

2nd SYMPOSIUM ON ANALYTICAL ATOMIC SPECTROMETRY

BOOK OF ABSTRACTS

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2nd SYMPOSIUM ON ANALYTICAL ATOMIC SPECTROMETRY

Zagreb, September 13–14, 2024

BOOK OF ABSTRACTS

IMPRESSUM

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Dear Colleagues, Participants, and Friends,

It is with great pleasure that we present to you the *Book of Abstracts* for the 2nd *Symposium on Analytical Atomic Spectrometry*, the international gathering dedicated to advancing the field of analytical atomic spectrometry.

The abstracts contained in this book represent modern analytical techniques and instrumentation advancements, novel applications in chemistry, biology, environmental science, and beyond.

Analytical atomic spectrometry plays a crucial role in addressing many of today's scientific and societal challenges, providing powerful insights in areas ranging from material characterization to pharmaceutical development, from environmental monitoring to forensic analysis. The research represented here not only deepens our understanding of fundamental processes but also opens new doors for technological advancements and real-world problem-solving.

We are incredibly proud of the diverse range of topics and the high quality of work that this year's conference brings together.

On behalf of the organizing committee, we would like to extend our heartfelt thanks to all the authors for their contributions, and to everyone who has made this conference possible.

We look forward to an inspiring and productive exchange of ideas and to the exciting innovations that will emerge from this symposium.

With warm regards,

Sanda Rončević Conference Chair/Organizing Committee

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PROGRAMME

	FRIDAY, September 13, 2024 Department of Chemistry, Faculty of Science, Horvatovac 102a, Zagreb
8:30 - 9:00	REGISTRATION
9:00 - 9:10	OPENING - Sanda Rončević
	Sponsors Section
9:10 - 9:30	Sébastien Sannac, Agilent Technologies, Automated Analysis of Low-to-High Matrix Environmental Samples using ICP-MS with Autodilution System
9:30 - 9:45	Lukas Schlatt, Nu Instruments, What is ICP-TOF and how does it improve upon current analytical methods?
9:45 - 10:00	Tanja Topić, ANALYSIS Adria Laboratory Equipment d.o.o., Products presentation
10:00 - 10:15	Bill Spence, Ciprian Stremtan, Teledyne Instruments Inc., Products presentation
10:15 - 10:35	Gianpaolo Rota, Milestone, How a total workflow approach to sample prep can help analytical labs to optimize their elemental analysis
10:35 - 11:15	Coffee Break
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11:15 - 11:50	Martin Šala, National Institute of Chemistry, Ljubljana, Slovenia, Refining LA-ICP-MS: Enhancements in Image Quality and New Methods for Accurate Quantification
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12:30 - 12:50	Hana Fajković, Department of Geology, Faculty of Science, University of Zagreb, Sequential extraction of CRM BCR lake sediment standard using two sequential extraction procedures
12:50 - 13:10	Zuzana Redžović, Department of Biology, Faculty of Science, University of Zagreb, Calcified structures in fish reveal metal exposure in wastewater-impacted ecosystems using LA-ICP-MS
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14:30 - 14:45	Tin Županović , Faculty of Science, University of Zagreb, Remediation of Gd ³⁺ ions from aqueous solutions using iron and carbon nanocomposites
14:45 - 15:00	Antonija Sulimanec, Institute for Medical Research and Occupational Health, Elemental composition and arsenic speciation in Croatian market rice
15:00 - 15:15	Karla Bogdan, Faculty of Science, University of Zagreb, Inductively coupled plasma-mass spectrometry (ICP-MS) analysis of lanthanides ions sorption on calcium alginate encapsulated iron nanoparticles
15:15 - 15:30	Bernardo Marciuš, Croatian Institute of Public Health, Evaluation of nutrition labeling and regulation compliance in infant formulas, fruit juices and food supplements regarding essential and trace elements
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11:30 - 12:00	Coffee Break + Discussion

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<u>Vesna Dvorski</u> , Sanda Rončević Elemental fingerprinting of selected sparkling wines by ICP-MS method
<u>Nina Kudumija</u> , Jelka Pleadin, Tina Lešić, Snježana Zrnčić, Greta Krešić, Ana Vulić Mineral composition of fresh farmed European sea bass and gilthead sea bream
Jelena Nikolić, Milica D. Nikolić, Violeta Mitić, Aleksandra Pavlović, Katarina Milenković, Milan Mitić, Vesna Stankov Jovanović Differences in elemental content in honey samples from Serbia
Vesna Stankov Jovanović, Milica D. Nikolić, Violeta Mitić, Aleksandra Pavlović, Stefan Petrović, Milan Mitić, Jelena Nikolić Elemental composition of oak honeydew from Serbia
Silva Žužul, Jasmina Rinkovec, Magdalena Vincetić, Gordana Pehnec Seasonal variations of Ni, As, Cd and Pb in the PM10 fraction of suspended particulate matter determined by indicative measurements
Lara Runje, Anita Pejić, Nikolina Ilić, Ivan Nemet, Sanda Rončević SEM and ICP-MS as characterization methods of iron nanoparticles used for removal of selected rare earth elements
Lovra Vuković, Nikolina Ilić, Ivan Nemet, Iva Juranović Cindrić, Michaela Zeiner, Heidelore Fiedler Elemental composition of dandelion from Croatia
Lela Martinaga, Maja Somogyi Škoc, Ernest Meštrović and <u>Iva Rezić</u> TLC Tracking of Nanoparticles Before Coupling to ICPMS for Investigation of Antimicrobial Coatings

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POSTER PRESENTATIONS

PLENARY LECTURE



REFINING LA-ICP-MS: ENHANCEMENTS IN IMAGE QUALITY AND NEW METHODS FOR ACCURATE QUANTIFICATION

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Recent advancements in LA-ICP-MS have significantly enhanced throughput, sensitivity, and image quality. In our laboratory, we have extensively studied the improvement in image quality by fine-tuning parameters based on a deep understanding of the fundamentals of LA-ICP-MS. This development, now widely accepted, will be described.

Despite these advances, the technique still faces challenges in precise quantification. One major issue is the need for matrix-matched standards, which are often difficult or impossible to obtain. To address this, we have developed two novel approaches for improving quantification in LA-ICP-MS: a semi-quantitative calibration protocol and a method for signal correction based on the volume ablated, measured in a separate experiment. These approaches will be discussed.

INVITED LECTURES



IMPORTANCE OF SPECTROSCOPIC CHARACTERIZATION OF ANTIBACTERIAL COATINGS ON PERSONALIZED MEDICAL DEVICES AND MEDICAL TEXTILES

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Spectroscopic characterization of antibacterial coatings on personalized medical devices and medical textiles is crucial for ensuring their effectiveness in preventing infections and maintaining biocompatibility. It provides detailed insights into the chemical composition, stability, and uniformity of the coatings, helping optimize their antimicrobial properties for safe and long-term medical use.

Medical devices are instruments, machines, implants, or tools designed to diagnose, prevent, treat, or manage medical conditions and diseases. These devices range from simple items like bandages and thermometers to complex technologies like pacemakers, artificial joints, and diagnostic imaging machines such as MRI scanners. Personalized medical devices are more enhanced – they are tailored solutions designed to meet the specific needs of individual patients, improving both treatment outcomes and comfort. These devices can include customized implants, prosthetics, and wearables that are precisely fitted or engineered based on a patient's unique anatomy, medical condition, or genetic profile. Advances in technologies like 3D printing, biomaterials, and digital health monitoring have made it possible to create personalized devices, ensuring better functionality, reduced risk of complications, and improved long-term effectiveness. By aligning with the patient's biology and lifestyle, personalized medical devices are revolutionizing the way healthcare is delivered, offering more targeted and patient-specific therapies.

In this work, therefore, we propose new biodegradable materials coated with nanoparticles in antimicrobial active coatings foreseen for medical and dental applications. By developing antimicrobial biodegradable polymers that prevent the onset of infections, we tried to respond to the World Health Organization's demands, which has highlighted this problem as a major problem to the world public health in this century. Coatings with mixtures of nanoparticles were designed to inhibit or eliminate microbial growth, reducing infection risks associated with medical textiles and devices, surgical implants, and dental materials. New dental and medical antimicrobial polymers were characterized by different spectroscopic techniques, such are UV-VIS spectroscopy, FTIR-ATR spectroscopy and ICP-MS. After modification of the polymers, and the results have shown that the antimicrobial surface was efficient against model microorganisms (*Escherichia coli, Staphylococcus aureus and Candida albicans*) after several hours of exposure, leaving a space for further development prior application in medical devices and textile materials.

Acknowledgements. This work has been supported by Croatian Science Foundation project ABBAMEDICA IP-2019-04-1381, project leader prof. Iva Rezić PhD



METAL CONTENT ANALYSIS OF PROKUPAC RED WINES FROM SOUTH-EAST SERBIAN VINEYARDS USING ICP-OES

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Metals play a crucial role in various biochemical and physiological functions, being essential for maintaining health throughout life. This study aimed to quantify the metal content in red wines made from the indigenous Prokupac grape variety, cultivated in the south-east Serbian wine-growing regions. Five red wine samples were analyzed for micro- and macroelements using inductively coupled plasma optical emission spectrometry (ICP-OES). Among the macroelements, potassium (517.5-854.1 mg/L) and phosphorus (78.90-201.2 mg/L) were the most abundant, with notable variability across samples. Regarding essential microelements, iron, zinc, copper, chromium, and selenium were present in the highest concentrations. Silicon (5.168-10.37 mg/L) and tin (0.018-0.051 mg/L) were the most and least prevalent among the probably essential microelements, respectively. Of the toxic trace elements analyzed (arsenic, cadmium, lead), only lead was detected, and its concentration remained within acceptable limits (0.006-0.024 mg/L). These findings provide a detailed profile of the metal content in Prokupac red wines, highlighting their nutritional value and confirming their safety regarding toxic elements.

Acknowledgements. This work has been supported by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia (451-03-66/2024-03/ 200124).



SEQUENTIAL EXTRACTION OF CRM BCR LAKE SEDIMENT STANDARD USING TWO SEQUENTIAL EXTRACTION PROCEDURES

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Sequential extraction is a widely used method to determine the binding sites and potential mobility of potentially toxic metals on various mineral phases. This analysis is typically employed to assess the environmental impact of metal mobility and accumulation. Since its introduction in environmental research, numerous procedures have been developed, each tailored to different materials and metals. The standardized method is the BCR sequential extraction, for which a certified reference material (CRM) was developed.

In this study, we used the standardized BCR procedure on BCR lake sediment CRM, alongside a newer seven-step sequential extraction method designed for soils impacted by acid mine drainage. The seven-step method is expected to provide a more detailed understanding of metal distribution across mineral phases compared to the BCR method. However, several questions arose during result interpretation:

- 1. How comparable are the extracted concentrations between different extraction procedures?
- 2. Can the measured concentrations be considered definitive?
- 3. What differences exist between the measured values?

To address these questions, we analysed nine elements: As, Ca, Cr, Fe, Mn, Ni, Pb, Zn, and a group of rare earth elements (REE) using an ICP-MS-QQQ instrument. After data preparation, the seven fractions were consolidated into four, based on targeted mineral phases. This approach aims to offer clearer insights into trends and potential differences in the results.

We observed differences in the extracted concentrations between the BCR and seven-step sequential extractions. The values varied from 7.6% to 98.5% of the average of the two measured concentrations. Generally, the seven-step extraction provided higher cumulative extracted concentrations for all elements except Pb, where BCR showed higher concentrations. For the exchangeable fraction, BCR extracted higher concentrations (except for Pb), while the seven-step extraction was more efficient for the oxidizable fraction across all elements. Results for the reducible and residual fractions varied depending on the metal, though the seven-step method typically yielded higher concentrations.

Further extraction of different samples is recommended to gain a better understanding of each method's efficiency.

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CALCIFIED STRUCTURES IN FISH REVEAL METAL EXPOSURE IN WASTEWATER-IMPACTED ECOSYSTEMS USING LA-ICP-MS

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In aquatic ecosystems, metals are considered important pollutants, since they are not biodegradable and can accumulate in fish tissues. Long-term environmental exposure can be considered using microchemistry of scales and otoliths, fish calcified structures from the inner ear.^[1] Different elements from the local environment can be permanently incorporated into their crystalline matrix during growth, as otoliths and scales are metabolically inert. We estimated metal accumulation in scales and otoliths of brown trout (Salmo trutta Linnaeus, 1758) from the Krka River, influenced by industrial and municipal wastewaters. Sampling was performed at the reference site (river source, KRS), downstream of the wastewater outlets (Town of Knin - 8300 inhabitants, KRK), and in the national park (KNP). Otoliths and scales were embedded, sectioned and analyzed by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) in line scan mode. Trends in metal content profiles along laser lines were similar for elements in the scales, confirming continuous metal accumulation with fish growth. Spatial differences were observed in otoliths, with Sr and Br being the highest in samples from KNP, and TI at KRS. These results were comparable to the differences in concentrations of these metals between sites in the water.^[2] Moreover, abnormal otoliths - indicative of stocked fish, were found in few fish individuals. As demonstrated by this study, LA-ICP-MS can facilitate unravelling the complex life histories of this species. These data will also contribute to the protection of trout population in the Krka National Park, as sensitive karst ecosystem.

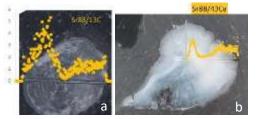


Figure 1. a) otolith, b) scale under the light microscope after LA-ICP-MS measurements

Acknowledgements. This work has been supported by Croatian Science Foundation under the BIOTOXMET project (IP-2020-02-8502).

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ORAL PRESENTATIONS



REMEDIATION OF Gd³⁺ IONS FROM AQUEOUS SOLUTIONS USING IRON AND CARBON NANOCOMPOSITES

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Gadolinium, a technologically important rare earths element, due to its widespread use, has caused concern in the world due to its potential toxicity to living organisms. Chelated forms of gadolinium accumulate in water and break down into the ionic form Gd³⁺, which is potentially toxic, so remediation is desirable.^[1,2] The removal of gadolinium can be achieved by using iron nanoparticles, which have high capacity to adsorb pollutants on their surface, and this property is improved by using carbon nanotubes as a carrier for iron nanoparticles.^[3,4]

Iron and carbon nanocomposites were synthesized and then characterized using scanning electron microscopy (SEM) and magnetic susceptibility measurement. Adsorption of chelate and ionic form of gadolinium on nanocomposite particles was observed using mass spectrometry with inductively coupled plasma, while varying the mass of the nanocomposite in the experiment. The experiment determined that the particles of the nanocomposite adsorb gadolinium very well in a narrow range of low concentrations, and at higher concentrations the adsorption of gadolinium decreases.

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ELEMENTAL COMPOSITION AND ARSENIC SPECIATION IN CROATIAN MARKET RICE

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Rice (Oryza sativa L.) is a high-calorie, starchy food that is a good source of various micronutrients, including minerals. Despite its high nutritional benefits, rice can accumulate undesirable levels of toxic inorganic As (iAs). This study aimed to determine the total concentrations of 26 elements (Al, As, B, Ba, Li, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Na, Ni, Hg, I, K, P, Pb, S, Se, Sr, V, Zn) and the fractions of four As species of different toxicity (As^{III}, As^V, DMA, MMA) in 58 samples of rice purchased in Croatian supermarkets. All air-dry (as sold) samples were milled and homogenized by mixer B-400 (BÜCHI Labortechnik AG, Switzerland). For multielement analysis, rice homogenates (≈0.20 g) were wet digested with 50% (v/v) HNO₃ in a highpressure microwave system UltraClave IV (Milestone, Italy). Before analysis, the samples were further diluted with a solution containing 1% (v/v) HNO₃ and $3 \mu g/L$ of internal standards (Ge, Rh, Tb, Lu, and Ir) (SCP Science, Canada) and analyzed by inductively coupled-mass spectrometry (ICP-MS) (Agilent 7500cx ICP-MS, Agilent Technologies, USA). Arsenic species were quantified in rice extracts using high-performance liquid chromatography (HPLC) (Agilent 1260 Infinity II LC System) coupled with Agilent 7900 ICP-MS (Agilent Technologies, USA). The methods were validated by determining the limits of detection (LOD) and quantification (LOQ). Certified reference material SRM 1568b, Rice flour (NIST, USA) was used to monitor the accuracy. Element concentrations varied by geographical origin, type of rice, and cultivation method. The study verified that rice, especially brown, is an important source of microelements Mn, Fe, and Co. Significant correlations were found among the concentrations of most elements. Regarding As species, the most toxic form, As^{III}, was predominant (mean value: 0.055 mg/g), with the order of abundance being $As^{III} > As^{V} > DMA > MMA$, However, in all tested samples the levels of iAs were below the established EU regulatory limit.^[1] It would be useful to expand this research to different rice-based products, milk, and dairy products as they were recognized as important contributors to dietary iAs exposure in the young population, particularly in children under three years old.^[2]

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INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY (ICP-MS) ANALYSIS OF LANTHANIDES IONS SORPTION ON CALCIUM ALGINATE ENCAPSULATED IRON NANOPARTICLES

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Lanthanides are used for the development of innovative technology and their increasing application in the modern world may impact the environment and drinking water resources. Therefore, it is important to find new ways of extracting those elements from water media. In this work a new technique is developed which uses encapsulated non zero-valent iron nanoparticles (nZVI). nZVI were functionalized by pyridine-2,6-dicarboxylic acid and encapsulated in alginate hydrogel and used for the sorption of lanthanum, europium, gadolinium and dysprosium. Pyridine-2,6-dicarboxylic acid forms stable complexes with lanthanoids, while the encapsulation enables the nanoparticles to be more mobile and more resistant towards agglomeration and oxidation in comparison to bare nZVI.^[1,2] The efficiency of sorption was tested on individual solutions and a mixture of lanthanoids using inductively coupled plasma-mass spectrometry (ICP-MS). The functionalized nZVI were compared with neutral nZVI, and showed a higher efficiency in sorbing a mixture of the four elements, while the neutral nZVI shower superior results in sorbing individual elements from water solution.

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EVALUATION OF NUTRITION LABELING AND REGULATION COMPLIANCE IN INFANT FORMULAS, FRUIT JUCIES AND FOOD SUPPLEMENTS REGARDING ESSENTIAL AND TRACE ELEMENTS

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Tolerances for nutrition labelling purposes are important, as it is not always possible for foods to contain exact labeled concentration due to natural and production variations. However, nutrient content of foods should not deviate substantially from labelled values to the extent that such deviations could lead to customer misleading. Therefore, Commission services and the representatives of Member states have drawn up a document in a form of a guideline to verify labeling compliance. This study aimed to show the laboratory process of nutrition labeling evaluation regarding Ca, K, Fe, Zn, Se, Cu, Mg and Mn in infant formulas and food supplements. Food supplements in form of tablets or capsules were weighted (n = 10) to determine average weight and then homogenized with agate mortar and pestle. For multi-element analysis, sample homogenates (approx. 0,30 g) were wet digested in a microwave digestion system (Multiwave GO, Anton Paar) with nitric acid (HNO₃) and diluted to approx. 50 g. Sample analysis was done by inductively coupled plasma mass spectrometry (ICP-MS 7900, Agilent Technologies). Quality control was done by using certified reference material NIST 3280 Multivitamin/multielement tablets to monitor accuracy. After measurement, sample compliance was assessed according to the European guideline.^[1]

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POSTER PRESENTATIONS



DETERMINATION OF ELEMENTAL COMPOSITION OF COCOA SAMPLES - EVALUATION OF GREENER ANALYTICAL APPROACHES

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Cocoa is an important raw material used in the chocolate industry and the production of other cocoa-related products such as beverages, cakes, cookies, and ice cream. The beneficial effects of cocoa on human health are well-known and are associated with its high content of flavonoids which play a key role in reducing the risk of or delaying the development of cardiovascular diseases, cancer, and other age-related diseases. Cocoa also contains essential trace elements such as copper, iron, manganese, and zinc, which in small amounts have important functions in various physiological processes in the human body. However, excessive accumulation of these elements in the body can cause intoxication and may lead to a number of human health disorders. Taking into account the wide use of cocoa in the human diet and the negative effects of excessive concentration of trace elements, there is a need to gather data on the elemental composition of cocoa to ensure the quality and safety of cocoa products.^[1,2,3]

The aim of this study was to determine the elemental composition of cocoa powder using different analytical techniques and different sample preparation methods. Total reflection X-ray fluorescence (TXRF), energy dispersive X-ray fluorescence (EDXRF), and inductively coupled plasma mass spectroscopy (ICP-MS) were used to measure the elemental content of cocoa powder samples, using the results obtained with ICP-MS as reference values and comparing them with the results of the X-ray fluorescence-based methods. In the case of TXRF analysis, two different sample treatment procedures were applied, namely suspension preparation and microwave digestion in a closed vessel. The samples for ICP-MS analysis were prepared by microwave digestion in a closed vessel, while the samples for EDXRF were prepared in the form of pellets. The methods of sample preparation for TXRF and EDXRF, in the form of suspensions or pellets, are cost-effective, easy to use, and environmentally friendly, which is in line with the principles of green chemistry. The results obtained with the different techniques based on X-ray fluorescence spectroscopy were comparable to those obtained with ICP-MS. The analysis also gave insight into the advantages and limitations of X-ray fluorescence-based techniques compared to ICP-MS, which opens up the possibility of a wider use of these techniques for the quality control of cocoa products.

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ELEMENTAL FINGERPRINTING OF SELECTED SPARKLING WINES BY ICP-MS METHOD

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Wine quality parameters are closely linked to metal ion levels, which can influence yeast nutrition during fermentation, redox processes, color stability, acidity, and flavor development. The fingerprinting of the content of trace metals in wines is a valuable method to authenticate their geographical origin.^[1] Sparkling wine production involves unique processing steps that can influence metal composition. Therefore, understanding the contribution of metal composition in sparkling wine, as well as its application to verification of authenticity, is increasingly relevant.^[2]

In this work, inductively coupled plasma mass spectrometry (ICP-MS) was used to determine the elemental composition of 70 samples of sparkling wine produced by several Croatian and Slovenian winemakers. The measured concentrations of Ca, Mg, K, Na, Al, P, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Cd, Tl, Pb and selected rare earth elements in samples of sparkling wines were processed using the *Statistica* software package. Multivariate statistical methods such as principal component analysis (PCA) and hierarchical cluster analysis (HCA) along with partialleast square analysis (PLS) allow classification of separate group of samples according to contribution of elemental concentrations. It was established that the variables of highest importance for the profiling of sparkling wines were Al, Ca, As and Fe.

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MINERAL COMPOSITION OF FRESH FARMED EUROPEAN SEA BASS AND GILTHEAD SEA BREAM

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Gilthead sea bream and European sea bass are among the most important fish species in the European aquaculture; apart from wild fish, both species are farmed on an industrial scale and have proven to be economically very important and have contributed to the development of aquaculture in the Mediterranean region. In addition, the nutrients contained in fish are important for vital functions and are responsible for numerous health benefits. The aim of this study was to determine and compare the mineral composition of sea bream and sea bass meat. For this purpose, 29 sea bream and 25 sea bass samples were collected from farms in the Republic of Croatia. After acid digestion of ~ 0.2 g of the sample with 7 mL of 60% nitric acid and 1 mL of 30% hydrogen in the microwave, the fish samples were transferred to a volumetric flask (50 mL) and filled up to the mark with water and further diluted depending on the mineral. The determination of the minerals sodium (Na), calcium (Ca), potassium (K), magnesium (Mg), copper (Cu), zinc (Zn) and iron (Fe) was carried out using flame atomic absorption spectroscopy (AAS), while the concentration of phosphorus (P) was determined using a spectrophotometer. The research results show that there is no statistically significant difference in the observed mineral composition of sea bream and sea bass ($p \ge 0.05$). The content of the analyzed minerals decreased in this study as follows: K > P > Ca > Na > Mg > Zn > Fe > Cu. For macroelements, the concentration ranged from 4,031.11 mg/kg for sea bream and 3,850.94 for sea bass (potassium) to 284.80 mg/kg for sea bream and 284.99 mg/kg for sea bass (magnesium), while for microelements, the analysis showed the highest concentration for iron at 9.99 mg/kg and 9.96 mg/kg for sea bream and sea bass respectively and the lowest concentration of copper for both species (1.63 mg/kg for sea bream; 1.10 for sea bass). The results show that the content of minerals is primarily influenced by the feed source and environmental conditions, but also that fish meat is a good source of minerals that are necessary for the vital functions of the human body and have better bioavailability compared to minerals of plant origin.

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DIFFERENCES IN ELEMENTAL CONTENT IN HONEY SAMPLES FROM SERBIA

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This study investigates the elemental composition of wild cherry honey and baker's honey from the Serbian market, utilizing microwave digestion and ICP-OES analysis. Toxic metal concentrations (Cd and Hg) were below limit of detection, while Pb levels ranged from 0.013- $0.027 \,\mu g \, g^{-1}$ for wild cherry honey and baker's honey respectively, which is below the permissible limit of 0.10 mg kg⁻¹. Strikingly, wild cherry honey exhibited tenfold higher Ca content (116.34 $\mu g \, g^{-1}$) compared to baker's honey (12.12 $\mu g \, g^{-1}$), along with elevated levels of Mg, Fe, Zn, and Cu. These findings suggest that wild cherry honey surpasses baker's honey in mineral richness, indicating superior quality. With its enhanced nutritional profile, wild cherry honey stands out as a compelling choice for consumers. This research underscores the significance of honey type in assessing its elemental content and underscores the potential of wild cherry honey as a premium dietary supplement.

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ELEMENTAL COMPOSITION OF OAK HONEYDEW FROM SERBIA

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Interest in and consumption of oak honeydew as a functional food product have surged among the food industry and consumers. This study aimed to establish the elemental profile of oak honeydew collected in Serbia. Using microwave-assisted sample preparation and ICP-OES analysis, we examined ten biologically important elements and three toxic elements. The results were reassuring. Calcium, for instance, was found in the highest concentration (181.50 μ g g⁻¹), higher than typical in blossom honey. Other notable elements included Fe (13.23 μ g g⁻¹), Mg (12.18 μ g g⁻¹), and Al (2.91 μ g g⁻¹), with the remaining elements below 1 μ g g⁻¹. Toxic metals Hg and Pb were detected at 0.021 and 0.031 μ g g⁻¹, respectively, while Cd was below LOD. The absence of significant toxic elements underscores the safety of oak honeydew, making it a superior alternative to traditional blossom honey. These findings highlight the nutritional value and safety of oak honeydew, supporting its growing popularity as a functional food.

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SEASONAL VARIATIONS OF Ni, As, Cd AND Pb IN THE PM₁₀ FRACTION OF SUSPENDED PARTICULATE MATTER DETERMINED BY INDICATIVE MEASUREMENTS

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Division of Environmental Hygiene of Institute for Medical Research and Occupational Health is the reference laboratory in the Republic of Croatia for determining the chemical composition of airborne particles. The analysis of nickel, arsenic, cadmium and lead in the PM₁₀ particle fraction is carried out using the accredited method HRN EN 14902:2007 with acid microwave digestion and analysis by the ICP-MS technique. This work presents the results of measurement of Ni, As, Cd and Pb in PM₁₀ inhalable fraction of suspended particulate matter, sampled during the 2022 and 2023 at Jakuševec special purpose monitoring station, located in the southeast part of Zagreb. Sampling was conducted on quartz fiber filters from 55 m³ of ambient air, during the 24 hours using the accredited method HRN EN 12341:2023. Indicative measurements were carried out during the fifteen consecutive days in each season.

Results show that nickel levels were very low, with 65% of the results below the detection limit, so it was omitted from further data analysis. Annual mean mass concentrations of As, Cd and Pb were 0.37 ng/m³, 0.19 ng/m³ and 6.79 ng/m³ in 2022 and 0.47 ng/m³, 0.25 ng/m³ and 6.59 ng/m³ in 2023 respectively. Significant seasonal differences were found for As, Cd and Pb in 2022 but not in 2023. Significant differences were also found between years, for cadmium during the summer period and for arsenic in winter and summer period. The lead levels were the lowest during the summer, for both sampling years. The data were further compared with the fixed measurements obtained at the nearby state network monitoring station Zagreb 3 showing very good agreement. The most pronounced difference was found for the winter period.

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SEM AND ICP-MS AS CHARACTERIZATION METHODS OF IRON NANOPARTICLES USED FOR REMOVAL OF SELECTED RARE EARTH ELEMENTS

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Rare earth elements (REEs) are a group of chemical elements crucial for modern technology and industrial applications. The demand for REEs has increased significantly in recent years, leading to more frequent release of these elements into the environment. Due to the high demand and challenges in their production, it is essential to develop an effective method for recovering these elements from aqueous systems. Innovative method in this field includes the testing of new materials like zero valent iron nanoparticles (nZVI) which are a special class of zero-valent iron whose particle size is less than 100 nm. Nanoparticles have a core-shell structure composed of a metal iron core wrapped by iron (hydroxyl) oxide shell, which enables nZVI not only to have the reducing property of Fe⁰, but also to have the adsorption property. To ensure better selectivity, nanoparticles are often surface modified.^[1,2]

The aim of our study is to examine the adsorption efficiency of metal ions from aqueous solutions using neutral zero-valent iron nanoparticles and nanoparticles modified with dipicolinic acid (PDCA). Nanoparticles were synthesized using borohydride reduction of iron ions followed by addition of dipicolinic acid with molar ratio Fe:PDCA=2:1. In order to confirm the surface modification, nanoparticles were also characterized by scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR). Both, neutral and modified nanoparticles were enscapsulated in alginate hydrogel. The adsorption efficiency of metal ions (Lu³⁺, Sm³⁺, Ho³⁺, Y³⁺, Tb³⁺, Yb³⁺) from aqueous solutions was monitored by inductively coupled plasma mass spectrometry (ICP-MS).

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ELEMENTAL COMPOSITION OF DANDELION FROM CROATIA

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Dandelion (lat. Taraxacum) belongs to the Asteraceae family, and it is known mainly for its medicinal properties. For many years it has been successfully used worldwide in the food industry as a completely non-toxic and edible plant. It is an extremely rich source of phenolic acids, flavonoids and terpenes. Dandelion is also a powerful source of vitamins and minerals (calcium, sodium, magnesium, iron, copper, silicon, zinc, manganese). Due to its high content of nutrients, dandelion is often used as an ingredient for preparing salads and as a substitute for coffee or tea.^[1] Soil and plant contamination with potentially heavy elements such as As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Sb, Sn, Zn is becoming the subject of scientific research due to their harmfulness to human health. Variations in concentration of these elements are caused by the chemical composition of the original rocks and anthropogenic activities as well as different soil properties such as sorption capacity.^[2]

The aim of this research was to determine the elemental composition of dandelion from various regions of Croatia by inductively coupled plasma mass spectrometry. The samples for ICP-MS analysis were prepared by microwave digestion in a closed vessel.

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TLC TRACKING OF NANOPARTICLES BEFORE COUPLING TO ICPMS FOR INVESTIGATION OF ANTIMICROBIAL COATINGS

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Metal and metal oxide nanoparticles have been extensively investigate for their antimicrobial properties. As such, they are already widely applied on different medical and dental items. However, their increasing usage has raised global concerns in particular for the aquatic environment. Therefore, there is a need to apply precise, accurate and appropriate quantification methodologies in order to determine their presence and quantity on different materials, as well as in the environment.

In this presentation, we propose a simple, rapid and sensitive method for the determination of size and mass concentration of silver nanoparticles (AgNPs) in aqueous suspension. The method can be established independently, as was done in our laboratory on colloidally stabilized certified reference materials, or by direct coupling of thin layer chromatography (TLC) with ICM-MS spectrometry which we would like to try in future experiments. The proposed TLC method allowed the quantification of differently sized AgNPs (10, 20, 40, and 100 nm). Various experimental parameters affecting the characterization of AgNPs, such as the composition of the solvent mixture for mobile phase, and the stationary phases were investigated. Under optimal conditions, the proposed method was successfully applied to the characterization of AgNP size and concentration in aqueous test samples. Additionally, comparative methods for tracking nanoparticles such are SEM, TEM, AFM, DLS, NTA and others will be discussed and the comparison to newly developed protocol will be presented.

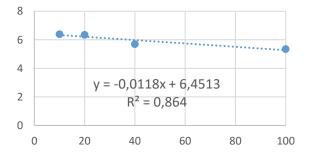


Figure 1. Linear correlation obtained by TLC separation and identification of silver nanoparticles of 10, 20, 40 and 100 nm

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