

IMYAC

1st International Meeting for Young Analytical Chemists
27-28th September 2021



Book of abstracts

IMYAC

1st International Meeting for Young Analytical Chemists

27th - 28th September 2021

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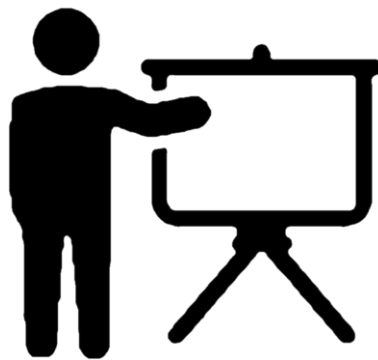
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Oral presentations

Capillary electrophoresis method for analysis of monosaccharides found in glycopeptides

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ABSTRACT: The glycosylation affects physicochemical properties of the protein, such as its conformation, biological activity and metabolism and therefore there is an increased interest in analysis of saccharides released from glycoproteins. Free monosaccharide analysis can provide useful information on the relative proportion of individual units in glycoproteins – changes in glycosylation may occur as a result of cancer, autoimmune disease or immunodeficiency [1], [2].

Acidic hydrolysis was used for the release of eight monosaccharides commonly found in glycoproteins, namely fucose, galactose, glucose, mannose, *N*-acetylgalactosamine, *N*-acetylglucosamine, *N*-acetylneuraminic acid and xylose [3]. The method used for their separation and determination was capillary electrophoresis with contactless conductivity detection in highly alkaline background electrolyte.

Total length of bare-silica capillary was 50.0 cm, effective length was 35.0 cm and inner diameter was 10 μm. Background electrolyte was 50 mmol/l sodium hydroxide, 22.5 mmol/l disodium phosphate and 0.2 mmol/l cetyltrimethylammoniumbromide. Samples were injected hydrodynamically with pressure of 5 kPa for 70 s, driving voltage was -30 kV and the pressure of 270 kPa was applied to the outlet vial during separation. An addition of an internal standard 4-(2-hydroxyethyl)-1-piperazinethanesulfonic acid increased the reliability of identification and determination of monosaccharides and the relative standard deviations of relative peak areas and relative migration times were lower than 3.5 %. The limits of detection were between 5–7 mg/l and the limits of quantification were between 16–22 mg/l. Fetuin was used as a model glycoprotein to be analyzed. Conditions for its hydrolysis were determined as 0.4M hydrochloric acid/80 °C/1 hour for *N*-acetylneuraminic acid and 4M hydrochloric acid/80 °C/5 hours for other monosaccharides.

Keywords: capillary electrophoresis, contactless conductivity detection, monosaccharides

Acknowledgements: This work has been supported by the Czech Science Foundation, Grant No 19-18005Y and by Specific University Research (SVV260560).

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Online labelling of monosaccharides for capillary electrophoresis

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ABSTRACT: Capillary electrophoresis is a suitable tool for the determination of carbohydrates [1,2]. Due to the lack of chromophores, the commonly used direct UV detection cannot be used. The carbohydrate structure also lacks ionizable groups. Therefore, a frequently used technique is labeling carbohydrates with charged chromophores or fluorophores. Conventionally, a saccharide is derivatized before the analysis by reductive amination using cyanoborohydride as a reducing agent. When analyzing a sample by capillary electrophoresis, it is possible to use the capillary as a reaction space where derivatization is performed. Sample and derivatizing agent are injected as separate zones and mixed inside the capillary by electrophoretic migration or diffusion. However, reduction with sodium cyanoborohydride releases hydrogen cyanide gas, which interrupts the continuous filling of the capillary with electrolyte and may affect the efficiency of online sample mixing.

In this work, glucose was derivatized with 7-amino-1,3-naphthalenedisulfonic acid monopotassium salt monohydrate (ANDSA) using electrophoretic mixing of the zones. It has been shown that the product can be obtained without the use of cyanoborohydride. The appropriate solvent for glucose and derivatizing agent was searched, sequence and length of injected plugs was optimized, and sufficient time for reaction was found. Measurements were conducted in a fused-silica capillary of 50 μm inner diameter with the total length 65.0 cm and effective length 56.5 cm. The background electrolyte was phosphate buffer, pH 3.5. Glucose in 4 mM concentration was injected hydrodynamically for 3 s by a pressure of 5 kPa, then 50 mM ANDSA was injected for 3 s by a pressure of 5 kPa (both dissolved in 2.5 M acetic acid). A voltage of -5 kV was applied for 90 s, then the mixed zones were allowed to react for 5 minutes. A separation voltage of -30 kV was applied. A UV-VIS detector operating at 254 nm wavelength was used. The method proved to be suitable for other carbohydrates - mannose, xylose, fucose, galactose.

Keywords: capillary electrophoresis, saccharides, online capillary electrophoresis

Acknowledgements: This work has been supported by Charles University, project SVV260560 and by the Czech Science Foundation, Grant No 19-18005Y.

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The electrophoretic separation of biologically active compounds with using modifiers based on imidazolium cation

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ABSTRACT: The application of modifiers like imidazolium ionic liquids can significantly extend the possibilities of the capillary electrophoresis method. They can be bonded to quartz capillary walls via linkers or can be added into background electrolyte as pseudo stationary phases. Thus, the modifiers typically provide electrophoretic separation of biologically active compounds including ones are similar in structure and even enantiomers.

It was established, *N*-alkylimidazolium coatings covalently bonded to the capillary wall allow to determine biogenic amines with good separation efficiency (up to 2×10^6 t.p.) and selectivity. Moreover, the use of a hybrid preconcentration technique (sweeping and field-amplified sample injection) in conjunction with coatings leads to a decrease of LODs of biogenic amines and their metabolites to 0.3-2.3 ng/mL [1].

The derivatives of β -cyclodextrin and imidazole in background electrolyte can act as pseudo stationary phases in the separation of corticosteroid hormones and nonsteroidal anti-inflammatory drug enantiomers (ketorolac and ketoprofen). Corticosteroids interact with the hydrophobic cavity of the derivative. Therefore, positively charged associates «modifier-corticosteroid» are formed. Due to this phenomenon separation of steroids occurred and a new approach for their preconcentration by electrokinetically injection into capillary was proposed [2]. It allows to concentrate steroids in 20-25 times (LODs are 35-50 ng/mL) and carry out an electrophoretic analysis of steroid hormones in human plasma after liquid-liquid extraction. Enantiomers of ketorolac and ketoprofen are also baseline separated and preconcentrated under field-amplified sample stacking mode with LODs 110-220 ng/mL.

Keywords: capillary electrophoresis, preconcentration, biologically active compounds, steroids, pharmaceutical drugs.

Acknowledgements: This work has been supported by the Russian Science Foundation (project No 19-13-00370).

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Determination and identification of antibiotic drugs and bacterial strains in post-operative wounds

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ABSTRACT: Surgical site infections (SSI) are common surgical complications, posing a real threat to the health and life of operated patients and significantly increasing treatment costs. It is estimated that 2-7% of all operations develop SSIs, and 11% of all deaths in intensive care patients are related to post-operative wound infections. Therefore, it is essential to quickly and accurately identify microorganisms that cause infections in post-operative wounds. Currently, many medical laboratories use the MALDI-TOF MS technique to identify bacteria. The primary purpose of the research was to select the conditions for the cultivation of microorganisms to obtain correct identification in a shorter time.

Microorganisms were isolated and identified from swabs from post-operative wounds. In order to identify microorganisms, four culture media were used: two non-selective (BHI, MHA) and two selective (BCP, VRE). Three species were selected for further research, which, according to the literature and the research performed, most often colonize post-operative wounds. These were *Staphylococcus aureus*, *Enterococcus faecalis* and *Escherichia coli*. Additionally, the identification level and quality of acquired mass spectra were compared for four solid culture media. The research results show that the type of substrate used and the method of preparation of bacterial extracts have an impact on the quality of the mass spectra obtained. The incubation time strongly influenced the bacterial identification; therefore, we concluded that the optimal time could significantly accelerate the microbiological diagnosis of post-operative wound infections and implement the individual therapy faster. Moreover, liquid chromatography coupled with mass spectrometry was applied for determination and identification of antibiotics from different therapeutic groups. Molecularly imprinted polymer (MIP)-coated solid-phase microextraction fibers were used on the sample preparation step in biological samples from patients in intensive care units. Finally, the obtained results demonstrate the potential of *in vivo* SPME as a useful sample preparation tool for chromatographic based metabolomics drug monitoring in the biomedical application from patients receiving therapeutic dosages.

Keywords: bacterial strain; antibiotic; MALDI-TOF MS; post-operative wound; SPME

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The catalytic influence of 2-thiocytosine on the electroreduction of Bi(III) ions in chlorates (VII) solutions with varied water activity; application of the R-AgLAFe electrode

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ABSTRACT: So far, the effect of „cap-pair” [1] has only been studied on mercury drop electrodes. The use of an electrode with a cyclic renewable film of liquid silver amalgam R-AgLAFe is an excellent alternative to HDME, as it guarantees similar quality and performance parameters to HMDE [2,3], and furthermore fits into the current trend of green chemistry, due to the significant reduction in the consumption of toxic mercury.

The effect of 2-thiocytosine (TC) on the kinetics and mechanism of Bi(III) ions electroreduction in chlorate(VII) solutions under various water activities using R-AgLAFe was investigated in aspect of the „cap-pair” effect. The results obtained with the innovative electrode using the different electrochemical techniques enabled to determine the magnitude of the catalytic effect of 2-thiocytosine and the correlation with changes in water activity. The multistep of Bi(III) ions electroreduction process in the presence of TC is controlled by the rate of formation of the nanosized active complexes on the R-AgLAFe electrode, mediating electron transitions. Changes in the Bi(III) ions electroreduction mechanism and in the presence of 2-thiocytosine in high water activity solutions compared to low water activity solutions were demonstrated.

Keywords: electrochemistry, kinetics, electroreduction, R-AgLAFe, cap-pair, 2-thiocytosine

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Influence of the doped ion on the properties of polyaniline nanofibers and the parameters of solid contact ion-selective electrodes based on them

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ABSTRACT: Ion-selective electrodes belong to the group of the most popular potentiometric sensors. In recent years, the ion-selective electrodes with solid contact have been subject to particular development, which allow to achieve very good parameters, comparable to classic electrodes with an internal solution, and often with even much better results, and at the same time allow for their miniaturization and construction change, easier storage, transport and use them in many configurations and positions. Apart from obtaining low detection limits, high slope of the calibration curves and good selectivity of sensors, particular attention is paid to ensuring very good stability and reversibility of the electrode potential. This is possible thanks to the appropriate selection of the substance that will be used as a solid contact in the construction of the electrodes and will allow the appropriate charge flow as an ion-to-electron transducer. Initially, for this purpose, compounds from the group of conductive polymers were used, while nowadays, various types of carbon nanomaterials, as well as nanoparticles, are most often used.

The research on the properties of synthesized polyaniline nanofibers doped with chloride and nitrate ions and their use as a solid contact in ion-selective electrodes sensitive to nitrates are described. For this purpose, many analytical techniques were used: SEM, UV-VIS spectroscopy, FTIR (for nanofibers) and potentiometric methods with electrochemical impedance spectroscopy (for constructed electrodes). It was concluded that the use of both types of nanofibers has a positive effect on the performance of the sensors, in particular the stability and reversibility of the potential. The obtained electrodes were also characterized by lower detection limits and a wider range of linearity of the calibration curves, and they also operated without disturbances in conditions of variable light intensity, presence of gases in the solution (O₂) and a wide pH range. The slight differences in the analytical parameters of the modified electrodes resulted from the differences in the structure of the obtained types of nanofibers.

Keywords: electrochemistry, ion-selective, solid contact, polyaniline, nanofibers

Electrochemical immunosensors for monitoring autoimmune diseases biomarkers

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ABSTRACT: Autoimmune diseases are a complex set of diseases characterized by the performance of the immune system that recognizes its own cells and tissues as foreign by mistake, and attacks it, instead of protecting it. Its unknown etiology and variety of pathogenesis trigger that a correct diagnosis and effective treatment difficult to achieve. The research of measuring the level of some predictive biomarkers may be the key for this to enhance¹. In this framework, the boom that electrochemical biosensors technology has reached in clinical analysis is due to their operational characteristics, being capable of monitoring, in real-time and at low cost, a wide variety of biomarkers with simple practical application and instrumentation. In this work, six electrochemical devices based on different functionalization strategies and electrochemical performance are presented. They were designed for the detection and quantification of several biomarkers for autoimmune diseases. In all cases, screen printed electrodes have been used for carrying out the electrochemical detection reaction by differential pulse voltammetry or amperometry. For the determination of important proteins -TGF- β 1², PYY³ or CXCL7⁴, IL-1 β ⁵- the functionalization of the electrode surface has been accomplished by electrografting techniques or click chemistry with modified nanomaterial, respectively. On the other hand, the development of two different dual devices for simultaneous determination of a pair of crucial autoantibodies RF and ACPA⁶, as well as CXCL7 and MMP3⁷ proteins, was possible by the use of magnetic micro beads for immunoreagent immobilization. Their application to biological sample analysis and good performance have shown their analytical usefulness, becoming an interesting alternative for monitoring autoimmune disease biomarkers in the clinical field.

Keywords: electrochemistry, autoimmune biomarkers, immunosensors, clinical analysis

Acknowledgements: This work has been supported by Spanish Ministry of Sciences, Innovation and Universities and TRANSNANOAVANSENS-CM Program.

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Flow amperometric biosensors based on the enzymatic mini-reactor and silver solid amalgam electrode

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ABSTRACT: A significant achievement of this work is the development of a perspective flow biosensing platform based on two key features:

i) the spatial separation of a bioreceptor and a transducer. It means that an enzyme (belonging to the oxidase family) is immobilized not at the surface of the working electrode but on some powdered support forming filling for co-called enzymatic mini-reactor. This mini-reactor is connected into flow system in front of the transducer. This approach enables the attachment of the much larger amount of enzyme and solves the limitations of the most biosensors given by their relatively low stability and short lifetime. Importantly, one of the main profits of non-attachment of the biorecognition element to the working electrode surface is a possibility of the fast replacing of one enzymatic mini-reactor by another one or using working electrode for other purpose;

ii) amperometric monitoring of the enzymatically consumed oxygen. This approach enables to avoid the interference effects that are common in detection of enzymatically produced hydrogen peroxide. For this purpose, the flow detectors based on silver solid amalgam have been proposed, developed and constructed in our laboratory and used to determine unconsumed oxygen via its sensitive four-electron reduction at the highly negative potential (-1.1 V vs. saturated calomel electrode).

Keywords: amperometric biosensor, enzymatic mini-reactor, flow injection analysis

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Chemical characterization and bioactivity evaluation of black mulberry and grape seeds

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ABSTRACT: Circular economy is increasingly seen as a crucial way to reduce food by-products and residues and obtain valuable raw materials. There is a growing demand for industrial products with clean labels and bio benefits, where natural bioactive compounds play an important role. Among these natural biomolecules, polyphenols stand out for their health benefits against diseases such as cancer or diabetes. Thus, the use of agro-industrial bioresidues as a rich source of polyphenols for the development of new natural preservatives, colorants and nutraceuticals is in the spotlight [1,2].

The aim of this work was the recovery of polyphenols from grape and mulberry seeds, usually considered as biowaste. Polyphenols were characterized by HPLC-DAD-ESI/MSⁿ, and the obtained polyphenol-rich extracts were analysed for their bioactive properties, namely antimicrobial and antioxidant capacities. Grape seeds were richer in catechin oligomers (36.0 ± 0.3 mg/g), and mulberry seeds in ellagic acid derivatives (3.14 ± 0.02 mg/g). In addition, both extracts exhibited high antimicrobial activity against multi-resistant *Staphylococcus aureus*. On the other hand, mulberry seeds showed the strongest antioxidant activity by the lipid peroxidation inhibition (IC₅₀ = 23 ± 2 µg/mL) and oxidative haemolysis inhibition (IC₅₀ at a 60 min Δt = 46.0 ± 0.8 µg/mL) methods [2]. Both by-products could be exploited for the recovery of added-value bioactive polyphenols and further application in the industry [2].

Keywords: Bioactivity, polyphenols, by-products, grape/mulberry seeds.

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Fluctuation of internal standard method calibration factors using GC-MS

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ABSTRACT: The research recorded changes in Relative Response Factors (RRF) values during the analysis of alcoholic products using GC-MS with traditional internal standard (IS) and "ethanol as IS" methods. It was shown that within a 20-96% ABV and 250-5000 mg L⁻¹ absolute alcohol (AA) volatile concentration range, the resultant RRFs for the standard IS method (8% RSD) were more stable than those for the "ethanol as IS" method (40% RSD). However, for 40% and 96% ABV matrices, the ethanol and standard IS methods showed nearly the same RSDs variation of no more than 1.5% within the 250-1000 mg L⁻¹ AA volatile compounds concentration range. Similar RRF stability under a wider concentration range would be achieved only when injections are made under identical conditions, particularly, with the same injection volume.

The reasons for relatively high instability of ethanol RRF values were also reviewed. To minimize the variability of RRFs during injection of alcoholic products it is suggested to use liners of bigger internal volumes, reduce injector temperature, and to inject smaller sample volumes. Samples with low ABV values contain high amounts of water and thus tend to produce a much larger vapour phase. For ethanol MS detection the influence of sample injection volume on RRF values was observed, especially a nonlinear relationship between the ethanol peak area and its quantity. This means that samples of the same ABV should not be injected in different volumes.

Although the "ethanol as IS" method demonstrated poorer RRF stability than the standard IS method the former is still recommended as a worthwhile method in practice. The reasons for this are, the method requires no manual addition of IS, and there is no necessity to establish strength and density of the testing sample which is required in the standard IS method. Using ethanol as an IS method has the distinct advantage of being the more rapid than standard IS and is the cheapest method for analysis of alcoholic products, especially using GC-FID.

Keywords: alcoholic products, calibration, GC-MS, internal standard method, relative response factors

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Abacavir: comparison of approaches to active pharmaceutical ingredient oxidation studies

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ABSTRACT: Forced degradation studies are one of the important steps in drug development. During forced degradation studies, the active substance or drug product is exposed to extreme physical and chemical conditions. The influence of temperature, humidity, pH and oxidation is studied [1]. The effect of oxidation on active pharmaceutical ingredient or drug product is commonly studied using a 0.1-3% peroxide solution at room or elevated temperature [2]. During this approach, oxidation products are formed mainly by electrophilic attack or nucleophilic addition and at elevated temperature, peroxy radicals are formed, which lead to oxidation by a radical mechanism. Another possibility is the use of radical initiators such as AIBN or AVCA, which are heat-initiated and the oxidation proceeds by a radical mechanism. Yet another possibility is the use of metal ions. In this approach, oxidation occurs by the electron transfer mechanism [3]. An alternative method is to use an electrochemical cell. During this approach, the active pharmaceutical ingredient or drug product is oxidized on a working electrode to which a constant potential is applied. Oxidation products are formed mainly by electron transfer and radical mechanisms. The advantages of this alternative approach are its speed, lower sample consumption and the ability to test multiple oxidation mechanisms at once. Within this project, a comparative study of oxidation mechanisms was performed. Abacavir was used as a model active pharmaceutical ingredient. Oxidation studies were performed using hydrogen peroxide, radical initiators and metal ions. These approaches were compared with an alternative electrochemical method. The effect of solvent on oxidation was also studied. The oxidation products were characterized by HPLC-MS. Electrochemical oxidation yielded the largest variety of oxidation products from all the tested approaches.

Keywords: abacavir, forced degradation studies, oxidation mechanism

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Separation of human IgG glycopeptides in mixed-mode hydrophilic interaction/ion-exchange liquid chromatography

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ABSTRACT: Glycosylation is one of the most frequent and complex post-translation modification of peptides [1]. It plays an important role in many biological processes such as protein folding and secretion or cell-cell adhesion. Furthermore, alterations of glycosylation are related to several inflammatory diseases, various cancer types or to Alzheimer's disease [2]. The macro- and micro-heterogeneity of glycopeptides complicates their analysis in spite the modern bioanalytical approaches [3]. In recent years, hydrophilic liquid interaction chromatography (HILIC) became a method of choice for glycopeptide separation before their identification by mass spectrometry [4].

In this work, we compared the separation potential of three recently developed HILIC columns developed by Advanced Chromatography Technologies (ACE) with a C18 reversed-phase column in the separation of human IgG glycopeptides. Each of these HILIC columns contain different stationary phase – HILIC-A with unfunctionalized silica, HILIC-N with polyhydroxy functionalized silica and HILIC-B with aminopropyl functionalized silica. Although in the reverse-phase mode we were able to separate the glycopeptides of IgG based on their peptide backbone, we were not able to separate different glycoforms attached to the same peptide. On the other hand, in the HILIC columns we were able to separate the glycoforms of IgG. Moreover, in case of sialylated glycoforms HILIC-A and HILIC-B columns showed a mixed-mode separation mode combining ion-exchange chromatography and HILIC separation mechanism.

Keywords: glycoproteomics, hydrophilic interaction liquid chromatography, mixed-mode chromatography, immunoglobulin G

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Voltammetric determination of the new growth regulator Revysol[®] (mefentrifluconazole) by using a boron doped diamond electrode

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ABSTRACT: Growth regulators are used to strengthen plants against natural phenomena. They are essential for growing plants in today's world. Revysol[®] is a new product that has unique chemical and biological properties. The main active substance of this preparation is mefentrifluconazole (MFZ) from the triazole group[1-3]. In this work, a method for the voltammetric determination of this substance was developed. The determination of MFZ was performed by differential pulse voltammetry using BDDE as an working electrode. The analysis was conducted in an alkaline medium, which was Britton-Robinson buffer (pH=9) in the presence of 33% acetonitrile. Quantitative and reproducible determination of MFZ was tested in three concentrations, in particular $1,27 \cdot 10^{-6}$ mol.L⁻¹, $2,54 \cdot 10^{-7}$ mol.L⁻¹ and $5,10 \cdot 10^{-8}$ mol.L⁻¹. Results with good reproducibility were obtained. Under the proposed conditions the limit of detection was $6,54 \cdot 10^{-9}$ mol.L⁻¹ and the limit of quantification was $2,26 \cdot 10^{-8}$ mol.L⁻¹. During the analysis of the real sample, which was REVYSTAR, a problem arose, there was an admixture in the preparation that distorted the results. After modifying the method of evaluation, the influence of the interfering component was minimized to such an extent that it did not affect the determination of mefentrifluconazole.

Keywords: growth regulator, DP voltammetry, BDDE, mefentrifluconazole

Acknowledgements: This work has been supported by the Czech Science Foundation (project 20-01589S) and by the University of Pardubice (project No. SGSFChT_2021_003).

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Electrochemical properties of screen-printed sensors with chemically deposited boron doped diamond electrode and their applications in electroanalysis

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ABSTRACT: The boron doped diamond electrode (BDDE) currently has been firmly established in the field of electroanalytical chemistry due to its excellent properties such as wide available potential window, low background current, low current noise, good chemical resistance, resistance to passivation and high mechanical stability [1]. In recent years, the trend towards miniaturization, acceleration of the analysis and cheapening has increased which brings the development of new types of electrodes and sensors, including printed sensors. Their main advantage consists in their low price and possibility of easy mass production, thanks to which they can be used as disposable sensors [2]. Therefore, the screen-printed (SP) sensors with chemical deposited BDDE as a working electrode (SP/BDDE) can be perspective alternative to bulk BDDE in the field of electroanalysis.

The subject of this work is the investigation of the electrochemical properties of newly prepared SP/BDDE and their comparison with commercially available printed sensors and bulk BDDE. For these studies mainly cyclic voltammetry of reversible redox systems ($[\text{Fe}(\text{CN})_6]^{4-/-3-}$ and $[\text{Ru}(\text{NH}_3)_6]^{3+/2+}$) was used. In addition to the width of the potential window, the difference between the potentials of the anodic and cathodic peaks and the ratios of their heights were also compared. Other parameters tested were repeatability and reproducibility of measurements both at one electrode and between electrodes. This work also shows the applicability of new tested sensors in the analysis of various compounds important environmentally (pesticides) and in term of human health (drugs).

Keywords: electrochemistry, voltammetry, screen-printed sensors, boron doped diamond electrode.

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Atorvastatin determination on glassy carbon electrode modified with carbon nanofibers and cobalt nanoparticles

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ABSTRACT: Atorvastatin (ATOR) is a medication belonging to the group of statins. Its therapeutic effect is focused on the reduction of ischemic attacks in people who suffered from acute coronary syndrome but might be also used for treatment of hypertension.

Among methods that might be used for ATOR determination are: high performance liquid chromatography [1], liquid chromatography [2], spectrophotometry [3] or capillary electrophoresis [4]. Great alternative for mentioned method is voltammetry, which might be characterized by high sensitivity, low limit of detection (LOD), simple process of sample preparation and relatively low cost of analysis.

We propose a new highly sensitive method for ATOR determination on glassy carbon electrode modified with carbon nanofibers and cobalt nanoparticles. Developed sensor might be characterized by good reproducibility (RSD = 9.0%, n = 5) and might perform not less than 700 measurements without compromising metrological parameters. Calculated LOD for ATOR was equal to 3.4 nM ($1.9 \mu\text{g L}^{-1}$) for accumulation time 50 s. Applicability of the method was proved by analysis of real samples containing ATOR.

Developed method for ATOR determination might be a useful tool in routine laboratory practice.

Keywords: voltammetry, carbon nanomaterials, cobalt nanoparticles, atorvastatin

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Graphene flakes modified with gold nanoparticles as intermediate layer for ion-selective electrodes

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ABSTRACT: Ion-selective electrodes are potentiometric sensors whose response is linearly dependent on the logarithm of the concentration of determined ion. Elimination of the internal solution from classical ion-selective electrodes initiated a lot of work on all-solid-state electrodes. The first proposed type of solid electrode, called coated-disc, unfortunately was characterized by a lack of potential stability. To eliminate this problem, a new type of electrode called solid-contact has been proposed, where a transducer layer is applied between the membrane and the electrode substrate. Since then, many materials have been proposed as a transducer layer, so that the obtained electrodes have the best parameters.

This work proposes electrodes that use nanographene flakes mediated by dispersed nanogold particles as a transducer layer.

The proposed material has been widely characterized. Its microstructure and parameters were determined, such as: hydrophobicity characterized by the contact angle with water - 115°, or the electric capacity equal to 1.80 mF. The determined parameters were better than those reported for unmodified graphene [1] from the point of view of using it as a solid-contact.

Ready to use electrodes with a nanocomposite layer had an electrical capacity of 280 μ F. Due to the high electrical capacity, the obtained electrodes showed a stable response over time, which is determined by the potential drift equal to 36 μ V / h. Moreover, the proposed electrodes showed good potential reversibility, close to the Nernstian response in the concentration range of $10^{-5.9}$ to 10^{-1} M K^+ ions, and were insensitive to light and pH changes in the range of 2 to 10.5.

Keywords: graphene; gold nanoparticles; potentiometric sensor; hydrophobic material; potassium determination

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How can we modify materials for solid-contact layers in ion-selective electrodes? - Modifications of ruthenium dioxide.

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ABSTRACT: The potentiometric sensor, also named ion-selective electrode, can be simply defined as an electrochemical sensor that transforms the effect of the electrochemical interaction between the ion and the membrane into a signal. The construction of a solid-contact electrode is characterized by the presence of three layers: electronic conductor at the bottom, ion-sensing membrane at the top, and solid-contact (mediation) layer in between.

In this work we tested three different types of RuO₂ based nanocomposite for the mediation layers: two nanocomposites composed of conducting polymer: poly(3-octylthiophene-2,5-diyl) (POT) and poly(3-octylthiophene-2,5-diyl) (PEDOT) and the entire group of composites made of ruthenium dioxide and carbon materials including graphene, nanotubes, and carbon black.

Each material was characterized by different parameters, yet all of them turned out to be perfect materials for application as mediation layers in ion-selective electrodes. With ruthenium dioxide as standalone composite of mediation layer, we were able to obtain a high electrical capacity of 1 mF. However, these layers turned out to be hydrophilic with a contact angle of only 17°.

The first modification was the addition of a conductive polymer, POT. The addition of POT allowed to raise the electric capacitance of the electrodes to 1.2 mF. Created mediation layer turned out to be a superhydrophobic layer with a contact angle of 150°.

The second step was the addition of carbon nanomaterials, which themselves are characterized by a high electrical capacity due to a very high surface area. The addition of graphene to ruthenium oxide allowed the electrical capacitance to increase to 2.6 mF. The contact angle of the ruthenium oxide-carbon composites was lower - the maximum of 100° was achieved.

The last material was the combination of ruthenium oxide with another conductive polymer: PEDOT. It turned out that such a composite made it possible to obtain electrodes with an extremely high electrical capacity parameter - up to 7 mF.

Keywords: ruthenium dioxide, solid-contact electrodes, potentiometric sensor, potassium determination

IMVAC



Poster presentations

Determination of silicon and cadmium concentrations in Pea plant

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ABSTRACT: The positive effect of silicon has been proven in plants under heavy metal stress (cadmium), by showing an increase in their leaves fresh weight [1]. While examining the influence of silicon on the Pea plant (*Pisum sativum* L) when subjected to stress (contaminated with cadmium), samples of roots and shoots were collected. Six types of samples were analyzed: 1) control plants (growing without stressor-cadmium and supplementation-silicon solution), 2) plants that were grown in a Cd medium, 3 and 4) plants that were grown in a Si medium (1mM and 2 mM), 5 and 6) plants that were grown in a medium with Cd and silicon solution at concentrations of 1 mM and 2 mM. The morphological parts were cut into small pieces and dried using the freeze-drying technique. The sample was mineralized using a microwave assisted mineralization technique. A mixture of solvents was used: HNO₃: H₂O₂: HF (5 mL: 2: mL: 1mL) in vessels made of PFA for silicon analysis and without HF acid in glass vessels for analysis of cadmium. The peak temperature during the digestion process is 180 degrees. Excess HF was neutralized with H₃BO₃ solution at 170 degrees. The solution was diluted to the analytical concentration range for each element and analyzed by ICP-MS spectrometry with a quadrupole mass analyzer using the standard addition method as calibration. The obtained results of silicon and cadmium content in the morphological parts of plant were analyzed in terms of the effect of silicon supplementation in the plant given to stress. We found that Si supplementation of Cd-stressed plants show simultaneous significant increase and decrease of Cd in roots and shoots, respectively, compared with non-Cd-stressed plants.

Keywords: trace element analysis, microwave - assisted digestion, sample preparation, ICP-MS

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Application of MIP-SPME-LC/MS for the therapeutic drug monitoring in biological samples from patients in the intensive care unit

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ABSTRACT: Determination of biologically active compounds from various matrices, including biological samples is a serious problem in a modern analytical chemistry. The most relevant matrices to be analyzed for this purpose are plasma or blood, due to providing a good correlation between their concentration and pharmacological effect. One of the major tools in the pharmacokinetic studies (PK) is the combination of high-performance liquid chromatography and mass spectrometry (LC-MS/MS). The main aim of this investigation was to apply a fast and sensitive extraction technique using electrochemically prepared a new polymeric coatings as sorbents for solid phase microextraction (SPME). SPME blood sampling technique was evaluated in human PK studies.

Polythiophene (PTh) and poly(3-alkylthiophenes) SPME coatings were used and evaluated their ability to extract selected antibiotic drugs. Mass spectrometric parameters were optimized for target compound in positive ion mode over the m/z 100-500 range. Quantitation was done using multiple reaction monitoring (MRM) mode to monitor precursor ion at $[M+H]^+$ to product ion transition. Validation data for accuracy and precision for intra- and inter-day were good and satisfied FDA's guidance: CV between 0.24% and 11.66% and accuracy between 93.8% and 108.7% for all compounds. The obtain results intends to give an overview of the process and bioanalytical tools for the *in vitro* and *in vivo* drug metabolism from different medical classes. Developed method can be used for the quantitative analysis of selected biologically active compounds, and provide and potential application to study the metabolism and pharmacokinetics of other drug from different medical classes from the biological matrices. The result demonstrate the potential of *in vivo* SPME as a useful sample preparation tool for chromatographic based metabolomic drug monitoring in the biomedical application from patients receiving therapeutic dosages.

Keywords: antibiotic, mass spectrometry; polythiophene; poly (3-methylthiophene); solid-phase microextraction

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Study of the of bacteria viability treated with an antibiotic by using capillary zone electrophoresis and flow cytometry approaches

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ABSTRACT: Rapid detection and identification of microorganisms is a challenging and important aspect in many areas of our life, beginning with medicine, ending with industry [1]. The aim of the work was to develop an innovative method of testing the survival of bacteria using capillary zone electrophoresis (CZE) and flow cytometry (CF) approaches. For this purpose, standard strains of bacteria from the ATCC collection were used: *Enterococcus faecalis* ATCC 14506, *Staphylococcus aureus* ATCC 11632, *Klebsiella pneumoniae* ATCC 10031 and *Pseudomonas aeruginosa* ATCC 27853 and *Escherichia coli* ATCC 25922 as well as a number of 7 antibiotics with different antimicrobial action mechanisms. The experiment was carried out in series depending on the concentration of the antibiotic and the incubation time. The survival rate of microorganisms was assessed each time using the electrophoretic and cytometric methods used simultaneously, and the results were compared to obtain a reference point for the electrophoretic method in the cytometric test. For the quantitative determinations of *Enterococcus faecalis* ATCC 14506, *Klebsiella pneumoniae* ATCC 10031 and *Pseudomonas aeruginosa* ATCC 27853, the CZE/CF differences did not exceed 15% of viable cells. For all tested strains, these values differed by more than 15% in only 6 out of 49 cases. The results obtained after 1.12.24 h in all cases showed a bactericidal tendency with high convergence between the CE and CF methods.

Keywords: capillary zone electrophoresis, flow cytometry, bacterium

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Investigation of the protein interactions with metal ions

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ABSTRACT: Interaction of metal ions with proteins may result in metal-proteins complexes which can find applications in many areas of human life. Metal ions can affect the biological properties of the protein, which extends the possibilities of their application especially in the field of medicine and food industry. Zinc ions, which naturally occur in living organisms and are necessary for the proper conduct of many changes taking place in the human body, deserve special attention. Moreover, zinc is a catalytic and structural component of many proteins. Therefore, determination of the mechanism involved in zinc ion binding to proteins could be crucial for preventing immune deficiencies or pathological changes. Furthermore, zinc ions bound by biologically active proteins can exhibit antiseptic and antibacterial properties [1]. Unfortunately, despite many studies on metal binding by proteins, the exact mechanism of this phenomenon still remains unclear. For this reason in the current study lysozyme was used as a model protein for description of protein-zinc interactions. Lysozyme is a small cationic protein with molecular mass of 14 kDa. This makes it an ideal model protein for investigations on protein structure and function. It is naturally present in human respiratory fluids and exhibit strong antibacterial activity [2,3]. The interactions between lysozyme and zinc ions was studied using advanced analytical methods including capillary electrophoresis coupled with inductively coupled plasma mass spectrometry (CZE-ICP-MS) and Fourier transform ion cyclotron resonance (FT-ICR). The obtained results confirmed the zinc ion binding by the model protein and provided a broader insight into the mechanism of metal-protein interaction.

Keywords: metal-protein complexes, capillary electrophoresis, mass spectrometry.

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Procedure design of sorption preconcentration of high-field-strength elements for routine ICP-MS analysis of ultramafic rocks

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ABSTRACT: The reproducibility and accuracy of determination high-field-strength elements (HFSE: Zr, Nb, Hf, Ta, Th, U) are important very much at geological and geochemical researches. The HFSE content in ultramafic rocks is very low and equals 10^{-7} - $10^{-5}\%$ (w/w) of each element. Due to the presence of refractory minerals (spinel) the most reliable digestion is achieved in bombs using strong acids. Considering the possible heterogeneity of ultramafic rocks at trace element analysis the minimum sample size for the bomb digestion should be at least 200 mg. So, large dilution is required for the measurement by ICP-MS due to strong acid medium and general salt content after the digestion. Consequently, HFSE concentration in the measured solutions may be close to the limit of quantification even when such highly sensitive equipment as sector field MS Element2 is used.

This research is dedicated to procedure design of sorption preconcentration of HFSE compatible with both bomb acid digestion of ultramafic rocks and ICP-MS analysis. Based on the studied elements are possible to be present in solutions obtained after the digestion in both cationic (Zr, Hf, Th, U) and anionic (Zr, Hf, Nb, Ta) forms several sorbents providing the various sorption mechanisms were investigated. They were AG 50W-X8 with sulfonic acid groups; TEVA with quaternary ammonium salt groups; Chelex-100 with tertiary amine and carboxyl groups and DGA resin with N,N,N',N'-tetra-*n*-octyldiglycolamide groups.

Quantitative (more than 95%) sorption degrees of Zr, Hf, Ta, Th and U from 3M nitric acid in the presence of the main ultramafic matrix components (Mg, Al, Ca, Fe) were obtained using the DGA resin (TrisKem International, France).

Keywords: ultramafic rocks, acid digestion, high-field-strength elements, sorption, sorption preconcentration, ICP-MS

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Application of CE-ICP-MS/MS for investigation of Fe₃O₄ nanoparticles and human serum proteins interactions

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ABSTRACT: Due to the low cytotoxicity, stability, biocompatibility, biodegradability, and unique magnetic properties of superparamagnetic iron oxide nanoparticles they have been extensively studied for nanomedicine applications, e.g., as drug carriers in cancer therapy. However, the obstacle to achieving this goal lies in the lack of appropriate methods to investigate nanoparticles behavior under a physiological environment.

This study aimed to develop novel capillary electrophoresis-inductively coupled plasma tandem mass spectrometry (CE-ICP-MS/MS) methodology for monitoring the behavior of SPIONs and their interactions with human serum proteins [1]. Use of tandem ICP-MS and selection of oxygen as collision gas allowed to minimize polyatomic interferences and simultaneous detection of both sulfur (a marker of proteins) and iron (a marker of SPIONs). To imitate physiological conditions, the temperature of tray and cassette and pH of background electrolyte in capillary electrophoresis were appropriately adjusted. Optimization of other parameters (type of background electrolyte, applied voltage, volume of sample) improved the quality of obtained signals and recovery of analytes from the capillary.

The developed methodology was used for the analysis of samples containing SPIONs incubated with human serum albumin. The obtained results confirmed the formation of conjugates and may provide the basis for further research of iron oxide nanoparticles behavior in biological samples using CE-ICP-MS/MS.

Keywords: capillary electrophoresis, superparamagnetic iron oxide nanoparticles, inductively couple plasma tandem mass spectrometry

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Determination of the zinc-casein binding using CE-ICP-MS

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ABSTRACT: Metal-proteins interactions are one of the most important issue attracting attention in many fields, e.g. analytical chemistry or medicine. Zinc participate in many biological processes and has exceptional coordination chemistry – in the acidic aqueous solution it forms the stable aqua complexes able to exchange water molecules when binding to other ligands. Due its high affinity for functional groups, such as carboxyl or amino, binding zinc to proteins create a new applications. Interestingly, except the crucial role of zinc for human health, the free Zn²⁺ might play a critical role in neuronal damage and neurodegenerative disorders [1]. Then, the specific binding of Zn²⁺ to proteins seems to be necessary to eliminate the toxic effect. Moreover, the use of specific proteins is also of ecological importance. An example could be whey or milk – using these raw materials as sources of biologically active proteins in an alternative way fits perfectly into the idea of sustainable development. The main protein of milk is phospho- and a glycoprotein called casein (CN), consisting of three subunits, each around 24 kDa. Previous work of our group [2,3] has shown that CN has a good affinity to metals such as zinc or silver. However, the exact mechanism of Zn binding to the CN is still unclear. Then, it is important to describe this process by using interdisciplinary and comprehensive methods. One promising approach might be capillary electrophoresis combined with inductively coupled plasma mass spectrometry (CE-ICP-MS). Coupling CE-based separation techniques to MS creates a powerful platform for analysis of a wide range of biomolecules because it combines the high separation efficiency of CE and the sensitivity and selectivity of MS detection. Therefore, the main aim of the present study was the identification of Zn-CN binding process based on CE-ICP-MS. As complementary methods, kinetic (including isotherms), spectroscopic (FT-IR and RAMAN) and microscopic (SEM) approaches were performed.

Keywords: protein-metal interaction, capillary electrophoresis, mass spectrometry

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Halogenated PAHs in the Ullmann on-surface reaction - theoretical model

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ABSTRACT: In recent years, the controlled polymerization of organic molecules on metallic surfaces has become an important and promising research topic, both in theory and practice. The poster presents the course and results of the Monte Carlo simulation in the canonical ensemble for polycyclic aromatic hydrocarbons (PAHs) halogen derivatives, which, through the Ullmann coupling, form organometallic compounds, which are precursors of the corresponding covalent polymers [1-3]. The systems studied in the simulations consisted of chosen polycyclic aromatic hydrocarbon molecules, represented by connected segments with assigned directional interactions, imitating the influence of the presence of halogen substituents, and divalent metal (copper) atoms. The elements of the system were placed on a triangular lattice, which corresponded to the surface of a metal crystal with symmetry of the type (111). In the conducted simulations, different topologies of the obtained structures were observed, depending on the number and position of halogen atoms in the molecule, as well as on the number of aromatic rings in the molecules. The influence of the chirality of the molecules on the morphology of the considered systems was also investigated by conducting simulations for enantiomerically pure compounds and racemic mixtures. The obtained results may be helpful in the synthesis of new compounds showing unprecedented properties and/or difficult to obtain by synthesis in the bulk phase.

Keywords: theoretical chemistry, computational chemistry, polymers, Monte Carlo method, on-surface synthesis

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Alternative method to study the bioaccumulation and biotransformation of BDE-47 using zebrafish larvae (*Danio rerio*)

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ABSTRACT: In recent years, several international institutions have been calling for a transformation in toxicity testing, seeking greater efficiency and a decrease in the use of animals. In this sense, an alternative method based on the official OECD guideline 305 [1], previously developed in the research group [2], is used to evaluate bioaccumulation of emerging pollutants with zebrafish larvae (*Danio rerio*), drastically reducing the time, the reagents and the suffering of the animals.

This work focuses on polybrominated diphenyl ethers (PBDEs), due to their persistent in the environment, bioaccumulation and endocrine disrupting effects (EDCs). In addition, they produce hydroxylated and methoxylated derivatives (OH-BDEs and MeO-BDEs) with similar toxic properties. The analytical protocol developed is based on a dependable ultrasonic extraction method followed to dispersive SPE clean-up procedure and GC-MS- μ ECD detection. The profiles found for BDE-47, one of the most abundant congeners, show a rapid uptake in the first hours of larval development and a high bioaccumulative power ($BCF > 5000$), $BCF 8000$ and 43000 at 10 and $1 \mu\text{g}\cdot\text{L}^{-1}$ ($< 1\% LC_{50}$), respectively. In addition, increasing concentrations of the metabolites BDE-28, 2'-OH-BDE-28 and 3-OH-BDE-47 were observed over the exposure time. These results show the feasibility of the method for bioaccumulative studies and open the possibility for metabolic studies with zebrafish larvae, which is a very underdeveloped field with no official tests or regulation.

Keywords: Bioconcentration, Biotransformation, Zebrafish, Metabolites, GC-MS, BDE-47

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Development of a SPE-GC-MS method for determining NSAIDs in water

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ABSTRACT: The aim of work is to analyze the impact and the daily intake of NSAIDs in wastewaters via GC-MS. Due to its increasing consumption [1], ibuprofen, clofibrac acid, salicylic acid, acetylsalicylic acid, naproxen and diclofenac were chosen as analytes.

Chromatographic analysis was carried out by using an GC instrument equipped with a MS detector operated by a computer software. The GC system was equipped with a polydimethylsiloxan (95%) cross-linked ZB-5 capillary column using Helium as carrier gas. The oven temperature was held at 70 °C for 1 min, then three temperature gradients were applied at a rate of 17°C/min to 120°C, a second rate of 5°C/min to 200°C and a third rate to 280 °C at 20 °C/min maintaining up to 3 min. Each chromatogram required 27 min. For the mass spectrometer conditions, ion source temperatures were of 230 and 150°C, for the quadrupole and 290°C for the transfer line. The scan range was from 50 to 550 m/z.

Since the selected analytes are not volatile enough, a derivatization step carried out by comparing three derivatization reagents as possible candidates for our analysis: Bis(trimethylsilyl)acetamide (BSA); N,O-Bis (trimethylsilyl)trifluoroacetamide (BSTFA) and N-(tert-butyltrimethylsilyl)-N-methyltrifluoro-acetamide (MTBSTFA) in 1 mg/L drug concentrations, concluding that MTBSTFA is the most suitable candidate reacting at 80°C for 30 minutes. LODs ranged from 5.3 to 8.5 µg/L. Calibration curves were linear in a wide range from 1 to 500 ng/mL with an $R^2 > 0.99$.

As pharmaceuticals found in wastewater are ranging from µg/L to ng/L, a pre-concentration step is needed. A detailed study of the most relevant parameters which affect the solid-phase extraction (SPE) and the recovery of the compounds selected -such as type of adsorbent, pH value of the sample and elution condition- has been carried out. Best recoveries were achieved using Extrabond EB2 cartridges with a pH of conditioning step of 7, eluting with methanol and an evaporation step optimized by heating the methanol extracts at 30°C with a gentle flow of N₂ until dryness. Before injecting the samples, a reconstitution step was achieved by adding acetone and following the derivatization step. This method was verified on wastewater samples using the optimized conditions.

Keywords: wastewaters, gas chromatography, NSAIDs.

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Application of nanostructured carbon electrodes modified with CuO-SiO₂ composite coating for voltammetric determination of H₂O₂

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ABSTRACT: A sensitive element of a voltammetric sensor for the determination of H₂O₂ based on the carbon screen-printed electrodes modified with CuO particles encapsulated in SiO₂ film was developed. The obtained CuO particles were synthesized by coprecipitation method, have spherical shape and their diameter was 100±50 nm. The carbon screen-printed electrodes (nanoSPCE) were modified with a CuO-SiO₂ composite film by the electro-assisted deposition method (EAD) method. [1] Obtained nanoSPCE-CuO-SiO₂ electrodes were used for further voltammetric research.

At cyclic voltamperograms of nanoSPCE electrodes the anodic and cathodic currents were observed at 1.0 V and -1.0 V, in presence of H₂O₂ they increased. Two new peaks at -0.3 V and -0.5 V were observed on CV of modified nanoSPCE-CuO-SiO₂ electrodes in background solution (pH 6.8). The cathodic current at -0.5 V highly increased in the presence of H₂O₂, while the anode current at -0.3 V decreases slightly, which confirms the presence of CuO particles onto electrode surface and their catalytic activity toward hydrogen peroxide. The linear range for H₂O₂ determination using nanoSPCE-CuO-SiO₂ electrodes was 0.01–0.1 mM, the detection limit was 0.01 mM, which is 0.1 mM compared to non modified nanoSPCE. The RSD under convergence conditions was 1.4% (C(H₂O₂) = 0.5 mM, n = 15). The relative error for hydrogen peroxide determination at nanoSPCE-CuO-SiO₂ electrodes in the presence of equimolar ratio interfering substances (ascorbic acid, urea, thiourea) was 9%, which is 4 times less than at nanoSPCE.

The developed sensor based on nanoSPCE-CuO-SiO₂ allows to detect microquantities of hydrogen peroxide in model solutions, is easy to use, and is also suitable for multiple measurements.

Keywords: electrochemistry, biosensors, cyclic voltammetry, carbon screen-printed electrodes, composite films, CuO nanoparticles, Hydrogen peroxide.

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How to choose the best material for solid-contact layer in ion-selective electrodes? - A comparative study.

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ABSTRACT: The construction of a solid-contact electrode is characterized by the presence of three layers: electronic conductor at the bottom, ion-sensing membrane at the top, and solid-contact (mediation) layer in between.

How do we know if the material is suitable to be used as mediation layer? We have three criteria. First: high electrical capacity, second: low hydrophilicity and the last but not the least: ion-to-electron transduction properties. When choosing the material, we need to take into consideration all mentioned conditions.

The most desirable feature of materials for ISE construction seems to be high electrical capacity. The ability of the layer to store the charge determined by the double layer/redox capacitance parameter enables it to sustain the potential equilibrium in the presence of external disturbances and protects the electrode from the impact of the current flow during the potentiometric measurement. Electrodes with layers characterized by the high electrical capacitance parameter exhibit stable potentiometric responses over time and insensitivity to the perturbations that may occur during the measurement.

Second condition concerns wetting properties of a material. The higher the contact angle value, the better. Water from solutions tends to penetrate the membrane and form a thin film between the membrane and electrode. The hydrophobic mediation layer was repeatedly shown to prevent the formation of such a layer. Consequently, since the water layer causes the delamination of the membrane, electrodes without such a layer live longer.

Last but not least, the condition involves ion-to-electron properties. Mediation layer acts as a connector between electrode of electronic transduction and membrane of ionic type of transduction. The presence of a mediation layer improves the analytical properties of electrodes.

These criteria were used in order to compare hydrous and anhydrous ruthenium dioxide and to indicate which of tested materials suits ion-selective electrodes best. Hydrous ruthenium dioxide, due to its higher electrical capacitance, higher contact angle, and more efficient ion-to-electron transduction processes, turned out to be a more favorable material in the context of potentiometric sensor design.

Keywords: solid-contact layer, electrical capacity, contact angle, hydrous ruthenium dioxide, anhydrous ruthenium dioxide

Modifications of the surface of working electrodes used in voltammetry

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ABSTRACT: Working electrodes used in voltammetry are a subgroup of chemical sensors, which are small devices that convert real-time chemical information into a measurable and analytically useful measurement signal. Chemical information, ranging from the concentration of a specific component of the tested sample, to the overall composition of the matrix, can come from both the initiated chemical reaction and be the result of physico-chemical transformations taking place in the tested object. Chemical sensors are equipped with two basic elements, i.e. receptor and transducer. The receptor is responsible for the conversion of chemical information from the tested object into a specific form of energy, in the converter this energy is transformed into a useful analytical signal. One of the main trends of modern analytics is the search for new electrode materials and various geometries of working electrodes. One way to improve the performance of working electrodes is to modify their surface, for example, by applying thin layers. One of the methods that allows obtaining materials with new properties is the plasma enhanced chemical vapor deposition method (PECVD). In this method, compounds, called precursors, are supplied to the plasma reactor as a gas phase. Thanks to plasma enhanced chemical vapor deposition, it is possible to obtain materials with unique properties.

This work concerns the design and implementation of innovative working electrodes modified with thin layers.

Keywords: electrochemistry, working electrodes, surface modification, voltammetry

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Application of carbon nanomaterials in the modification of glassy carbon electrodes

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ABSTRACT: The glassy carbon electrode (GCE) is a popular type of sensor used in electrochemical methods. Glassy carbon might be characterized by properties like good mechanical and chemical resistance and high electrical conductivity what makes it an excellent electrode material. Another advantage of the electrode mentioned is also the possibility of its modification with different kinds of surface modifiers. Thanks to this, parameters such as selectivity, sensitivity, and limit of the detection might be improved.

In the work application of carbon nanomaterials in different compositions (e.g. with hydrated ruthenium dioxide or with Nafion) will be presented. The composition of each modifier was optimized, as well as its volume applied on the surface of the sensor. Performance of each sensor was also determined.

The applicability of the developed modified electrodes was confirmed by analysis of pharmacological substances in real samples [1,2]. Parameters such as the limit of detection and recoveries for each tested analyte were also determined.

Keywords: voltammetry, carbon nanomaterials, carbon black, hydrated ruthenium dioxide

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Methods for pyridoxine determination – an overview

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ABSTRACT: Pyridoxine (PA) is one of the vitamers of vitamin B₆ (VB₆), which due to its outstanding chemical stability is added to dietary supplements and fortified food products. In the human body, PA is converted into phosphate esters which act as cofactors in miscellaneous enzymatic reactions, including the metabolism of amino acids and fats [1]. VB₆ supports the functioning of the immune system, reducing the risk of viral infections [2]. In particular, it alleviates the course of COVID-19 illness and associated complications [3]. Due to that, the determination of PA, as the most common form of VB₆, in pharmaceuticals and food products is essential for providing its safe supplementation.

In this work, numerous methods of pyridoxine determination have been collected and reviewed in terms of the provided linear range, the limit of detection, precision, accuracy, and possible applications. The listed methods include various chromatographic, spectroscopic, and electrochemical techniques. The latter gain more and more attention due to the relatively low cost of apparatus, short time of analysis, and easy sample preparation. In this context, a multiplicity of carbon-based nanomaterials, natural polymers, and metal- and metal-oxide nanoparticles have been proposed for the modification of the working electrodes with the aim to improve its response towards PA.

Keywords: chemical analysis, electroanalysis, pharmaceuticals, pyridoxine, vitamins

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Deep learning for voltammetry

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ABSTRACT: Deep learning is a part of machine learning based on artificial neural networks. This computational strategy is called deep because of the network architecture. It consists of many layers of input, output, hidden layers, and convolutions, and the learning process occurs with the use of a large amount of data. In voltammetry, the received data have the structure of 1D signals. Due to the development and interdisciplinarity of science, it is possible to solve complex chemical problems with the use of machine learning. For the analysis of a database of voltammetric signals using deep learning methods, convolutional neural networks are used, which are mainly used for the analysis of two-dimensional data, but can also be used for the analysis of one-dimensional data [1-3].

The commercialization of the market and the desire to reduce costs while increasing profits encourage food producers to modify the composition of their products. Although there is no formal definition of 'food fraud' in European Union law, it is the term used to describe any act that intentionally misleads consumers for the benefit of the producer.

In this work, proposals for the use of deep learning in the problem of falsification of fruit juices will be presented. Four different neural network architectures for multivariate data analysis will be compared using root mean square error of calibration (RMSEC), cross-validation (RMSECV), and prediction (RMSEP).

Keywords: electrochemistry, chemometrics, deep learning

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