POSTER SESSION II

THURSDAY, JUNE 2nd, 2016

CHAIRPERSONS: Jelena Trifković and Agata Kot-Wąsik

1.

Speciation and determination of trace and ultratrace amount of arsenic and selenium on the graphene oxide decorated with cerium oxide

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Heavy metal ions are one of the harmful substances in environment (water, air, plants). They can be created in environment by a mine and car industry or a metallurgical process. Because the heavy metal ions are cancerous the concentration of them are required on trace levels.
The aim of the work was synthesised a new nanocomposide based on the graphene oxide (GO) prepared using modified Hummers method [1]. The next step of synthesis included the surface modification of GO using cerium(III) nitrate [2]. The structure of graphene oxide decorated with cerium nanoparticles (GO/CeO_2) was investigated by spectroscopy and microscopy technique. The structural research confirmed that the GO was covered by cerium nanoparticles (CeO_2) on the whole surface.
Further researches were based on investigation the influence of pH, contact time, sample volume, influence of coexisted ions and humic acid (HA) on the recovery of determined elements. The As(V), Se(IV), Cu(II) and Pb(II) ions were adsorbed by functional groups of GO/CeO_2 and the methodology dispersive micro-solid phase extraction with final measurement energy dispersive X-ray fluorescence spectrometry as non-destructive and eco-frendly technique (DMSPE/EDXRF) was developed. The obtained detection limit (LOD) are 0.072, 0.100, 0.175 and 0.074 for As(V), Se(IV), Cu(II) and Pb(II), respectively. The proposed methodology DMSPE/EDXRF was applied to determine the selected heavy metal ions in the natural water samples.

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2.

Novel insights into pH-dependent retention behavior of analytes in chaotropic chromatography

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Complexity of chromatographic systems modified with chaotropic salts poses numerous challenges both for practitioners, and for those involved in developing a rigorous theoretical description of these systems. Numerous factors that affect retention – type and concentration of the chaotropic salt and organic modifier, and choice of column – have been recognized. Up until recently, however, mobile phase pH was thought to have negligible effects on retention of analytes once their full protonation is achieved. Our group has recently provided experimental evidence that even when no significant changes in analytes' ionization occur, variance in mobile phase pH can exhibit profound effects on their retention. We hypothesized that the observed effects are essentially governed by changes in organic modifier's surface adsorption and magnitude of the surface potential created by chaotrope's adsorption on the stationary phase.

To further test this hypothesis, we profiled the retention behavior of 13 structurally diverse analytes under chromatographic conditions chosen to assure full protonation of the solutes: pH was varied from 2 to 4, sodium hexafluorophosphate concentration from 1 mM to 50 mM, while acetonitrile content in the mobile phase was kept constant at 40%. To discern the contribution of changing ionic strength (*I*) to variance in retention occurring as function of pH, two sets of experiments were performed – one, in which *I* was held constant, and another where it was allowed to vary with concentration of chatrope and additives for mobile phase pH adjustment. The obtained data was modeled using the extended thermodynamic approach by Cecchi *et al*.

The obtained results quantitatively support our previous findings regarding the pH-dependent increased affinity of analytes for the stationary phase, caused by differential adsorption of the organic modifier and chaotrope. Furthermore, difficulties in modeling this effect are highlighted. Insights offered by the extended thermodynamic treatment of retention data provided a basis for the development of a physically well founded, empirical model which can be used to predict retention in the studied systems, based on analyte's chemical structure alone. The developed model incorporates both parameters of the chromatographic system, and molecular descriptors which account for key phenomena affecting retention; namely, interactions with the electric double layer and ion pair formation. It, therefore, presents a potentially very useful tool in both fundamental understanding of chaotropic chromatography and its practical application.
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3.

A comparative study of chromatographic behaviour and lipophilicity of selected imidazoline derivatives

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Chromatographic behavior and lipophilicity of 20 selected imidazoline derivatives was examined by thin layer chromatography using CN, RP-2, RP-8 and RP-18 stationary phases and a mixture of methanol, water and ammonia as mobile phase.

In all the examined chromatographic systems, linear relationships were established between retention parameters and the volume fraction of the methanol in mobile phase ($r>0.985$, 0.978, 0.981, 0.988 for the CN, RP-2, RP-8 and RP-18, respectively). The highest correlation between the obtained R_M^0 values was observed for RP-2 and RP-8 stationary phases. The experimental lipophilicity indices (R_M^0, m and C_0) obtained from the retention data were used in a correlation study with the calculated logP values. Experimentally determined R_M^0 values for all the investigated chromatographic systems exhibited the highest correlation with the calculated ClogP values (r: 0.880, 0.872, 0.897 and 0.889 for the CN, RP-2, RP-8 and RP-18 stationary phases, respectively). The performed QSRR analysis showed that frequency of C-C at topological distance 1 and CATS2D Lipophilic-Lipophilic at lag 01 were important descriptors with an influence on the R_M^0 values in all the examined chromatographic systems, while the differences in the retention behavior of compounds on the examined stationary phases can be distinguished, based on their specific geometrical, electronic and constitutional properties.

4.

Determination of microbiological activity of hop extracts from different varieties of *Humulus lupulus* by TLC + direct bioautobiographic method

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History of beer brewing dates back to 4000 years BC. The first mention of this brewing comes from Mesopotamia, inhabited by the culture of the Sumerians. The first beer was prepared with bread and water. A small amount of ethyl alcohol was created as a result of alcoholic fermentation. Hop as a beer component for the first time was used by the ancient Babylonians.

The content of ethyl alcohol and compounds found in hops allows for longer storage brewed beer.

The aim of our work was comparison of bacteriostatic/antibacterial properties of various hops varieties (*Humulus lupulus* L.) and in next step, isolation of biologically active compounds/groups of compounds from examined hop extracts. There was two solvents used to extraction process: water and ethyl alcohol. Extracts were prepared from two commercially available types of granulates: T-90 (qualitative and quantitative very similar to cone hops) and T-45. Water extracts were prepared using percolation process, choice of method was due to similarity to hopping beer. Ethanolic extracts were obtained by continuous extraction in Soxhlet apparatus. The next, both types of extracts were evaporated and dissolved again to needed volume.

Chromatographic separation was performed on TLC systems: silica/mixture of organic solvents, under earlier found conditions. The samples were introduced as narrow bands (automatic applicator with evaporation of solvent) on silica and TLC plates were developed and dried.

Bioautographic visualization method allowed to find separated fractions of extracts containing substances with bacteriostatic/antibacterial properties.

After isolation (scraping the important bands and washing out it content from bed) of found fractions, the next planned step is re-chromatography in various chromatographic systems and after bioautographic confirmation of its biological properties, prepared to mass spectrometry analysis.

5.

Application of TLC, HPLC and GLC in the analysis of metronidazole and secnidazole

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6.

Studying the changes of excise duty components in diesel oil samples under influence of a reducing agent using gas chromatography with nitrogen chemiluminescence detector

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In EU countries, diesel oil is spiked with chemical substances to indicate tax level and further use. In Poland, diesel oil designated for regular transport contains Solvent Yellow 124 (a marker compound) and Solvent Red 19 or 164 (a red dye) [1]. Even though these substances are considered to be stable, there are many illegal attempts to modify basic physico-chemical properties and thus to eliminate their role as specific fuel markers.
The major goal of this study is to gain knowledge of changes in the content of excise duty components in diesel oil samples induced by a reducing agent.
In the course of experiment 36 different diesel oil samples were analyzed. To describe the studied process, gas chromatographic fingerprints registered with nitrogen chemiluminescence detector were considered since the selected excise duty components contain diazo group(s). In total, 144 fingerprints were collected: (1) for 36 raw diesel oil samples, (2) 36 for their methanol extracts, (3) 36 for diesel oil samples after influence of a reducing agent, and (4) 36 for their methanol extracts. It is important to emphasize that each diesel oil same sample is characterized by four chromatographic fingerprints.
In order to identify differences in the chemical composition of diesel oil samples partial least squares discriminant analysis extended with variable selection based on the selectivity ratio [2-4] was used.

Acknowledgement
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7.

Investigation of micro- and nanostructures spontaneously formed in monocomponent proteinogenic amino acid solutions

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The research presented in paper [1] showed that the amino acids dissolved in aqueous organic solvents spontaneously undergo two parallel processes of chiral conversion and peptidization. As a result of peptidization, peptides are formed giving the nano- and microstructures. Some of spontaneous reactions running in living organisms and resulting in formation of novel peptides are recognized as producing erroneous and harmfully folded proteins. As a result, deposits of such reaction products in form of insoluble fibers are formed, which are considered as a cause of many grave health conditions [2].

In the reported experiment, we focused our attention on the monocomponent amino acid systems: *L*-phenylalanine (*L*-Phe), *L*-methionine (*L*-Met) [3], *L*-phenylglycine (*L*-Phg) and *L*-cysteine (*L*-Cys) [4] dissolved in 70% aqueous methanol. The main tool of investigating peptide micro- and nanostructures was scanning electron microscopy (SEM). As auxiliary techniques, high-performance liquid chromatography (HPLC), and mass spectrometry (MS) were applied. Observations of the oscillatory peptidization reactions of amino acids were possible with use of HPLC. With MS, we confirmed the presence of the spontaneously formed peptides in the investigated solutions.

The obtained results demonstrate that the investigated amino acids can undergo an spontaneous oscillatory condensation, with a consequence that these compounds may form peptide nano- and microstructures in an abiotic system. Furthermore, an evident difference among the peptides originating from different amino acids apparently is due to their different molecular structures.

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8.

The ways of detecting counterfeit plant protection products

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The presence on the market of counterfeit and illegal plant protection products (PPPs) has become a global problem in recent years. Data published by the European Crop Protection Association (ECPA) show that more than 10% of the world pesticide market are composed of illegal and counterfeit products. There are services in the member states of the European Union (EU) whose a one of main goal is an official quality control of plant protection products introduced to the market. In Poland, this task is performed by the Main Inspectorate of Plant Health and Seed Inspection. Samples of plant protection products collected in the official quality check of pesticides by inspectors of the Main Inspectorate of Plant Health and Seed Inspection are sent to the Quality Research Laboratory of Plant Protection Products in the Institute of Plant Protection National Research Institute, Sośnicowice Branch. It is for conducting laboratory studies whose aim is to check whether the samples meet the technical requirements established in the process of their registration. Introducing the illegal and counterfeit pesticides on the market has resulted in the need for steady improvement of methods and using different analytical techniques in order to verify the origin of the delivered to the laboratory samples of PPPs. The subject of research were chemical PPPs which came from all over the country in the years 2011 - 2015 in the official control and individual orders. There were used a few techniques to determine active substances such as: gas chromatography (GC-FID, GC-MS) and liquid chromatography (HPLC, RR-HPLC, LC-MS/MS). The following physicochemical parameters such as: stability of suspension (MT 184 CIPAC K), stability of emulsion (MT 36.3 CIPAC K), wetting time (PN-87/C-04662), sieve analysis (MT 185 CIPAC K), pH (MT 75.3 CIPAC J), density (MT 3 CIPAC F), dissolution degree and solution stability (MT 179 CIPAC H) were examined in the formulations.

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9.

Fatal poisoning of 3-MMC

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The issue of sudden deaths due to acute 3-MMC (3-Methylmethcathinone) poisoning is presented in the report. The analysis included case autopsied. A 20-year-old woman was found dead after her suicide. Biological material were delivered to the Toxicological Laboratory ToxLab placed in Katowice, during the autopsy were subjected to chemical-toxicological analysis. Samples analyzed by performance liquid chromatography coupled with mass spectrometer and PDA detector (LC-PDA-MS). Analysis of blood samples present concentration of the 3-MMC were 800 ng/ml. Analysis of urine present 3-MMC concentrations were 150ng/ml. Analysis of stomach contents samples present concentration of the 3-MMC were 5,5 μg/ml.

10.

Determination of caffeine content in fat-burning supplements

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Obesity is a chronic condition, which increasingly gains ground among the inhabitants of fast-developing countries. BMI values of 25-29.9 kg/m^2 are classified as overweigh range, values above 30 kg/m^2 fall within the obese range, and values greater than 40 kg/m^2 are typically referred to as severe obesity. Obesity is closely related to lifestyle. Extended working hours are conducive to having so called “quick meals”, snacking and having little physical activity. It is often the case that in order to maintain focus for longer periods of time, one reaches for caffeine, often consumed in the form of coffee or tea. It is caffeine that is responsible for alertness, reducing weariness, and decreasing the need for sleep, but its large doses actually conduce to the reduction of body mass. Both scientific evidence and historical reports show that among a healthy population of adults, the consumption of caffeine limited to 400mg a day does not cause negative health effects. Due to the fact that the pharmaceutical market is currently lacking an ideal product for reducing body mass, manufacturers are competing in producing new sets of substances registered as food supplements. The consumption of caffeine, mainly in form of food supplements aimed at reducing the body mass, should not cause dangerous side effects as long as it does now exceed the recommended dose.

11.

Determination of ziprasidone and its impurities by thin-layer chromatography

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Ziprasidone belongs to the second generation of so-called atypical antipsychotic drugs, having the G protein-coupled receptor binding profile. Five ziprasidone impurities representing degradation products of ziprasidone (impurities II, III, and V) or originating from the synthesis (impurity I and IV) are the compounds significantly different in polarity. A thin-layer chromatographic method for simultaneous determination of ziprasidone and its main impurities was developed and validated. Separation of the examined compounds was performed on chromatographic plates precoated with silica gel $60F_{254}$ and using toluene-methanol-glacial acetic acid, 7.5:0.5:0.5 (v/v/v) as mobile phase. The ascending development mode was performed in the twin-trough chromatographic chamber, which was presaturated with mobile phase vapors for 15 min. The developed chromatographic plates were dried in air and densitometrically scanned at the wavelengths of 250 and 320 nm. Regression coefficient ($r \geq 0.992$), recovery (94.94-106.70%), precision (RSD 0.41 to 8.45 %), limit of quantification of impurities (25 ng band-1 equivalent to the 0.14% impurity level), and robustness were validated and found satisfactory. The developed method is convenient for quantitative analysis and the purity screening of ziprasidone in pharmaceutical formulations.

12.

Chromatographic methods for qualitative evaluation of oxidative stress markers in urine samples

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Oxidative stress is regarded as an imbalance in oxidative status of living organism between antioxidant defense and the production of reactive species (e.g. free radicals). It occurs when certain pathological conditions like environmental pollution, stress or limited access to natural sources of antioxidants (e.g. provided with food) influence the system being studied. Reactive species interact with basic components of organisms, i.e. DNA, lipids and proteins. Products of these interactions are considered as oxidative stress markers. The most studied oxidative stress markers are 8-hydroxy-2'-deoxyguanosine, isoprostanes, and dityrosine formed as a result of DNA, lipids and proteins damage. Increased levels of these compounds indicate imbalance in the oxidative status. They can also provide information about increased risk of certain diseases, since reactive species influence regular biochemical pathways [1].

Urine is a product of blood filtration that can describe biochemical changes and as biofluid sample has a number of desired properties. It is (i) less complex matrix with respect to organic and inorganic compounds compared with blood or plasma fluids, (ii) more stable with respect to increase of oxidative markers formed in the course of collection and storage of samples, and (iii) relatively easy to collect.

There are only a few oxidative stress markers bearing in mind 4000 compounds found in urine metabolom [2]. Their quantitation requires separation form the sample matrix, and thus chromatographic techniques are valuable for such studies. In this work we focus of the presentation of methods of preparation and the chromatographic analysis of urine samples of such oxidative stress markers as 8-hydroxy-2'-deoxyguanosine, isoprostanes, and dityrosine.

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13.

Thermal stability of silica based stationary phases for liquid chromatography by vibrational spectroscopy techniques

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Searching for novel approaches to the separation problems reveals numerous limitations related to the instrumentation and materials. Special techniques, like supercritical fluid chromatography, ultra-fast liquid chromatography or high-temperature liquid chromatography set extraordinary requirements when it comes to the instrumentation and employed materials. Many authors underline miscellaneous advantages of silica material as a support material for the chromatographic bed. The high mechanical strength, the rigidity, the large achievable surface areas and the ability to modify the surface chemistry in a highly controlled way, makes silica ideally suitable as packing material in chromatographic columns [1]. At the same time, in the case of silica based stationary phases, higher temperature (60 – 80^{o}C) accelerates stationary phase degradation in the mobile phase even with neutral pH much more than does increased buffer concentration [2-5].

For a number of reasons, chromatographers want to improve chemical and thermal stability of the chromatographic bed [4,6]. Several authors suggest tests based on chromatographic retention and selectivity combined with the programmed column aging for the stability evaluation. Results obtained in the course of chromatographic tests usually concern temperature (extend) ranging up to 150^{o}C. Usually much less then 100^{o}C [5]. Heating the reversed-phase liquid chromatographic beds causes also changes in the intensity of vibrational spectra bends attributed to the particular fragments of covalently bonded ligands. Changes in vibrational spectra of the chromatographic bed sample resulting from heating at temperature above 150^{o}C indicate the decrease of the alkyl ligands content and, in some cases, occurring the bends attributed to structural fragments of carbonyl, vinyl or aromatic functionalities. Changes in *Raman* scattering intensity, particularly in the range from 3000 to 2800 cm^{-1} may indicate a loss of the stationary phase ligands or even of their chemical transformation occurring during the aging process.

Raman spectrometry is a promising alternative to chromatographic tests performed in the study on the stability of chromatographic beds for reversed-phase liquid chromatography.

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14.

RP-18 thin layer chromatographic study of selected biological and physicochemical properties of substances

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This paper is a part of broader research on the application of Thin Layer Chromatography to prediction of bio-availability of compounds. 21 Randomly selected drugs and excipients of different molecular structures (propylparaben, methylparaben, benzophenone-3, methylbenzylidene camphor, triclosan, diethylamino hydroxybenzoyl hexyl benzoate, nifuroxazide, thioridazine, quetiapine, sulpiride, perazine, zuclopenthixol, flupentixol, telmisartan, hymecromone, capeticabine, acenocumarol, drotaverine, emedastine, atropine, clemastine) were subjected to thin layer chromatography on the RP-18 stationary phase using 30:70 (v/v) binary mixtures of pH 7.4 phosphate-buffered saline – organic modifier (acetonitrile, tetrahydrofuran, 1,4-dioxane, methanol, ethanol or isopropanol) as mobile phases. Selected physicochemical and biological properties of these compounds: lipophilicity (log P), blood and brain barrier penetration ability (log BB), skin permeability (log K_p), human intestinal absorption (%HIA) and plasma protein binding ability (%PPB) were predicted *in silico* using Pre-ADMET server available *via* the Internet. The relationships between the retention of compounds listed above and their predicted properties were investigated. It was concluded that log P, log BB and %PPB of compounds investigated throughout this study are in better agreement with their retention than log K_p and %HIA and that methanol, acetonitrile and ethanol as the organic modifiers give much better correlations than 1,4-dioxane, tetrahydrofuran or isopropanol.

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15.

RP-18 thin layer chromatographic investigations of lipophilicity of selected steroid hormones

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Retention parameters R_f and R_m were obtained for 16 steroid hormones and other drugs, containing the steroid moiety (cortisol, hydrocortisone acetate, methyltestosterone, progesterone, testosterone propionate, testosterone heptanoate, cortisone acetate, prednisolone, estrone, estradiol benzoate, desoxycorticosterone acetate, tibolone, spironolactone, eplerenone, digoxin, dexamethasone) by thin-layer chromatography on the RP-18 stationary phase using pH 7.4 phosphate-buffered saline - acetonitrile 30:70 (v/v) mixture as the mobile phase. R_f and R_m values were correlated with lipophilicities calculated *via* different algorithms (ALOGPs, AClogP, milogP, ALOGP, MLOGP, XLOGP2, XLOGP3, ACDLab) and with experimental $logP_{o/w}$ obtained from the literature sources. Analysis of correlations of R_m values with $logP_{exp}$ proved that the single chromatographic run approach used throughout this study gives sufficiently good result (R = 0.95) and using R_m^0 values extrapolated to zero concentration of the organic modifier is not necessary.

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16.

Chromatographic investigations of plasma protein binding of selected drugs

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21 Structurally diverse drugs (acetaminophen, acyclovir, amoxicillin, aspirin, bromazepam, carbamazepine, chlorpromazine, cimetidine, clonidine, diazepam, famotidine, ibuprofen, indomethacin, naproxen, phenytoin, piroxicam, propranolol, ranitidine, spironolactone, trazodone, zolpidem) were investigated by single-run RP-18 TLC using pH 7.4 phosphate-buffered saline - acetonitrile 30:70 (v/v) mobile phase. R_m values determined for these drugs were correlated with their experimental plasma protein binding ability (%PPB) taken from the literature sources. Linear correlations of R_m (RP-18 TLC) with %PPB explained 64% of the total variance. Moderate as they might appear, the results of the RP-18 TLC experiments prove that this cheap and readily available technique may be a good starting point to obtain chromatographic descriptors useful in generating more complex and (hopefully) predictive models of the compounds' ability to bind to plasma proteins.

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17.

The development of the conditiond for thin-layer chromatographic separation and the detection of bioactive flavonols and depsides in plants

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Phenolic compounds are the most numerous group of chemical compounds in the world of plants. Many scientific studies have shown that they posses a wide range of biological and pharmacological activities. Plant phenolics show antimutagenic, antiproliferative, antioxidant, antiinflammatory, antibacterial and antiviral properties [1-3].
Similarities of chemical structures and physicochemical properties between catechins and depsides cause major difficulties in isolating these compounds from plant materials. The aim of this work was to develop the conditions for the chromatographic separation of (-)-epicatechin, (+)-catechin, cynarin, epigallocatechin gallate, chlorogenic acid, cichoric acid and rosmarinic acid.
As an analytical method thin layer chromatography (TLC) was used. The mixture of compounds were separated by using cellulose plates in 18 developing systems, silica gel plates in 19 developing systems and HPTLC RP18F_{254} plates in 4 systems. The data obtained were used for the simulation analysis in two dimensial chromatography. The optimized separation conditions were used to identify these compounds in the herb and roots of *Lamium album* L., herb of *Echinacea purpurea* (L.) Moench, roots of *Taraxacum officinale* Web. and rhizome of *Polygonum bistorta* L.

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18.

Finding a set of orthogonal solvents for effective plant extraction by chemometric analysis of chromatograms

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Extraction of plant material is a crucial part of the phytochemical study and changing the extraction solvent can change the chemical composition of the extract dramatically. Instead of finding the one optimal solvent, which is often far away from ideal extraction performance, we propose a methodology to choose an "orthogonal" set of several (as few as possible) solvents for separated extraction of the material. These extracts can be merged (mixed) after this process, resulting in extract which is more rich for active plant ingredients belonging to various classes. The choice of orthogonal set is done by chemometric analysis of chromatograms obtained for the same plant material, but various solvent used for extraction. The idea consists of: chromatogram preprocessing (if needed: denoising, baseline removal, warping), principal component analysis, identifying most "extraction-sensitive" peaks by inspection of loading vectors for several first PC (plotting the variance of k first loading values at one wavelength, as a function of the wavelength; for example for 4 PCs, four loading values are taken for each wavelength and the variance of these values is plotted in function of wavelength) and then principal component analysis on heights of identified peaks. As we present the application of this approach to fingerprinting of fruits and roots of *Angelica sylvestris* L. From 17 investigated solvents we chose benzene and toluene as most orthogonal extractants. Other solvents were intercorrelated, so the third solvent can be freely chosen from them.

19.

Photocatalytic degradation study of tiapride by ESI-LC-MS method

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Ultraviolet and visible radiation are one of the most important factors affecting the stability of drug substances. Formed photoproducts may be more toxic than parent molecules, what is problematic also from the environmental point of view. However, radiation could be also used in wastewater treatment to remove pharmaceuticals especially with the use of catalytic agent. In this context, photocatalytic degradation of drugs can be very useful in environmental research as well as in the stability study of pharmaceuticals.

In this study the photocatalytic degradation of tiapride – an atypical antipsychotic drug acting as a selective D_2/D_3 receptor antagonist with the use of titanium dioxide as a catalyst was performed. Water solutions of tiapride hydrochloride were irradiated (0 – 400 min) with the use of solar simulated radiation (UV-VIS), and then analyzed with the use of UHPLC-DAD/ESI-Q-TOF coupled system. Reversed phase chromatographic column (RP-18) and gradient elution of mobile phase consisting of acetonitrile and water with addition of 0.1% formic acid were used. Mass spectrometer was set in a dynamic range and auto MS/MS mode to enable simultaneous qualitative and quantitative analysis. Total time of the LC-MS analysis was 9.5 minutes.

As a result of the above study, four main photoproducts were identified. Three of them were the effect of photolysis reaction and one of photooxidation process. It was also found that the photocatalytic decomposition of tiapride yields the second-order kinetics reaction (k = 0.0011 min^{-1}, $t_{1/2}$ = 90 min). The comparison of the reaction kinetics between the samples with and without addition of titanium dioxide revealed that the presence of the catalyst accelerates the photolysis reaction over four times.

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