Proceedings of the 21st International Students Conference "Modern Analytical Chemistry"

Prague, 18—19 September 2025

Edited by Karel Nesměrák

FACULTY OF SCIENCE
Charles University

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Preface

Effective scientific communication – both oral and written – is a fundamental competence across all disciplines of science. To support the development of this essential skill among early-career researchers, the Department of Analytical Chemistry at the Faculty of Science, Charles University, hosts an annual conference dedicated to Ph.D. students in analytical chemistry. The present volume contains the proceedings of the 21st edition of this event, held on September 18–19, 2025. This gathering brought together 50 doctoral students from Croatia, Germany, Poland, the United Kingdom, and the Czech Republic, offering them an opportunity not only to present and discuss their current research, but also to connect, exchange ideas, and foster collaborations that contribute to the progress of analytical science. Moreover, the event provided a valuable context for enhancing their scientific English proficiency.

This issue includes four full-length papers; the remaining 46 participants opted to publish abstracts of their presentations. All contributions are arranged alphabetically by the family name of the main author, and are supported by indexes to facilitate navigation. The scope of the submissions spans the major domains of instrumental analysis – namely electroanalytical, separation, and spectroscopic techniques – and illustrates their diverse applications in addressing real-world problems. We trust that readers will find this collection intellectually stimulating and enjoyable to explore.

We gratefully acknowledge the patronage of the Division of Analytical Chemistry of the European Chemical Society and the Working Group of Analytical Chemistry of the Czech Chemical Society. Finally, we sincerely thank all sponsors for their generous contributions, which enabled the realization of this conference and continue to support our broader activities.

doc. RNDr. Karel Nesměrák, Ph.D.
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Electrolytic fingerprint visualization on metals: Comparing the effectiveness of methylene blue

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Keywords
Britton-Robbinson buffer
fingerprint visualization
metal
methylene blue

Abstract
Under specific conditions, metal surfaces undergo chemical passivation or corrosion. By selecting a suitable electrolyte, oxidation processes can be used to visualize latent fingerprints. Fingerprints were deposited on clean metal substrates (copper, brass, aluminum), and an electrolytic method was evaluated using Britton–Robinson buffer at pH values of 2, 7, and 12, with and without methylene blue. The visualization efficiency was evaluated using a stereomicroscope in relation to deposition time. The best contrast was achieved on brass at neutral pH with methylene blue, while copper and aluminum showed reactions depending on the pH and the presence of dye. Methylene blue was effective only under certain conditions; otherwise it caused staining or blurring of ridge details. This simple and low-destructive method shows the potential for fingerprint visualization on metals and offers scope for further optimization for forensic purposes.

1. Introduction

Latent fingerprints are considered of significant forensic value due to their uniqueness and permanence. In practice, the visualization of latent fingerprints most commonly occurs through the use of fingerprints powders [1], cyanoacrylate fuming [2], or dye application [3, 4]. In recent years, there has been an increasing interest in alternative approaches, particularly those that expand the possibilities of fingerprints visualization on metal surfaces. One such approach involves the use of electrolytes and dye solutions, which can enhance contrast between metal surfaces and fingerprint residues.

Although the behavior of metals in electrolyte solutions is well understood, their interactions with latent fingerprints remain underexplored. Nizam et al. [5] investigated the effect of electrolysis on the visualization of fingerprints on brass cartridge cases, employing concentrated hydrochloric acid as the agent for this process. It was found that the method's efficacy is time-dependent, with its effectiveness diminishing over time following fingerprint deposition.

Further research by Jasuja et al. [6] investigated the effect of different pH levels of aqueous sulfuric acid and sodium hydroxide solutions on the visualization of eccrine and sebaceous fingerprints on metal substrates. A substantial effect was observed in the presence of a second metal in the system, which promoted ion migration and accelerated substrate corrosion, thereby enhancing the visibility of the fingerprints. In a subsequent study, Jasuja et al. [7] explored silica gel-based electrolytes with calcium chloride and potassium permanganate, revealing results that demonstrated comparable efficacy to conventional dactyloscopic methods, such as cyanoacrylate fuming or dye suspension methods.

In addition to electrolytes, dyes also play an important role, especially in enhancing the fingerprint visibility on specific substrate types. Organic dyes such as gentian violet [8], Sudan black B [9], and methylene blue [10] have been employed for the detection of greasy components, lipids, or blood residues in fingerprints. Methylene blue serves not only as a pH indicator but also as a component of newly developed fingerprint powders that provide improved clarity and contrast of ridge details in the visible spectrum [10].

The present study focuses on the visualization of latent fingerprints on metal substrates using an electrolytic method with Britton-Robinson buffer at various pH values. In addition to the pure buffer, the effect of adding methylene blue was investigated. Methylene blue serves both as a dye, enhancing print contrast, and as an electroactive species influencing interactions at the metal surface. The objective of this study is to contribute to the development of simple, more effective, and less destructive methods for fingerprint visualization on metal surfaces.

2. Experimental

2.1 Chemicals and substrates

Methylene blue was purchased from Lachema (Czech Republic). The solutions were prepared using Britton-Robinson buffer, sodium hydroxide solution and redistilled water from the University of Chemical Technology, Prague. Acetone and 96% p.a. ethanol used for substrate cleaning were supplied by Lach-Ner (Czech Republic).

To optimize fingerprint visualization conditions, three metal materials commonly found in everyday life were selected: brass, aluminum, and copper. These 0.5 mm thick materials were cut into plates of approximately 15×25 mm.

2.2 Chemical cleaning of metal substrates and fingerprint collection

All metal substrates underwent sequential chemical cleaning using a series of solvents (redistilled water/acetone/warm soapy water/ethanol) according to the literature [3]. Following cleaning, the substrates were air-dried at laboratory temperature. This procedure ensures optimal surface conditions for subsequent processing.

Fingerprint samples were collected from a single donor and applied according to the procedure described in the literature [11]. The fingertips were intentionally contaminated with sebaceous secretions from facial skin to preserve the natural lipid composition of human sebum.

2.3 Preparation and application of electrolytic solutions

A 0.04 M Britton-Robinson buffer pH = 1.6 was alkalized with a 0.2 M sodium hydroxide solution to pH 2, 7, and 12 monitored by a pH meter (Labio, Czech Republic), equipped with a combined glass electrode. Three 0.01 M methylene blue solutions dissolved in Britton-Robinson buffer were prepared with the same pH values. These six Britton-Robinson buffers were tested on brass, copper, and aluminum.

Fingerprint samples were immersed in 6 vials, each containing 5 ml solution, for time intervals of 10, 30 and 120 minutes, as well as 1 and 5 days. Deposition time for each electrolyte and material was optimized, and the quality of the visualized fingerprints were evaluated using a stereoscopic microscope for a comprehensive comparison of the effectiveness of the individual electrolytes.

3. Results and discussion

Fingerprints were successfully visualized on all substrates; however, the quality of visualization depended on the pH, deposition time, and type of solution. The presence of methylene blue had a beneficial effect only under certain conditions, whereas in others it resulted in reduced contrast or non-specific surface staining. A detailed evaluation of fingerprint quality under each set of conditions (Britton-Robinson buffer/Britton-Robinson buffer with methylene blue) is summarized in Table 1.

3.1 Copper

According to a study by Jasuja et al. [6], a duration of 10–30 minutes was sufficient to achieve high-quality fingerprint visualization in the alkaline medium. In contrast, the acidic medium resulted in only partial visualization after 30 minutes. A notable discrepancy was observed at neutral pH. While previous literature reports suboptimal results under such conditions, the present study (Fig. 1a)

Table 1
Summary of fingerprint quality assessment for all substrates. Results are shown as Britton-Robinson buffer/Britton-Robinson buffer with methylene blue. Rating scale: (5) well-visualized fingerprints including minutiae, (4) good-quality fingerprints with minor imperfections, (3) visible fingerprints with more pronounced imperfections, (2) partially visualized fingerprints with very faint minutiae, (1) fingerprints not visualized, n.e. = not evaluated.

Substrate	pH	10 min	30 min	2 h	1 day	5 days
Copper	2	2/2	2/2	2/2	2/3	n.e./n.e.
	7	3/3	4/4	3/4	3/3	4/3
	12	3/2	3/3	3/3	4/3	3/2
Brass	2	2/3	2/3	2/4	3/3	3/n.e.
	7	3/4	3/3	5/3	3/4	n.e./2
	12	5/4	4/5	4/5	4/5	3/4
Aluminum	2	1/1	2/1	2/2	2/2	5/n.e.
	7	2/2	2/2	2/2	3/3	4/3
	12	2/2	2/2	2/3	2/2	n.e./3

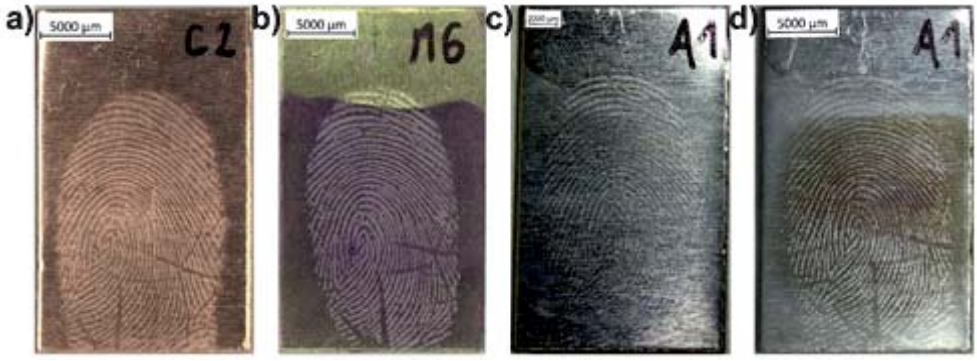

Fig. 1 Visualization of fingerprints using Britton-Robinson buffer: a) copper at pH = 7, b) brass with methylene blue at pH = 7, c) aluminium at pH = 2, and d) aluminium at pH = 2 after 5 days.

demonstrates that pH = 7 yields optimal outcomes, with considerable fingerprint stability maintained over several days.

The incorporation of methylene blue into acidic medium did not improve the fingerprint quality, probably due to the dye's low affinity for fingerprint residues. The highest contrast was again observed at neutral pH, becoming more pronounced after 24 hours. In the alkaline medium, methylene blue exhibited a tendency to bind after a shorter exposure period; however, prolonged exposure led to non-specific staining and reduced ridge clarity.

3.2 Brass

The results on brass aligned with Jasuja et al. [6], whereas copper alloys exhibited behavior similar to that of pure copper. In the acidic medium, visualization was limited; prints began to emerge only after several days and were often accompanied by surface oxidation. The most favorable outcomes were obtained at neutral pH, where a thin film formed around the ridges within two hours. In the alkaline medium, visualization was rapid (within 10 minutes), although the quality did not improve over time.

Methylene blue-enhanced visualization improved in the acidic medium due to the dye's protective effect against oxidation, achieving sufficient contrast after 2 hours. At neutral pH, the imprint appeared after 24 hours but faded within 5 days due to uneven dye deposition. The best contrast was observed under alkaline conditions with methylene blue (Fig. 1b) after 24 hours.

3.3 Aluminum

Aluminium yielded the best results in the acidic medium, with the fingerprints becoming visible after just 2 hours (Fig. 1c). After 5 days, oxidation led to a noticeable browning of the substrate (Fig. 1d). Compared to the findings of Jasuja et al. [6], our results demonstrated improved contrast with longer deposition times. In the neutral medium, the fingerprints remained barely visible and did not improve over time. The alkaline medium proved unsuitable due to the consistently poor visibility of the imprint, regardless of exposure duration.

When used alone, methylene blue proved unsuitable for enhancing fingerprint visualization under most tested conditions. In the acidic medium, the papillary lines darkened, and a matte film formed without clear visualization of the imprint. At neutral pH, good initial contrast was observed, but this diminished over time due to dye leaching. In the alkaline medium, the print became visible after 24 hours; however, methylene blue stained the entire surface non-specifically, obscuring the fingerprint.

To evaluate the forensic applicability of fingerprints visualization, minutiae were assigned to selected substrates, consistently meeting the Czech Republic legal threshold of ten characteristic points. A total of 65 minutiae were identified on the fingerprints developed on brass with Britton-Robinson buffer and methylene blue (Fig. 2).

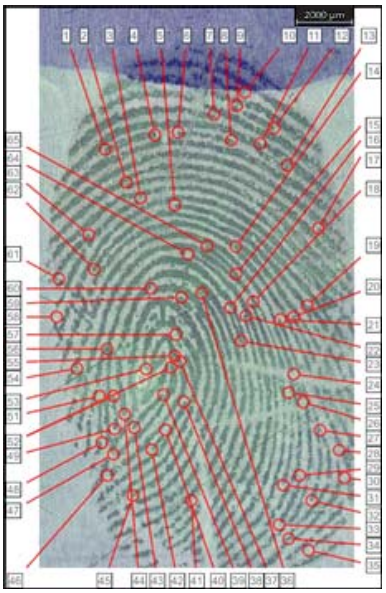

Fig. 2 Fingerprints visualized on brass using Britton-Robinson buffer with methylene blue after 24 hours deposition; assigned minutiae are indicated.

4. Conclusions

The effectiveness of latent fingerprint visualization in an electrolytic medium depends on a combination of factors, including the type of metal substrate, the pH of the solution, and the presence of methylene blue as a contrast agent with substrate-specific interactions. Brass was identified as the most versatile substrate, with a neutral pH containing methylene blue providing the most effective and stable visualization. For copper and aluminum, rapid visualization was achieved in an acidic buffer without a beneficial effect from the dye. From a practical perspective, it is essential to select visualization conditions appropriate to the chemical properties of the substrate. Future research should focus on evaluating the temporal stability of the visualized fingerprints and applying the method to real-world objects.

Acknowledgments

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Mass spectral structure elucidation by neural network model: A proof of concept demonstrated on esters

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Keywords
mass spectrometry
neural network
structure elucidation

Abstract
The aim of this study was to develop a neural network capable of suggesting chemical structures based on electron impact mass spectra. The model was trained on a dataset of esters, using their mass spectra and SMILES structures. Its architecture combines convolutional layers for spectral encoding and long-short term memory for structure generation, with teacher forcing applied during training. As a proof of concept, the model was tested on known esters from the NIST library and validated using experimental spectra measured by GC/MS. The predicted structures were mostly similar to the original ones, often differing only by minor substituents such as methyl groups. These results show that even though the model is not yet accurate enough for real identification, the approach is promising and could be further developed into a useful tool for structure elucidation in GC/MS analysis.

1. Introduction

Beer contains several thousand compounds, many of which have been identified in the past. Even so, many of them remain unknown. Some of these unidentified compounds may have a major impact on the quality of beer or their identification may push the boundaries of knowledge in this field. For these reasons, there is a need for tools and methods that would significantly streamline and speed up the process of identifying unknown substances, not only in beer. Such a tool could be neural network capable of suggesting chemical structures of compounds based on experimentally obtained mass spectra and retention characteristics in gas chromatography of unknown compounds.

The aim of the study is to develop a neural network model suggesting chemical structures based on electron impact mass spectra of unknown compounds, and the proof of concept would be demonstrated on esters.

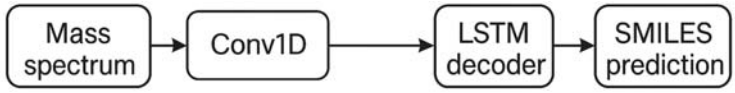

Fig. 1 Architecture of the neural network (LSTM = long-short term memory layer).

2. Experimental

2.1 Data processing

Data (mass spectra and chemical structures) of selected esters of monocarboxylic acids were obtained from NIST 14 library [1]. Dataset was divided into two subdatasets: training (810 esters), test (10 esters). And, mass spectra of the 5 selected esters were experimentally obtained by GC/MS (section 2.4). Mass spectra were limited to maximum *m/z* 600. Chemical structures were in the simplified molecular input line entry system (SMILES, [2]) strings and were transformed into canonical form by RDkit package [3]. SMILES strings were vectorized by tokenizer. The maximal length of the SMILES strings was limited to 100 tokens, and padding was used so each sequence has the same length.

2.2 Neural network architecture and training

Firstly, autoencoder was pretrained, the aim of the pretraining was that the model could code mass spectrum into latent space without loss of any information. Secondly, the pretrained part of autoencoder – encoder, was used in the suggested model. This part contains 5 convolutional layers, where only last 3 were further trainable. The output from pretrained encoder was connected to another convolutional layer and to global average pooling layer so the output was in the right shape for the decoder part. The decoder part contains long-short term memory layer and the teacher forcing [4] was used. A schematic representation of the architecture is shown in Fig. 1.

2.3 Chemicals

In this work, the following chemicals were used: ethyl caprate (≥98%, Sigma-Aldrich), ethyl myristate (≥98.5%, Merck), hexane (≥99%, Sigma-Aldrich), isoamyl acetate (≥99%, Merck), isobutyl acetate (≥98%, Merck), phenylethyl acetate (≥98%, Sigma-Aldrich).

2.4 Instrumentation

Gas chromatography and mass spectrometry with triple quad (Agilent Technologies 7000D) was used to obtained experimental mass spectra of the chosen

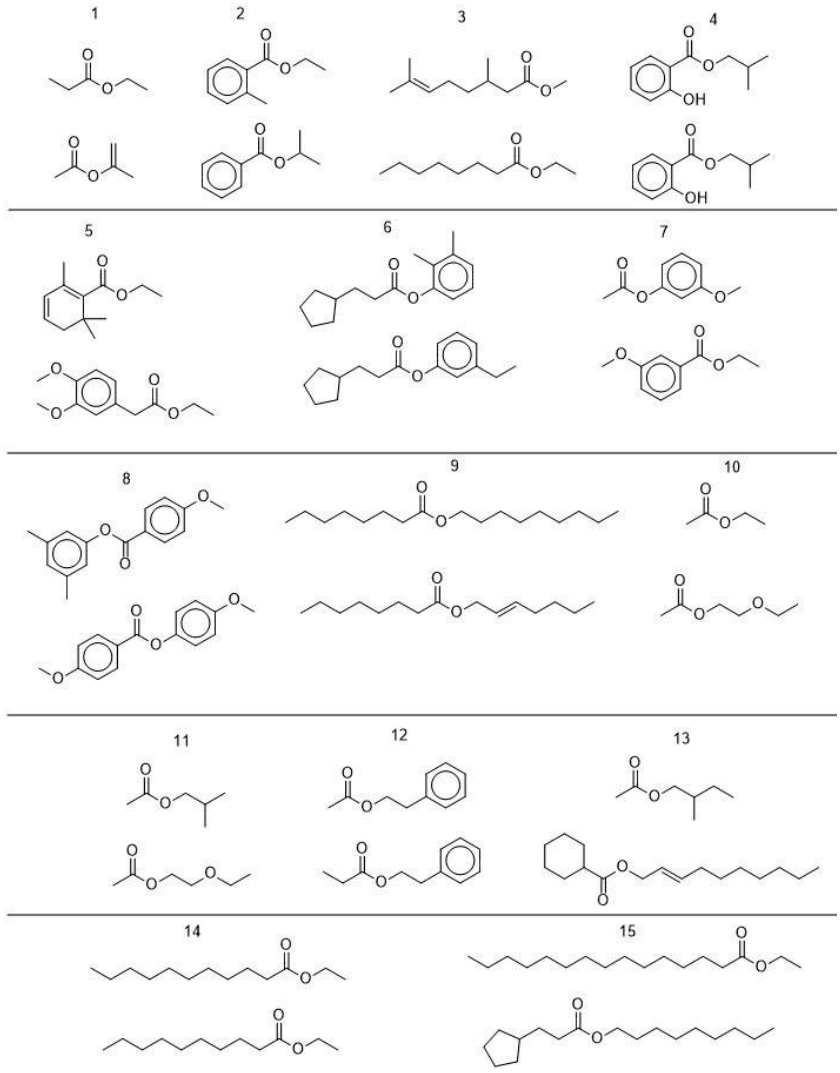

Fig. 2 Molecular structures of true molecules (upper) and suggested molecules (lower). Numbers 1–10 are molecules from test dataset and 11–15 are molecules from validation dataset.

esters. Analysis was performed using an HP-5MS UI column (30 m × 0.25 mm × 0.25 µm). Injection volume was 2 µl in split mode (5:1) at 250 °C. The oven temperature program was: 50 °C (1.5 min), ramped at 20 °C/min to 150 °C (5 min), then 10 °C/min to 210 °C (3 min), and finally 10 °C/min to 320 °C (5 min). Helium was used as the carrier gas (1 ml/min). The mass spectrometer operated in SCAN mode with electron ionization (70 eV) and ion source temperature of 230 °C.

Table 1
True and suggested SMILES strings and their calculated Tanimoto similarity. Molecules from test and validation dataset are divided by a line.

Number in Fig. 2	True SMILES	Suggested SMILES	Tanimoto index
1	CCOC(=O)CC	C=C(C)OC(C)=O	0.55
2	CCOC(=O)c1ccccc1C	CC(C)OC(=O)c1ccccc1	0.86
3	COC(=O)CC(C)CCC=C(C)C	CCOC(=O)CCCCCCC	0.63
4	CC(C)COC(=O)c1ccccc1O	CC(C)COC(=O)c1ccccc1O	1.00
5	CCOC(=O)C1=C(C)C=CCC1(C)C	CCOC(=O)Cc1ccc(OC)c(OC)c1	0.23
6	Cc1cccc(OC(=O)CCC2CCCC2)c1C	CCc1cccc(OC(=O)CCC2CCCC2)c1	0.84
7	COc1cccc(OC(C)=O)c1	CCOC(=O)c1cccc(OC)c1	0.44
8	COc1ccc(C(=O)Oc2cc(C)cc(C)c2)cc1	COc1ccc(OC(=O)c2ccc(OC)cc2)cc1	0.88
9	CCCCCCCCCOC(=O)CCCCCCC	CCCC/C=C/COC(=O)CCCCCCC	0.58
10	CCCOC(C)=O	CCOCCOC(C)=O	0.52
11	CC(C)COC(=O)C	CCOCCOC(C)=O	0.52
12	CC(=O)OCCc1ccccc1	CCC(=O)OCCc1ccccc1	0.95
13	CC(=O)OCC(C)CC	CCCCCCC/C=C/COC(=O)C1CCCCC1	0.38
14	CCOC(=O)CCCCCCCCCC	CCCCCCCCCC(=O)OCC	1.00
15	CCOC(=O)CCCCCCCCCCCCCC	CCCCCCCCCOC(=O)CCC1CCCC1	0.86

3. Results and discussion

The performance of the neural network was tested by prediction of chemical structure on 10 mass spectra from NIST library (test dataset) and on 5 mass spectra experimentally obtained (validation dataset) which contain a noise. Hence, it was also tested how would the neural network act if the input be the raw noisy experimental mass spectrum. The true chemical structures and suggested structures are on Fig. 2. There can be seen that suggested structures are quite similar to true structures (except example number 5). At most cases the difference are extra methyl groups or their position (example number 2, 3 ,6, 12). In order to quantify similarity between the true and the suggested structure, the Tanimoto index [5] was calculated (Table 1). The mean Tanimoto index for the test dataset was 0.65, while for the validation dataset it reached 0.74. Despite the presence of unfiltered noise in the validation spectra, the model demonstrated robust performance, indicating its ability to extract the key structural features from the spectra.

4. Conclusions

The proof of concept was demonstrated on the neural network suggesting chemical structures of esters based on their mass spectra. Even though that it is not suggesting the right structures in all cases, it could be very useful and helpful

tool in structure identification of unknown molecules in GC/MS as the model is able to find the main structural characteristics of the identified molecule. Yet, this neural network is not usable in real identification of the unknown compounds, but the results confirm that this approach is the right way towards a more comprehensive model trained for a wider range of chemical structures.

Acknowledgments

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Study of thermal-induced chemical transformations of hop essential oils in model samples

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Keywords
aroma
essential oils
hops
GC-MS
transformation

Abstract
This study investigates thermal-induced chemical transformations of 27 hop essential oils using model aqueous solutions analyzed by headspace gas chromatography–mass spectrometry (HS-GC–MS). After a simulated boiling process (90 min in a water bath), principal component analysis and retention-time-based mapping revealed that most esters and ketones remained relatively stable, with the exception of 2-dodecanone. Significant compositional changes were observed in α-pinene, β-pinene, myrcene, β-caryophyllene oxide, farnesol, irone, and others. Three transformation scenarios were identified: (i) single precursor to single product, (ii) structurally related precursors forming the same product, and (iii) multiple distinct compounds yielding a shared product. Interestingly, α-terpineol consistently appeared as a newly formed compound in samples not originally containing it. Newly formed products, currently labeled by retention time, are planned to be structurally identified in the upcoming phase of the research. The findings contribute to understanding thermal behavior of hop volatiles and may support the rational design of hop-forward beer flavor profiles.

1. Introduction

Hop essential oils are important secondary metabolites found in the lupulin glands of mature hop cones from female plants [1]. These are volatile compounds with a characteristic aroma that are transferred into beer during wort boiling or subsequent stages of the brewing process. To date, hundreds of such compounds have been identified and characterized [2].

Available studies indicate that the transfer of hop oils into beer during wort boiling and subsequent hopping stages (such as whirlpool hopping or dry hopping during fermentation or maturation) is highly complex and depends on multiple factors [3, 4]. Among the most significant and currently described are: (i) chemical reactions (e.g., oxidation, isomerization), (ii) interactions with beer components (e.g., ethanol), and (iii) reactions mediated by yeast enzymes.

Although some individual steps in the transfer of essential oils into beer have been described, there are still no established rules or predictive methods to determine the final hop aroma profile of beer based on the essential oil composition of hops and brewing parameters (e.g., hop addition regime, mashing program, wort boiling duration and intensity, yeast strain, maturation time, dry hopping dosage).

The main objective of this study is to elucidate a number of these still unclear processes in order to facilitate the selection of appropriate hop varieties for the production of beer with a targeted sensory profile.

2. Experimental

2.1 Reagents and chemicals

Used chemicals: isobutyl isobutyrate (≥98.0%), methyl hexanoate (≥98.0%), α-pinene (≥97.0%), isoamyl isobutyrate (≥98.0%), methyl heptanoate (≥99.8%), 2-nonanone (≥99,0%), linalool (≥99.0%), methyl octanoate (≥99.8%), methyl nonanoate (≥99.8%), nerol (≥97.0%), methyl geranate (AldrichCPR), 2-undecanone (≥99.0%), geranyl acetate (≥99.0%), 2-dodecanone (≥98.5%), β-farnesene (≥90.0%), irone (≥99.0%), β-caryophyllene oxide (≥99.0%), farnesol (≥95.0%), β-pinene (≥99.0%), myrcene (≥90.0%), limonene (≥97.0%), ocimene (≥90.0%), 2-decanone (≥99.5%), terpinen-4-ol (≥98.0%), α-terpineol (≥97.0%), methyl decanoate (≥99.0%), α-humulene (≥99.0%), *cis*-3-hepten-1-ol (≥97.0%) all from Merck and ethanol (≥99.8%) from Lach-Ner.

2.2 Sample preparation

Stock solutions of individual essential oils were first prepared by dissolving the corresponding analytical standards in 10 ml of ethanol. From these stock solutions, individual 10 ml model aqueous solutions with an approximate concentration of 10 mg l^{-1} were prepared in gas-tight 20 ml headspace vials. The model solutions were then divided into two groups: control samples and samples subjected to a boiling process. The latter underwent thermal treatment in a water bath for 90 minutes to simulate heat exposure.

Both control and thermally treated model solutions were subsequently analyzed using headspace gas chromatography–mass spectrometry (HS-GC–MS).

2.3 Instrumentation

The samples were analysed on the Thermo fisher chromatograph Trace 1310, equipped with capillary column TG-WAXMS (30 m, 0.25 mm ID and 0.25 film of acid-deactivated polyethylene glycol). Sample injections were performed using solid-phase microextraction (SPME Fiber assembly 65 µm PDMS/DVB, fused

silica). The fiber was thermally desorbed in the injector port set at 250 °C. The desorption time was 1 minute to ensure complete analyte release. Injections were carried out in split mode with a split ratio of 1:8, enabling controlled analyte transfer onto the chromatographic column. Helium was used as the carrier gas and maintained at a constant flow rate of 1.0 ml min^{-1} throughout the analysis. A fast and simple temperature program was chosen for its ease of implementation and reliable repeatability when analyzing a high throughput of samples. The program was as follows: 40 °C (1min); 30 °C min^{-1}; 260 °C (2 min). Detection was carried out by a Thermo Fisher mass spectrometer ISQ 7610 operating in scan mode over the mass range of 35–400 amu, with a dwell time of 0.2 seconds. Data acquisition was performed from the 2nd to the 12th minute of the chromatographic run.

2.3 Data processing

Raw GC-MS data were processed by eRah package [5] in Rstudio for automatic extraction of peaks, deconvolution, alignment and missing compound recovery.

The resulting processed data were subjected to principal component analysis by FactoMineR [6]. Loading plot was used for identification of peaks influenced by boiling process. Peaks with lower change between boiled and unboiled samples than 50% of area were filtered out of dataset. Identification of linalool, nerol and geraniol was then carried out by comparing the obtained spectra with spectra of reference analytical standards and data from the NIST library.

3. Results and discussion

Following the analysis and data processing of model solutions containing 27 hop essential oils, it was observed that compounds classified as esters exhibited relatively high thermal stability, as no statistically significant changes in their concentrations were detected after heat exposure.

A similar trend was observed for ketones, with the exception of 2-dodecanone, which showed a notable deviation. This finding suggests a potentially higher reactivity or volatility of this compound under thermal stress conditions. An overview of the concentration changes of 2-dodecanone is provided in Fig. 1.

In total, 15 essential oils were identified that did not undergo significant changes exceeding a 50% difference in peak area between control and heat-treated samples. These include: isobutyl isobutyrate, methyl hexanoate, isoamyl isobutyrate, methyl heptanoate, 2-nonanone, linalool, methyl octanoate, methyl nonanoate, methyl geranate, 2-undecanone, limonene, ocimene, 2-decanone, methyl decanoate, and *cis*-3-hepten-1-ol.

The most pronounced changes were observed in the following essential oils: α-pinene, β-pinene, myrcene, β-caryophyllene oxide, α-humulene, terpinen-4-ol, α-terpineol, β-farnesene, geranyl acetate, 2-dodecanone, farnesol, and irone.

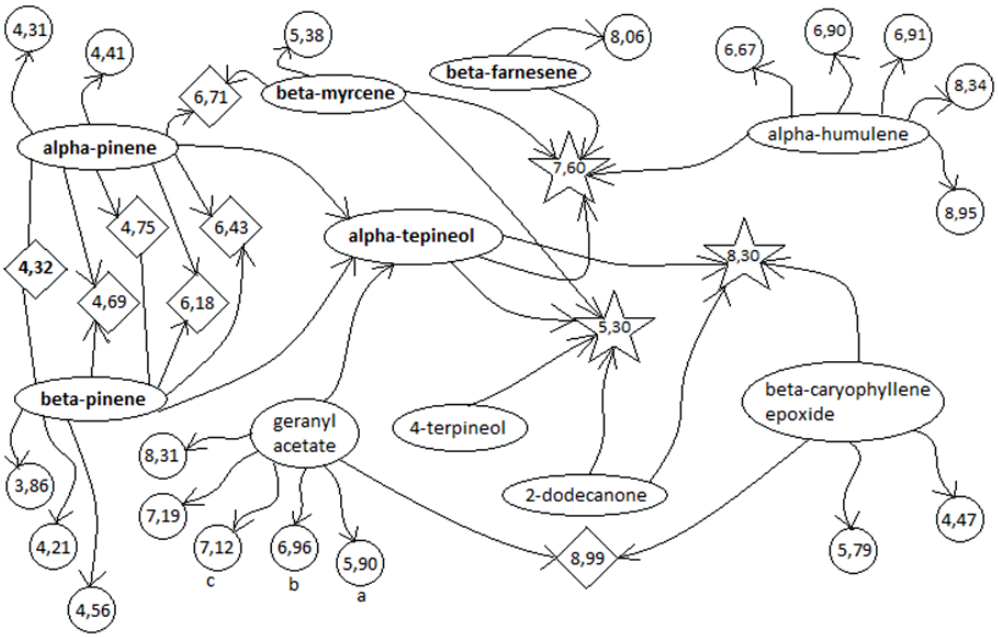

Fig. 1 The scheme of essential oils is represented with compound names shown in ellipses, and newly formed compounds are labeled by their retention time (in minutes). The letters *a*, *b*, and *c* indicate known compounds, identified by comparison of their mass spectra with those of authentic standards: (a) linalool, (b) nerol, (c) geraniol.

Based on the observed thermal transformations, three typical scenarios were identified:

1. The formation of a new compound from a single precursor after thermal exposure.
2. The formation of the same product from two structurally similar precursors, independently.
3. The conversion of several structurally distinct essential oils into the same product, regardless of their origin.

For example, farnesol gave rise to six new compounds after boiling process, while irone produced four novel products, each with a relative increase in abundance exceeding 50%.

A comprehensive mapping of the remaining essential oils, which exhibited multiple transformation pathways across all experimental variants, led to the development of a schematic representation of thermal conversions, presented in Fig. 1. The figure illustrates all three transformation scenarios observed in the model solutions of essential oils.

- Scenario I (formation of a new compound from a single precursor) is represented by retention times labeled within circles.
- Scenario II (formation of the same product from two structurally similar compounds) is indicated by retention times labeled within diamonds.

- Scenario III, where new products are shared across multiple essential oils, is marked with a star symbol (star).

Interestingly, an increase in α-terpineol was observed in several model solutions, even though these independent model systems did not originally contain α-terpineol as one of the monitored essential oils. This suggests that α-terpineol may be a common thermal degradation or rearrangement product formed from these essential oils.

The new compounds, currently labeled only by their retention times in minutes, are planned to be identified for the upcoming phase of the research.

4. Conclusions

The results of this study demonstrate that while many hop essential oils, particularly esters, exhibit high thermal stability, certain compounds such as 2-dodecanone, α-pinene, and farnesol undergo substantial transformation upon thermal treatment. The identification of three distinct transformation scenarios suggests the existence of predictable pathways influenced by compound structure. Notably, the recurrent formation of α-terpineol across multiple samples indicates its role as a potential thermal degradation or rearrangement product. These insights deepen the current understanding of volatile compound dynamics during beer production and may assist brewers in tailoring hop profiles for desired aromatic outcomes. Further identification of newly formed compounds is underway in the next research phase.

Acknowledgments

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A novel atmospheric pressure glow discharge-based hydride atomizer for atomic absorption spectrometry

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Keywords
atmospheric pressure glow discharge
atomic absorption spectrometry
hydride generation

Abstract
A novel hydride atomizer for atomic absorption spectrometry based on an atmospheric pressure glow discharge was constructed and its voltage-current characteristics measured. Subsequently, atomization of seven elements, introduced into the atmospheric pressure glow discharge by hydride generation, was optimized. The atmospheric pressure glow discharge performance was compared, in terms of sensitivity and limits of detection, to the other hydride atomizers. An externally heated quartz tube atomizer, the most common atomizer in hydride generation-AAS, was used as a reference, while a dielectric barrier discharge plasma atomizer, was employed for comparison.

1. Introduction

Several analytically important analytes such as As, Se, Sb, Sn, Pb, Bi, Te or Ge can be converted from liquid sample into their corresponding volatile hydrides with 100% efficiency and introduced into the atomic spectrometric detector to reach ultratrace determination of these elements. Sensitivity can be increased by an order of magnitude with hydride generation when compared to liquid sample nebulization. Atomic absortion spectrometry is still the most common detector for routine use in trace element analysis. The most frequent hydride atomizers used in atomic absortion spectrometry are the externally heated quartz tubes. Recently, the dielectric barrier discharge, was proven a promising hydride atomizer for some of the hydride forming elements including As, Se, Te and Sb [1, 2]. On the contrary, the hydrides of Pb, Bi, Sn or Ge were found difficult to atomize in dielectric barrier discharge. As a consequence, alternative types of atmospheric plasma discharges have been investigated. Among them, atmospheric pressure glow discharge seems to be promising.

Atmospheric pressure glow discharge is a non-equilibrium discharge formed between two electrodes powered by high DC or pulsed voltage (1–10 kV). The discharge gap varies between 1–5 mm with 10–100 mA discharge current [4]. The most explored design is atmospheric pressure glow discharge with one electrode liquid. This set-up, referred to as a liquid electrode atmospheric pressure glow discharge was proven compatible with detection by optical emission spectrometry allowing direct trace metal determination in liquid samples. Atmospheric pressure glow discharge arrangement with two solid electrodes coupled to hydride generation, would lead to a simpler experimental set-up and, at the same time, to higher sensitivity and lower limits of detections owing to the quantitative analyte introduction. The applicability of atmospheric pressure glow discharge to hydride atomization and excitation of free atoms and its compatibility with optical emission spectrometry detection has been proven [3]. The feasibility of the coupling of the atmospheric pressure glow discharge hydride atomizer to other atomic spectrometric detectors and the performance of such arrangement remain unexplored.

The aim of this work was to construct an atmospheric pressure glow discharge hydride atomizer including its power supply source compatible with atomic absorption spectrometer, study its voltage-current characteristics and assess its potential.

2. Experimental

2.1 Chemicals

All reagents were of analytical grade or higher purity. The solutions and dilutions were made with deionized water (< 0.1 mS cm, Ultrapur, Watrex, USA). Working standards were prepared from 1000 mg l^{-1} stock solutions of As(III) (Merck, Germany), Sb(III) (Fluka, Germany), Pb(IV) (BDH, United Kingdom), Se(IV), Sn(IV), Bi(III) (Sigma-Aldrich, Germany) and Te(IV) (Analytika, Czech Republic). Diluted HCl, prepared from 37% HCl (p.a., Merck, Germany), served as the matrix for working standard solutions as well as the blank. The reductant was a solution of $NaBH_4$ (Sigma Aldrich, Germany) stabilized in 0.4% (*m/v*) KOH (Lach-Ner, Czech Republic). Solid $K_3[Fe(CN)_6]$ (p.a., Lachema, Czech Republic) was added to both the standard and blank to reach its 1% concentration (*m/v*) when hydride generation of Pb was investigated. Solid NaOH pellets (p.a., Penta, Czech Republic) were used as a filling of the gas phase dryer (see below). Either Ar (99.996%), or He (99.998 %), purchased from SIAD Czech (Czech Republic), were used as carrier and discharge gas.

2.2 Instrumentation

A Varian SpectrAA 300/400 (GBC, Australia) atomic absorption spectrometer equipped with hollow cathode lamps and without background correction was

Table 1
Optimum hydride generation and atomic absorption spectrometry detection conditions.

Analyte	Hydride generation conditions			AAS parameters		
	c(HCl)/mol l^{-1}	w(NaBH$_4$)[b]/%	Dryer	λ/nm	Slit/nm	Lamp current/mA
As	1.0	1.0	NaOH	193.7	0.5	10.0
Se	1.0	0.5	Nafion	196.0	1.0	10.0
Sb	1.0	0.5	Nafion	217.6	0.2	10.0
Sn	0.1	1.5	–	286.3	0.5	12.0
Pb	0.1[a]	2.0	Nafion	283.3	0.5	10.0
Te	3.0	2.0	Nafion	214.3	0.2	10.0
Bi	1.0	0.5	Nafion	223.1	0.7	12.0

[a] 1% $K_3[Fe(CN)_6]$ added.
[b] Stabilized in 0.4% (*m*/*v*) KOH.

employed. Table 1 summarized the operation conditions. The peak area of the signals was recorded from which sensitivity of the measurement was calculated as the peak area divided by the analyte mass.

2.3 Hydride generation

An in-house made, flow injection hydride generation system based on a peristaltic pump (Ismatec, Switzerland), analogous to that described in ref. [5] was employed. Analyte standards were injected by a six port manual injection valve (V-451, IDEX Health-Science, USA) with a 0.50 ml loop into the flow of the carrier liquid (4.0 ml min^{-1}) before mixing with the reductant (1.2 ml min^{-1}). The optimum concentration levels of the carrier liquid (HCl) and the reductant ($NaBH_4$) were analyte dependent as stated in Table 1. The reaction mixture was merged downstream with a flow of carrier gas (Ar if not stated otherwise) controlled by a mass flow controller (Omega Engineering, USA) and directed to the quartz gas-liquid separator with a forced outlet. If not stated otherwise, analyte hydrides were introduced into the atmospheric pressure glow discharge atomizer through a dryer, while liquid waste was drained from the bottom of the gas-liquid separator. The dryer was realized either by a polypropylene cartridge (100 mm long, 15 mm i.d.) filled with NaOH pellets, or a Nafion™ membrane tube model MD-110-12P (12″ long, 0.11″ i.d., Perma Pure, USA). The latter one used 1.0 l min^{-1} Ar as a drying gas.

2.4 Atmospheric pressure glow discharge

The design of the atmospheric pressure glow discharge atomizer is derived from the quartz tube atomizer atomizer using exactly the same quartz body. This allows direct comparison of analytical performance of both atomizers. Atmospheric pressure glow discharge differs from quartz tube atomizer by two holes drilled

against each other in the center of its optical arm through which the electrodes are inserted. Both were made of tungsten and were tip shaped. An in-house DC power supply source was employed. Its input voltage (0–12 V DC) was converted to a high voltage in a pulsed mode (18 kHz, 50% duty cycle) used to power the atmospheric pressure glow discharge.

2.5 Voltage-current characteristics

A model Infiniium DSO-S 204A oscilloscope (Keysight Technologies, USA) equipped with a Tektronix (USA) model P6015A high voltage probe, and a Pearson Electronics (USA) model 2877/6585 current probe were employed to investigate the time resolved voltage and current characteristics of the atmospheric pressure glow discharge discharge.

3. Results and discussion

3.1 Effect of discharge gas and dryer

In plasmas such as atmospheric pressure glow discharge or dielectric barrier discharge the carrier gas serves also as a discharge gas affecting thus the formation of energetic species (ions, metastables, etc.) and electron number density as well as the analyte hydride atomization processes. Apart from Ar, also He was investigated. Taking the sensitivity reached for given analyte in Ar as a reference (100%), the sensitivity observed in He was 14% for Se, 25% for As, 44% for Te, 50% for Pb, 70% for Sb, 75% for Sn and 85% for Bi. Ar was selected as the discharge gas.

A universal dryer compatible with all hydride forming elements does not exist since each hydride has different, analyte-dependent, physico-chemical properties. These analyte dryer combinations have been previously shown not to cause analyte losses in the dryer [1, 5]: As and Sn with NaOH dryer and Se, Sb, Pb, Te and Bi with Nafion dryer. The optimum dryers found for the hydride generation-atmospheric pressure glow discharge-atomic absorption spectrometer arrangement are listed in Table 1.

3.2 Effect of argon flow rate

The effect of argon flow rate on analyte sensitivity was investigated with the results depicted in Fig. 1. The same trend can be observed for all analytes studied except for Se. The sensitivity is increasing with increased flow rate, reaching a plateau, followed by sensitivity decrease at higher flow rates due to dilution. A monotonous decrease of sensitivity was observed for Se. Optimum flow rate of 50 ml min^{-1} Ar was chosen for Se and As and 75 ml min^{-1} Ar for Bi. An optimum of 100 ml min^{-1} Ar was selected for the remaining analytes.

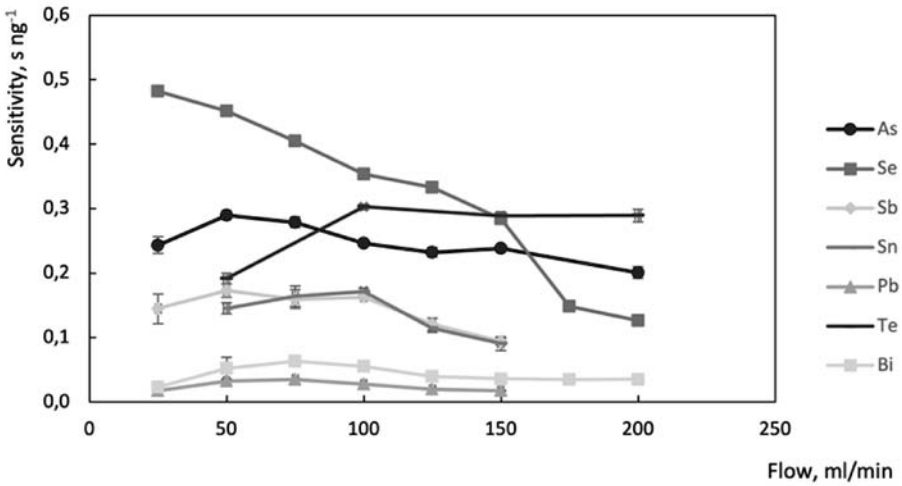

Fig. 1 Effect of argon flow rate on sensitivity. Standard concentration 5 ng ml^{-1} Sn, 10 ng ml^{-1} As, Se, Sb, 20 ng ml^{-1} Pb, and Te, 40 ng ml^{-1} Bi. Nafion dryer for Se, Sb, Pb, Te and Bi, NaOH dryer with As an Sn. Power source input voltage 12 V, except for Bi (7 V).

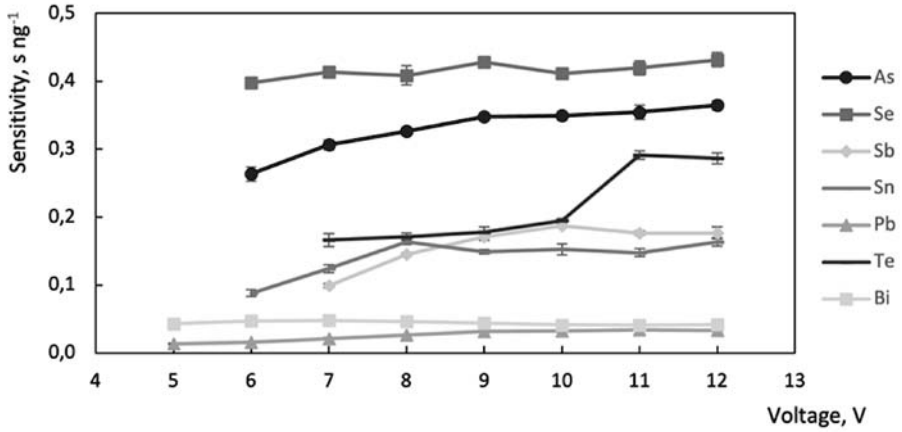

Fig. 2 Effect of input voltage on sensitivity. Standard concentration 5 ng ml^{-1} Sn, 10 ng ml^{-1} As, Se, Sb, 20 ng ml^{-1} Pb and Te, 40 ng ml^{-1} Bi. Nafion dryer for Se, Sb, Pb, Te and Bi, NaOH dryer with As an Sn. Power source input voltage 12 V, except for Bi (7 V). Argon flow: 50 ml min^{-1} for As, Se, 75 ml min^{-1} for Bi and 100 ml min^{-1} for Sb, Sn, Te, Pb.

3.3 Effect of discharge voltage

The effect of DC input voltage delivered to the atmospheric pressure glow discharge power supply source was investigated in the range from 6 to 12 V with the results depicted in Fig. 2. Voltage values above 12 V were not investigated in order to eliminate the risk of power source damage. Voltage values below 6 V were investigated only if a stable plasma discharge could be sustained. An increase of the sensitivity with increasing input voltage followed by a plateau was observed

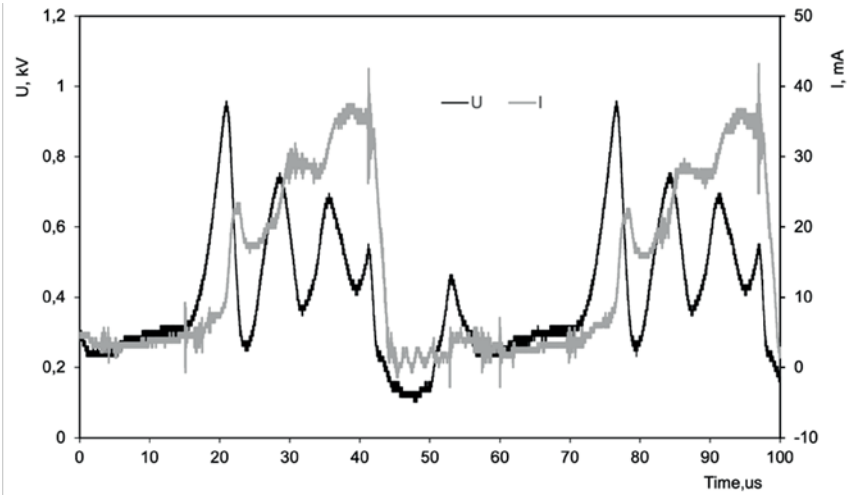

Fig. 3 Atmospheric pressure glow discharge voltage-current characteristics. Hydride generation conditions: 1 mol l^{-1} HCl, 0.5% $NaBH_4$ in 0.4 % KOH, 100 ml min^{-1} Ar, NaOH dryer.

for As, Sb, Pb and Te while the sensitivity for Se remained constant regardless of the voltage applied. The maximum sensitivity for Bi was reached at 7 V selected as optimum for further measurements. The optimum voltage of 12 V was chosen for all other analytes.

The important features of the discharge are given by its voltage-current characteristics. These were measured under optimum conditions (12 V input voltage, 100 ml min^{-1} Ar) being presented in Fig. 3. The pulsed character of the discharge can be seen with voltage and current maxima of 1 kV and 40 mA, respectively. The discharge period (52 s) corresponds to the 18 kHz excitation frequency.

3.4 Analytical figures of merit

Calibration curves were measured in the hydride generation-atmospheric pressure glow discharge-atomic absorption spectrometer arrangement under the optimum atomization conditions. limits of detection and sensitivity were quantified (Table 2). For comparison, the results found previously for the same analytes in dielectric barrier discharge and quartz tube atomizer atomizers [1] with the same hydride generation system in the same laboratory are included in Table 2.

Table 2
Sensitivity and limits of detection (LOD) found in atmospheric pressure glow discharge (APGD), quartz tube atomizer (QTA), multiple microflame quartz tube atomizer (MMQTA) and dielectric barrier discharge (DBD) atomizers.

Analyte	APGD			MMQTA		DBD	
	Sensitivity/s ng^{-1}	*LOD* /ng ml^{-1}	APGD as QTA / s ng^{-1}	Sensitivity/s ng^{-1}	*LOD* /ng ml^{-1}	Sensitivity/s ng^{-1}	*LOD* /ng ml^{-1}
As	0.41	0.18	0.31	0.48	0.15	0.48	0.16
Se	0.37	0.09	0.42	0.53	0.15	0.32	0.24
Sb	0.17	0.21	0.21	0.36	0.14	0.46	0.15
Sn	0.17	0.19	0.12	0.20	0.33	0.03	3.60
Pb	0.03	1.53	0.42	0.29	0.20	0.04	2.60
Te	0.23	0.1	0.27	0.32	0.10	0.31	0.20
Bi	0.06	0.33	0.42	0.40	0.10	0.15	1.00

4. Conclusions

Atmospheric pressure glow discharge can compete well with quartz tube atomizer or multiple microflame quartz tube atomizer, respectively, when used for As, Se, Te, Sb or Sn. In contrast, the sensitivity of Bi and Pb determination in atmospheric pressure glow discharge is an order of magnitude lower compared to quartz tube atomizer.

Acknowledgments

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Abstracts

Determination of silver nanoparticles in products of personal hygiene

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Keywords
cosmetics
nanoparticles
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Nanoparticles are solid particles of nanometre-scale size representing a subgroup of insoluble or biopersistent and intentionally manufactured materials with one or more dimensions on the scale from 1 to 100 nm. Nanoparticles are not only used in scientific fields, but also used in everyday life. This includes electronics, textiles, food and cosmetics. The second most common type of nanoparticles, silver nanoparticles, are used because of their antimicrobial, antifungal, anti-inflammatory and preservative properties. Thus, the primary use of silver nanoparticles is in medical cosmetics including creams, shampoos, toothpastes, hand wash or wound treatment products. Even though the standard dermatology tests showed complete safety for dermal use, there is still concern about the fate of nanoparticles and their impact on human health. Therefore, monitoring the human exposition to nanoparticles is necessary driving the innovations in sample preparation and in determination methods. Single particle inductively coupled plasma mass spectrometry can detect metal-based particles in various media including dissolved metal background and mixtures of other particles. This surpasses other techniques used for nanoparticles detection and determination, e. g., electron microscopy and field flow fractionation. Sample preparation and stabilization have to overcome several problems. Specifically, silver nanoparticles are liable to aggregation and dissolution, which could lead to misrepresentation of results, both in particle diameter and number concentration. This work focuses on methods of stabilization, sample preparation and ultimately, the determination of silver nanoparticles in products of personal hygiene accessible on the Czech market. Several stabilization and extraction agents were examined. The optimal stabilization and extraction agent were selected, along with the optimal sample preparation procedure. Preceding the final determination of silver nanoparticles in chosen products, the validation of the methods was performed.

Improvement in Native Mass Spectrometry: Optimization of ESI-Emitters

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Keywords
emitters
enterobactin
lipocalin
mass spectrometry

The study of non-covalent complexes relies essentially on native mass spectrometry. Prior to the standard settings of the instrument, various characteristics influence the quality of spectra including sample purity (proteins, ligand and solvent buffer), emitter shape and conductivity. Optimizing the gold-coated capillaries for sample insertion was the goal of the investigation. The non-specific binding may be caused by the big orifice of emitter, which can be changed to smaller diameters for better results. The capillary pulling configuration was adjusted based on the instrument's ramping temperature (Sutter instrument P-97). Pure gold was applied to the capillaries by twice under the following parameters: current 30 mA (target value 2.5 kV), Argon 0.12 Torr and duration 120 s. The diameter of orifice was measured by scanning electron microscopy (Nova Nanosem 450). The electrospray ionization quadrupole time-of-flight mass spectrometry (Synapt G2Si, Waters) was used to analyse the non-covalent complex Lipocalin1-enterobactin. The Ramp value 355 generates the emitters with orifice ≈ 874.6 nm which showed a decrease in non-specific binders such as sodium or potassium. The modification was significant in comparison to the prior pulling settings, which produced a tip with a longer shaft having a diameter of ≈ 750 nm, it was unusually fragile and small particles could clog, in that case the only solution is to construct a small incision that would increase the orifice diameter (4.296 μm) and increase sodiated adducts. Therefore, a smaller diameter of emitters improves the quality of native MS data by decreasing non-specific binding.

Application of analytical techniques in assessing biochar interactions with soil environment and contaminants

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Keywords
bioaccumulation
constructed wetlands
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NSAID
water treatment

Pharmaceutical pollutants, particularly non-steroidal anti-inflammatory drugs (NSAIDs) such as ibuprofen, represent a significant concern due to their persistence, bioactivity, and potential ecological impact. Constructed wetlands are increasingly explored as sustainable systems for wastewater treatment, yet their efficiency in removing micropollutants remains largely unknown. This research focuses on the use of analytical and separation techniques to evaluate the bioaccumulation of ibuprofen in selected plant species under controlled conditions simulating wetland environments. Radiolabelled ibuprofen was used to quantify uptake and mobility within plant tissues, by utilizing scintillation counting and autoradiography. In parallel, the potential of biochar produced and modified through pyrolysis of biomass – as an adsorbent for ibuprofen and related compounds was assessed. Beyond its sorption capacity, biochar application to soil systems is also being investigated for its long-term impact on carbon sequestration, water and nutrient retention, and mitigation of greenhouse gas emissions. However, knowledge gaps remain, particularly regarding its long-term behaviour under field conditions, effects on soil biota, and surface transformations over time. Results to date indicate notable ibuprofen accumulation in wetland plant species and promising sorption efficiency of modified biochars, supporting their role in integrated remediation strategies. This work contributes to a broader understanding of micropollutant dynamics in artificial and terrestrial ecosystems, and the potential of biochar in sustainable water and soil management.

Optimization of suspension preparation for elemental analysis of topical formulations using TXRF and Box–Behnken design

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suspension
topical formulation
TXRF

Gels, lotions, creams, and ointments are among the most commonly used topical cosmetic formulations that consumers around the world use on a daily basis. Exposure to potentially toxic elements in cosmetic products is a serious concern, as their repeated and prolonged use may increase the risk of adverse health effects, including skin irritation and allergic reactions, as well as negative systemic effects due to their absorption through the skin. Therefore, routine elemental analysis is essential to ensure the safety and quality control of cosmetic products. Atomic absorption spectroscopy and inductively coupled plasma mass spectrometry (ICP-MS) are extensively applied techniques for elemental analysis of cosmetic products. However, the increasing importance of environmentally friendly analytical methods has driven the development and introduction of more environmentally friendly alternatives. Among these, total reflection X-ray fluorescence spectrometry (TXRF) has emerged as a promising technique, that offers minimal sample preparation, low reagent consumption, and reduced environmental impact. This study describes the development of a simple, rapid, cost-effective, and environmentally friendly method for the preparation of suspensions for multi-elemental analysis of gel for topical application using TXRF. A Box-Behnken design was employed to determine the optimal method parameters through a response surface methodology. Three variables were evaluated in the optimization study: the type of dispersant, sample deposition volume, and the homogenization method. The elemental composition of the gel sample used in the

optimization study was first determined by ICP-MS after microwave-assisted digestion in a closed vessel. To optimize the conditions for the preparation of the sample suspension, the results obtained by TXRF analysis following the suspension preparation method were compared with those obtained using ICP-MS after the established microwave digestion method for recovery studies.

An electrochemical study of pinene

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Keywords
pinene
voltammetry

In this work, we have investigated the electrochemical behaviour of pinene in the ionic liquid 1-ethyl-3-methylimidazolium ethyl sulfate in acetonitrile as a supporting electrolyte by cyclic voltammetry and its quantitative determination by square-wave voltammetry. Pinene is an unsaturated bicyclic monoterpene of natural origin (pine trees) excreted by varroa mites. They are among the most destructive pests of honeybees globally, capable of killing entire colonies of honeybees if left untreated. Therefore, early detection of the presence of varroa mites is essential in protecting honeybees. Although eDNA analysis is a commonly used method for detecting the presence of invasive pests including varroa mites, this technique is time-consuming, costly, and can provide false positive or false negative results. Notably, pinene exists as α-pinene and β-pinene isomers, but the former is more abundant. Previously, pinene was electrochemically detected at a metallic-organic framework-immobilised platinum and glassy carbon electrodes, where the structural isomers were discriminated. However, there was no report on the reaction mechanism, nor the identity of product(s). In our work, cyclic voltammetry revealed that (α- or β-) pinene is irreversibly oxidised at relatively high potential (ca. +1.80 V versus Ag|AgCl) with no reduction peak observed. Meanwhile, severe electrode fouling was encountered during the voltammetric experiments. From a calibration study using square wave voltammetry, the lowest quantifiable concentration (based on a signal-to-noise ratio of 3) of β-pinene was 1 mmol L^{-1}.

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Application of boron-doped diamond electrode for the determination of penoxulam

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Keywords
boron-doped diamond electrode
penoxulam
voltammetry

The boron-doped diamond electrode has gained considerable attention in electroanalysis thanks to its outstanding electrochemical properties, including a wide potential window, low background current, high chemical and mechanical stability. These features make boron-doped diamond electrode particularly well-suited for detecting environmental pollutants, especially pesticides, which are becoming increasingly prevalent in ecosystems due to intensive agricultural practices. Among these, herbicides like penoxulam are of growing concern due to their widespread use and environmental persistence. Penoxulam, a triazolo-pyrimidine herbicide, acts by inhibiting acetolactate synthase and is widely applied in cereal production. Given its increasing application, there is a strong need for sensitive and reliable analytical methods to monitor its presence in environmental samples. In this work, the electrochemical behavior of penoxulam was studied using cyclic voltammetry on a boron-doped diamond electrode in Britton-Robinson buffer across a pH range of 2.0–10.0. The compound showed clear electrochemical activity throughout the tested pH range, with the most pronounced oxidation peak at pH = 2.0. The oxidation process was found to be irreversible and diffusion-controlled. Based on these findings, a quantitative determination method was developed using differential pulse voltammetry. Key parameters of the supporting electrolyte and differential pulse voltammetry technique were optimized to achieve the best analytical performance. The method was validated by establishing a calibration curve and evaluating figures of merit,

including limit of detection and limit of quantification. Possible interferences from coexisting ions and selected pesticides were also assessed. The developed procedure proved effective in analyzing real environmental samples, confirming its potential for practical applications.

Novel HPLC buffer blending method for weak electrolyte pK_a determination

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Keywords
buffer blending
HPLC
mixed mode chromatography
pK_a determination
weak electrolyte

Analyte pK_a determination via HPLC is advantageous in early stages of drug discovery. The advantages of this method stem from the small amount of analyte required and the dispensability of sample purity, an otherwise essential requirement in potentiometric or spectrophotometric pK_a determinations. The HPLC approach commonly utilises reversed phase chromatography, leveraging the fact that the analyte's ionisation state affects its hydrophobicity and therefore retention. Estimation of the analyte pK_a value in this setting is done either in isocratic conditions, by plotting the retention factor as a function of pH, or by generating a pH gradient, in less chromatographic runs but utilising more complex equations. Typically, an organic modifier is necessary in the mobile phase, an addition that distorts the observed pK_a value. Hereby, we present a novel mobile phase blending method aimed to fully automatise the pK_a determination process for weak bases and acids via HPLC. The method uses buffer blending by pumps to produce mobile phases in the range of pH 2.5–8.6, within the liquid chromatography system. Furthermore, we demonstrate that utilising this method in mixed mode chromatography, combining reversed phase and ion exchange chromatography while in isocratic conditions, brings the benefits of working with a solely aqueous mobile phase. The method also enables a linear pH gradient generation, likewise applicable for pK_a determination.

Use of analytical methods for the oxidation mechanisms of synthetic selaginpulvilins study

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Keywords
IR spectroelectrochemistry
liquid chromatography
mass spectrometry
oxidation mechanism
selaginpulvilins

Selaginpulvilins are natural biologically active substances found in plants, e.g., *Selaginella pulvinata*, as their secondary metabolites, along with selaginellins, neolignans, and biflavonoids. Some of their synthetic derivatives were found to form stable radicals in air, which is quite rare. In this contribution, the oxidation mechanisms of four synthetic selaginpulvilins were proposed using analytical methods, namely IR spectroelectrochemistry and HPLC/MS analysis of oxidation products obtained by exhaustive electrolysis at constant potentials corresponding to the oxidation waves of the studied substances. The composition of the mobile phases and the sample preparation of the oxidation product mixture were optimized to improve the ionizability of the analytes. In addition, the spatial distribution of HOMO orbitals was calculated using the Spartan program. All results suggest that the first electron transfer, followed by hydroxylation, occurs on the fluorene skeleton.

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Nitrate detection using a single-piece electrode based on a black PVC membrane

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Keywords
carbon nanomaterials
ion-selective electrode
potentiometry
single-piece electrode

The development of ion-selective electrodes started in 1906 when Max Cremer demonstrated opportunities of the glass electrode. Ion-selective electrodes are electroanalytical sensors with a membrane whose potential reflects the activity of the ion. They are a robust tool for ion detection due to their unique parameters such as high degree of selectivity and sensitivity. In this study, graphene, carbon black, and carbon nanotubes were employed as modifiers of a PVC-based membrane. The sensor's construction involved incorporating carbon nanomaterials directly into the polymeric membrane. Chronopotentiometry and Electrochemical Impedance Spectroscopy were applied to evaluate electrical properties, while potentiometric measurements assessed analytical parameters such as sensitivity, repeatability, detection limit, and redox sensitivity. The modified electrodes exhibited a near-Nernstian response (54 mV/pNO_3^-) to nitrate ions over a broad linear concentration range (10^{-1} to 10^{-6} mol dm^{-3} NO_3^-). Despite the presence of carbon materials, the electrodes remained insensitive to redox-active species. The newly developed ion-selective electrode enables fast, simple, and cost-effective analysis of environmental samples. Modified electrodes exhibit stable potential, good repeatability, and high selectivity. The designed ion-selective electrodes find theirs use in water quality monitoring. This research has created new opportunities to design efficient potentiometric sensors with improved performance parameters for environmental monitoring.

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Reductive electrochemical grafting of carbon-based electrodes by 4-nitrobenzenediazonium salt

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Keywords
boron-doped diamond
diazonium salts
electrochemical grafting
electrochemical reduction
surface functionalization

Boron-doped diamond electrodes are greatly treasured in different electroanalytical applications and developing biosensors because of their excellent chemical stability, wide potential window, low background current, fouling resistance, and promising biocompatibility. Thus, boron-doped diamond electrodes can be used to make long-term and reusable biosensing platforms in this case. A stable surface modification supporting the electrode's chemical specificity and stability is achieved. Diazonium salt grafting to boron-doped diamond electrodes creates stable, covalently C–C bound functional layers, giving a versatile platform to immobilise a biorecognition element for the target substrate. The 4-nitrobenzenediazonium tetrafluoroborate was used in this study to covalently modify a boron-doped diamond electrode using cyclic voltammetry in 0.1 mol dm^{-3} sulfuric acid. The surface modification was characterised by cyclic voltammetry using a $[Fe(CN)_6]^{3-/4-}$ redox marker. Following modification, the disappearance of the quasireversible redox signal of this marker was noticed, thus showing minimal electrokinetic activity of the boron-doped diamond surface because of the grafted layer. It proved that the phenylnitro-functionalized surface offers a general platform for immobilising a biorecognition element, such as biomolecules, through post-modification approaches, like electrochemical or chemical reduction to amine functionalities.

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Indirect electroanalysis of anticancer drug docetaxel at liquid|liquid interfaces using thin organic film electrode platform

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Keywords
interfacial electrochemistry
membrane-modified carbon-based electrodes
mitotic inhibitor

Thin organic film electrodes are emerging electroanalytical platforms designed to mimic biological membrane environments, enabling the study of charge transfer at two distinct interfaces: the electrode│membrane and membrane│aqueous phase boundaries. A typical thin organic film electrode configuration consists of a thin membrane deposited on a carbon electrode substrate, composed of a water-immiscible organic solvent that forms a stable liquid|liquid interface upon immersion in an aqueous electrolyte. Despite their promising capabilities, thin organic film electrode systems remain an underrecognized tool in electrochemical research. Notably, their applicability to anticancer drug analysis has not yet been explored. In this work, a thin organic film electrode system was employed for the electrochemical investigation of docetaxel, a chemotherapeutic agent from the class of mitotic inhibitors. Direct electrochemical detection of docetaxel on thin organic film electrode was unfeasible, as its high oxidation potential exceeds the operational window of the system. Therefore, an alternative indirect detection strategy was adopted. Systematic optimization of the organic and aqueous phase compositions, as well as the electrode substrate, was first conducted in the absence of docetaxel to ensure reliable and reproducible interfacial conditions. The optimized thin organic film electrode system was then applied to evaluate the effect of docetaxel on ion transfer processes at the liquid|liquid interface using

cyclic voltammetry and square-wave voltammetry. It was found that the presence of docetaxel results in a pronounced suppression of the redox mediator signal. Kinetic analyses by square-wave voltammetry indicated that docetaxel imposes constraints on interfacial charge transfer. The system exhibits a linear analytical response in the 10.0–100.0 μmol dm^{-3} docetaxel concentration range, with low detection and quantification limits achieved via square-wave voltammetry. These findings highlight the thin organic film electrode platform as a robust and versatile tool for the indirect electrochemical detection of redox-inactive anticancer agents.

UV-photochemical vapor generation of silver and gold: Optimisation of experimental setup

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Keywords
gold
inductively coupled plasma mass spectrometry
photochemical vapor generation
silver

Photochemical vapor generation under UV irradiation is an emerging sample introduction technique offering enhanced sensitivity and reduced matrix interferences in inductively coupled plasma mass spectrometry. This study explores the photochemical vapor generation under UV irradiation of silver and gold from acidic aqueous solutions, focusing on the nature of the volatile species formed and their efficient transport to the plasma. Using a low-pressure mercury lamp as the UV source, silver and gold were exposed to formic acid and other photoreductants to initiate vapor generation. The volatile species generated were directed to inductively coupled plasma mass spectrometry for quantitative analysis. Experimental variables such as acid type and concentration, photolysis time, and matrix effects were systematically optimized. The photochemical vapor generation efficiency was found to be highly dependent on the redox chemistry of the metal precursors. Preliminary evidence suggests the formation of ultra-fine particulate species, possibly metal nanoparticles, as key carriers in the vapor phase. While the generation of classical molecular species (e.g., hydrides) could not be confirmed for silver and gold, the volatility and transport efficiency under UV conditions point toward a nanoparticle-mediated mechanism. However, definitive identification of these species remains a subject of ongoing investigation, involving off-line trapping and characterization techniques. These findings contribute to a deeper understanding of photochemical vapor generation mechanisms for noble metals and support the development of reagent-efficient, green methodologies for trace-level analysis of silver and gold by inductively coupled plasma mass spectrometry.

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Automation of biosensor preparation based on screen printed electrode

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Keywords
automatic benchtop electrochemical system
electrochemical biosensor
phenolic compounds
screen-printed electrodes

This study focuses on the automation of the development of an electrochemical biosensor using screen-printed electrodes for the detection of total phenolic compounds in wine. By optimizing conditions and utilizing immobilized laccase, combined with transferring the process to an automated system, we aim to increase the efficiency and reproducibility of the biosensor while reducing the risk of human error. Optimization steps include the characterization of laccase and enhancement of its activity through the optimization of parameters such as pH, temperature, and enzyme concentration. Further optimization involves the electrochemical deposition of chitosan, characterization of the chitosan film using fluorescence microscopy, and immobilization of laccase onto the screen-printed electrode surface. Measurement protocols for phenolic compounds will be further refined to achieve optimal performance. Upon completion of all optimization steps, the electrode modification process will be transferred to an automated benchtop electrochemical system. This approach has the potential to enable efficient and cost-effective biosensor production suitable for various analytical applications in food analysis and environmental monitoring.

Method development for antibody analysis by CZE: From UV detection towards native CE-MS

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Keywords
antibodies
background electrolyte
capillary electrophoresis
coating

Therapeutic antibodies are biologics widely used to treat various diseases. Their thorough characterisation is essential for ensuring quality and efficacy in drug development. Among the key aspects are post–translational modifications, which can significantly affect antibody activity. Native proteomics aims to analyse proteins under conditions that preserve their noncovalent interactions, which are crucial for functional assemblies such as antibody–antigen or protein–protein complexes. This project focuses on developing analytical methods for native protein analysis by coupling capillary electrophoresis with high–resolution mass spectrometry using a nanospray interface. Capillary electrophoresis is employed as an initial separation technique to reduce sample complexity prior to mass spectrometry analysis, with separation conditions optimised to maintain native-like environments and compatibility with mass spectrometry. In this study, we examined the monoclonal antibodies Trastuzumab (pI = 9.1), Cetuximab (pI = 8.1), and Rituximab (pI = 9.4). Method development was initiated using capillary zone electrophoresis with UV detection. Tested capillary coatings included polyvinyl alcohol, hydroxypropyl cellulose, polyacrylamide, polyethylene oxide, a cationic polyacrylamide derivative (APTAC, 5% and 30% of the cationic component), and five layer successive multiple ionic polymer layer coatings based on diethylaminoethyl-dextran and poly(diallyldimethylammonium chloride) both in combination with poly(sodium styrene sulfonate). Background electrolytes included formic acid (0.12 M, 0.5 M, 1.0 M; pH = = 1.87–2.35) and acetic acid (0.83 M, 1.69 M, 4.0 M; pH = 2.07–2.41). Based on

performance and repeatibility, polyethylene oxide, successive multiple ionic polymer layer, and APTAC (30%) were selected for further use. For background electrolyte, we decided to proceed with 0.12 M formic acid, along with 0.83 M, and 1.69 M acetic acid. Currently, separations at varying pH values are being explored. This research lays the foundation for a robust capillary zone electrophoresis–mass spectrometry method for native protein analysis, with ongoing efforts to refine conditions and transfer the system to mass spectrometry detection.

Expanding the potential of printed electrodes for portable electrochemical sensing

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Keywords
electrochemistry
modified electrodes
salinomycin
voltammetry

The development of low-cost, portable sensing platforms is a growing priority in modern analytical chemistry, especially for on-site detection of biologically relevant substances. In this work, screen-printed electrodes based on silver substrates were explored and modified to expand their electrochemical performance, particularly to achieve a wider cathodic potential window. Several modification strategies were evaluated to improve their applicability for voltammetric sensing, aiming to mimic the behavior of traditional electrodes while offering miniaturization and field usability. The electrochemical properties of the resulting electrodes were characterized under various conditions. The approach showing the most favorable performance was selected for proof-of-concept sensing of a biologically active compound. Salinomycin, a polyether ionophore antibiotic (coccidiostat), was chosen as an analyte for the pilot study, stemming from its reduction at fairly negative potential. The results demonstrate the potential of these modified printed electrodes as accessible, sensitive tools for electroanalysis in diverse environments, from laboratories to remote testing sites. By fine-tuning the electrode composition and optimizing the modification conditions, we achieved reliable performance suitable for detecting biologically active compounds such as salinomycin. The platform's portability and cost-effectiveness make it especially promising for decentralized applications, including food safety monitoring and environmental screening.

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Prostate cancer diagnosis based on chemical analysis of human scent

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Keywords
gas chromatography
GC×GC-TOF/MS
human scent
olfactronics
prostate cancer

Human scent comprises a variety of chemical compounds that can provide valuable information about an individual. By using sensitive analytical methods, such as gas chromatography, which accounts for the volatile nature of these substances, and appropriate detectors, the characteristic scent profiles of individuals can be identified. This facilitates the identification of an individual's gender, blood type, and Rh factor. It is believed that these characteristics originate primarily from what is known as the primary scent, which remains largely unchanged throughout a person's life and is probably genetically determined. Genetically determined diseases include conditions such as Parkinson's disease, diabetes types I and II, as well as various forms of cancers. The most commonly diagnosed cancer among men is prostate carcinoma. With early diagnosis, which follows a tissue biopsy and blood tests, the survival rate for this type of cancer can reach up to 99%. Given that cancer is a degenerative disease, it is plausible to assume changes in genetic material that could also alter the primary scent of a patient. This variation could potentially be used to differentiate between patients based on their health status. Scent samples were collected from both ill and healthy individuals by absorbing scent components onto a suitable sorbent, in this case, glass beads. These samples were then extracted from the sorbent using a special methodology. The prepared substrates were analysed using a chromatographic technique (GC×GC-TOF, Pegasus BT-4D, LECO, USA). Eventually, the resulting chromatographic data were evaluated using a combination of statistical methods, including PCA (Principal Component Analysis), CA (Cluster Analysis), KNN (*k*-nearest neighbors algorithm), and SVM (Support Vector Machine). This

method of obtaining scent samples is non-invasive and stressless compared to surgical procedures, which have associated health risks such as infections and anaesthesia. The process of obtaining the sample itself is undemanding; therefore, it would be possible to do the sampling directly at the doctor's office.

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Electrochemical performance of additively manufactured metal meshes with doped diamond coatings

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Keywords
additive manufacturing
boron-doped diamond
electrochemical characterization
titanium mesh

Additively manufactured metal structures offer novel architectures for advanced electrochemical devices. In this work, titanium meshes with varying pore sizes, produced by additive manufacturing, were used as substrates for boron-doped diamond (BDD) coatings deposited via microwave plasma-enhanced chemical vapor deposition using a linear antenna delivery system. The resulting BDD-coated titanium meshes underwent comprehensive electrochemical characterization. Cyclic voltammetry was performed in supporting electrolytes of varying composition and pH to determine the widths of potential windows. In addition, redox probes differing in standard redox potential, electron transfer mechanism (outer- *vs.* inner-sphere), and charge were used to evaluate heterogeneous electron transfer kinetics, as reflected by peak-to-peak separation values. Electrochemical impedance spectroscopy was performed to evaluate double-layer capacitance and charge transfer resistance of the individual mesh electrodes. As a reference, the electrochemical behavior of bare (uncoated) additively manufactured titanium meshes was also investigated. This work demonstrates the potential of combining additive manufacturing with advanced electrode materials for the development of novel electrochemical platforms.

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Using non-aqueous capillary electrophoresis with amperometric detection in veterinary drug analysis

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Keywords
amperometric detection
capillary electrophoresis
separation technique

Animal welfare is an important part of modern agriculture and responsible pet ownership. Consequently, quality control in veterinary medicine is essential to ensure accurate diagnoses, effective treatments, and overall health. It also protects public health by preventing the spread of diseases and ensuring food safety through proper care of livestock, utilizing specialized medication. Reliable and robust analytical methods are of central importance in the routine analysis of veterinary drugs to facilitate the proper application of these substances. Capillary electrophoresis is a powerful separation technique characterized by high separation efficiency and low sample and solvent consumption, making it applicable to a wide range of analytical problems. Furthermore, it provides a highly adaptable, cost-efficient alternative to liquid chromatography in many applications. Non-aqueous capillary electrophoresis provides excellent long-term stability and low electrophoretic currents, relying exclusively on organic solvents and electrolytes. Non-aqueous capillary electrophoresis is widely used in pharmaceutical, environmental, and agricultural analysis, particularly when dealing with lipophilic, non-polar, or poorly water-soluble substances. Commonly, non-aqueous capillary electrophoresis is coupled with a powerful detection principle like conductivity, mass spectrometry, or UV detection. Amperometric detection, while less prominent, has also proven to be advantageous in various non-aqueous capillary electrophoresis applications. The use of organic solvents in non-aqueous capillary electrophoresis offers several benefits for amperometric detection, including improved detection of analytes, lower noise levels,

enhanced sensitivity, selectivity, and long-term stability. Herein, we present the successful determination of two prominent veterinary drugs, namely nitenpyram (insecticide for flea and tick control) and nicarbazin (coccidiostat in poultry management), utilizing non-aqueous capillary electrophoresis and oxidative amperometric detection at platinum electrodes.

Analysis of macro- and microelements and heavy metals in confectionery products using the ICP-MS method after extraction with deep-eutectic solvents

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Keywords
deep eutectic solvents
inductively coupled plasma–mass spectrometry
multi-elemental profile

Nowadays, the central premise of "green chemistry" is the reduction of environmental risks. Deep eutectic solvents fit into the "green chemistry" concept. They are mixtures of two or more compounds with a melting point lower than their components, including a hydrogen bond acceptor and a hydrogen bond donor that associate with each other by hydrogen bonding. Recently, deep eutectic solvents have been prepared by mixing natural components (sugars, organic acids, and amino acids), which are non-volatile, have a low toxicity, are biodegradable, sustainable, and inexpensive. In the present study, three deep eutectic solvents – (i) xylitol and malic acid, (ii) choline chloride and malic acid, and (iii) choline chloride and lactic acid – have been involved in the extraction of macro- (Na, Mg, K, Ca), microelements (Mn, Fe, Cu, Zn) and representative of heavy metal (Cd) from confectionery products including uniced and iced gingerbreads. This proposed ultrasound-assisted extraction was considered an environmentally friendly alternative to the gingerbread sample pretreatment procedure based on microwave digestion. The elements present in deep eutectic solvent-based extracts and wet-digested gingerbread samples were determined by inductively coupled plasma-mass spectrometry. It was found that deep eutectic solvent, synthesised from choline chloride and malic acid, provided the highest extraction efficiency in the extraction of macroelements, whereas deep eutectic solvent, containing choline chloride and lactic acid, most effectively extracted microelements from confectionery products. Interestingly, iced gingerbread was a richer source of macro- and micronutrients than uniced gingerbread. Moreover,

toxic cadmium was not found in the studied confectionery products. However, control of nutritional and toxicological quality is essential to ensure safe consumption.

Determination of antibiotics using silver nanoparticles and smartphone-based detection

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Keywords
aminoglycosides
gentamicin
silver nanoparticles
smartphone-based detection

The spread of antibiotics across human life and the ecosystem is becoming more pervasive. One of the popular group of antibiotics are aminoglycosides, which include gentamicin, kanamycin, streptomycin, and kanamycin, among others. These antibiotics are used to treat severe diseases caused mostly by Gram-negative bacteria. Aminoglycosides could be commonly found in the form of eye drops, ointments, and injectable solutions. Due to the narrow therapeutic index, monitoring the blood concentration of aminoglycosides is essential to ensure therapeutic efficacy and prevent adverse effects such as nephrotoxicity and ototoxicity. Additionally, the growing presence of aminoglycosides in the environment contributes to increasing bacterial resistance, making it important to monitor their levels in environmental and food samples. In recent years, nanomaterials, especially silver nanoparticles, have gained considerable attention in analytical applications, including aminoglycoside antibiotic determination due to their high reactivity and the possibility of using colorimetric detection. To verify the application of silver nanoparticles for the determination of aminoglycosides, a gentamicin determination method was developed using silver nanoparticles and a smartphone-based detection. The research was focused on selecting reagents for nanoparticle synthesis, optimising their concentrations, reaction conditions, and time, and determining the concentration of nanoparticles. Gallic acid, as a natural reducing and stabilizing agent, was used for nanoparticle synthesis. For the proposed method, analytical parameters such as linear range, limit of quantification, precision, and accuracy were established for

both the smartphone-based and spectrophotometric methods. The influence of potential interferents was also assessed. The proposed method was validated using model samples and applied to pharmaceutical formulations of gentamicin, with results compared to those obtained through spectrophotometry. The method demonstrates potential for broader application across different sample types.

A combined microextraction-voltammetric method for determination of trazodone in biological fluids

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Keywords
hollow fiber liquid-phase microextraction
screen-printed boron-doped diamond electrode
square wave voltammetry
trazodone

A novel method based on hollow fiber liquid-phase microextraction was developed for detecting the antidepressant trazodone in biological samples. Trazodone is a medication with various therapeutic uses. At lower doses, it serves as a sleep aid, while at much higher doses, it acts as an antidepressant by blocking the reabsorption of serotonin in the brain. Since trazodone's therapeutic effects are closely tied to its effective therapeutic levels, monitoring its concentration in biological fluids is essential. This approach combined with square wave voltammetry using a screen-printed boron-doped diamond electrode. The optimal hollow fiber liquid-phase microextraction conditions included isoamyl benzoate as the supported liquid membrane immobilized in a porous polypropylene hollow fiber Accurel Q3/2, 0.1 mol dm^{-3} sulfuric acid as the acceptor phase, a Britton Robinson buffer (pH = 10) as the donor phase, and an extraction time of 35 minutes. The method achieved limits of detection and quantification of 12 and 42 nmol dm^{-3}, respectively. Its effectiveness was validated using human urine samples. Overall, this project highlights the effectiveness of hollow fiber liquid-phase microextraction combined with square wave voltammetry for determination trace levels of basic drugs in human urine using a portable system suitable for clinical applications.

Conformational analysis of selected kratom alkaloids using NMR spectroscopy

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Keywords
alkaloid
conformation
coupling constant
kratom
NMR

Kratom (*Mitragyna speciosa*) is a well-known medicinal plant native to Southeast Asia that has been used for centuries to alleviate pain, cough, and hypertension. Nowadays, kratom is receiving increased attention as a potential herbal medicine for pain relief as well as an alternative approach to managing opioid addiction, or as a recreational drug. Mitragynine, a major kratom alkaloid, is primarily associated with its biological effects. However, minor alkaloids may also contribute to them, possibly causing side effects and risks associated with kratom usage. Therefore, further research on both major and minor alkaloids and their structures is needed. An important part of the structural analysis of organic compounds is the determination of conformation since this property has a major influence on the chemical reactivity and biological activity of compounds. The crucial part of the conformational analysis applying NMR spectroscopy is the determination of coupling constants, especially those between protons separated by three bonds ($^3J_{HH}$). Such constants are directly related to dihedral angles between protons through the Karplus equation. However, signal overlapping, a common problem in the interpretation of NMR spectra, makes the extraction of homonuclear couplings rather difficult. Possible solutions of this issue involve, for example, measuring at different temperatures or using solvents with varying magnetic properties. To interpret the obtained characteristics correctly, molecular modelling is necessary, i.e., finding all conformers, determining their structural parameters (interatomic distances and angles), and calculating desired NMR properties. This presentation provides current results from the NMR analysis of selected kratom alkaloids (mitragynine, speciogynine, speciociliatine and paynantheine).

RP-HPLC method development and analysis of twelve expired analgesic preparations from the 20th century

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Keywords
analgesic preparation
degradation
RP-HPLC
stability
tandem mass spectrometry

The aim of this study was to develop a versatile reversed-phase high-performance liquid chromatography (RP-HPLC) method for the analysis of twelve expired pharmaceutical analgesic preparations – comprising six single-component and six multi-component formulations. These preparations contained a total of twelve active pharmaceutical ingredients, whose stability was subsequently evaluated. Two types of detection were employed: UV detection for the quantification of the active pharmaceutical ingredients, and tandem mass spectrometry for the verification of analyte identity and the detection of potential degradation products. Chromatographic separation was achieved using a Phenyl-Hexyl stationary phase in combination with a gradient elution of 0.1% aqueous acetic acid (adjusted to pH = 5.00 with ammonia) and methanol. All analytes were successfully separated, with the exception of aminophenazone and phenobarbital, which coeluted. Their quantification was resolved using mathematical correction based on dual-wavelength UV detection. Calibration models were constructed using analytical standards, with limits of quantification ranging from 3.0 to 70 mg dm^{-3}. The historical tablet samples were analyzed in triplicate, and the results were statistically evaluated. A remarkable long-term stability – within ±10% of the declared content – was observed for the majority of active pharmaceutical ingredients. Notable exceptions were found for codeine and acetylsalicylic acid in specific formulations. Of particular interest was the stability of bromisoval, whose tandem mass spectrum and proposed fragmentation pathway are presented here

for the first time, despite the fragile physical condition of the corresponding tablets. The analysis of acetylsalicylic acid effervescent tablets highlighted the influence of dosage form on stability, while the importance of storage conditions was illustrated by the analysis of three different types of Alnagon tablets manufactured in 1990.

Identification of volatile species of iridium and rhodium generated by photochemical vapor generation using direct analysis in real time mass spectrometry

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Keywords
direct analysis in real time
high resolution mass spectrometry
iridium carbonyl
photochemical vapor generation
rhodium carbonyl

Photochemical vapor generation is an efficient sample introduction technique for atomic spectrometry. The analyte (element) is converted into a volatile species during UV irradiation of the liquid photochemical medium containing low-molecular-weight organic acid, such as formic acid. To thoroughly understand the reaction pathways for individual elements, it is crucial to identify the final volatile products. In this study, a direct analysis in real time ion source coupled to an Orbitrap high-resolution mass spectrometer (DART-HRMS) was used to identify volatile species of iridium and rhodium generated in a thin-film flow-through photoreactor from the HCOOH-based photochemical media, spiked with Co^{2+}, Cu^{2+}, or Cd^{2+} as mediators. It was assumed that only volatile compounds of the general formula $M_x(CO)_yH_Z$ can be formed during UV photolysis of formic acid, satisfying the 18-electron rule. Using nitrogen as the discharge gas, extensive decarbonylation, hydration, oxidation, and formation of nitrogen-containing ions were observed in both positive and negative ion modes. When photochemical vapor generation was conducted from 10 mol dm^{-3} HCOOH with the addition of

50 mg L^{-1} Cd^{2+}, the dominant ions in the positive ion mode were $[C_3H_4O_6Ir]^+$ (100%) and $[C_2H_5O_5Ir]^+$ (42%). The presence of $[C_4H_2O_6Ir]^+$ (9.2%) and $[C_4H_5O_6NIr]^+$ (6.9%) in the high-resolution mass spectrum likely indicated four CO groups. In the negative ion mode, the most abundant ions were $[O_2Ir]^-$ (100%), $[O_3Ir]^-$ (36%), and $[C_2O_3Ir]^-$ (14%). Using 0.01 mol dm^{-3} HCOOH with the addition of 5 mg L^{-1} Cd^{2+} for photochemical vapor generation and argon as the discharge gas resulted in "cleaner" spectra and softer ionization. This is evidenced by the detection of $[C_3O_3Ir]^-$ (26%) and $[C_4O_4Ir]^-$ (6.4%). The latter ion suggests that the mononuclear $Ir(CO)_4H$ is most likely the volatile species. Identification of the volatile species of rhodium is even more challenging since it is monoisotopic and lacks a characteristic isotopic pattern. The preliminary DART-HRMS data will also be presented.

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Advancing gut microbiome metabolomics: A derivatization-based approach

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Keywords
derivatization
germ-free
metabolomics
microbiome
3-nitrophenylhydrazine

Microbiota-associated metabolites play a crucial role in host physiology and disease by mediating host-microbiota communication, providing essential nutrients, and regulating metabolism and immune functions. Understanding these interactions requires comprehensive chemical analysis of the metabolites. However, their low abundance, diverse physicochemical properties, and analysis in complex matrices present significant challenges, leaving us with no universal method to analyze them all. Chemical derivatization is a powerful approach particularly for polar metabolites. By modifying the analyte structure, it decreases their polarity and makes them compatible with conventional reverse-phase liquid chromatography. 3-Nitrophenylhydrazine is a widely used derivatization agent, which was previously employed in studies targeting well-known microbial metabolites such as short chain fatty acids and other primary metabolites. However, the potential of its applicability can be extended and go beyond to larger datasets, covering the majority of polar primary metabolites as well as known products of microbial metabolism. Here, we present a large-scale analysis of nearly 600 gut microbiome-related chemical standards, derivatized using 3-nitrophenylhydrazine. Standards were systematically classified based on structural similarities, biological relevance, and metabolic pathway associations using a Python-based automated categorization pipeline and public metabolomic databases. For streamlined identification, the recently introduced *in-silico*

Derivatization Tool in MetaboScape by Bruker was employed for automated targeted search. To validate the applicability of this derivatization strategy, we utilized the library of derivatized standards for the targeted analysis of microbiota associated metabolites in stool samples from mice with different statuses of microbial colonization, including germ-free models. Our results demonstrate the utility of this approach in providing valuable insights into host-microbiota metabolic interactions.

Comparison of succinite from various geological deposits using molecular spectroscopy

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Keywords
deposits
fossil resins
Fourier-transform infrared spectroscopy
Raman imaging
Raman spectroscopy
succinite

The research materials consisted of fossil resins – Baltic amber (succinite) of different geological origin: Gdańsk Delta and Parczew Delta. Fossil resins are biogenic and amorphous materials formed as a result of natural polymerization of ancient tree resins. The age of the samples is presumably approximately 40 million years. The aim of the research was to compare the spectra of both fossil resins: Fourier-transform infrared spectroscopy and in Raman and highlighting the signature differences. Nowadays infrared spectroscopy is used to authenticate Baltic amber, whereby a characteristic shape in the range of 1250–1150 cm^{-1} called "Balic shoulder" occurs. Raman imaging was performed to identify variability in the chemical structure in different areas of monolithic samples. The samples collected in Poland were transported to Kwansei Gakuin University in Japan and analysed. Raman spectroscopy comes across one of the non-destructive. However, it is rarely selected for fossil resin identification, as its applicability is constrained by factors such as the low diagnostic value and the limited number of identifiable spectral bands. Infrared and Raman spectra were collected and analysed for 10 samples from Gdańsk Delta and 10 samples from Parczew Delta. Obtained spectra were overlayed and compared to identify differences between them. Such differences were interpreted based on available geochemical data for stratigraphic layers in which fossil resins occur.

A sensitive UHPLC-MS/MS method for simultaneous quantitation of topotecan lactone and carboxylate in plasma and vitreous and its application in hydrogel implant drug delivery

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Keywords
drug delivery system
hydrogel implants
retinoblastoma
topotecan
UHPLC-MS/MS

Topotecan is used in the treatment of retinoblastoma, the most common malignant intraocular tumor in children. Topotecan undergoes pH-dependent hydrolysis of the lactone ring to the ring-opened carboxylate form, with the lactone form showing antitumor activity. A selective, and highly sensitive ultra-high performance liquid chromatography-tandem mass spectrometry method was developed for the determination of both forms of topotecan in one mobile phase composition in plasma and vitreous humor matrices. The method showed an excellent linear range of 0.375–120 ng mL^{-1} for the lactone. For the carboxylate, the linear range was from 0.75 to 120 ng mL^{-1}. The matrix effect and the recovery for the lactone ranged from 98.5% to 106.0% in both matrices, for the carboxylate form, it ranged from 94.9% to 101.2%. The dynamics of the transition between topotecan lactone and topotecan carboxylate were evaluated at different pH environments. The stability of topotecan forms was assessed in plasma and vitreous humor at 8 and 37 °C and a very fast conversion of lactone to carboxylate form occurred at 37 °C in both matrices. The developed method facilitates the investigation of topotecan pharmacodynamics and release kinetics in the development of innovative local drug delivery systems. The new method was

recently applied in both *in vitro* and *in vivo* studies using hydrogel-based implants for localized topotecan delivery in retinoblastoma treatment. *In vivo*, lens-shaped bi-layered implants, comprising a drug-loaded poly(HEMA) layer and an outer poly(EOEMA) barrier, were implanted into the posterior segment of rabbit eyes, enabling release via transscleral diffusion while minimizing exposure to surrounding tissues. The UHPLC-MS/MS method allowed separate quantification of lactone and carboxylate forms in vitreous humor and blood, confirming sustained, pharmacologically relevant lactone levels. In vitro, implants made from poly(HEMA), poly(HEMA-*co*-MOETACl), and poly(HEMA-*co*-DMAEMA) were compared for release profiles in porcine plasma, showing significant effects of copolymer composition on release kinetics. Future in vivo studies will compare this local delivery approach to intravitreal injection, which carries a notable risk of metastatic spread in pediatric patients.

Assay of selected micro- and macroelements in biomaterials: poly-γ-glutamic acid enriched *Pleurotus* spp. mycelia from *in vitro* cultures

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Keywords
analysis
concentration
desorption
metals
sorption

Mushrooms are an essential part of the ecosystem, serving the role of decomposers by breaking up organic matter before its properly absorbed back into the environment. Their excellent sorption and pH dependent desorption properties allow them to properly digest, assimilate and/or return micro- and macroelements from decomposing biomass. For this reason, mushrooms serve as great indicators for environmental pollution, as they are sensitive to all matter of heavy metals and toxic substances present in the soil. As edible mushrooms are known for their culinary applications, due to being source of bioactive organic substances such as phenolic acids and indole compounds, proper monitoring of concentration of various elements in their structure is vital for proper safety of the potential consumer. Poly-γ-glutamic acid is a natural polymer form of amino acid

glutamic acid. Poly-γ-glutamic acid is derived from bacterial fermentation that forms L-glutamic and D-glutamic monomers joined via γ-glutamine bond. Poly-γ-glutamic acid possesses great chelating properties, being able to bind metal ions in its structure, which was shown to improve plants' absorption, increase their salt and cold resistance and might prove useful in soil and sewage treatment applications. In the presented work the focus was put on applications of combination of both *Pleurotus djamor* and *Pleurotus ostreatus* mushroom species, due to their characteristic health-promoting properties, with natural poly-γ-glutamic acid. The feed used for these cultures was enriched with micro- and macroelements (magnesium and zinc). The concentration of these subsidized elements, both in the harvested biomass and the feed post-cultivation, was assayed in an effort to prove the effectivity of sorption and desorption of this natural biomaterial. The assay was conducted using AAS method (flame technique) and the results showed that the effectiveness of sorption depends on physicochemical properties of the material, type of the analyzed element and their concentration.

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Unlocking soapwort's secrets: Tracking saponins via liquid chromatography-mass spectrometry

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Keywords
glycosides
LC-MS
Saponaria officinalis L.
saponins
soapwort

Saponaria officinalis L., commonly known as soapwort, is a plant with a broad distribution that is renowned for producing high levels of triterpene saponins, mainly in its roots, rhizomes, and shoots. These are typically applied in medicines and cosmetics. Although over 20 saponins have been structurally characterized using NMR techniques, many glycosides synthesized by this species remain unidentified. This study presents a thorough analytical approach for identifying, characterizing the structure and determining soapwort saponins using high-performance liquid chromatography coupled with mass spectrometry.

Plant extracts were prepared using methanolic extraction, followed by purification and reversed-phase chromatographic separation on a C18 column, with formic acid-modified water and acetonitrile eluted in a gradient manner. Electrospray ionization was used for mass spectrometric detection in both positive and negative modes. The approach enabled the detection of over 200 glycosidic species containing 11 different triterpenoid aglycones, with identification based on their mass-to-charge ratios and characteristic fragmentation patterns. Additionally, a multiple-reaction monitoring method was developed to investigate how extraction and purification conditions affect the saponin composition.

It was found that acidification, alkalinization, and elevated extraction temperatures boosted the overall yield of glycoside but at the same time

accelerated the de-esterification of oligosaccharide side chains, especially those containing pentoses and deoxyhexoses. The developed method demonstrated good sensitivity, reproducibility, and selectivity, offering a reliable tool for saponin profiling and advancing the phytochemical analysis of complex plant matrices.

Fractional factorial optimization of methylmercury determination and regional discrimination in marine organisms

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Keywords
fractional factorial design
marine organisms
methylmercury
regional discrimination
thermo-oxidative analysis

Methylmercury is the most toxic mercury species and poses significant health risks owing to its high bioaccumulation potential in marine organisms. Its quantification typically relies on advanced techniques such as gas chromatography-mass spectrometry or high-performance liquid chromatography-mass spectrometry, which are time-consuming and resource-intensive. As a more accessible alternative, thermo-oxidative quantification can be used, provided that methylmercury is selectively extracted beforehand. In this study, we developed a simplified, time-efficient extraction protocol that minimizes both sample and reagent consumption. A fractional factorial design was employed to evaluate eight experimental variables simultaneously and identify the optimal extraction conditions. The method was validated with certified reference materials (ERM-BB422 and DOLT-5) and applied to 50 squid samples collected from the Mediterranean Sea and the Atlantic Ocean. Methylmercury concentrations were generally higher in Mediterranean specimens. To assess regional differences, a support vector machine classifier was trained on the analytical data and successfully distinguished samples by provenance. The method exhibits good repeatability and analytical robustness, making it suitable for routine monitoring of methylmercury in marine biota.

Determination of organic acid anions in fermented food samples using capillary electrophoresis: A functional approach to gut health supplementation

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Keywords
capillary electrophoresis
fermented food
gut health
organic acid anions
short-chain fatty acids

TShort-chain fatty acids are a group of fatty acids with fewer than six carbon atoms in the aliphatic chain. Primarily, they are produced in the colon through the microbial fermentation of dietary fiber and play a crucial role in body homeostasis. Short-chain fatty acids have an important role in modulating inflammation, influencing immune responses, and maintaining gastrointestinal health, which makes them promising dietary supplements. Fermented plant-based foods, such as pickled vegetables, are natural sources of these metabolites and may serve as functional components of gut health-oriented diets. The aim of this study was the transfer, development, and validation of a capillary electrophoresis method with indirect UV detection for the determination of twelve organic acid anions, including short-chain fatty acids and their precursors. The analytical method was validated following the ICH Q2 requirements. The method demonstrated good linearity (*LOQ*–100 μg ml^{-1}), precision (*RSD* ≤6.5 %), trueness (≤8.9%), low limits of detection (<1.2 μg ml^{-1}) and quantification (≤3.98 μg ml^{-1}). Additionally, the method presents high selectivity in the occurrence of inorganic anions (e.g., chloride, phosphate, and sulfate). Analysis of real samples of fermented vegetable juices demonstrated diverse acid profiles, with formic, acetic, and propionic acids as dominant analytes. The results prove the use of a capillary electrophoresis method with indirect UV detection as a reliable, low-cost, and environmentally sustainable method for profiling organic acid anions in fermented food samples and highlight their potential as functional supplements in gut health strategies.

Comparison of on-line and off-line approaches to monitoring drug degradation

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Keywords
boron-doped diamond electrodes
degradation
pharmaceuticals
UHPLC-MS

Oxidative degradation represents a promising approach for the degradation of pharmaceutical compounds, leading to their rapid transformation into degradation products or complete mineralization. Electrochemical methods offer an environmentally friendly alternative to chemical oxidation, as they generate reactive oxygen species, especially hydroxyl radicals, directly on the electrode surface without requiring external chemical reagents. Among available materials, boron-doped diamond electrodes are particularly well-suited for this purpose due to their stability and wide potential window. In this study, an on-line coupling of an electrochemical degradation cell with mass spectrometry was tested, enabling real-time monitoring of emerging degradation products. The study employed a custom-made flow-through electrochemical cell fabricated via 3D printing, which allows for precise control of the contact time between the analyte and the boron-doped diamond electrodes, while also facilitating system miniaturization. Degradation products identified by on-line mass spectrometry analysis were compared with those obtained by off-line HPLC-MS analyses of samples from both batch and flow electrochemical cells experiments. This study provides a detailed analysis of degradation products formed at various stages of pharmaceutical compound breakdown and aims to contribute to the development of fast, environmentally friendly, and efficient approaches for their degradation in the environment.

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Development of Cu-film modified silver solid amalgam electrode for voltammetric analysis of fluoren-9-one

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Keywords
copper film electrode
fluoren-9-one
silver solid amalgam
voltammetry

This study focuses on the voltammetric investigation of fluoren-9-one, a genotoxic and electrochemically active compound, using two types of working electrodes: a polished silver solid amalgam electrode (p-AgSAE) and its copper film-modified version (CuF-AgSAE). The primary objective was to develop sensitive and reliable voltammetric methods for the determination of fluoren-9-one by employing both direct current voltammetry and differential pulse voltammetry. A 1:1 volumetric ratio of organic (ethanolic/methanolic) to aqueous phase was found to be optimal for preparing fluoren-9-one solutions at a concentration of 5×10^{-5} mol dm^{-3}. The optimal medium for the voltammetric determination of fluoren-9-one was investigated using Britton-Robinson buffer solutions across a pH range from 2.0 to 12.0. For the p-AgSAE, the best performance in direct current voltammetry was observed at pH 6.0 and 10.0, while differential pulse voltammetry provided the most well-defined peaks at pH 5.0 and 12.0. In each case, calibration curves were constructed down to the lowest possible analyte concentration, and repeatability was assessed to determine the limits of detection and quantification. This work serves as a pilot study in the development of novel intermetallic phase electrodes combining silver solid amalgam with copper as a less noble metal. For the optimization of copper film deposition on the p-AgSAE, various combinations of deposition time and deposition potential in a copper(II) chloride solution were used. Modification of the p-AgSAE surface by electrochemical deposition of a copper film significantly enhanced the electrode performance. The CuF-AgSAE exhibited improved definition of the fluoren-9-one reduction peak, along with lower limits of detection/quantification values and an expected broader linear dynamic range.

Development of an LC-MS method for the analysis of oligosaccharide profile in human milk

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Keywords
colostrum
human milk
LC-MS
oligosaccharides

Human milk constitutes an optimal source of nutrition for infants, providing essential nutrients necessary for their growth and development. Human milk oligosaccharides, which are complex glycans, represent the third most abundant component in human milk. Human milk oligosaccharides are resistant to digestive processes and reaching the intestinal tract largely unaltered, where they principally function as prebiotics, facilitating the development of a healthy gut microbiota by selectively promoting bifidogenic bacteria. The primary metabolites resulting from human milk oligosaccharides fermentation are short-chain fatty acids, which play a role in the maturation of intestinal epithelial cells and enhance intestinal barrier integrity. Furthermore, human milk oligosaccharides contribute to host defense mechanisms against pathogens through their anti-adhesive and antimicrobial properties, and are also implicated in neurodevelopment. This study reports the development of a liquid chromatography-tandem mass spectrometry method for the profiling of oligosaccharides in human milk. Given the high polarity of the analytes, an amide-based chromatographic column was employed. The inclusion of certain isomeric human milk oligosaccharides presents analytical challenges, necessitating the optimization of the gradient elution protocol. Under optimal separation conditions, ten compounds, including four isomeric groups, were successfully resolved. Additionally, optimal mass

spectrometric parameters – including ionization source and collision cell settings – were established to ensure high sensitivity and reproducibility. The described method enables the analysis of specific human milk oligosaccharides in human milk samples within a run time of less than 19 minutes, and, when combined with a streamlined sample preparation procedure, allows for quantification at physiological concentrations.

Forensic differentiation of black polyester fibers: a comprehensive study

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Keywords
black fibers
differentiation of fibers
forensic fiber analysis
polyester fibers

The forensic examination of black polyester fibers is particularly challenging due to their widespread use, complex dye compositions, and low evidential value when analyzed with limited methods. This study presents a protocol that reflects the procedures used in forensic casework, combining non-destructive and destructive techniques to enhance the value of the evidence. Non-destructive methods included optical microscopy in white, polarized, and UV light, enabling morphological assessment and detection of optical effects related to dyes or fiber treatments. Micro spectrophotometry in the UV and visible ranges provided information about dyes, while micro-FTIR enabled the identification of the polymer type. Destructive analysis involved capillary electrophoresis coupled with TOF mass spectrometry (CE-TOF-MS), which enabled the identification of individual dyes with high mass resolution and accuracy. This was especially useful for complex dye mixtures in black fibers. Additionally, GC-MS/MS in multiple reaction monitoring mode was used for the targeted screening of aromatic amines derived from azo dyes. Non-destructive techniques are fast and preserve evidence but offer limited chemical specificity. In contrast, CE-TOF-MS and GC-MS/MS provide detailed chemical data crucial for forensic identification, although at the cost of sample consumption and longer preparation times. This integrated approach significantly improves the forensic evidence value of black polyester fibers, allowing more confident comparisons and group identification in criminal investigations.

Studying electrochemical oxidative degradation of venlafaxine in lab-scale 3D-printed cells

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Keywords
boron-doped diamond
lab-scale 3D-printed cells
oxidative degradation
venlafaxine
wastewater treatment

The persistent occurrence of pharmaceuticals in aquatic ecosystems has become a major environmental concern, as these compounds often withstand conventional wastewater treatment processes. Even at low concentrations, they can pose ecotoxicological threats. Electrochemical advanced oxidation processes, which generate strong oxidants such as hydroxyl radicals, have gained attention as promising and environmentally friendly methods for efficiently degrading these pollutants. Among available electrode materials, boron-doped diamond anodes are particularly notable for their outstanding stability, resistance to aging, and high efficiency in generating reactive species. This study investigates the oxidative degradation of venlafaxine – a commonly prescribed antidepressant and one of the most frequently detected pharmaceuticals in rivers worldwide. To improve degradation performance, two custom lab-scale electrochemical cells were developed and fabricated using stereolithographic 3D printing, allowing for precise, customizable designs suited to experimental needs. One batch-type cell was used for initial degradation experiments, while a dual-function cell enabled both degradation and voltammetric monitoring of residual venlafaxine. Degradation products were identified and quantified using ultra-high performance liquid chromatography coupled with mass spectrometry after treatment in each cell.

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A novel chemiluminescence point-of-need prototype for rapid adiponectin detection

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Keywords
acridinium ester
adiponectin
chemiluminiscence immunoassay
nagnetic beads
point-of-need diagnostics

Adiponectin is a clinically relevant biomarker with great potential in early diagnosis and monitoring of metabolic diseases. However, current detection methods typically laboratory-based immunoassays are time-consuming, complex, and unsuitable for decentralized or time-critical testing. Here, we present a novel chemiluminescent point-of-need prototype for rapid adiponectin quantification from small-volume biological samples. This approach aims to combine analytical precision of laboratory assays with the speed and portability required for on-site applications. Our instrument named MALIA (Magnetic-Assisted Chemiluminescence Immunoassay) is a portable chemiluminescence analyzer tailored for low-volume immunodiagnostics. The analytical principle is based on a magnetic bead sandwich immunoassay, in which adiponectin is selectively captured by antibody-coated magnetic microparticles and subsequently detected using acridinium ester-labeled secondary antibodies (ACR). The light generated by the ACR-triggered reaction is measured by an integrated photomultiplier tube. Key innovations include an optimized ACR labeling protocol ensuring sufficient signal-to-noise ratio, and a streamlined workflow with rapid magnetic separation in a disposable cartridge. The total assay time is under 15 minutes and the platform achieves a detection limit in the low ng ml^{-1} range. Calibration using recombinant adiponectin yielded a curve with excellent fit ($R^2 = 0.99$). Comparative analysis with commercial methods revealed strong correlations: $R^2 = 0.90$ versus ELISA, and $R^2 = 0.92$ versus the CLIA-based KleeYa platform. This novel point-of-need prototype represents a significant advance in accessible diagnostics for metabolic health monitoring. Its compact design, rapid turnaround, and minimal sample requirements offer a compelling solution for use in primary care, home settings, or remote environments.

Application of 3D printing technology for the production of working paste electrodes

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Keywords
3D printing
paste electrode
voltammetry

3D printing technology has been a dynamically developing field for several decades and is now widely used in various areas of life and science, such as medicine, industry, engineering, and chemistry. Due to its ability to create three-dimensional objects based on digital computer models, 3D printing enables fast, precise, and flexible production – both single-unit and serial – often eliminating the need for expensive molds, tools, and complex manufacturing processes. This technology allows for the layer-by-layer construction of objects from a wide range of materials, including plastics, metals, ceramics, composites, and even biological substances, which significantly broadens its application potential. One innovative application of this technology is the creation of specialized holders for paste electrodes, which play a crucial role in electrochemical research. The general aim of the research was to apply 3D printing technology to the production of holders used for carbon paste electrodes. The holders were designed and printed using various materials available for 3D printing. The design allowed for the placement of carbon paste and a wire connecting the electrode surface to the measuring device. To compare chemical properties of the produced electrodes, measurements were carried out with traditional carbon paste, in different environments: acidic, neutral, and alkaline. Potassium ferrocyanide and ferricyanide were used as a model system for electrochemical measurements, and cyclic voltammetry was employed as the measurement technique. The obtained voltammograms were compared with results obtained using a traditional carbon paste electrode holder.

EDTA-stabilised silver nanoparticles as a tool for Fe(II) ion detection

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Keywords
Fe(II) determination
silver nanoparticles
smartphone-based detection

Silver nanoparticles have become widely used in chemical analysis due to their distinctive optical and chemical characteristics, such as high reactivity and stability. Their surfaces can be functionalized with different chemical groups, enhancing both the selectivity and sensitivity of analytical techniques, which makes them effective tools for detecting and quantifying various analytes. To achieve consistent and desirable physicochemical properties, the synthesis of silver nanoparticles demands careful regulation of reaction conditions, including concentrations of reagents, pH, temperature, and process duration. Flow-based synthesis methods have proven particularly effective in maintaining stable conditions during nanoparticles production. In this research, silver nanoparticles stabilized with EDTA were produced to enable the determination of Fe(II) ions. The concentration of silver nitrate was optimized for the specific application of Fe(II) detection. The resulting nanoparticles were characterized using transmission electron microscopy. A method for Fe(II) determination was developed employing the synthesised silver nanoparticles, with detection performed through both spectrophotometry and smartphone-based analysis. The influence of potential interferents on the measurement was also assessed. Key analytical parameters, such as the linearity, quantification limits, precision, and accuracy, were established. The method's practical applicability was verified by measuring Fe(II) content in white wine and water samples, with the results compared to those obtained using the 1,10-phenanthroline as a reference method.

Racemization of animal glue in paintings

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Keywords
aspartic acid
cultural heritage
enantioseparation
racemization

Material research in cultural heritage is one of the most reliable sources of information about historical artifacts. There is a plethora of well-established techniques for studying composition of painted artwork. Yet only a handful of dating techniques exists. The radiocarbon method is routinely applicable to materials of substrates (wooden panels, canvas) and frames. Only recently, dating of lead white from color layers was reported. However, required sample size and exclusion of some time periods, due to the fluctuations in calibration curve, substantially limits its potential. Amino acid racemization is a chemical method for dating materials of biological origin used in forensic and quaternary science as well as archaeology. Although proteinaceous binders (eggs, animal glues, casein) are widely used in painting, to our best knowledge this method has never been used for dating of painted artworks. Due to its nature, we believe it has great potential to complement existing methods. Most living organisms throughout their life maintain L-amino acids homochirality, although it is an energy-intense process as racemization naturally occurs, and defective proteins are usually repaired or replaced. In event of death, there are none or negligible D-amino acids and racemization starts to proceed unimpeded. That is the starting point to which age estimation is linked and if the reaction rate is known, and a racemization ratio is determined, the age can be estimated. This work focuses on the aspartic acid due to its relatively fast racemization, which makes it suitable for dating paintings hundreds of years old. To determine enantiomer ratio the technique of choice in this work is capillary electrophoresis with fluorescence detection, as required sample size can be reduced to microliters and offers very low limit of detection. Cyclodextrins were used as chiral selectors and we were able to enantioseparate nine pairs of amino acids, which represents most of the primary structure of

collagen from a skin. Animal glues were extracted in multiple steps from mock-ups of grounds as they are likely a target for sampling in historical paintings. These experiments create a base for upcoming research in this area and development of amino acid racemization method for dating painted artworks.

Development of structured boron-doped diamond electrodes for anodic oxidation of phenol

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Keywords
boron-doped diamond
cyclic voltammetry
degradation
phenol

Boron-doped diamond is an effective electrode material for the electrochemical oxidation of various organic compounds due to its superior physical and chemical properties. However, its exceptional hardness and chemical inertness make structuring challenging, even though it can be crucial for improving electrochemical performance in degradation and sensing applications. In this work we prepared boron-doped diamond on roughened titanium support to obtain structured boron-doped diamond surfaces and explored the properties of these structured boron-doped diamond on roughened titanium support electrodes for anodic phenol oxidation. A set of boron-doped diamond electrodes with varying [B]/[C] ratio was fabricated using microwave plasma-enhanced chemical vapor deposition (in particular, its linear antenna variation) to study the influence of doping levels on the electrochemical performance. Boron-doped diamond on roughened titanium support electrodes were characterized structurally, morphologically, and electrically, followed by electrochemical evaluation under different pH conditions. Morphological analysis using scanning electron microscopy revealed uniform nanocrystalline diamond films. Raman spectroscopy confirmed the incorporation of boron. Electrical measurements confirmed a general increase in specific conductivity with increasing boron concentration. Cyclic voltammetry showed a higher boron doping and pH affected the potential window of the electrodes, with increased boron slightly reducing potential window but improving conductivity. Phenol degradation was performed by

galvanostatic oxidation in aqueous sodium sulfate electrolyte. The degradation efficiency was estimated using chemical oxygen demand measurements, which suggest that it is influenced by boron content. It should be noted that this method estimates total mineralization of organic molecules rather than specific oxidation of phenol molecules, which, for example, is better suited to evaluate performance of wastewater treatment. Notably, higher boron doping enhanced degradation efficiency at high current density, whereas the difference was less pronounced at low current density.

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Smartphone-assisted fluorescent detection of chloride ions on a paper-based microfluidic platform

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Keywords
biomedical analysis
chloride ion determination
microfluidic analytical devices
miniaturization of analytical methods

Modern analytical chemistry increasingly concentrates on miniaturised, low-cost, and environmentally sustainable solutions. One such approach involves microfluidic paper-based analytical devices, which align well with the principles of Green Analytical Chemistry due to their simple design, low production costs, and minimal reagent and sample consumption. Integrating these devices with widely accessible mobile technologies, such as smartphones, facilitates their use outside of laboratory settings by non-specialists. In this study, a paper-based microfluidic device was developed for the determination of chloride ions. The method relies on changes in the fluorescence intensity of a citric acid–cysteine complex in the presence of chloride ions. Signal detection was performed using a smartphone placed in a custom 3D-printed holder equipped with LED diodes emitting light at 365 nm. Images captured during the analysis were processed with the ImageJ software. Preliminary studies involved optimizing both instrumental parameters and the chemical reaction conditions underlying the detection process. The obtained analytical performance suggests that the proposed system has the potential for practical application in determining chloride ions in biomedical and environmental samples, particularly under field conditions.

The research was conducted with the financial support of the Anthropocene Priority Research Area as part of the Strategic Programme Excellence Initiative at the Jagiellonian University.

Chemometric insight into spiciness of hot peppers

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Keywords
capsaicin
chemometrics
dihydrocapsaicin
spiciness

There are numerous pepper varieties worldwide differing in shape, colour, size, taste and ripening time. Peppers also vary significantly in content of health-promoting compounds, such as capsaicinoids. Capsaicinoids offer several benefits to human health, including supporting body thermoregulation, usage in treating various diseases, and having potential anti-cancer properties. What is more, capsaicinoids are known for giving peppers their characteristic pungency. Among the capsaicinoids group, capsaicin and dihydrocapsaicin are the most predominant, collectively comprising approximately 90% of the total capsaicinoid content in peppers. It is also worth noting, that the content of these compounds may differ not only between specific pepper species, but also within phenotypically different varieties. Studies were conducted to determine the content of capsaicin, dihydrocapsaicin and the total content of these two compounds in three species of hot peppers, which were Carolina Reaper, Bhut Jolokia and Big Mama. Each species contains many colour varieties, including: white, yellow, brown, green and, the most famous – red. The measurements showed that, depending on the variety of pepper, the content of capsaicinoids differed between the colour variants. Moreover, there is a noticeable trend among all three species, in which red and darker peppers are characterized by the highest content of capsaicin and dihydrocapsaicin. This work presents a chemometric analysis of capsaicinoid content in various varieties of three hot pepper species.

The research results show in a simple and clear way the relationship between the colour of the pepper and the levels of capsaicin and dihydrocapsaicin in each colour variant. Using several data analysis methods, the contents were also compared across colours within individual species, revealing an upward trend in capsaicinoids concentration.

Design and characterization of 3D-printed potentiometric sensor platforms

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Keywords
3D printing
conductive polymers
fused deposition modeling
potentiometry
solid-contact electrodes

The importance of accurate and precise analytical methods is undeniable. Analytical chemistry is applicable in many fields including medicine, pharmacy, industry or environmental science. As a result, there is a growing demand for low-cost and reliable techniques and devices for the detection of various analytes, including ions, which are essential in quality control, environmental monitoring, and healthcare. One of the effective methods for such measurements is potentiometry, which is commonly used for the detection of ions such as potassium, sodium, calcium, chlorides, and nitrates. A major advancement in this field was the discovery of the conductive properties of certain polymers, enabling their use as intermediate conductive layers in solid-contact ion-selective electrodes. This innovation made it possible to eliminate the internal solution typically required in conventional sensors and facilitated the miniaturization of potentiometric devices. In this work, I focus on the development of multi-electrode sensors capable of simultaneously detecting multiple analytes. The project involves studying the electrochemical properties of these sensors, which are fabricated using rapid prototyping techniques – specifically, fused deposition modeling 3D printing. The sensors are designed for single-step manufacturing using a multi-extruder 3D printer. Several commercially available filaments were used to reduce production costs, including non-conductive polylactide and two types of conductive polylactide filaments: carbon black-based polylactide from ProtoPasta and graphene-infused polylactide from Advanced Graphene Products. The experimental phase involved designing the sensor models in Autodesk Inventor and preparing them for printing using two 3D printers: the Flashforge Creator Pro 2 and the Original Prusa XL 5-Head. The electrochemical performance of the

sensors was evaluated in solution using chronopotentiometry and electrochemical impedance spectroscopy. The results demonstrate the potential of this approach for developing miniaturized, cost-effective sensors suitable for remote and field applications.

Application of the atomic absorption spectroscopy method to monitor the content of bio-elements in natural biological material with sorption properties (biomass from *in vitro* cultures)

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Keywords
atomic absorption spectroscopy
bio elements
in vitro cultures
Pleurotus spp.
sorption

Atomic absorption spectroscopy is an analytical technique increasingly used to monitor essential bio element content in biological materials, including *in vitro* cultured *Pleurotus* spp. fungal biomass (with exceptional sorption properties). Atomic absorption spectroscopy enables precise, quantitative assessment of both macro- and micronutrients in biological matrices, allowing for real-time tracking of the accumulation and mobilization of elements such as magnesium, zinc, copper, and iron during the growth of this exceptionally sorption biomass. The methodology involves sampling the culture media and using atomic absorption spectroscopy to determine temporal changes in element concentrations that facilitate bioaccumulation during the *in vitro* culture stages of *Pleurotus* spp. biomass. Non-invasive or minimally invasive sampling techniques preserve culture integrity and provide accurate monitoring of metal uptake and retention in living biomass systems. This analytical strategy is particularly valuable for optimizing bio element supplementation in *in vitro* culture protocols and for

investigating the mechanisms underlying biosorption and bioaccumulation phenomena under controlled biotechnological conditions. The use of atomic absorption spectroscopy to determine bio element content in *in vitro* cultures of *Pleurotus* spp. allows for high sensitivity in the detection of trace elements. This study examined the use of atomic absorption spectroscopy to determine bio element content in biomass from *in vitro* cultures. *Pleurotus* spp. mushrooms were characterized by varying degrees of bioaccumulation of elements such as magnesium, zinc, iron, and copper.

Immobilisation of single-stranded DNA capture probes on a chitosan leaky waveguide designed to detect single-stranded circulating tumour DNA biomarkers

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Keywords
bladder cancer
chitosan
label-free detection
leaky waveguide
ss-ctDNA

Bladder cancer ranks as the world's tenth most diagnosed cancer and is the most expensive in terms of patient care due to the extensive follow-up required to monitor recurrence. Early detection is crucial for reducing mortality rates associated with bladder cancer, and the detection of circulating tumour DNA shows promise for identifying cancer at early stages. In this study, we are developing a chitosan leaky waveguide biosensor designed to detect single-stranded circulating tumour DNA (ss-ctDNA) biomarkers. A leaky waveguide consists of three layers: the cover or sample layer, the waveguide layer, and the substrate layer. Chitosan hydrogel is utilised as the waveguide layer due to its amine groups, which can be easily modified to immobilise a recognition element. Preliminary studies, including glycerol sensing tests and porosity tests (using PEG), indicate that chitosan hydrogel demonstrates high sensitivity (RIS_{gly} =118.73 ± 0.25 deg/RIU) and relatively high porosity. These characteristics are beneficial for enhancing sensing performance, specifically by improving sensitivity and lowering the limit of detection. A single-stranded DNA capture probe with an amine modification (ssDNA capture probe) serves as a recognition element to capture the complementary ss-ctDNA target analyte. The ssDNA capture probe was immobilised on chitosan leaky waveguide via physical adsorption. When the ss-ctDNA target analyte is present, the immobilised ssDNA

capture probe hybridises with it, forming double-stranded DNA. This hybridisation causes a shift in the resonance angle, which is influenced by changes in the refractive index due to the formation of the double-stranded DNA. The immobilisation of the ssDNA capture probe was investigated under various conditions, including blocking reaction time, concentration of the ssDNA capture probe, addition of sodium ions, and temperature. These factors were found to influence the signal obtained from the immobilisation of the ssDNA capture probe. Additionally, the selectivity study revealed that the chitosan leaky waveguide immobilised with the ssDNA capture probe demonstrated good selectivity over mismatched ssDNA (ssDNA wild type) with a signal of 0.067 ± 0.013 deg for the ss-ctDNA target analyte compared to just 0.007 ± 0.004 deg for the ssDNA wild type.

Author Index

Keyword Index

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