4.54)	0.33 (0.10 – 2.93)	<0.001
U-Cd (ng/mL)	0.21 (0.015 – 1.75)	0.17 (0.015 – 3.83)	<0.001
U-Cd/Cea (µg/g)	0.16 (0.03 – 1.14)	0.36 (0.02 – 2.79)	<0.001
U-Cd/SG (ng/mL)	0.22 (0.03 – 1.11)	0.21 (0.04 – 3.65)	0.153
U-IgG/Crea (mg/g)	1.84 (0.53 – 145)	3.99 (0.28 – 535)	<0.001
U-Alb/Crea (mg/g)	5.05 (0.50 – 1791)	10.0 (0.18 – 3227)	<0.001
U-A1M/Crea (mg/g)	3.67 (0.82 – 60.1)	4.81 (0.47 – 38.1)	<0.001
U-NAG/Crea (µkat/g)	22.0 (1.15 – 283.0)	33.6 (0.17 – 295)	<0.001

Reference values: B (U)-Cd <1 ng/g (µg/g Crea); Critical levels: U-Cd > 4 mg/g Crea, U-IgG > 12.8 mg/g Crea, U-Alb > 30 mg/g Crea, U-A1M >10 mg/g Crea, U-NAG > 81 mg/g Crea

❖ **ASSOCIATIONS:**

- Moderate associations → between U-Cd and renal function biomarkers **(Table 2)**
- Corrections for diuresis (U-Crea or SG) changed associations into the weak

Table 2: Pearson's correlation coefficients between renal function biomarkers and Cd exposure (U-Cd, B-Cd) stratified by gender.

		uncorrected	Crea corrected	SG corrected	uncorrected	Crea corrected	SG corrected
biomarker	gender	lnU-Cd			lnB-Cd		
lnU-Cd	M	1	1	1	**0.134****	**0.221****	**0.214****
	F				**0.224****	**0.236****	**0.279****
lnU-IgG	M	**0.267****	**0.191****	**0.129***	0.028ns	0.091ns	0.072ns
	F	**0.366****	**0.145***	**0.140***	0.000ns	-0.014ns	-0.010ns
lnU-Alb	M	**0.433****	**0.105***	**0.189****	-0.024ns	0.033ns	0.042ns
	F	**0.453****	**0.141***	**0.188****	0.014ns	-0.001ns	0.001ns
lnU-A1M	M	**0.396****	**0.279****	**0.222****	***0.106****	***0.157****	***0.166****
	F	**0.252****	0.089#	-0.024ns	***0.098****	0.028ns	0.046ns
lnU-NAG	M	**0.363****	**0.218****	**0.233****	-0.033ns	-0.001ns	0.022ns
	F	**0.383****	**0.267****	**0.209****	***0.104****	0.058ns	***0.104****

** p < 0.001, * p < 0.05, # p< 0.1, ns, not significant;

AFTER MULTIVARIABLE REGRESSION:
- A1M no longer correlated with B-Cd
- NAG marginally correlated with B-Cd

CONCLUSION

❖ Observed associations between U-Cd and renal function biomarkers could be attributed to physiological and other factors (smoking, age) rather than Cd renal effects → U-A1M vs. B-Cd associations disappeared after testing for cofounders difficulties due to U-Crea or SG correction → incomparable results

❖ B-Cd may be more appropriate biomarker at low levels of exposure, although also with considerations

This work was supported by the National Human Biomonitoring program financed by the Ministry of Heath, Chemical Office of the Republic of Slovenia

The fate of zero valent iron nanoparticles after their use in wastewater remediation by single particle ICP-MS

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Providing clean and affordable water to meet human needs is a major global challenge of the 21st century. Current water and wastewater treatment technologies and facilities are reaching their limit for providing adequate water quality to meet human and environmental needs. Therefore, the sustainable use of water, including the efficient use of renewable sources of water, is needed. Nanotechnology with the use of zero valent iron nanoparticles (nZVI) exhibits great potential in efficient wastewater treatment, enabling the reuse of wastewater for secondary purposes. After their use in nanoremediation, nZVI can either agglomerate – lose their nano properties and settle, or they can remain dispersed in water. Their small size and high redox reactivity make them potentially harmful to living organisms. In order to ensure that the use of nZVI does not present a risk to living beings and the environment, single particle ICP-MS method was used for following the removal efficiency and nZVI behaviour after their use in the nanoremediation.

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RusaLCA

INTRODUCTION

Providing clean and affordable water to meet human needs is a major global challenge of the 21st century. Nanotechnology by the use of **zero-valent iron nanoparticles (nZVI)** exhibits great potential in **efficient removal** of **metal contaminants in wastewater treatment.** Despite their extensive use in the wastewater remediation, risk exists that nZVI potentially remain in remediated waters, which presents "nano threat" to the environment and living organisms. The aim of this study was to follow the **Cd^{2+} removal** with nZVI as well as **aggregation, dissolution and settlement of nZVI** after their usage for the remediation of synthetic wastewater.

Materials and methods

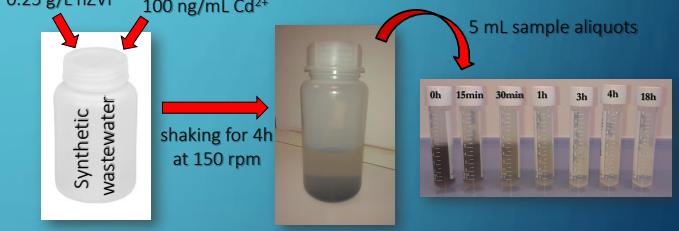
ICP-MS operating parameters for measurement of Fe

Parameter	Type/Value
Nebuliser	MicroMist
Spray chamber	Scott
Skimmer and sampler cone	Ni
Reaction gas flow	5.5 mL H_2 min^{-1}
Nebulizer pump	0.1 rps
Data acquisition mode	TRA
Integration time per isotope	3 ms
Total acquisition time	120-180 s
Isotope monitored	$^{56\rightarrow56}$Fe

Agilent 8800 Triple Quadruple ICP-MS

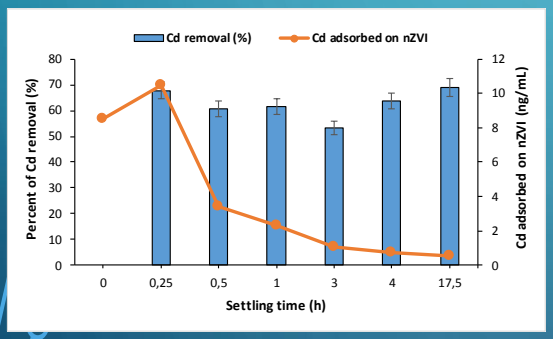
$LOD_{nZVI\ size}$ = 30 nm
$LOD_{nZVI\ conc}$ = 0.980 ng/L
$LOD_{Fe\ diss}$ = 329 ng/L

Simulated nanoremediation experiment



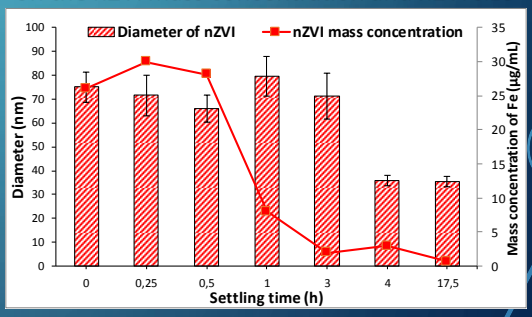
Results and discussion

Influence of settling time on Cd^{2+} removal and the amount of Cd^{2+}adsorbed on nZVI



- The initial rapid adsorption of Cd^{2+} on nZVI
- Adsorption of Cd^{2+} starts to decrease after half hour of settling
- Expected concentrations of Cd in wastewaters are below 10 ng/mL

Influence of settling time on the nZVI mass concentration and nZVI size



- 97 % of nZVI is removed at the end of settling

CONCLUSIONS

- **Sensitive, interference-free** measurements of nZVI by SP-ICP-MS was achieved by detecting the most abundant ^{56}Fe isotope with the use of **H_2 as a reaction gas** in **MS/MS mode.**
- The use of nZVI **does not present environmental threat** due to their **rapid aggregation** and **settling.**
- Understanding the processes of the **nZVI behaviour** after the treatment of contaminated waters and **mechanisms of Cd^{2+} removal** is essential to achieve **effective nanoremediation** and to ensure conditions, which **prevent nano threat** towards environment and living beings.

Speciation of mercury and microbial communities in the seawater of the Central Adriatic Sea

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Among the trace metals, mercury is one of the contaminants of most concern because of its high toxicity, persistence and accumulative behaviour in the environment and biota. Mercury can reside in the atmosphere for a long time and be transported over a large geographical distance and is therefore considered a global environmental problem. Due to transformation and transport processes mercury can travel between environmental compartments; from atmosphere to water, soil and biota. Natural bacterial processes in seawater and in sediments can convert inorganic Hg into its most toxic form, methylmercury, where it can be rapidly incorporated into the food web. The uptake of methylmercury by organisms is much quicker than its elimination from the body, so MeHg concentrations will increase with continuing exposure as organisms grow older. This increase with age is referred to as bioaccumulation. Species with longer lifespan are more likely to bioaccumulate higher amounts of methylmercury with continued exposure. Persistent bioaccumulative contaminants, like methylmercury, build up in much greater levels in predators than in their prey. This increase with each step up the food web (trophic level) is called biomagnification. So, in the marine food chain, methylmercury is bioaccumulated and biomagnified with the highest levels found in older predatory fish. But the initial bioaccumulation of methylmercury by phytoplankton represents the biggest single contribution to overall bioaccumulation in marine food webs.

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Mercury and microbes' relationships in the seawater of the Central Adriatic Sea during cooler and warmer season

Igor Živković, mag. chem.

Study programme: Ecotechnology

Jožef Stefan International Postgraduate School

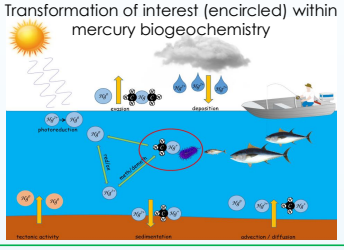
Mentor: prof. dr. Milena Horvat

Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana

Introduction

- Biological processes can transform mercury species
- Bioaccumulation and biomagnification of Hg species (especially methylmercury, MeHg)
- MeHg production is connected to the specific configuration of the ecosystem
  - It depends on the organic carbon remineralisation processes
  - MeHg connection with the basic structure of marine food web
- Hypothesis:
  - MeHg accumulation follows the same scavenging path for nutrients at low concentration in the microbial biomass
  - Critical step in the marine food web might be prokaryotic microbes

Transformation of interest (encircled) within mercury biogeochemistry



Objective

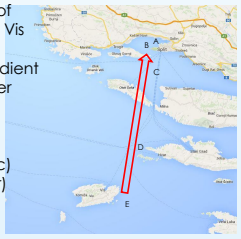
- Biotic methylation of Hg in oxic media (sea)
- Hg species are produced by different microorganisms
- Role of the microbial web structure
  - Which microorganisms are the most important for MeHg production?
- Formation of MeHg depends:
  - Structure of the food web
  - Extent of Hg accumulation in the marine food web

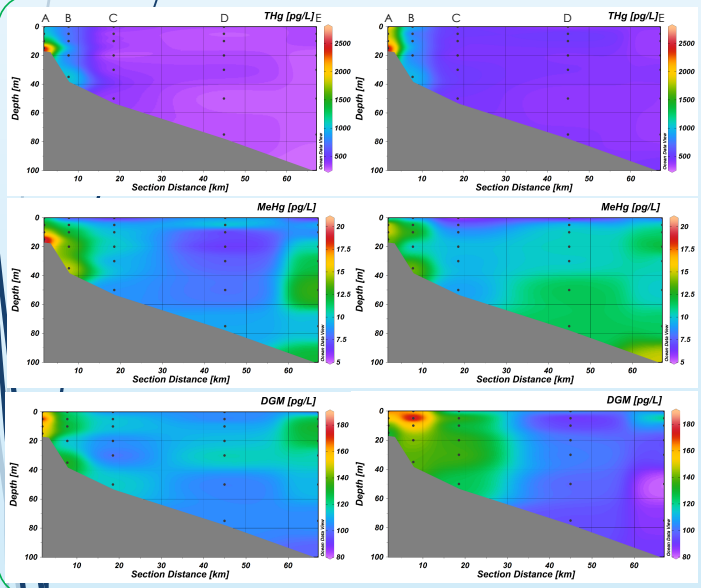
Methods

- Monthly sea water sampling
- Analysis of Hg species
  - Total mercury (THg)
  - Dissolved gaseous mercury (DGM)
  - Methylmercury (MeHg)
- Microbiological measurements
  - Total number of bacteria
  - Picoeukaryotes
  - Heterotrophic nanoflagellates
  - Autotrophic nanoflagellates
  - Bacterial production

Sampling locations

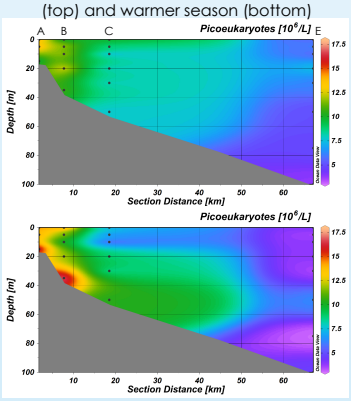
- Transect from the Bay of Kaštela to the island of Vis (Croatia)
- THg concentration gradient
  - Kaštela Bay – former chlor-alkali plant
  - Vis – pristine environment
- A – Kaštela Bay (Vranjic)
- B – Kaštela Bay (center)
- C – Split Channel
- D – Island of Hvar
- E – Island of Vis





THg, MeHg and DGM seasonal transect profiles during cooler season (left) and warmer season (right)

Picoeukaryotes transect profiles during cooler season (top) and warmer season (bottom)



Graphs:

- Letter on each graph corresponds to sampling point as indicated on the map
- Measurements were performed from March 2014 to December 2015

Conclusions

1. Vranjic (in Kaštela Bay) is the closest station to mercury source and shows the highest values for THg, while lowest are found at Island of Vis.
2. MeHg has similar values for both stations in the Kaštela Bay, except after strong wind which might have changed distribution.
3. Kaštela Bay has the highest number of picoeukariotes due to eutrophic conditions for which surrounding cities are responsible.
4. For future work, we will try to establish correlations between mercury and microbial species.

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Informacijske in komunikacijske tehnologije (Information and Communication Technologies)

NLOS Channel Detection with Multilayer Perceptron in Low-Rate Personal Area Networks for Indoor Localization Accuracy Improvement

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Wireless localization takes important part in several application areas. It can be used for indoor industrial robot navigation, visitor navigation at a fair, inventory monitoring, etc. One way to correctly position devices or people in space is to measure ranges from several points in space (in this case with wireless sensors communication) and combine this distances to a relative or an absolute position with method called multilateration.

Multilateration is efficient mathematical method to calculate position but is sensitive to distance measurement errors. Wireless ranging devices are susceptible to non-line-of-sight distance measurement bias. This happens because of longer signal traveling path caused by reflections in environment compared to actual shortest distance between devices which is not obstructed by obstacles.

To eliminate or at least mitigate the effects of non-line-of-sight distance measurements impacting positioning accuracy we proposed signal classifier based on multilayer perceptron machine learning algorithm which in 90% cases correctly decides on a nature of distance measurement (line-of-sight or non-line-of-sight) according to available frame quality indicators.

Correctly classified non-line-of-sight distances can be removed from localization set and thus preventing positioning accuracy degradation. In experimental setup this improved the localization accuracy from 1.93 m to 0.59 m.

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NLOS Channel Detection with Multilayer Perceptron in Low-Rate Personal Area Networks for Indoor Localization Accuracy Improvement

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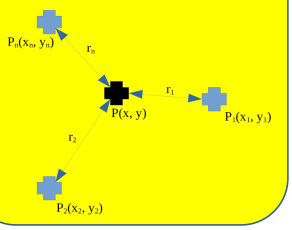
Study programme: Information and Communication Technologies
Mentor: Assoc. Prof. Dr. Mihael Mohorčič

Motivation:

- NLOS range measurements (high range error) impact localization accuracy
- Positioning accuracy can be improved by eliminating NLOS range measurements
- NLOS ranges can be predicted from current communication channel condition

Node position:



Locating node with multilateration:

Distance between unknown position and anchor node:

$$r_i = \sqrt{(x_i - x)^2 + (y_i - y)^2}$$

Linearizing system by substracting last equation from the first n-1:

$$x_1^2 - x_n^2 + y_1^2 - y_n^2 + r_n^2 - r_1^2 = 2(x_1 - x_n)x + 2(y_1 - y_n)y$$
$$\vdots$$
$$x_{n-1}^2 - x_n^2 + y_{n-1}^2 - y_n^2 + r_n^2 - r_{n-1}^2 = 2(x_{n-1} - x_n)x + 2(y_{n-1} - y_n)y$$

Reordering system in the form $\mathbf{A}x = \mathbf{b}$:

$$\mathbf{A} = \begin{bmatrix} 2(x_1 - x_n) & 2(y_1 - y_n) \\ \vdots & \vdots \\ 2(x_{n-1} - x_n) & 2(y_{n-1} - y_n) \end{bmatrix}$$

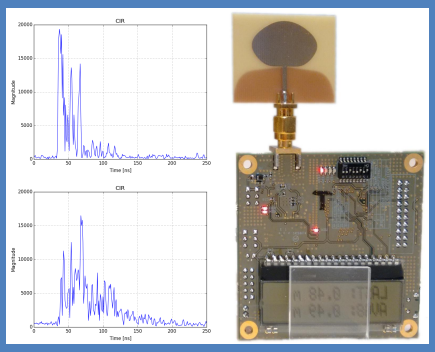
$$\mathbf{b} = \begin{bmatrix} x_1^2 - x_n^2 + y_1^2 - y_n^2 + r_n^2 - r_1^2 \\ x_{n-1}^2 - x_n^2 + y_{n-1}^2 - y_n^2 + r_n^2 - r_{n-1}^2 \end{bmatrix}$$

Solving system using standard least-squares approach:

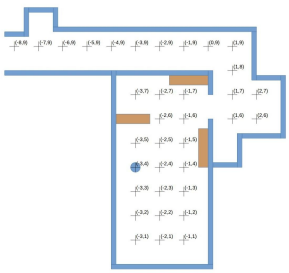
$$\mathbf{P}(x, y) = \hat{\mathbf{x}} = (\mathbf{A}^T\mathbf{A})^{-1}\mathbf{A}^T\mathbf{b}$$

DecaWave DWM100 IEEE 802.15.4-2011 UWB Radio:

- Using bandwidths from 499.2 MHz to 1331.2 MHz
- Communication and ranging capability
- Low power spectral density (< -41.3 dBm/MHz)
- Channel center frequencies from 3.5GHz to 6.5 GHz
- ***Channel impulse response estimation***
- Low interference with existing technologies
- High multipath effect immunity
- 10 cm ranging accuracy



Range acquisition map:



Conclusions:

- LOS/NLOS range classification with 90% accuracy when using simple frame quality indicators
- Improved localisation accuracy with signal classification
- Multilateration unsuitable for practical use where anchors are placed in straight line or at the same height
- For real life applications more numerically stable method than multilateration is needed or multilateration with smart anchor selection algorithm should be used

	Mean [m]	Std_dev [m]	Max [m]
3 anchors: LOS and NLOS	1.93	3.98	122.05
4 anchors: LOS and NLOS	1.13	1.41	65.70
3 anchors: LOS only	0.28	0.29	4.23
4 anchors: LOS only	0.19	0.14	2.78
3 anchors: with classifier	0.59	0.97	33.36
4 anchors: with classifier	0.40	0.51	21.92

Passive Ankle Exoskeleton: Design and Practical Evaluation

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Exoskeletons or wearable robotic mechanisms are assistive robots, which now face intensive development. They can improve the quality of lives for patients with disabilities, older people, workers and even healthy people. Because of a rapidly aging population of industrial societies, the proportion of older people is getting larger. Exoskeletons could improve their lives and prolong their individual social independence, which could have benefits for the users as well as long-term benefits for the society.

Right now, many different actuated exoskeletons exist, some are also commercially available, but are not yet widely affordable. The high prices result from complicated mechanics, actuators, sensors, complicated controllers, electronics and the need for batteries. Unpowered passive exoskeleton solutions exist that have some distinct advantages over the actuated solutions, since they are simpler, lighter, easier to operate and do not use electronics or controllers, and are consequently cheaper. Because of this, they possess a better chance of integration and end-user acceptance.

In this paper a passive exoskeleton is presented with results from a study of its effect on the user during walking. The unpowered ankle exoskeleton reduced the metabolic cost of walking, when correct clutch timing was setup and when a spring with a proper stiffness was selected. The mechanism of clutch operation is at this stage not yet fully robust, so the average metabolic consumption reduction differs greatly from subject to subject. Additional research is still needed and the exoskeleton design could still be improved. The current results will help improve the concept, the design and robust clutch operation and bring the exoskeleton closer to the usage.

The concept could potentially be extended to other human joints, instead of only the ankle, which could result in novel new types of exoskeletons that work in a hybrid unpowered and powered combination to achieve greater energy efficiency and performance. The exoskeleton could be used by any user, that is able to walk, and would like to walk with less effort.

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A passive unpowered ankle exoskeleton for walking assistance

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Supervisor: dr. ANDREJ GAMS
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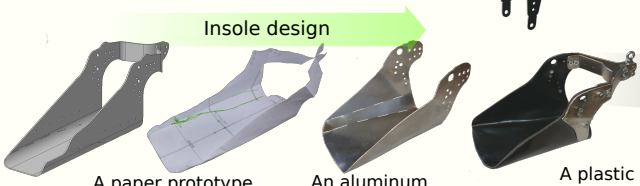
Motivation:

- Recent achievements in the research of unpowered exoskeletons (Collins 2015)
- **Advantages** of passive solutions over actuated solutions, because they are simpler, lighter, more available, cheaper
- Potential **wide range of applications**
- Because, **anyone** who wants to walk with less effort **can use it**

Exoskeleton design:

- **Safety, comfort and ergonomic design are important**
- Simple is more likely to be accepted by the end user
- Exoskeleton should be light-weight, have minimal inertia, and not impede on the user
- It should have a proper size and a proper number of kinematic degrees of freedom

Designed insole must:
- be comfortable
- fit in a shoe
- be strong enough

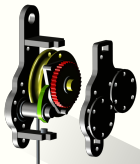


A rough 3D-model

A paper prototype insole to better estimate the correct insole shape

An aluminum prototype insole manufactured based on an improved 3D-model

A plastic insole made with heat-forming process and reinforced with stainless steel



Mechanical clutch

Outer metal frame

Fig.: Exoskeleton prototype

Pilot study:

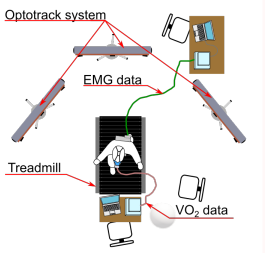


Fig.: The measurement system.

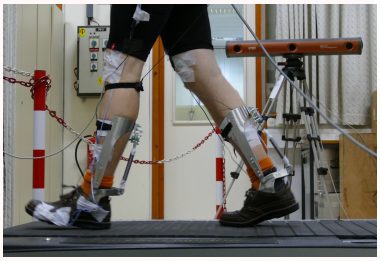


Fig.: Subject using the exoskeleton.

- **Exoskeleton was tested in a randomized cross-over pilot study**
- **Four participants** performed five 10-min walking sessions each
- The walking sessions included a referential (exoskeleton free) walk; a walk with the spring-less exoskeleton and three walks with springs of different stiffness (5, 12, 20 N/mm)
- **Oxygen consumption (VO_2) and muscle EMG activity were measured**, to asses the physiological effect of the exoskeleton on the user

Results:

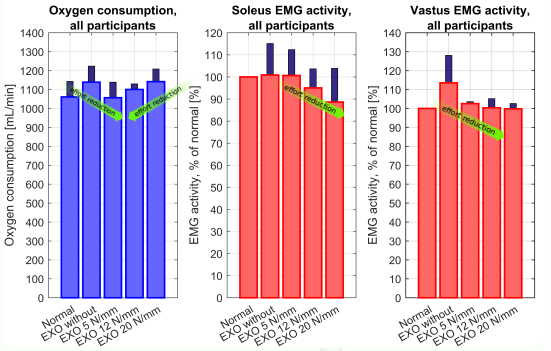


Fig.: Graphs of oxygen consumption (VO_2) and muscle EMG activity for different boundary conditions

- **Metabolic cost reduction can be observed** between walks of different boundary conditions
- **Muscle effort reduction can be observed**, when walking with springs of increasing stiffness

Conclusion:

- The collected **data shows** that the exoskeleton **can reduce** the metabolic cost of walking, if the clutch timing is correct and a spring has a suitable stiffness
- The exoskeleton **design can influence the metabolic cost reduction** greatly
- The appropriate spring stiffness was narrowed down to be smaller than 12 N/mm and near 5 N/mm
- The pilot study confirmed the potential of unpowered exoskeleton for reducing the energy cost of walking

Future outlook:

- Current design improvement
- Weight/strength optimization
- Improving robustness of operation
- Extending the concept to other joints
- Combining unpowered and powered solutions

References:

Collins S. H. , et al. (2015), “Reducing the energy cost of human walking using an unpowered exoskeleton,” Nature, vol. 522, no. 7555, pp. 212–215

Knowledge extraction of evidence-based dietary recommendations

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Food-based dietary guidelines (FDBGs) are simple advices on healthy eating, aimed at the general public. They give an indication of what a person should be eating in terms of foods, and provides a basic framework to apply when making healthy dietary choices and planning meals. The main goal of FBDGs is to improve public health and well-being.

The European Food Safety Agency (EFSA) is an example of the authority, which provides dietary reference values (DRVs) as a complete set of nutrient recommendations and quantitative reference values for nutritional intakes.

Most countries have established their own national DRVs and FBDGs that consider beside international recommendations and guidelines also local conditions and national eating culture and habits and are reviewed and updated from time to time.

In several chronic diseases, like diabetes, celiac disease, chronic kidney disease, some cancers, Parkinson's disease etc., nutritional therapy is used to help patients get energy and nutrients they need to deal with the effects of disease and its treatment.

Personalized dietary recommendations consider genetic predisposition to chronic disease and phenotypic information on anthropometry, physical activity, clinical parameters and biochemical markers of nutritional status, and give strategies to dramatically reduce the chronic–disease risk.

In public health as well as in clinical practice, dietary recommendations should be based on evidence-based principles, considering scientific knowledge, expert consensus and clinical experience. In case of chronic patients, the best available evidence must take into account individual circumstances, preferences, and cultural and ethnic preferences, and the patient should be involved in the decision-making process.

As today amount of information is massive and is quickly increasing, computer-based tools for systematic knowledge identification, extraction and exploration are welcome to support human experts in decision-making about appropriate nutritional care for specific disease states or conditions in typical settings.

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Knowledge extraction of evidence-based dietary recommendations

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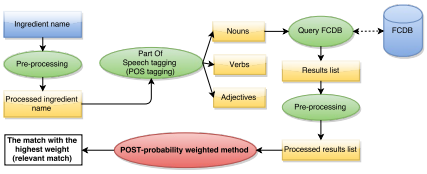
ISO Fd Food ERA Chair — Safety Quality Traceability

Motivation

- Unhealthy diet can lead to diseases such as diabetes, cardiovascular disease and stroke, and some type of cancer, among other health-related problems.
- Dietary Reference Intakes (DRIs) are values that are quantitative estimates of nutrient intakes that can be used for planning and assessing the diets for healthy people.
- Food-composition studies are carried out to determine the chemical nature of components in food that affect human health.
- Complete mapping of the human-genome sequence has introduced a possibility of personalized dietary recommendations based on the individual's genetic profile.

Food matching

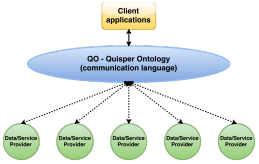
- People provide names of recipe ingredients and names of food analyses as unstructured data.
- Recipe ingredients -> Food composition databases (FCDBs)
- An information retrieval method, called POS tagging-probability weighted method, is used for matching Internet recipe ingredients with food composition data.
- 91.82% of 1,615 different ingredients were matched with food composition data.

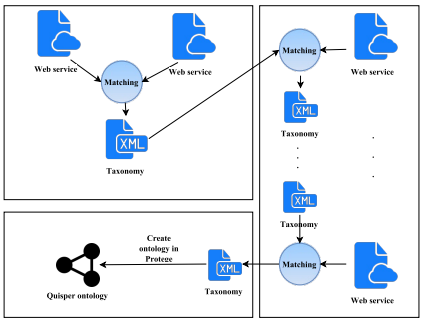


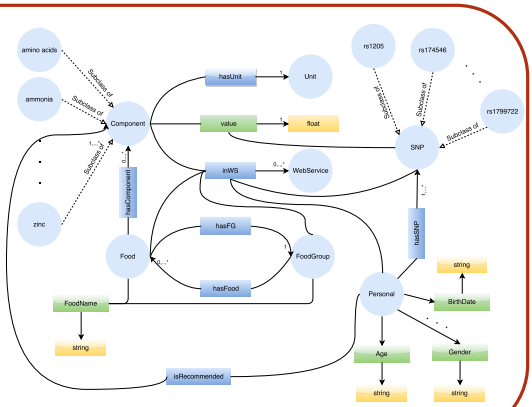
Recipe	FCDB	Code
gibanica	prekmurska gibanica	RECMEM000162
omaka sojina	sojina omaka tamari (iz soje)	16124
pomarančе	pomaranča	P0402
melona	melona casaba melona honeydew	9183 9184

Ontology Learning

- How to extract knowledge from heterogeneous data sources using different ways of describing and classifying the data?
- Ontology, semi-automatic

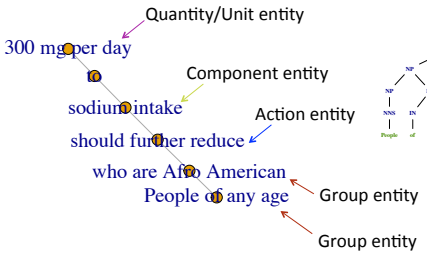


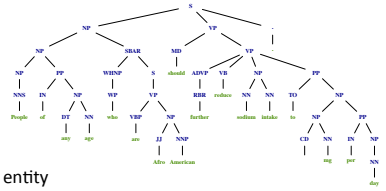




Named-Entity Linking

- Grammar and dictionary based named-Entity Linking is used to help people to follow new knowledge about healthy diet.
- "People of any age who are Afro Americans should further reduce the sodium intake to 300 mg per day."
- Entities: Food, Component, Quantity/Unit, Action, Group





Activity and stress monitoring using smartphone and wrist device

Martin Gjoreski[1,2], Vito Janko[1,2], Hristijan Gjoreski[1], Božidara Cvetkovć[1,2], Mitja Luštrek[1], Matjaž Gams[1]

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Physical and mental health are closely related and impact the overall quality of life simultaneously. The need for health monitoring was confirmed by the European Commission by estimating the costs of work-related stress at €20 billion a year due to absence from work and decreased productivity.

Regular physical activity has a positive impact on one's life, yet only a small fraction of the modern population exercises sufficiently. To appropriately motivate people for increasing their physical activity, it is important to quantify it first. Similarly, the stressful environment of today's world introduces another problem, stress, which should be addressed in order to prevent negative health consequences of chronic stress.

We propose a smartphone application capable of monitoring physical activity and mental stress using data provided from smartphone sensors and a commercial wrist device. The application consists of two modules, an activity recognition (AR) module and a stress detection module. The AR module continuously recognizes user's activity with accuracy of 91%.

The stress detection module uses data provided by the AR module and a commercial wrist device equipped with standard bio-sensors and an accelerometer. The stress detection module was trained on 21 subjects in a laboratory setting and tested on five subjects in a real-life setting achieving accuracy of 92% for detection of stressful events.

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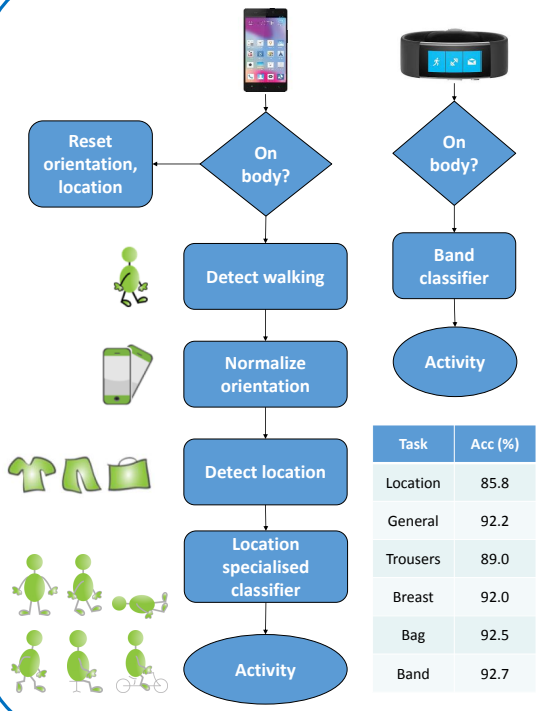
Motivation

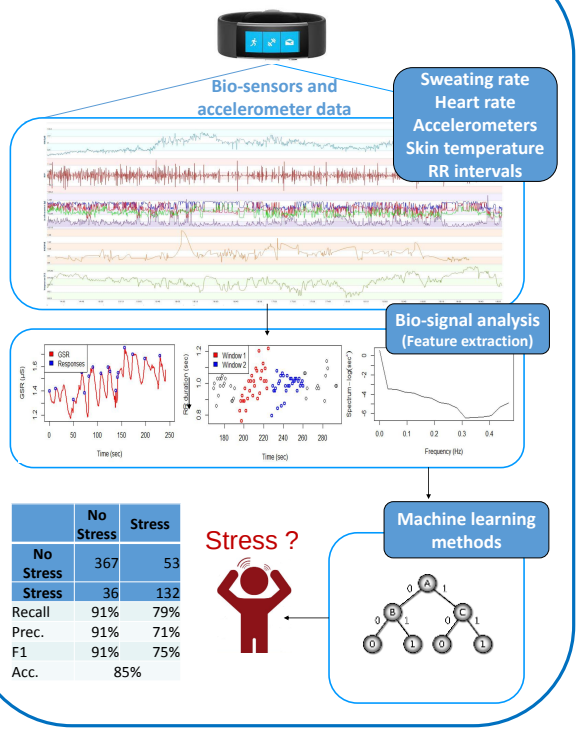
- Physical and mental health are closely related and impact the overall quality of life simultaneously.
- The need for health monitoring was confirmed by the European Commission by estimating the costs of work-related stress at €20 billion a year due to absence from work and decreased productivity.
- Regular physical activity have a positive impact on one's life, yet only a small fraction of the modern population exercises sufficiently. To appropriately motivate people for increasing their physical activity, it is important to quantify it first.
- Similarly, the stressful environment of today's world introduces another problem, stress, which should be addressed in order to prevent negative health consequences of chronic stress. .

Activity recognition



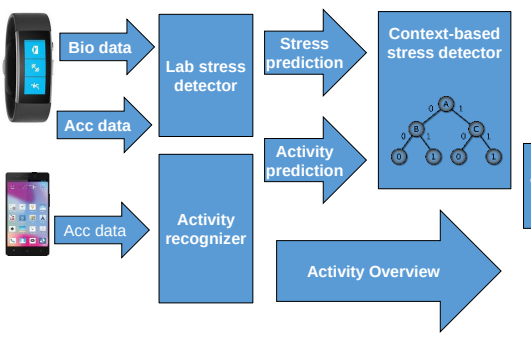
Task	Acc (%)
Location	85.8
General	92.2
Trousers	89.0
Breast	92.0
Bag	92.5
Band	92.7

Stress detection



	No Stress	Stress
No Stress	367	53
Stress	36	132
Recall	91%	79%
Prec.	91%	71%
F1	91%	75%
Acc.	85%	

Combination of modules



Smartphone application

Integrating predictive and decision modelling in decision support system for water protection from phytochemicals

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In this paper we demonstrated an approach for integration of predictive and decision modelling into a decision support system. The described approach employed machine learning and data mining methodology for predictive modelling tasks, and DEX methodology for decision modelling task. The former is applied, in order, to build models that accurately predict uncertain conditions of the state of the world in decision making process, while the latter use such predictions in order to make a better evaluation of the defined alternatives. Finally, the approach of integration is implemented in a web-based decision support system for decision problem from the domain of water protection from pesticides used in agriculture. The web-based decision support system includes four steps in the workflow: description of the planned application of pesticides, prediction of drainage outflow (quantity) and periods of intensive drainage events (time period), risk evaluation, and, if the planned application of pesticides is evaluated as risky, generation of mitigation measures (alternatives) that leads to the solution of the given decision problem.

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Integrating predictive and decision modelling in decision support system for water protection from phytochemicals

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Marko Debeljak (supervisor)

Abstract

Most real-world decision problems over multiple criteria are facing uncertain conditions during the decision making process. Such uncertainty appears mainly due to lack of information about the state of the world and possible outcomes of a decision. Therefore, additional analysis are required in order to estimate the risk of uncertainty that influences the decision making process. We propose an integration of predictive and decision modelling within a decision support system, in order to avoid additional analysis. The former is proposed to take the role of oracle that will bring more accurate information within the decision making process and quantify its uncertainty. The latter considers such predictions and uncertainty quantification, and provides decision models that consume additional information. The proposed integration is applied on a decision problem from the domain of water protection from pesticides used in agriculture, which results in web-based decision support system.

Predictive modelling

The predictive modelling of water flows from the fields and drainage periods has been done using machine learning and data mining methodology. Precisely, we use a bagging approach for building ensembles models of both regression and model trees.

Decision modelling

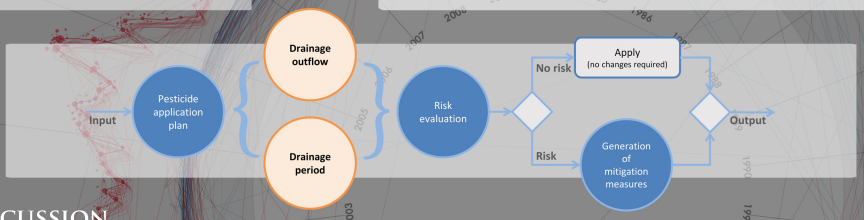
Decision modelling task for building qualitative multi-criteria decision models, is done using DEX methodology. The methodology is implemented in the DEXi software package

Data & Expert knowledge

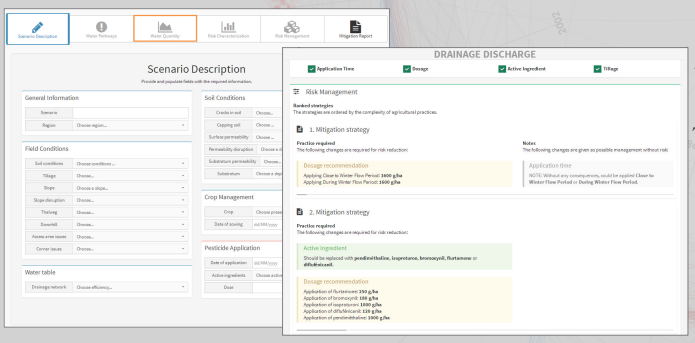
The data we used in our study are from the experimental site La Jaillière, run by the technical institute ARVALIS - Institut du Végétal. It is situated at the southern end of the Armorican massif in western France. The site has been dedicated to the study of the influence of agricultural management practices on water quality since 1987. It is a reference site for the European Commission FOCUS working group.

Data from the experimental site of La Jaillière are collected since 1987 and include data about the agricultural practices (tillage, sowing, fertilizing and pesticides application dates), the amount of water flows and the concentration of the water solution (mineral and active substances) in the water pathways (drainage and runoff).

For the decision modelling, we used expert knowledge for water and pollutant pathways through the soil under certain crop management, field and landscape conditions, provided by experts from ARVALIS.



Results & discussion



The predictive modelling task covers predictive models built for both uncertain conditions on the field, drainage outflow and drainage period. They are further incorporated into the final web-based DSS with a role to extract as much as possible valuable information about the uncertain conditions on the field.

The decision modelling task involves building DEX decision models for ecological risk evaluation of planed applications of pesticides at the field scale. These models also evaluate each possible mitigation measure in coordination with previously evaluated ecological risk and feasible crop management actions on the field, out of which mitigation measures (alternatives) are constructed.

The DSS is implemented as a web-based application where DSS's graphical user interface contains two main parts: input (or scenario description) and evaluation report.

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)

Multi-dimensional analysis of PPMI data

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The major goal in Parkinson's disease treatment is to look for a disease-modifying treatment that will hopefully slow, prevent or even reverse the effects of the disease. A crucial step towards that goal is the discovery and validation of disease biomarkers. The current set of identified biomarkers is not fully validated and is not optimal.

In this work, we used data acquired from the Parkinson's Progression Markers Initiative (PPMI). The goal is to search for groups of subjects that exhibit similar behavior in terms of their motor assessment scores. These scores tell us how much a person has a motor impairment in a certain region of his body (left arm, right leg, speech etc.). On the identified groups/clusters of subjects, their motor assessment scores were described using imaging data information from fMRIs (functional magnetic resonance imaging) and DaT scans (specialized imaging technique for detecting levels of dopamine in the brain).

The results from the use of predictive clustering trees for analysis of such data are promising. With this technique, we are able to predict all of the patients' motor scores from their imaging scans. This can save time, money and effort from specialists and can also give us an insight or even detect the biomarkers that indicate Parkinson's disease at a person before the disease even starts to manifest.

Multi-dimensional analysis of PPMI data

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Problem Definition

- The search for a disease-modifying treatment is the major goal of Parkinson's Disease (PD) research
  - discovery and validation of disease biomarkers is a crucial step
- The Parkinson's Progression Markers Initiative [3] is an observational clinical study for verification of the discovered biomarkers
  - combines the knowledge from multiple worldwide cohort studies offering an exhaustive set of clinical, imaging and biosample data
- The identification of a valid set of biomarkers for PD is not completed

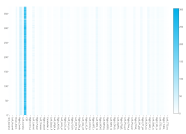
Goal: Identify groups of subjects that exhibit similar behaviors in terms of motor assessment scores and describe them with fMRI and DaTscan features

The dataset concerns 4873 subjects described with:

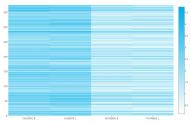
- 135 Regions of interest (ROIs) from fMRIs represented as volumes from different parts of the brain [4]
- 4 Caudate and putamen's striatal binding ratio results from DaT (dopamine transporters) scans
- 35 motor examination scores from the Unified Parkinson's Disease Rating Scale [5]

Data Visualizations

Motor assessment scores



ROIs



DaTscan

Procedure

Two sets of examples:

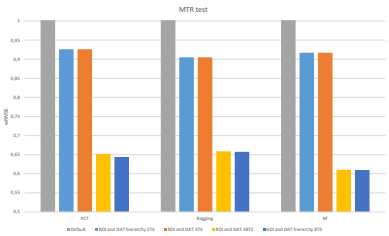
- Earliest scores only (baseline) for each patient, 374 examples
- All instances for each patients, 4873 examples

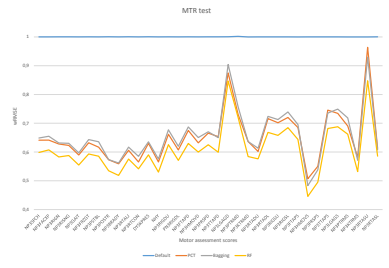
Evaluation performed for both regular and hierarchical regression (the sums of all of the scores, and the sum of the scores for individual parts of the body used for clustering)

Predictive accuracy assessed by using 10-fold cross-validation

Results and Conclusion

The lowest error is achieved using random forest, 0.616 when we use all of the scores whereas the default error is 1



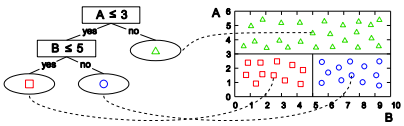


- ***Caudate*** and ***putamen*** appear highest in the tree, which corresponds with other studies
- Hierarchical regression does not improve the results significantly
- The single model is **valid for all motor scores** and exploits the inter-dependencies between the scores

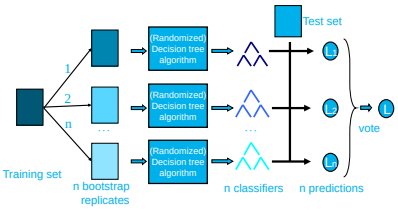
Methodology

Predictive Clustering Trees

- PCTs are a generalization of decision trees for predicting structured outputs



- Constructed with standard top-down induction of decision trees algorithm
- Distance measure: minimization of intra-cluster aggregated Gini indices



Bagging: Uses standard decision tree building algorithm as base classifier

Random Forests: At each node the best test is selected from random feature subspace

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PARKINSON'S PROGRESSION MARKERS INITIATIVE
Play a Part in Parkinson's Research

Centre Hospitalier Universitaire Vaudois

Model-based fault diagnosis with Gaussian process regression of nominal model residuals

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Fault detection, isolation (FDI) is a subfield of control engineering which concerns itself with monitoring a system, identifying when a fault has occurred, and pinpointing the type of fault and its location. It is an important, but challenging problem in chemical, nuclear, aerospace, and automotive engineering.

An interesting subfield is machine fault diagnosis, concerned with finding faults arising in machines. To identify the most probable faults leading to failure, model-based methods have been developed in order to check consistency between the monitored system and its model.

Discrepancy between a process and its model affects reliability of the diagnostic system, either through decreased sensitivity or frequent false alarm rates.

The problem tackled in this paper is how to handle unmodelled effects, caused by imperfect nominal models. We propose nonparametric statistical modelling of the error in nominal model. The Gaussian process model is used to predict the discrepancy between process and nominal model. Hence, the the two models together may represent a refined model of the plant. Since the Gaussian process model prediction is normally distributed, each realisation of (refined model) residual is a random variable with associated normal probability distribution.

The onset of a fault is inferred by comparing the statistical pattern of the refined model residuals, collected under current operating mode with the pattern in the nominal (fault-free) condition. Major novelty of the approach is the application of Jensen-Renyi divergence as a means to quantify the difference between the two corresponding ensembles of distributions.

The ideas of the approach and their potentials are demonstrated in an illustrative example of simulated solid oxide fuel cell system.

Model-based fault diagnosis with Gaussian process regression of nominal model residuals

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Fault detection is about timely indication of malfunctioning system component.

How it works? We compare the process with its (model of) normal operating condition.
Imperfections in process models, if ignored, may affect reliability of the diagnostic system either as excessive false alarm rates or insensitivity. Reducing the destructive impact that the model errors might degrade diagnostic reliability is challenging.

The problem is how to handle the unmodelled portion of reality left from nominal model.

The solution consists of:

- accounting unmodelled nonlinearities in z with Gaussian process-based finite impulse response model [2] (with possibility of universal application),
- placing the detection rule (based on Jensen-Rényi measure of diversity over a distribution ensemble)
- directly from the given probability of false alarm [1].

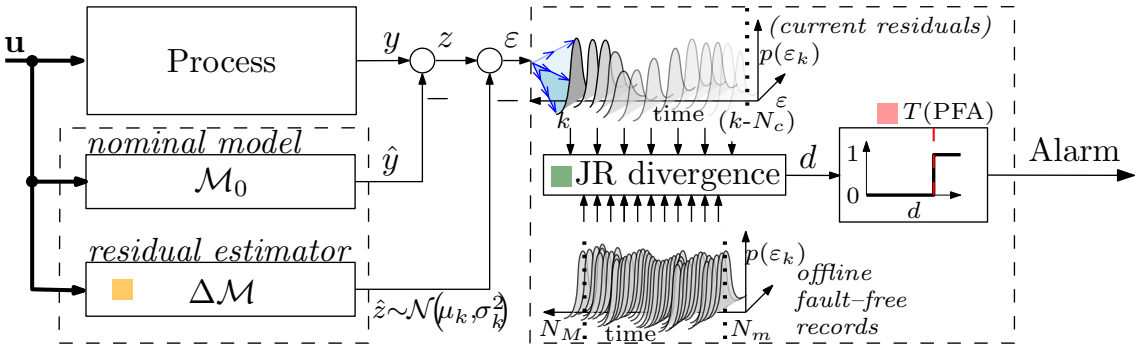

Figure 1: The idea of accounting for modelling error (left) and statistical detection procedure (right).

Results are demonstrated on a simulated solid oxide fuel cell (SOFC) power generating unit (80-cell SOFC stack with total of 550 cm^2 of active area, balance of plant (BoP) module [3]) operating within 3V peak-to-peak voltage.

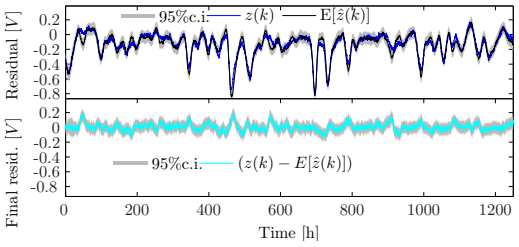

Figure 2: Fault-free simulation. (top) residual z and its estimate, and (bottom) final residual ε along the confidence intervals.

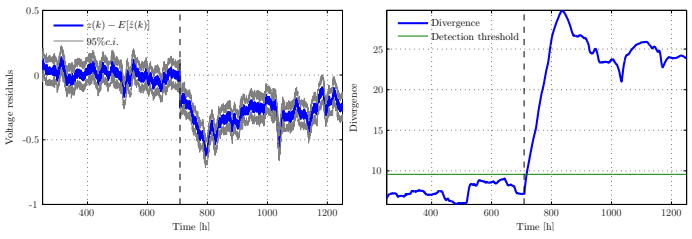

Figure 3: Fault simulation. Final residual ε (left) and Jensen-Rényi divergence (right). The fault occurs at dashed line.

Conclusions. The residual estimator $\Delta\mathcal{M}$ is able to capture unmodelled nonlinear dynamic effects, but we need rich enough training data set and (ii) considerable computational load in the identification stage. Strikingly simple selection of the diagnostic thresholds by only one design parameter and superb detection reliability indicate significant practical potentials of the approach.

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Low-cost spectrum sensor for ultra-narrowband transmissions

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There is only a limited amount of useful radio frequencies that can be used for wireless communications. Rapid increase in demand for wireless technologies in recent years has made this limitation evident. Ultra-narrowband is a new technology that is optimized for sensors and other devices that only occasionally transmit small amounts of data. Compared to existing mobile networks or Wi-Fi it is capable of accommodating many more devices in the same amount of radio spectrum.

Spectrum sensing is a special method of radio reception where instead of extracting information being sent by a transmitter we are only interested in the fact that a transmission exists. The most basic and widely used method is detecting the energy emitted into the electromagnetic field. However physical laws impose limits on how weak a signal can be reliably detected with energy detection. More sophisticated methods, like those based on statistical covariances, can reliably detect transmitters even when their signals are many times weaker than noise.

Spectrum sensing can be used to provide real-time information on which radio frequencies in an area are in use and which are vacant, independent of the radio technology. This can help network planners in manually optimizing their wireless networks. More interestingly, it opens a possibility for intelligent devices that can autonomously and dynamically adapt to environment, avoiding interference from other devices. Early application of this technology can be seen for example in automatic channel selection in modern Wi-Fi routers.

Spectrum sensors were traditionally complex devices. Just as new radio technologies continuously decrease the cost of wireless devices, to the point where billions of are now predicted to be in use in the near future, so must spectrum sensors follow this trend if they are to be included on such devices. In this paper we present a custom designed spectrum sensor that was developed using off-the-shelf components intended for use in TV receivers. We show that advanced spectrum sensing algorithms can be implemented on low-cost hardware and that they are effective in detecting the kind of radio transmissions that will likely be widely used in the future by smart wireless sensors and other devices in the future Internet of things.

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Low-cost spectrum sensor for ultra-narrowband transmissions

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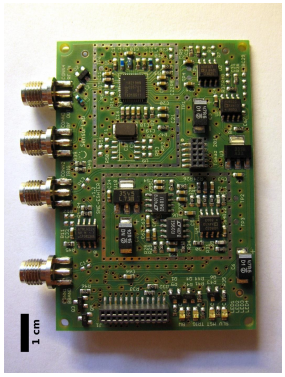
Study programme: *Information and communication technologies*

Mentor: *doc. dr. Tomaž Javornik*

VESNA SNE-ESHTER

Custom designed spectrum sensor using off-the-shelf components intended for use in DVB-T receivers.

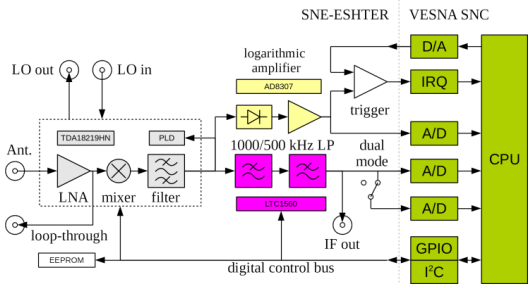
Based on VESNA, a low power sensor network platform developed at IJS.

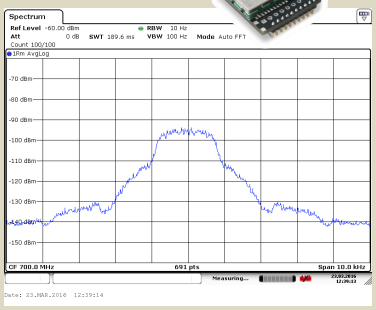


Ultra-narrowband (UNB) transmissions

Transmissions using low bit-rate binary phase- or frequency-shift keying modulations with bandwiths below 1000 Hz on sub-1 GHz frequencies. High range, high spectrum efficiency, low battery use.

This is an emerging technology for small devices infrequently transmitting short packets of data - *Internet of Things*





Covariance-based detection

A basic method of spectrum sensing is detecting the energy emitted into the electromagnetic field. However physical laws impose limits on how weak a signal can be detected.

Methods based on signal sample covariances are computationally simple and can detect transmitters even when their signals are many times weaker than noise.

$$\sigma_l = \frac{1}{N_s}\sum_{n=0}^{N_s-1} x_n \cdot x_{n-l} \quad l \in [0, L-1]$$

$$[r_{ij}] = \begin{bmatrix} \sigma_0 & \sigma_1 & \cdots & \sigma_{L-1} \\ \sigma_1 & \sigma_0 & \cdots & \sigma_{L-2} \\ \vdots & \vdots & \ddots & \vdots \\ \sigma_{L-1} & \sigma_{L-2} & \cdots & \sigma_0 \end{bmatrix}$$

$$\gamma_{MAC} = \frac{\max_{i,j}|r_{ij}|}{|r_{11}|} \qquad \gamma_{CAV} = \frac{\sum_{i=1}^{L}\sum_{j=1}^{L}|r_{ij}|}{\sum_{i=1}^{L}|r_{ii}|}$$

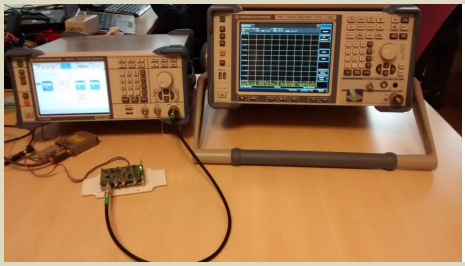
What is spectrum sensing?

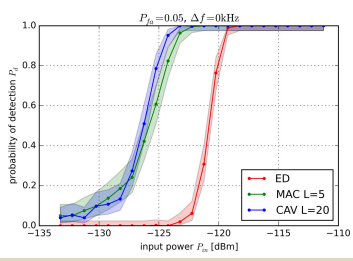
A method of radio reception where instead of extracting information being sent we are only interested in the fact that a transmission exists.

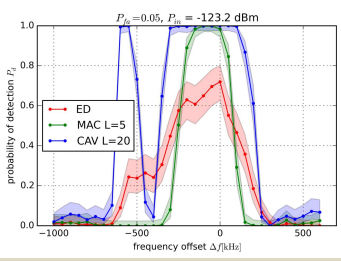
Real-time information on which radio frequencies are in use enables intelligent devices that can autonomously adapt to radio environment and avoid interference from other devices.

Evaluating UNB signal detection with VESNA SNE-ESHTER and covariance-based detection methods.

A test ultra-narrowband signal was generated using an RF vector signal generator. With a computer-controlled experiment, probability of detection was estimated for different signal power levels and frequency offsets.







The research leading to these results has received funding from the European Horizon 2020 Programme under grant agreement n°688116.

Nanoznanosti in nanotehnologije (Nanosciences and Nanotechnologies)

New method for C-O and C-N bond formation catalysed by *N*-halo compounds under green reaction conditions

Njomza Ajvazi[1] and Stojan Stavber[1,2,3]

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[2] Department of Organic and Bioorganic Chemistry, Jožef Stefan Institute, Ljubljana, Slovenia

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- New green chemical approach of the synthesis of aryl alkyl ethers and *N*-alkylated products could be of considerable interest to producer of these kinds of chemicals often used as active ingredients in fragrances, cosmetics, dyestuffs and pharmaceutical industry.
- In comparison with known related methods and processes, considerably improved green chemical profile of our original methodology offers a potential impact to environmental effect, in related production processes.

MEDNARODNA PODIPLOMSKA ŠOLA JOŽEFA STEFANA
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New method for C-O and C-N bond formation catalyzed by *N*-halo compounds under green reaction conditions

Njomza Ajvazi[1] and Stojan Stavber[1,2,3]

Study program: Nanosciences and Nanotechnology
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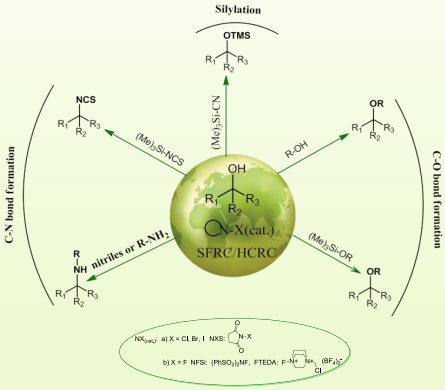
INTRODUCTION

Alkyl aryl ethers are important solvents and synthetic building blocks for the production of fragrances, cosmetics, pharmaceuticals, and dyestuffs[1], while nitrogen containing compounds are important buiiding blocks in organic synthesis[2]. Numerous related methodologies up to now suffer some disadvantages in their green chemical profile.

Aim of this work: Investigation, development and application of new methodology for the construction of the direct ***C-O*** and ***C-N bond*** under reaction conditions which follow as much as possible the principles of green chemistry.

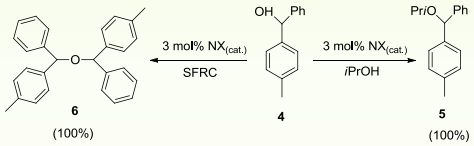


General concept and work-plan of the research

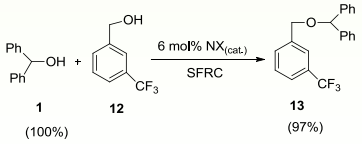
RESULTS

C-O bond formation

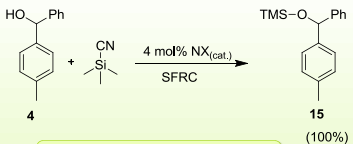
Scheme 1. Transformation of 4-methylbenzhydrol **4** with *i*PrOH catalyzed by *N*-halo compound under **SFRC** and in **solution.**



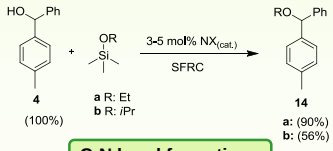
Scheme 2. Etherification of diphenylmethanol **1** with primary benzyl alcohol **12** catalysed by *N*-halo compound under **SFRC**.



Scheme 3. Trimethylsilylation of 4-methylbenzhydrol **4** with TMSCN catalyzed by *N*-halo organic compound under **SFRC**.

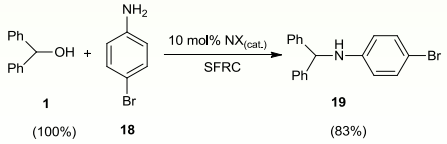


Scheme 4. Etherification of 4-methylbenzhydrol **4** with TMSOEt or TMSO*i*Pr catalyzed by *N*-halo compound under **SFRC**.

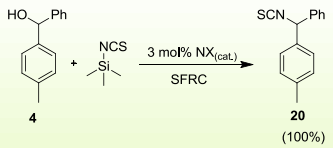


C-N bond formation

Scheme 5. Direct coupling of diphenylmethanol **1** with 4-bromoaniline **18** catalyzed by *N*-halo compound under **SFRC**.



Scheme 6. Isothiocyanation of 4-methylbenzhydrol **4** with TMSNCS catalyzed by *N*-halo compound under **SFRC**.



CONCLUSION

•We have demonstrated a novel, efficient and selective, metal- and acid-free method for **C-O bond formation** through the direct transformation of alcohols to dimeric ethers using *N*-halo compound as a catalyst under SFRC, while under alkyl alcohol HCRC, alkyl aryl ethers were obtained. Etherification could also be achieved by cross coupling of two different benzyl alcohols catalyzed by *N*-halo compounds under SFRC. Additionally, we have demonstrated that etherification of secondary alcohol could also be achieved using TMSOEt, TMSO*i*Pr or TMSCN in the presence of *N*-halo compound as a catalyst under SFRC. On the other hand, we have developed convenient **C-N bond formation** reactions of phenyl substituted alcohols with acetonitrile or anilines and TMSNCS as nucleophile sources, under solvent-free reaction conditions or in solution catalyzed by *N*-halo compound. Newly developed methods present a significant contribution from a green chemistry viewpoint, economy of time and reagents.

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Building thick spinel iron oxide layer onto the hexaferrite core nanoparticles using multiple co-precipitation of iron ions

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Composite nanoparticles are composite materials, where one of their dimension is in nanometre range (1 nm = 10^{-9} m). Within the individual composite nanoparticle at least two different materials displaying different composition, crystal structures and properties are combined. Such nanoparticles have potential to exhibit novel physical and chemical properties.

Applications of magnetic materials are based on their response to a magnetic field. The response of the magnetic material to the external magnetic field can be described with hysteresis loop. According to the shape of the loop, the magnetic materials can be classified as magnetically hard or soft materials. The soft magnetic materials are those where relatively low external field is required for their saturation. Typically they exhibit strong saturation magnetization (M_S) and low coercive field (H_C). Contrary, the hard-magnetic materials display large H_C, however low M_S. With coupling between properties of hard- and soft-magnetic materials in single composite nanoparticle, the shape of magnetic hysteresis can be tuned. The coupling means, that one property of the material can be tuned with influence on the other. The bi-magnetic nanoparticles usually exhibit core-shell (CS) structure, since it was found that coupling between different magnetic materials is stronger than in the other composite structures. The hysteresis loop of the bi-magnetic composite nanoparticles possessing CS structure, can also be tuned with the varying the thickness of the shell.

Generally for synthesis of CS nanoparticles, high temperature (<200 °C) and toxic, expansive chemicals are required. In our work used environmentally-friendly, inexpensive method based on the co-precipitation of the Fe^{3+}/Fe^{2+} ions and heterogeneous nucleation of the soft-magnetic maghemite layer onto the hard-magnetic HF core nanoparticles in the aqueous suspension at 60 °C.

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Introduction

- Composite nanoparticles: different functional materials combined in the single nanoparticle.
- Coupling between the different materials → new chemical and physical properties.
- **Bi-magnetic** materials consist of two different magnetic materials.
- Majority of bi-magnetic nanoparticles posses core/shell structure → strong coupling effect due to large contact area between the materials
- Thickness of the shell can influence on the magnetic properties of the composite nanoparticles

SYNTHESIS OF THE CORE/SHELL NANOPARTICLES
- high temperatures (> 200 °C).
- toxic and expensive reactants.

ALTERNATIVE
- Low temperature synthesis of the magnetic spinel iron oxide (maghemite γ-Fe_2O_3) shell/layer deposited onto the hexaferrite core nanoparticles.
- Method based on the co-precipitation of Fe^{3+}/Fe^{2+} ions and heterogeneous nucleation of the product onto the core nanoparticles [1,2].

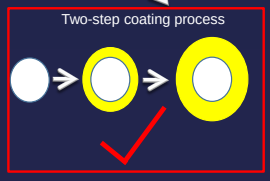
Our work

Increasing the layer thicknes

Increasing the n(Fe^{3+}):A(HF) ratio

Maximum layer thickness: 2 nm

Two-step coating process



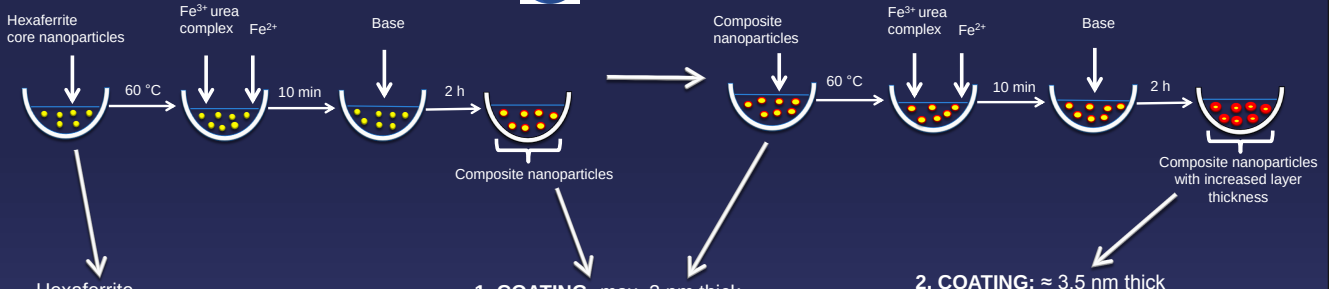
- Investigation of the synthesis procedure aiming to increase the maghemite layer coated onto the hexaferrite core nanoparticles.
- **METHOD:** two-step co-precipitation process of the Fe^{3+}/Fe^{2+} ions in colloidal suspension of the core nanoparticles [2].

PROBLEMS

Agglomeration of the composite nanoparticles in the second step.

Decreasing of the surfce area available for the growth of the maghemite layer Agglomeration could promote formation of the homogeneously-nucleated maghemite nanoparticles.

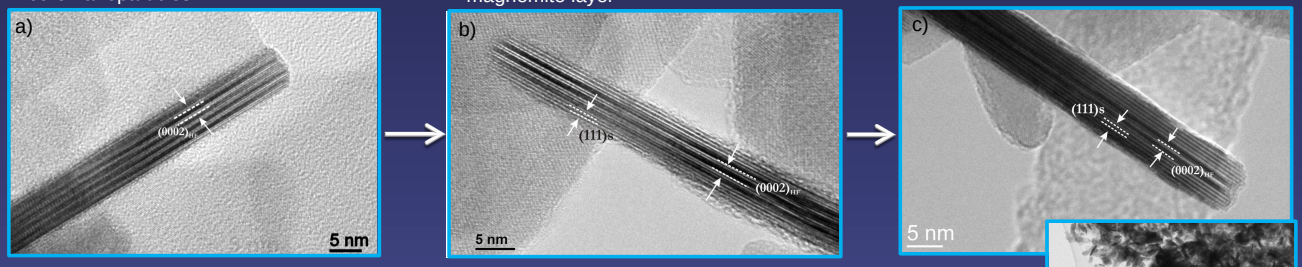
Synthesis



Hexaferrite core nanoparticles

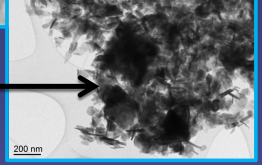
1. COATING: max. 2 nm thick maghemite layer

2. COATING: ≈ 3.5 nm thick maghemite layer



Images represent all stages of the two-step synthesis of the composite nanoparticles with increased thickness of the maghemite layer, from (a) the beginning trough (b) first stage of coating and (c) second stage of coating. (HF …. Hexaferrite core nanoparticles, S …. Spinel ferrite-maghemite).

Homogeneously-nucleated maghemite nanoparticles



Conclusion

- With the two-step approach of coating the core nanoparticles it is possible to increase the thickness of the maghemite layer.
- Further optimization of the synthesis in needed to obtain the homogeneous product, containing only the composite nanoparticles

References

[1] Primc, D. and D. Makovec; Composite nanoplatelets combining soft-magnetic iron oxide with hard-magnetic barium hexaferrite. Nanoscale. 7: p. 2688-2697 (2015).
[2] Primc, D., B. Belec, and D. Makovec; Synthesis of composite nanoparticles using co-precipitation of a magnetic iron-oxide shell onto core nanoparticles. J. Nanopart. Res. (18:64): p. 1-13 (2016).

Acknowledgment

Suport of the Ministry of the Higher Education, Science and Technology of the Republic Slovenia (PR-05558).
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The formation of silica coatings on barium hexaferrite nanoparticles and functionalization with 3-aminopropylsilane

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Magnetic nanoparticles (MNP) have been widely studied because of their wide range of applications: magnetic liquids – ferrofluids (e.g., in car brakes and speakers as vibration dampers), MNP are being used in computer science for storage and recording media. MNP have a potential in (environmental) cleaning and separation processes, for example, in ocean oil spillage MNP with modified surface can be dispersed in oil and then used to remove oil from ocean surface magnetically. Recently there has been an increasing interest for biomedical applications of MNP: in therapy for targeted drug delivery and hyperthermia and in diagnostics for magnetic resonance imaging (MRI) and magnetic particle imaging (MPI).

Our work is focused on the functionalization of MNP for biomedical applications. For such application materials have to express specific surface and magnetic properties, suitable size distribution of nanoparticles, and biocompatibity.

The magnetic properties are controlled by the choice of material. Barium hexaferrites is distinguished from other ferrites by high intrinsic coercivity and good chemical stability. Size distribution can be controlled by appropriate synthesis route such as hydrothermal synthesis, a reaction in hot water under high pressure.

The surface properties of nanoparticles are tuned with organic/inorganic coatings (e.g., thin layer of amorphous silica). The coating prevents the agglomeration of nanoparticles and further enables easier preparation of their dispersion in various liquids. For biomedical applications, biomolecules (e.g., polysaccharides like dextran) have to be attached - conjugated on the nanoparticles. To enable conjugation of biomolecules, first specific functional groups (amino, carboxyl, etc.) have to be introduced onto the nanoparticle surfaces. This can be done with grafting organic molecules (such as 3-aminopropyltriethoxysilane) onto the nanoparticles surfaces in the process usually referred to as "functionalization". In our work the surface of barium hexaferrites nanoparticles was modified by coating with silica. Silica

introduced reactive silanol groups, -Si-OH on the surface which were then be used in functionalisation reaction with 3-aminopropyltriethoxysilane, so that amino groups are now on the surface of the nanoparticles. In the future amino groups will be conjugated with biomolecules.

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Tanja Goršak [1,2], Slavko Kralj[1], Darko Makovec[1], Darja Lisjak[1]

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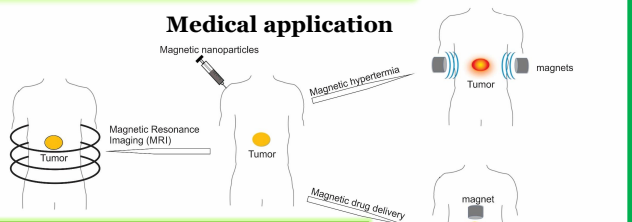
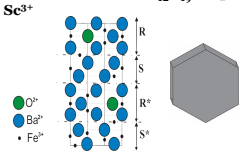
Recently there has been an increasing interest for medical applications of magnetic nanoparticles.
For such application materials must to have specific properties:

- magnetic properties → barium hexaferrites has high coercivity compared to other ferrites,
- suitable size distribution → size distribution can be controlled by synthesis hydrothermal synthesis,
- surface properties → tuned with organic/inorganic coatings (silica) and functionalization (APS),
- biocompatibity → conjugation with biomolecules.

Medical application



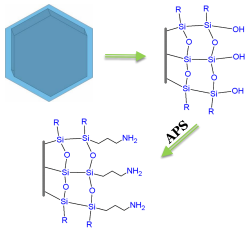
Barium hexaferrite ($BaFe_{12}O_{19}$) doped with Sc^{3+}



Crystal structure of $BaFe_{12}O_{19}$

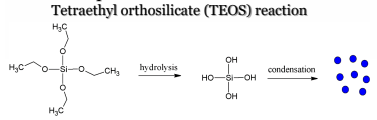
Part of Fe^{3+} is substituted by Sc^{3+}

Silica coated barium hexaferrite



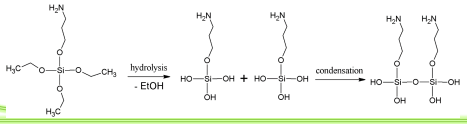
Amorphous silica - Stöber reaction

Tetraethyl orthosilicate (TEOS) reaction



Reactions are catalysed by an acid or a base

3-aminopropyltriethoxysilane (APS) reaction



Synthesis

Core nanoparticles

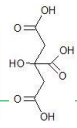
Barium hexaferrite doped with Sc^{3+} (BSc) [1]
- Hydrothermal synthesis
- T = 240°C

Coating of the nanoparticles with CTAB as surfactant

Cetyltrimethylammonium bromide - CTAB

Silica coating
- water/ethanol dispersion (40 : 1)
- 0.115 wt% of BSc nanoparticles
- 2.68 mM CTAB
- 16.1 mM TEOS
- pH 2.9 $\xrightarrow{1h}$ pH 4.1 $\xrightarrow{2h}$ pH 8.5
- Mixing overnight

APS grafting
- water/ethanol/ ammonium hydroxide (5/1/0.3)
- 1.6 mM of APS
- heated 50 °C and stirred for 5 h



Citric acid - CA

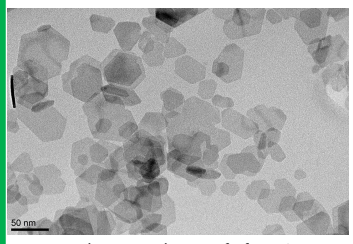
Coating of the nanoparticles with CA as stabilizing agent [2]

CA adsorption
- water dispersion of 0.5 wt% BSc, + 3,2 mL of CA (0.5 g/mL)
- pH to 5.1 with $NH_4(OH)$
- heated to 80 °C for 90 min
- pH to 10.1 with $NH_4(OH)$

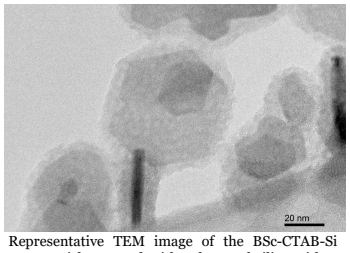
Silica coating
- water/ethanol solution (1 : 4)
- 1 % of concentrated $NH_4(OH)$
- 0.05 wt% of BHFS nanoparticles
- 7.46 mM TEOS
- Mixing overnight

APS grafting
- water/ethanol/ ammonium hydroxide (1/1/0.06)
- 4.8 mM of APS
- heated 50 °C and stirred for 5 h

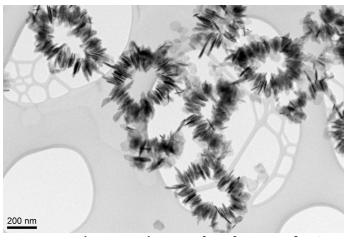
Results



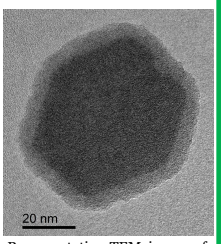
Representative TEM image of the BSc core nanoparticles with size 43 nm ± 15 nm.



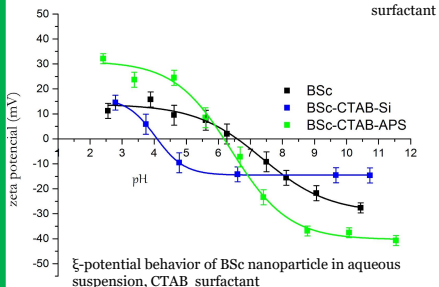
Representative TEM image of the BSc-CTAB-Si nanoparticles coated with a layer of silica with a thickness of 7-8 nm, prepared using CTAB as surfactant



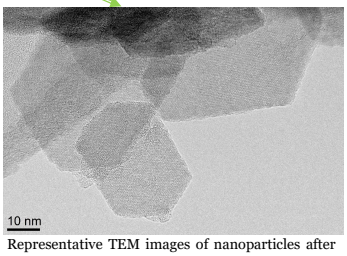
Representative TEM image of agglomerated BSc-CTAB-Si nanoparticles coated with a layer of silica, prepared using CTAB as surfactant



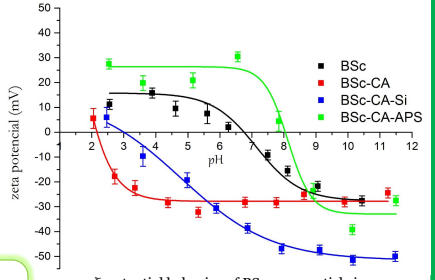
Representative TEM image of the BSc-CA-APS nanoparticle coated with a layer of silica with a thickness of 5-6 nm, prepared using CA



ξ-potential behavior of BSc nanoparticle in aqueous suspension, CTAB surfactant



Representative TEM images of nanoparticles after an attempt to graft them with APS (BSc-CTAB-APS)



ξ-potential behavior of BSc nanoparticle in aqueous suspension, CA stabilizing agent

Conclusion

The coating of BSc nanoparticles with silica was performed with the use of two different surfactants CTAB and CA. During the grafting with APS, the silica formed in the presence of CTAB degraded. We successfully coated BSc with a layer of silica, when CA was used as a stabilizing agent. BSc-CA-Si nanoparticles were further graphed with APS

Acknowledgement:
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Influence of concentration and size of Al_2O_3 particles on their distribution in reinforced austenitic stainless steel.

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It is well established that the steel matrix composites commonly have a good combination of hard ceramic reinforcement particles (e.g. TiC, TiB_2, WC and Al_2O_3) and ductile metallic matrix, which make them a promising candidate in wear resistance applications. Generally, there are several methods for fabricating the particulate reinforced steel matrix composites, such as powder metallurgy, conventional melting and casting, reactive sintering and self-propagating high-temperature synthesis. The casting process is more economical than the other available routes for integration of nanoparticles into microstructure of steel. However, it is extremely difficult to obtain uniform dispersion of ceramic nanoparticles in liquid metals due to the poor wettability and the specific gravity difference between the ceramic particles and metal matrix. Furthermore, low concentrations and only few nanometers size limit the possibility of identifying presence, distribution and effect of ceramic nanoparticles in the steel matrix.

The aim of the present work is to identify the distribution of particles in the steel matrix introduced through conventional melting and casting method, and above all to determine the influence of different concentrations and sizes of Al_2O_3 particles on the distribution of Al_2O_3 in reinforced austenite stainless steel. In the frame of this work the steels dispersed with Al_2O_3 particles were produced by conventional casting method and their microstructure investigated by light microscopy (LM), scanning electron microscopy (SEM) and auger electron spectroscopy (AES) techniques. To calculate and determine the particle distribution we used ImageJ. Based on the experimental results the dispersion of the Al_2O_3 particles in the steel matrix is non-homogeneous and concentrated in certain areas. With the EDS and AES analysis it was confirmed that the bright, small spot-like features represent the Al_2O_3 particles without any intermetallic reactions observed between the particles and the steel matrix. The results of the particle distribution show that at the mass fraction 0,5 to 1,0 wt% of Al_2O_3 with a mean particle size of 500 nm and 50 nm, the distribution of Al_2O_3 particles is relatively homogeneous with only a small deviation.

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Influence of concentration and size of Al_2O_3 particles on their distribution in reinforced austenitic stainless steel

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Mentor: izr. prof. dr. Bojan Podgornik

Materials for automotive, aerospace, wear and cutting applications.

They have a combination of hard ceramic (e.g. TiC, TiB_2, WC, Al_2O_3) reinforcement and ductile metallic matrix.

Ceramic reinforced steel matrix composites

Processing rutes: powder metallurgy, infiltration, spray deposition, **conventional melting and casting**

Microstructure characterization with LM, SEM, TEM and AES.

Aims: To study the influence of Al_2O_3 particles on the microstructure of a steel matrix using a conventional casting method. Focus was on the influence of concentration and size of Al_2O_3 particles on their distribution in reinforced austenite stainless steel.

Experimental work:

Material:

Austenitic stainless steel has been used for the work. The chemical composition of this alloy is given in Table 1.

Table 1: Chemical composition of austenitic stainless steel 304 in mass fractions (wt.%).

Alloying element	C	Mn	Cr	Ni	Cu	Mo	V	Si
wt %	0,02	1,24	17,4	10,1	0,36	1,29	0,08	0,33

As reinforcement particles commercial Al_2O_3 powder with a mean particle size of 500 nm and 50 nm has been used.

Specimens preparation

We prepared six different experiments in which we used two different particle sizes (500 nm and 50 nm) and three different concentrations (0,5 wt%, 1,0 wt% and 2,5 wt%) of Al_2O_3. Al_2O_3 particles were wrapped into the aluminium foil and put into the mould and the molten metal was poured over it.

Characterization

The microstructural changes and the dispersion of Al_2O_3 were observed and analysed by light microscopy (LM), scanning electron microscopy (SEM) and auger electron spectroscopy (AES) techniques. Samples for microstructure analysis were taken from the bottom (N), middle (S) and top (G) portion of the cast piece, as shown in Figure 1 below.

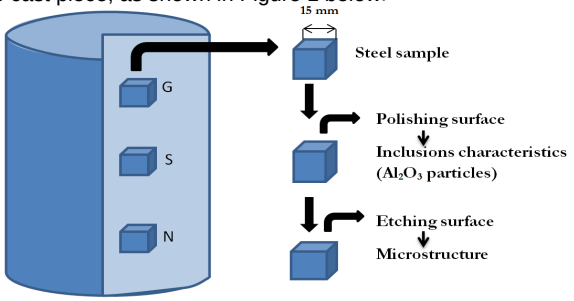


Figure 1: Schematic diagram of subtraction and preparation of metallographic steel samples.

Results:

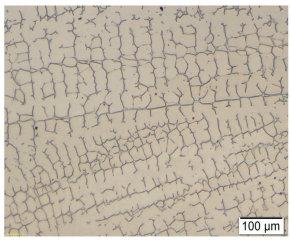


Figure 2: Cast microstructure of austenitic stainless steel with 6% of δ-ferrite.

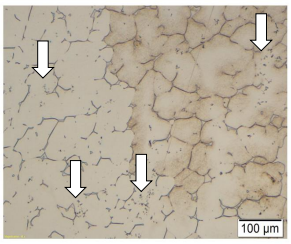


Figure 3: Cast microstructure of austenitic stainless steel with 6% of δ-ferrite and Al_2O_3 particles.

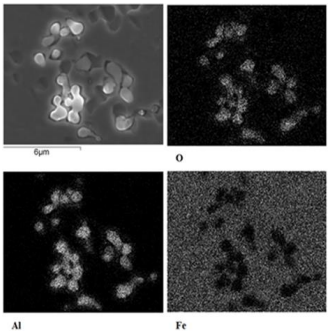


Figure 5: SEM elemental analysis of Al_2O_3 particles in the cast microstructure of austenitic stainless steel.

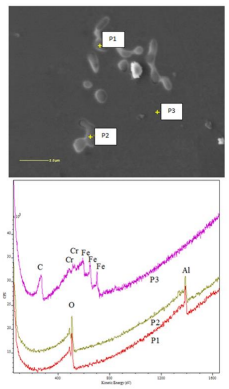
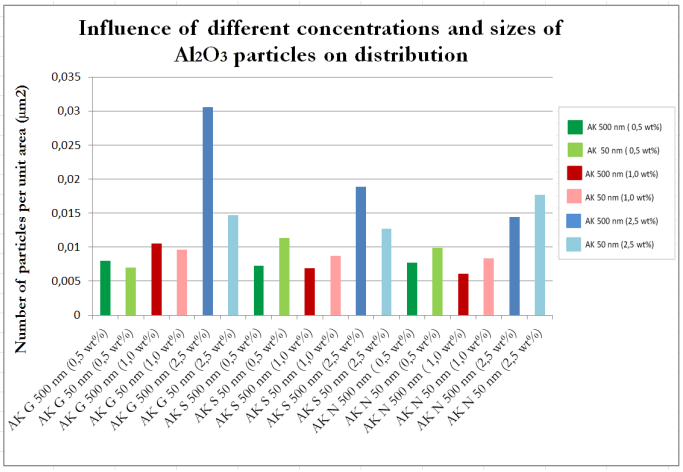


Figure 6: AES spectrum of the Al_2O_3 particles in the cast microstructure of austenitic stainless steel.



Conclusions: The results show that regardless of particles size and concentration no reactions take place between the particles and steel matrix. Furthermore, at the mass fraction 0,5 or 1,0 wt% of Al_2O_3 the distribution of all Al_2O_3 particles is relatively homogeneous with a very small deviation through the ingot. However, when mass fraction increases to 2,5 wt% the concentration ratio for larger particles starts to decrease toward the bottom of the ingot.

An infrared study of Concanavaline A aggregation at pH 5 and 9

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Protein aggregation is very important process associated with conformational diseases such as Alzheimer or Parkinson Disease or stability of protein drugs. The protein aggregation is a very complex process characterized by a remarkable polymorphism, where soluble amyloid oligomers, amyloid fibrils and amorphous aggregates are found as final product. This polymorphism is further related with the existence of multiple independent and competing assembly pathways leading to aggregation. Some of those oligomers are considered to be major initiators of the neurodegenerative cascades of corresponding diseases. However, not all oligomers are equally harmful, and several amyloidogenic proteins have been shown to form nontoxic oligomers, some of which were efficient fibrillation inhibitors.

In order to find a method, which can accurately spectroscopically determine the formation of fibrils, we systematically utilise infrared spectroscopy on the structural study of thermal aggregation of model protein (Concanavaline A). We have shown that proper application of the vibrational spectroscopy (ATR experiment) and accurate processing of recorded spectra (band fitting algorithm, deconvolution, second derivatives, and difference spectroscopy) provide a deeper insight into formation of the protein aggregates and fibrils. We found the markers in Amide I region, which uniquely expresses the presence of fibrils during the aggregation. Moreover, analysis of Amide I and Amide III regions by modelling of the intrinsic bands gives us an opportunity to monitor structural changes upon protein-protein interaction. The developed methodology presented in this manuscript will be applied in aggregation studies of proteins connected with neurodegenerative diseases.

Since FTIR spectroscopy allows fast and easy determination of protein secondary structure and in particular a very sensitive detection of conformational changes, it has important application values. The methods of FTIR spectroscopy described in

this paper can be used in pre-formulation and formulation studies, forced degradation studies, quality control and binding studies to name a few.

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An infrared study of Concanavaline A aggregation at pH 5 and 9

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Introduction:

Amyloid fibrils and amorphous aggregates are two types of aberrant aggregates associated with protein misfolding diseases. Although they differ in morphology, the two forms are often treated indiscriminately.

Structure of Concanavaline A is remarkably similar to the structure of human serum amyloid P component, a protein which is constituent of almost all amyloid deposits. Con A is able to induce programmed cell deaths on cortical neurons by a mechanism similar to programmed cell deaths induced by amyloid β-peptide [1].

Objective:

To show, that infrared spectroscopy offers an opportunity to distinguish between two similar and related processes; aggregation and fibrillation. Properly processed infrared spectra provide valuable information about the protein structure and structural changes during the process of aggregation. Moreover, difference spectra provide details about hydrogen bonding.

Methods:

- The aggregation of Concanavaline A was induced by heating the protein solution at two different pH values, pH 5 and pH 9.
- Before any spectral analysis the spectrum of pure buffer/water was subtracted.
- Spectra were simplified by applying difference spectroscopy, a spectroscopic method, which is sensitive to small band-shape changes [2].
- The band overlapped regions were additionally analysed using the Grams band fitting procedure by modelling the sum of the bands with the mixed Lorentzian and Gaussian band shapes.
- The assignment of the structural sensitive bands in Amide I, II and III regions is based on previous results on blocked dipeptides [3] and vibrational spectra of proteins in solution with known structure [4, 5].

Table 1. **The assignment of the model bands from the Amide I, II and III region [5].**

conformation	Frequency (cm^{-1}) Amide I	Amide II	Amide III
turn	1664–1674	1563–1572	1257–1260
P_{II}	1648–1654	1543–1546	1308–1311
P_{II}-conformation	1634–1640	1560–1550	1308–1311
α	1643–1645	1550–1552	1290–1295
α-conformation	1648–1654	1560–1550	1290–1295
β-conformation	1648–1654	1560–1550	1270–1280
β-strand	1625–1630	/	1240–1243
β-sheet	1685, 1630–1640	/	1230
aggregated β-sheets	1692, 1618	1530	1219–1222

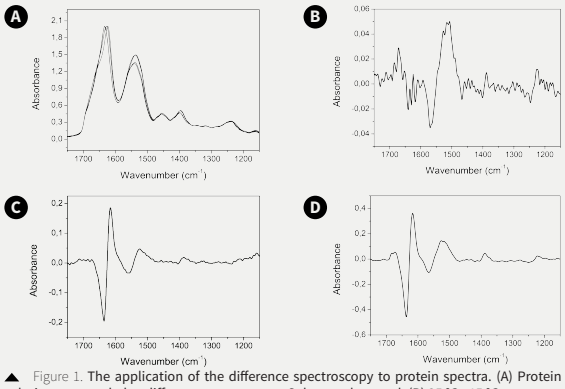

Figure 1. **The application of the difference spectroscopy to protein spectra. (A) Protein solution as recorded at different temperatures. Solvent subtracted. (B) 35 °C - 15 °C, (C) 75 °C - 60 °C, and (D) 75 °C - 15 °C.**

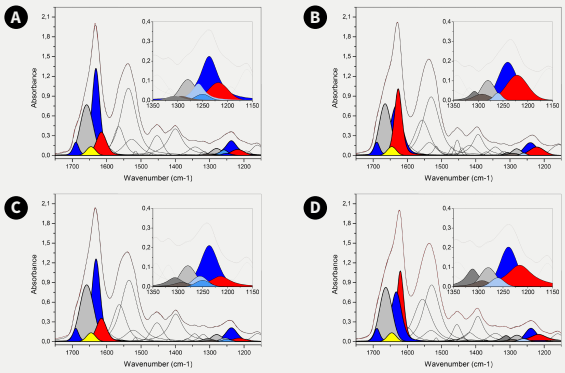

Figure 2. **Decomposition of the Amide I, II, and III region of (A) Con A (pH 5) at *T*=15 °C, (B) Con A (pH 5) at *T*=75 °C, (C) Con A (pH 9) at *T*=15 °C and (D) Con A (pH 9) at *T*=75 °C.**

Table 2. **The summary of the conformational changes observed by analysis of the Amide I and Amide III region applying band fitting algorithm.**

	Aggregation pH=5 (cm^{-1})	*T*=15 °C (%)	*T*=75 °C (%)	assignment	Fibrillation pH=9 (cm^{-1})	*T*=15 °C (%)	*T*=75 °C (%)
Amide I	1690	5	5	β-sheet	1690	5	5
	1664	36	30	turns, loops	1660	40	34
	1632	44	35	β-sheet	1630	41	31
	1626	15	30	β-sheet agg.	1620	13	30
Amide III	1310	3	7	P_{II}	1310	10	15
	1290	4	5	α	1290	5	6
	1280	15	15	β_{120}	1280	17	13
	1260	13	3	β_{150}	1260	8	5
	1250	4	0	β-strand	1248	5	0
	1236	45	39	β-sheet	1230	42	31
	1220	16	30	β-sheet agg.	1220	13	30

Conclusions:

The presented study showed that we are able to distinguish between the protein aggregation and fibrillation. The appearance of the Amide I component at 1620 cm^{-1} indicates the presence of fibrils. Difference spectra present a useful method for following spectral changes. Moreover, together with the analysis of the Amide III region reveals the structural changes of the protein during aggregation.

Application value:

- Pre-formulation and formulation studies: determine the effects of differing formulations on protein stability, quantify protein aggregation, analyse protein conjugates
- Forced degradation studies: examine protein stability and aggregation, perform accelerated stability tests (pH, temperature, mutations, etc…)
- Quality control: test protein concentration, structure, stability and purity in the production environment
- Binding studies: analyse the effects of protein ligand binding on protein structure

Advantages of vibrational spectroscopy:

- Sensitive to β-sheet structure,
- Opaque samples, suspensions, solids allowed
- No limitation by buffer components (e.g. Chloride)
- Fast analysis

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Chemical speciation of third-row elements via valence-to-core x-ray emission spectroscopy

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The particle induced x-ray emission (PIXE) is well established non-destructive analytical technique for rapid multielemental detection. The technique is based on the detection of characteristic x-ray emission following inner shell ionization induced in collision with MeV protons. Solid state detectors with energy resolution of ~150 eV are commonly applied in such analysis, which is enough to separate characteristic x-ray lines from different elements. However, if we push the energy resolution on the level of the natural linewidth, the valence-to-core x-ray emission spectra reflects the chemical environment of the x-ray emitting atom.

In present work, valence-to-core x-ray emission spectra of phosphorus, sulphur, and chlorine are studied experimentally and theoretically. In order to record Kβ spectra with high energy resolution an in-vacuum curved-crystal spectrometer was employed. Theoretical model spectra were built using calculations based on the density functional theory (DFT) and the main spectral features were explained in a molecular orbital picture. In particular, detailed analysis of P, S, and Cl in compounds with T_d local symmetry is presented, demonstrating that valence-to-core XES is a sensitive probe of electronic structure, symmetry of the molecule and ligand bonding. Finally, the first-principle DFT calculation of the S Kβ spectra of lithium polysulfide (Li_2S_x) compounds were performed, which can be used to study Li-S batteries in operando conditions.

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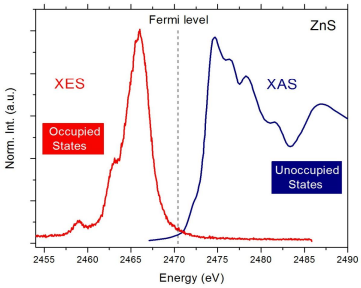
CHEMICAL SPECIATION OF THIRD-ROW ELEMENTS VIA VALENCE TO CORE X-RAY EMISSION SPECTROSCOPY

MARKO PETRIC

Study program: Nanosciences and Nanotechnologies,
Jožef Stefan International Postgraduate School
MENTOR: doc. dr. MATJAŽ KAVČIČ
Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana

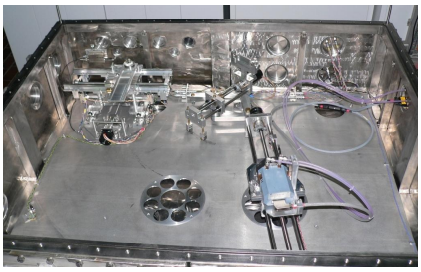
MOTIVATION

Local electronic structure of bulk materials can be studied by inner-shell x-ray spectroscopy.



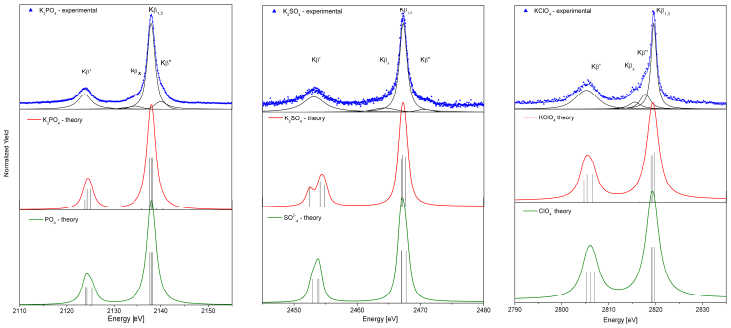
EXPERIMENT

- Wavelength dispersive x-ray emission spectrometer in Johansson geometry was used [1].
- Targets were irradiated by 2MeV protons and 3 keV photon beams.
- Thermoelectrically cooled CCD camera was used for position sensitive detection of x-rays.

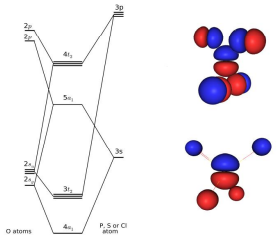


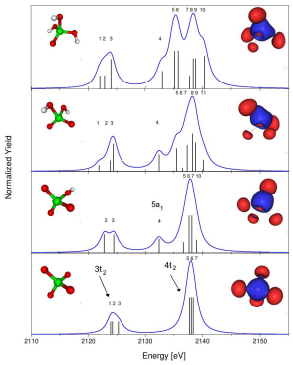
The spectrometer resolving power E/ΔE ≈ 7000!

RESULTS: T_d local symmetry



The P, S and Cl Kβ x-ray emission spectra measured from K_2PO_4, K_2SO_4 and $KClO_4$ compounds are presented in the top part of upper Figure and are compared with two theoretical spectra calculated for neutral molecule and first coordination sphere around the center atom [3].





The main characteristics of the emission spectrum can be modeled only with the first coordination sphere around the center atom and explain in molecular orbital picture.*(upper right Figure)*

If the hydrogen atoms is bonded to phosphate ion, the original tetrahedral symmetry is broken leading to different mixing of the atomic orbitals and changing the dipole transition matrix elements that contribute to the spectrum[2]. *(left Figure)*

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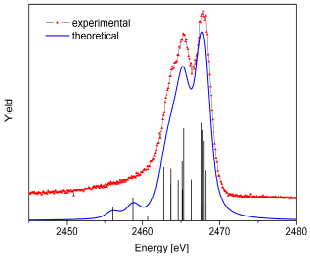
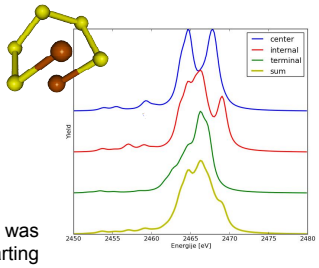
[3] M. Petric, R. Bohinc, K. Bučar, S.H. Nowak, M. Žitnik, and M. Kavčič, *Inorg. Chem.* DOI: 10.1021/acs.inorgchem.6b00237

APPLICATION: Li-S batteries



The theoretical model of the elemental S which was compare with measurement, was used as starting point for modeling the Li_2S_x spectra.

The theoretical S Kβ spectrum of the Li_2S_5.



ACKNOWLEDGMENT

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The effect of benzene ring and mercapto group in imidazoles on the corrosion inhibition of copper alloy with 10% zinc

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Corrosion has an important role in diverse fields of industry and everyday life. Loss due to corrosion are estimated between 2 to 5 % of the word´s gross national products. The main goal of research is to search for new methods for the minimization and prevention of corrosion. The aim of the to find a cheap, non-toxic and efficient inhibitor which prevents corrosion. That was the main reason why we studied the inhibition efficiency of different types of imidazoles as corrosion inhibitors of copper alloy which is widely used material in many applications. The mercapto group beneficially affects the inhibition efficiency of imidazoles as corrosion inhibitors of Cu90Zn10 alloy in chloride solution but only in combination with benzene ring. On the other hand, imidazole combined with methyl group acts as a corrosion activator.

Institut "Jožef Stefan" Ljubljana, Slovenija

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Univerza v Ljubljani Fakulteta za kemijo in kemijsko tehnologijo

THE EFFECT OF BENZENE RING AND MERCAPTO GROUP IN IMIDAZOLES ON THE CORROSION INHIBITION OF COPPER ALLOY WITH 10% ZINC

Monika Žnidaršič[1,2], Črtomir Podlipnik[1] and Ingrid Milošev[2,3]

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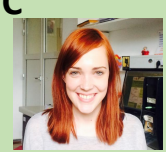
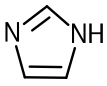


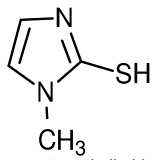
INTRODUCTION

- The main goal of research - to find methods for the minimization and prevention of corrosion.
- The most effective inhibitor of copper corrosion was benzotriazole - which has been used for decades.
- The research is focused on alternative corrosion inhibitors for copper and its alloys – to find less toxic compounds with similar inhibition efficiency.
- We focused on copper alloy with 10 wt.% of zinc, i.e. Cu10Zn alloy.

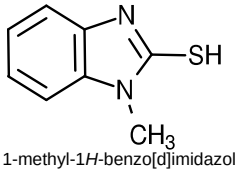
INHIBITORS



Imidazole (**ImiH**)



2-mercapto-1-methylimidazole (**SH-ImiMe**)



1-methyl-1*H*-benzo[d]imidazole-2-thiol (**SH-BimiMe**)

EXPERIMENTAL

Samples

↓

Ground at a circulating device

↓ Ultrasound for 2 minutes

0.1 M NaCl

↙ ↘

blank

With inhibitors:
1. **ImiH**
2. **SH-BimiMe**
3. **SH-ImiMe**

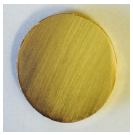
$$IE(\%) = \frac{R_p^* - R_p}{R_p^*} \times 100$$

IE ..... inhibition efficiency
R_p^* ..... inhibitor
R_p ..... blank

- 1h at the open circuit potential (OCP)
- Linear polarization 10 mV vs. OCP, 0.1 mV/s
- Potentiodynamic polarization -250 mV vs. OCP, 1 mV/s

➢ **Electrochemical parameters**
- R_p – polarization resistance
- j_{corr} – current density
- E_{corr} – corrosion potencial

➢ **Optical images of Cu10Zn before and after electrochemical measurements**



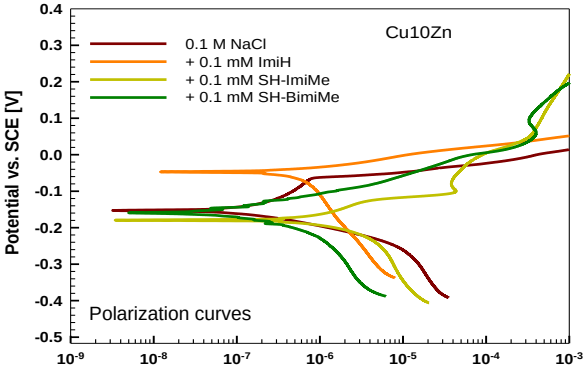
Cu10Zn

Cu10Zn in NaCl

Cu10Zn in NaCl with addition of SH-BimiMe

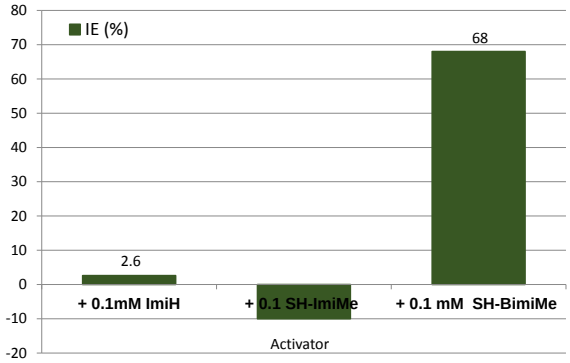
RESULTS

➢ **Electrochemical results**



	OCP [V]	R_p[Ωcm²]	j_{corr} [μA/cm²]	E_{corr} [V]	IE/%
0.1 M NaCl	-0.143	32506	0.453	-0.096	-
+ 0.1 mM ImiH	-0.090	33389	0.471	-0.042	2.6
+ 0.1 SH-ImiMe	-0.162	11807	2.876	-0.183	-
+ 0.1 mM SH-BimiMe	-0.144	101800	0.389	-0.156	68

Inhibitor efficiency



CONCLUSION

- According to the electrochemical results - the mercapto group beneficially affects the inhibition efficiency of Cu10Zn alloy
  - ↳ only in combination with benzene ring
- When combined with methyl group it acts as corrosion activator.

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Kazalo Avtorjev (List of Authors)

Sodelujoča podjetja ˝Od ideje do uspeha˝:

Sodelujoča podjetja in organizacije:


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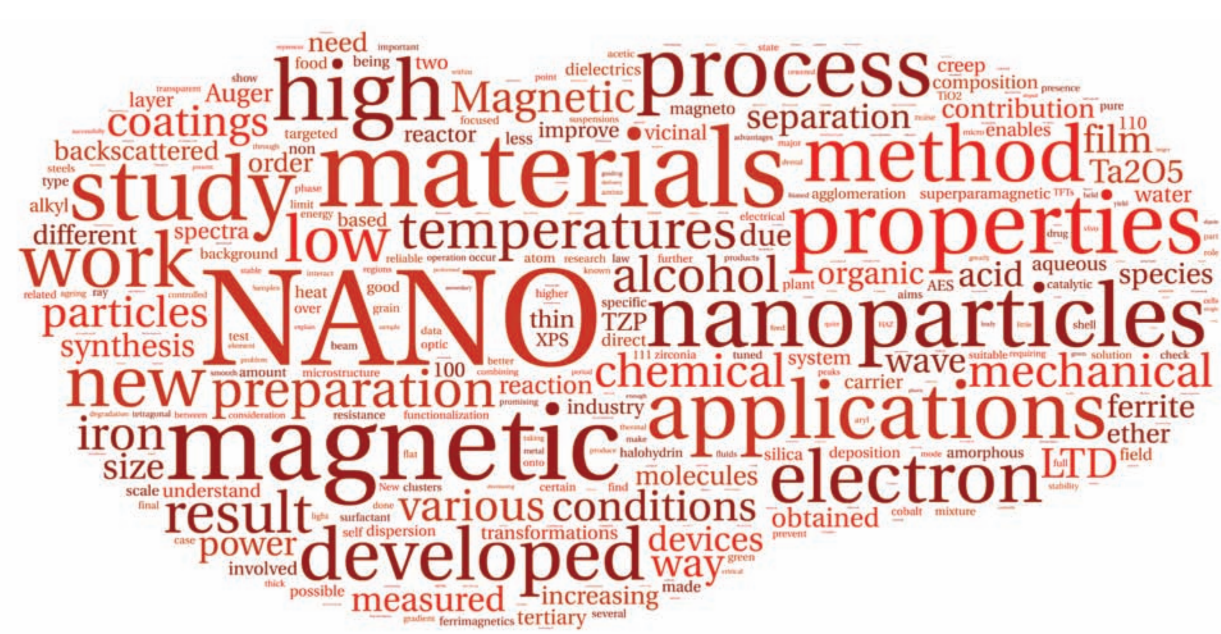
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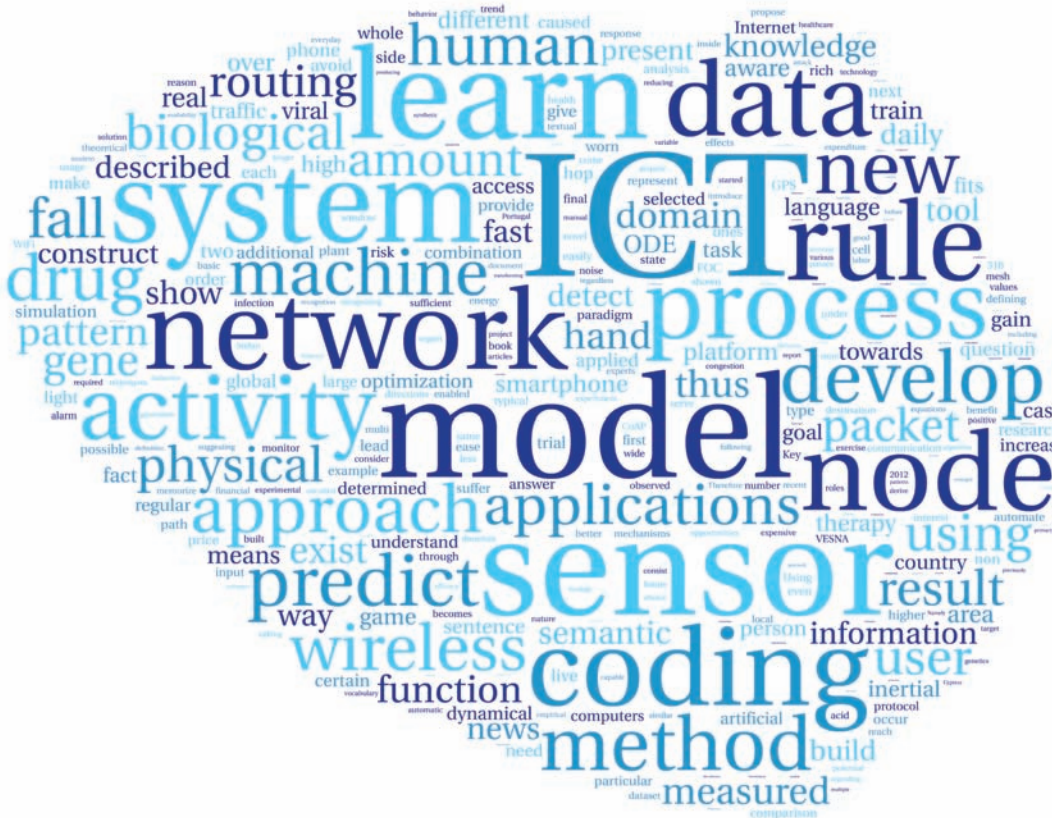
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