Abstracts

for

The 7th Scientific Session of Undergraduate, Master and PhD Students, Iasi, Romania

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P1. Mono- and Multimodal Distributions of Water Soluble Ionic Species in Urban Particulate Matter from Iasi, Romania

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Particulate matter is a ubiquitous component of the atmosphere and plays a significant role in many areas including human health, climate, visibility, atmospheric depositions and air quality. Water soluble ions can change size, composition, number-density and lifetime of aerosols. In the present work, the size distribution of water soluble ionic species was investigated in urban particulate matter from Iasi, north-eastern Romania. Size distribution of the species of interest in the 0.0276-9.94 µm size range was appropriately investigated by using 13 specific fractions collected with a cascade Dekati Low-Pressure Impactor (DLPI). Water soluble ionic species of the collected particles were investigated with an ICS-5000 DC DIONEX ion chromatograph. Data analysis revealed that the average mass concentration was 21.9 ± 13.0 µg m⁻³ for the PM₂.₅ (particles with a diameter <2.5 µm) fraction and 23.3 ± 13.4 µg m⁻³ for the PM₁₀ (particles with a diameter <10 µm) fraction. For both sulphate and ammonium ions, clear monomodal mass concentration distributions were observed, with maxima at 381 nm. Moreover, the significant statistical correlation (r² = 0.92) between sulphate and ammonium ions would suggest possible common sources. The size distribution of nitrate mass concentration resembles bimodal features, having one dominant fine mode with maxima at 381 nm (the condensation mode) and one supermicron mode between 1.60 and 2.39 µm. Such behaviour would suggest that nitrate is most likely produced either by gas-particle condensation or by in-cloud processing.

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References:
P2. Elemental and Morphological Analysis of Airborne Particulate Matter Collected in Iasi, North-Eastern Romania

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Morphology and elemental chemical composition of airborne particulate matter (PM) have been investigated by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). PM airborne samples were collected in the atmosphere of Iasi area, north eastern Romania, using a Dekati Low Pressure Impactor (DLPI), providing 13 particle fractions ranging from 27.6 nm to 9.94 μm. Investigations were conducted on the characteristics of the PM collected on various filter batches (i.e., aluminium, polycarbonate, and quartz). Punctual EDX analysis of similar morphological particles allowed us to discriminate between contributions brought by elements such as C, N, O, Na, Mg, Al, Si, S, Pb, Cl, K, Ca, Ti, and Fe. However, in order to extract meaningful information for each batch filter type possible, blank contributions were taken into account. The data obtained from the aluminium filters seemed to be the most important in terms of the size distribution intercomparison with similar information obtained by ion chromatography (IC) (especially for N, Na, S, Ca and K). Mono- or multimodal distributions were identified for the abovementioned elemental species, in full agreement with the IC data for the ionic species tracing those elements. Moreover, interesting behaviour was observed for C and Pb. While Pb still needs to undertake a quality control check procedure, C distribution revealed the existence of a dominant C fraction in the accumulation mode. In our opinion, several elements might be of natural (Ca – dust resuspension present in the coarse fraction, Na – salty environment or long range transport of sea-sprayed aerosols) or anthropogenic origin (S – traffic and coal burning).1 In some samples, the presence of spherical Fe-rich particles, with diameters between 2.5 μm and 10 μm, were identified. The observed behaviour for iron would reflect either contribution from dust (Saharan dust event on the aluminium batch) or from high temperature processes2 at other punctual sources (local emissions from heating purposes on the polycarbonate batch).

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The authors acknowledge the financial support provided by UEFISCDI within the PN-II-PCE-2011-3-0471 Project (EVOLUTION-AIR). CERNESIM Center is also grateful acknowledged for the infrastructure used in this work.

References:

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P3. On how the Lack of Experience in HPLC Measurements of Aspirin, a Selected Medicine, can Bring you into the Trap of Elaborating Erroneous Conclusions

Ana-Maria Rusu, Mihaela Matei, Elvira Malu, Georgiana Iustina Ababei, Dumitrela Cucu, Raluca-Mihaela Șîmadici, Loredana Oana Badragan, Carmen Aonigioaiei, Gianina Bivol (Augustin), Anca Florina Crețu, Roxana Petronela Damaschin, Romeo Iulian Olariu, Cecilia Arsene

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Aspirin, one of the most accessible medications, seems to be the magic tablet, being recommended for preventing heart attack and, possible, colorectal cancer. The potential of an active ingredient in the willow bark, to act as a pain reliever, has been documented in a publication from Philosophical Transactions as early as 1763. Although for a while aspirin had been pushed aside by the more stomach-friendly medicines (e.g. paracetamol, known as acetaminophen in the US, ibuprofen or diclofenac), the drop in aspirin's fortune was countered within the last decades, and aspirin has become the focus of extensive investigations into its antiproliferative and anticancer activities.

In the present work, a simple, rapid and sensitive reversed phase-high performance liquid chromatographic (RP-HPLC) analysis method has been employed in order to perform a quantitative assay of the active ingredient aspirin (acetylsalicylic acid) and its hydrolysis product (salicylic acid) in Sanosan (RO), Zentiva (RO), Aspenter (RO), Bayer effervescent (RO), original Bayer (D) and Aspar (UK) pharmaceutical products. Separation of the interest compounds was achieved in chromatographic runs of 10 min under isocratic conditions (70% buffered aqueous phase:30% organic phase) on a Zorbax SB-C18 (150 × 4 mm, 5 µm) column. Quantification of the active ingredients of interest was carried out by acquiring the signal at 235 nm. Experiments were undertaken by three working teams (WT1: AMR, MM, EM, LOB; WT2: CAN, GB, RPD, RMS; WT3: GIA, AFC, DC, GP) and a reference working team (RWT: AMR, MM, RIO, CA) within training periods of 12 hours each. Poor accuracy was obtained by each of the WTs involved in the experiment, with estimated errors varying in the 10-80% range. The RWT reported errors for the measured values within 1-5%. Each pharmaceutical formulation revealed the existence of ~1.5% salicylic acid. It was shown by the RWT that the conclusion drawn initially based on each of the three WTs’ data i.e. mainly the fault of the drug suppliers, was erroneously elaborated. The data obtained by the RWT proves that the quantification process is extremely sensitive to the performance of the experimenter (starting with the use of appropriate calibration curves etc.).

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CERNESIM Center is gratefully acknowledged for the infrastructure used in this work.

References:

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Aromatic hydrocarbons are an important class of volatile organic compounds (VOCs) present in the atmosphere, with important contributions to the chemistry of urban air. Primary pollutants emitted by anthropogenic activities (chemical industry, use of fossil fuels) such as benzene, toluene and xylene, are known to produce hydroxylated aromatics in significant yields (e.g. phenol, cresols and dimethylphenols, respectively) through atmospheric oxidation. The major atmospheric loss process for phenolic compounds is the gas-phase reaction with hydroxyl radicals (OH) that greatly contributes to the formation of photooxidants and secondary organic aerosols (SOA).

As a part of a systematic study of the gas-phase atmospheric chemistry of aromatic hydrocarbons, we report preliminary kinetic results on the reaction of 2,6-dimethylphenol with OH radicals. Investigations were performed using long path FT-IR spectroscopy in the newly designed Environmental Simulation Chamber made of Quartz from the “Alexandru Ioan Cuza” University of Iasi (ESCQ-UAIC). Kinetic experiments were performed at 298±2 K and atmospheric pressure in synthetic air. The rate coefficient was determined by using a relative rate method. The hydroxyl radicals were produced by the photolysis of methyl nitrite. Tetrahydrofuran and p-xylene were used as reference compounds in this study. The average rate coefficient obtained within the present work (\( k_{OH} = (5.46±0.60) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \)) is discussed in comparison with reported literature data and Structure Activity Relationship (SAR) estimated values. Residence lifetime of 2,6-dimethylphenol (\( \tau(h) = 3.18 \)) was calculated based on a daytime tropospheric OH radicals average concentration ([OH] = 1.6 x 10^6 molecule cm^{-3}).

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References:
P5. Synthesis and Analysis by NMR and MS of two Fragments Derived from the Amyloid-β Peptide

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Peptide chemistry has an important role in the study of proteins and their functions. Solid-phase peptide synthesis (SPPS) has been largely used and is an excellent method to get large amounts of synthetic biomolecules. Amyloid-β peptides (Aβ) are major components of senile plaques and soluble oligomers, which are considered to play the main role in Alzheimer’s disease (AD). Aβ peptides can form fibres associated with the AD pathology under the influence of Cu²⁺, Zn²⁺, Fe³⁺ and Cd²⁺ ions. The interaction of Al³⁺ and Fe³⁺ ions with Aβ(1-28) peptide was investigated by ¹H-NMR and ESI-MS under pH conditions close to physiological ones.

Consequently, we synthesized the Aβ peptide fragments H₂N-GYEVHHQK-CONH₂ and H₂N-GGEVHHQK-CONH₂, which contain the sites for metal ion binding. The structure of the peptides was characterized by MS and NMR, and the reaction with metal ions was also investigated.

Acknowledgements:
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References:

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P6. Structural Characterization of a Synthesized Peptide with Potential Neuroprotective Activity

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The aggregation of amyloid-β (Aβ) peptide in the presence of aqueous metal ions such as copper, zinc, iron or aluminium, contributes to neuronal damage and therefore to the appearance of diverse pathologies. 1 Neuronal loss in Alzheimer’s disease leads to memory deficit, the main factor responsible for this being the neurotoxic effect of the Aβ peptide. 2 Experiments including co-incubation of a neuropeptide type NAPVSIPQ and amyloid peptide fragments showed that NAP inhibits Aβ(25–35) and Aβ(1–40) fibril formation. 3 These neuropeptides are able to cross the blood–brain barrier and act as neurotransmitters in the intercellular communication network. 4

In this work we present the synthesis and characterization of a new peptide which could have therapeutic properties in neurodegenerative diseases. The NAPVAIPQ peptide was obtained using solid phase peptide synthesis chemistry methods and analysed by mass spectrometry, NMR and FT-IR spectroscopy.

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Photodegradation of the Rhodamine 6G (R6G) dye was investigated on 6 samples of titanium dioxide doped with cerium oxide, prepared by the EISA technique, using Ce(III) nitrate – labelled as N and ammonium Ce(IV) sulphate – labelled as S. Titanium isopropoxide was used as precursor and hexadecyl-trimethyl-ammonium bromide (CTAB) as surfactant. The release of the pores was carried out by calcination at 500, 600 and 700°C for 6 hours at a heating rate of 1°C/minute. The solids were characterized by BET adsorption for investigation of the porous structure. The photocatalytic tests were carried out in photoreaction under UV irradiation.

All samples are porous and have specific surface areas between 25 and 184 m²/g. The results from the photocatalytic oxidation reaction show different behaviour of the samples from the N and S series. While specific areas are higher in the N series, the activity is higher in the S series. This indicates that doping with Ce(IV) compared to Ce(III) might be more advantageous when the optimal calcination temperature is 500°C. After 2 hours of UV irradiation, a degree of conversion of 72% was achieved.

References:
P8. A Multi-component Protein-Based System for Copper Determination

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The now-abandoned ore-processing plant in Tarnita, located in the Eastern Carpathians, remains abundant in waste material.¹ This mine waste contains toxic heavy metals such as cadmium, arsenic, zinc, copper etc., as determined by ICP-OES. Heavy metals have accumulated in plant tissues, inhibiting a number of physiological processes and presenting high risk for surrounding forests and waters.² Environmental pollution of the Tarnita site and its impact on human health are still not fully estimated.

The present study aimed to develop a spectrophotometric method for copper quantification in waste material from the Tarnita site. This method is based on the complex formation reaction between protein and copper in presence of resorcinol and ammonia. In contrast to casein, bovine serum albumin (BSA) reacts much easier, as it only requires mixing of the four components and stirring for 5 minutes. The reaction with casein requires heating, boiling [3] and centrifugation. The amount of bound copper was monitored at 450 nm from the resulting supernatant solutions.

References:

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P9. Study on Toluidine Blue and Rhodamine 6G Dyes’ Adsorption on Several Mesoporous Solids

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Toluidine blue (TB) and rhodamine 6G (R6G) dyes are a significant source of pollution in wastewater. These dyes are also used as model compounds for testing adsorbents and (photo)catalyst decomposers.

The mesoporous materials synthesized in this work are SBA-15, Ti-MCM-41 and Ti-MCM-48. The characterization of the materials was performed by specific methods: BET nitrogen adsorption at 77K, FT-IR.

Tests on the adsorption equilibrium were carried out according to the adsorbent mass, the dye concentration and dye solution volume. Dye concentrations were monitored by means of UV-Vis spectroscopy. In addition, the sorbents with good adsorptive capacities were regenerated by calcination at 500 °C (1 °/minute) and then retested.

The results of the adsorption tests were fitted by applying the Langergren and Ho kinetic models. For pseudo-second order kinetic (Ho model) a very good correlation (R² ≅ 1) data was obtained (Figure 1b).

In conclusion, the mesoporous materials are excellent adsorbents for the two studied dyes, the best being Ti-MCM-41 and Ti-MCM-48.

References:

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P10. Use of Mg3Al Hydrotalcite in the Adsorption Process of Organic Compounds of Biological Interest from Wine

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Wine is a complex product, containing a multitude of chemical compounds, many of which are biologically active (especially antioxidants).1 The adsorption tests in order to capture some compounds from wine on anionic clay came from the initial premise that these compounds could be immobilized on hydrotalcite (HTc) by anionic exchange. The study was designed from two perspectives: the first aimed to uptake organic compounds with bioactive potential (possibly they could be separated and subsequently used for therapeutic purposes) on this non-toxic, biocompatible mineral, and another perspective targeted the use of such a solid in the wine industry as an adjuvant material in the clarification and stabilization processes of wine.

A wine sample, previously characterized through specific tests,2 was maintained in contact for an hour with Mg3Al-HTc under vigorous stirring. The mixture was kept in static conditions overnight (16 hours, cold), then the slurry was filtered, yielding the adsorbant which retained compounds from wine, and the post-treatment wine in solution (fig.1). Both the solid and wine were analysed by specific appropriate methods (BET adsorption, FT-IR, XRD (Figure 2), thermal analysis, AES, UV-Vis spectrometry, HPLC).

The tested Mg3Al-HTc had a complex behaviour in wine: decrease of particle size, adsorption of significant amounts of organic compounds, induction of mutual transformations between wine compounds (by catalytic effects). However, the partial dissolution of the sorbent released aluminium ions in wine, an undesired side-effect which restricts the practical use of the material in the oenological treatment.

References:
1. Cotea, V. D., Zănoagă, C. V., Cotea, V. V., Oenochemistry, Published by Romanian Academy, Bucharest, 2009, vol. 1and 2.

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P11. Students’ Perception on Factors which Influence Professional Route

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One focus of contemporary education, with effect on training of highly qualified workforce, is illustrated by the issue of transition from one stage to another in higher education, issues concerning both the education provider (university) and the beneficiary of this extensive, systemic and lasting process (student).

In terms of a comprehensive educational plan, with coverage of skill training and cognitive acquisitions, monitoring the beneficiaries’ perception is a logical requirement, and especially imperative for any education provider. For this goal, the present study was carried out in March-May 2016 on a representative sample of 72 students from the “Alexandru Ion Cuza” University of Iasi, Faculty of Chemistry, by applying a questionnaire and direct interview. The respondents were selected among the undergraduate and master students. The data were processed and interpreted by the multivariate statistical analysis technique – “analysis of clusters in two steps” method, one cluster including students from Undergraduate studies (Cluster I), and the other one students from Master Courses (Cluster II)\(^1,2\).

The questionnaire sought to identify the most motivating aspects of the training period of earlier education,\(^3\) highlighting the professional experiences inside or outside the students’ specialization, and to gather opinions in favour of or against maintaining the current training route, outlining the respondents’ expectations on the most desirable occupations in the labour market that require specialization through courses at Faculty of Chemistry. As a rule, the students of both university cycles are satisfied with their choice and want to continue the selected professional route in chemistry or related fields. However, none of the response options to the syntax item “You want to continue studies at Masters / PhD” was imposed on respondents’ preferences in cluster I.

References:

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