

## **POSTER SESSION I**

**MAY 25<sup>th</sup>, 2010**

**CHAIRPERSONS:** W. Verschelde and Ł. Komsta

1.

## **Effect of mobile phase composition on the overall elution process in thin-layer chromatography**

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The solute retention and its band profile in the TLC system are strictly dependent upon the mobile phase composition. Determination of this dependence seems to be especially complex in the case of that kind of adsorbents that possess variety of active sites on their surface. Such heterogenic surface usually provides adsorption sites of different ability to interact both with molecules of solute and with more polar component of the mobile phase. The example of such popular adsorbent having at least two different active sites on its surface is alumina. This stationary phase is very common in numerous TLC applications. We have found that for binary mobile phase, there is a range of stronger component concentration that gives both peaks of Gaussian shape and triangle-like shape as well. Mobile phase composition determines the scope of interaction between analyte (solute) and active sites of adsorbent and therefore affects observed isotherm of adsorption. Profound insight in modeling of this process should reflect the fact of competitive adsorption of solute and components of mobile phase. This phenomenon is not observed in the TLC as frequently as in the LC mode of chromatography because concentrations applied here are usually in low level. Nevertheless we observed non-Gaussian peaks in our TLC study of phenylacetone on alumina chromatographed with mixture of toluene and 1,4-dioxane with relatively low concentration of the last one. We also suggested an appropriate model describing observed retention process.

2.

## **Study of Porous Materials by IGC/flash Thermodesorption**

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Inverse Gas Chromatography (IGC) became very popular method for the measurement of physico-chemical properties of solid materials. In contrast to analytical chromatography the stationary phase is the sample under investigation, while a substance in the mobile phase acts as a probe molecule. This means the roles of the phases are inverted.

The combination of IGC and thermal desorption method allows to determine the type of solid structure and estimate the contributions of micropores, mesopores and outer surface area to the adsorption process. Adsorption mechanism in micropores is completely different in comparison to behavior of the adsorbate in the mesopores and at the outer surface area. The adsorption in the smallest pores can be described by so-called “theory of volume filling of micropores” (TVFM), while in the mesopores and the outer surface prevails mono-/multilayer sorption mechanism (BET equation).

In combined IGC/flash thermodesorption experiment different zeolites were investigated. The obtained chromatograms show two peaks: the first corresponds to the elution, while the second – to the thermodesorption. The first peak, representing the mesopore and outer surface adsorption, is associated with desorption of only physisorbed probe molecules. Some probe molecules, due to their increased adsorption potential, are retained in the micropores. Therefore, after the increase of temperature the thermodesorption peak (micropore sorption) is observed.

The combination of IGC with flash thermodesorption proved to be a very good method for the characterization of porous materials and separation micropore and mesopore/outer surface adsorption due to different adsorption mechanisms.

## Increasing the reproducibility of gc retention indices by modifying their measurements

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Calculating the gas chromatographic retention indices (**RI**) usually implies the registration of the maxima of chromatographic peaks. The column overloading or non-linearity of sorption isotherms cause a distortion of peak shapes and shift the positions of their maxima, however the profiles of fronts of chromatographic peaks often remain undistorted.

We recommend to reconsider the idea of RI calculations using retention times measured not at the maxima of chromatographic peaks, but at the points on their fronts corresponded to the same levels of analytical signals, which was proposed first by A.I.M. Keulemans at the end of 1950s. It permits us to compensate RI variations caused by different relative quantities of target analytes and reference compounds. It can be illustrated by data for nitrobenzene, analyzed on the packed column with standard non-polar phase (see Table), where  $\gamma$  [1] is the following ratio:

$$\gamma = \frac{S_x}{S_n + S_{n+1}}$$

where  $S_x$  is peak area of the target component,  $S_n$  and  $S_{n+1}$  are peak areas of reference alkanes with  $n$  and  $n+1$  carbon atoms in the molecules.

**Table.** The reproducibility of **RI**s of nitrobenzene calculated in the maxima of peaks ( $RI_{\max}$ ) and at the different levels of the signals at their fronts.

$RI_{\max}$	RI (8 mV)	RI (4 mV)	RI (2 mV)	$\gamma$
1052	-	1081	1076	0.04
1084	1086	1079	1075	0.27
1096	1093	1082	1078	0.43
1111	1090	1082	1077	0.95
1110	-	1083	1077	1.20
1118	1085	1078	1074	1.75
1126	-	1082	1077	2.20
1143	-	1080	1077	3.10
<b>Average values</b>				
<b>1108 ± 28</b>	<b>1088 ± 4</b>	<b>1081 ± 2</b>	<b>1077 ± 1</b>	

As we can see, the fewer level of registration of signals leads to decreasing of absolute **RI** values and increasing of their reproducibility ( $S_{RI}$  values decrease from 28 to 1 i.u.). The values RI (2 or 4 mV) indicate no dependence on  $\gamma$  at all. The proposed method of **RI** calculation permits us to compensate partially both the influence of overloading of GC systems and non-linearity of sorption isotherms.

### References:

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### Hydrophilic Interaction Planar Chromatography of Geometrical Isomers of Some Co(III) Complexes

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Hydrophilic interaction liquid chromatography (HILIC) has recently been introduced as a highly efficient chromatographic technique for the separation of a wide range of polar solutes [1]. In the HILIC mode, an aqueous-organic mobile phase combined with a polar stationary phase was used to provide normal-phase retention behavior. HILIC is often considered as a normal-phase separation in a reversed-phase fashion mode. Studies on the separation mechanisms in different chromatographic systems were the topic of our long-term investigations and the results were reported in numerous papers. Among these studies, examinations of chromatographic behavior of different classes of metal complexes are of a special significance because their environmental and biomedical interest [2]. Continuing these investigations in this work the applicability of hydrophilic interaction chromatography to the analysis of geometrical isomers of some Co(III) complexes was explored.

The chromatographic behavior of series of cobalt(III) complexes of the anionic, cationic and neutral type were investigated under HILIC conditions on thin-layer of silica-gel. The chromatography was carried out with solvent systems: water (0-100%)/organic solvents and water (0-100%)/organic solvents/various amounts of electrolytes.

On the basis of the results obtained, possible retention mechanisms were considered.

#### References:

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5.

**Comparison of chromatographic retention parameters of several basic compounds obtained on different stationary phases i.e. C18 and Phenyl bonded silica and various ionic liquids added to organic aqueous eluent systems**

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Ionic liquids (ILs) were firstly applied in liquid chromatography by Poole et al. in 1986. They are most commonly applied as additives in low concentration (smaller than 60 mM) in organic aqueous solutions in reversed-phase mode. It is obvious that the chromatographic results are affected by either cations or anions of a modifier. Activity of anions could be explained using the theory of chaotropicity, while action of cations is connected with suppression of silanophilic interactions. In this work the measurements of chromatographic parameters of several basic compounds revealing retention and efficiency were performed on different hydrophobic stationary phases i.e. C18 and Phenyl bonded silica gel whereas the mobile phase containing organic solvent/water/ionic liquid remained constant. Obtained results were compared and discussed according to retention mechanism appearing at applied conditions. Blocking of silanophilic interactions was also taken into account in conclusions.

**References:**

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- [2] A.Berthod, M.J.Ruiz-Angel, S.Cardá-Broch, *J.Chromatogr. A* 1184 (2008) 6.
- [3] J.Flieger, *Anal.Letters*. 42 (2009) 1632.

## On Spontaneous Oscillatory Condensation of Phenylacetic Acids in Aqueous Ethanol

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It is generally believed that condensation of amino acids and hydroxy acids (resulting in peptides and poly(hydroxy acids), respectively) is rather difficult because energetically unfavourable, as it needs a considerable energetic input in order to split one water molecule from each pair of binding compounds [1]. This conviction affects many present-day presumptions regarding, e.g., prebiotic condensation of amino acids resulting in formation of peptides coupled through peptide bonds (NH-C=O). Hence, the experiments are still devised which involve ion irradiation of amino acid solutions to imitate the presumable prebiotic conditions of peptide formation [2]. Moreover, computational simulations are carried out to prove that energetically, polycondensation of amino acids (and hydroxy acids) would be more favourable, if carbon, oxygen, and/or nitrogen atoms in amino acid and hydroxy acid molecules were replaced by their respective analogues, i.e., silicon, sulphur, and phosphorus atoms [3].

In this study, an experimental evidence is provided to prove that condensation with certain low-molecular-weight amino acids and hydroxy acids carried out at ambient temperature can be effortless, if it is carried out in 70% aqueous ethanol. We present the results of the investigation carried out with use of the non-chiral high-performance liquid chromatography with diode array detector (HPLC-DAD) and mass spectrometry (LC-MS) on the dynamics of condensation of *S*-, *R*-, *rac*-phenylglycine, and *S*-, *R*-, *rac*-mandelic acid dissolved in 70% aqueous ethanol and stored for the longer periods of time.

It seems that energetically effortless condensation of amino acids and hydroxy acids is inseparably linked with an ability of these acids to undergo a spontaneous oscillatory chiral conversion, first described in papers [4-6]. With the obtained experimental results, we managed to convincingly demonstrate that condensation of phenylglycine and mandelic acid is the oscillatory process.

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## On Spontaneous Oscillatory Condensation of *S*-(+)-Ketoprofen in Acetonitrile

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This study is continuation of our earlier investigations of chemical stability of the ketoprofen, when dissolved in the low-molecular-weight solvents and stored for the longer periods of time in a solution (1-5). In those earlier experiments, we have discovered an ability of this profen to undergo a spontaneous oscillatory *in vitro* chiral inversion and also to undergo condensation. The kinetic-diffusive model was proposed to illustrate formation of the oscillatory time and space waves of the locally changing concentration of the respective antimer pairs.

In this study, experimental evidence is provided to prove that condensation with ketoprofen carried out at ambient temperature can be effortless, if this profen is dissolved in acetonitrile. We present the results of the investigation carried out with use of the non-chiral high-performance liquid chromatography with diode array detector (HPLC-DAD) and mass spectrometry (LC-MS) on the dynamics of condensation of *S*-(+)-ketoprofen dissolved in acetonitrile and stored for certain period of time.

It seems that energetically effortless condensation of ketoprofen is inseparably linked with its ability to undergo a spontaneous oscillatory chiral conversion. With the obtained experimental results, we managed to convincingly demonstrate that condensation of ketoprofen is the oscillatory process.

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## **Chromatographic behavior of chosen basic drugs on cyanopropyl bonded silica gel eluted with organic aqueous eluent systems modified with ionic liquids**

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Recent years have been characterized by the increase of the application of the so called "ionic liquids" (ILs). Ionic liquids have very unique properties of a new class of solvents that make them fashion in organic synthesis, catalysis, electrochemistry or green chemistry. However, when used diluted in a chromatographic mobile phase, ILs lose all their fashion properties and become just salts. The ions, being the components of salts may incite in the chromatographic system both a synergistic effect and an antagonistic effect, providing improvement of efficiency and separation selectivity. Not meaningless, as for the benefit of the achieved effects, is the possibility of suppressing of silanol interactions.

The aim of the following study is the use of the chosen ionic liquids (1-ethyl-3-methyl-imidazolium hexafluorophosphate (EMIM PF<sub>6</sub>), 1-butyl-3-methyl-imidazolium hexafluorophosphate (BMIM PF<sub>6</sub>) and 1-butyl-3-methyl-imidazolium chloride (BMIM Cl) as the additives for the mobile phase in RP-HPLC of ionogenic basic compounds. By the application of HPLC technique and Cyanopropyl bonded silica gel, chromatographic parameters expressing efficiency of the system were established.

In this work, the retention mechanisms (solute interactions in ionic liquids modified systems) of solutes of different nature was demonstrated.

### **References:**

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## Application of micellar TLC in studying lipophylic properties of organic compounds

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Hydrophobic character of organic substance is important physico-chemical property in relation to its biological activity. The most widely accepted hydrophobicity index is octanol-water distribution constant,  $\log P$ . Because this value is extremely difficult to measure experimentally due to problematic and tedious procedure, different computational methods are applied. Moreover, reversed-phase liquid chromatography (column and planar) is used for estimation of chromatographic hydrophobicity indices. In isocratic RPLC extrapolated retention to pure water,  $\log k_w$ , or  $\varphi_0$  parameters are proposed for the purpose. Although RPLC is a simple technique and permits to obtain reproducible data, using it in hydrophobicity measurements is not perfect. The value of extrapolated  $\log k_w$  parameter strongly depends on organic modifier and residual silanols of alkyl-bonded stationary phases. To overcome these difficulties new stationary phases imitating biosystem are proposed for studying hydrophobicity - immobilized artificial membranes IAMs, immobilized proteins, ceramides, keratin or cholesterol. Moreover alternative techniques such as counter-current chromatography (CCC) or micellar liquid chromatography (MLC) are applied in such investigations. Micellar liquid chromatography is a mode of conventional RPLC using surfactant solution above critical micellization concentration (cmc) as the mobile phase. The retention of solute in this technique depends on the type of interactions with the micelles and the surfactant modified stationary phase. In MLC two values, i.e., retention parameter  $k$  and  $k_m$  (the retention parameter at zero micellar concentration), are proposed as hydrophobicity indices and correlated to  $\log P$  values.

In our investigations micellar TLC was proposed to study hydrophobic properties of newly synthesized organic substances. Two surfactants, Brij35 and SDS, were applied as mobile phase components and different organic solvents, i.e., methanol, acetonitrile, acetone, dioxane and tetrahydrofuran, were used as the mobile phase modifiers. As stationary phase RP-CN HPTLC plates were utilized. Very interesting correlations between chromatographic parameters and  $\log P$  values calculated from molecular structures of test solutes confirm the importance and usefulness of micellar TLC in studying hydrophobicity of new substances.

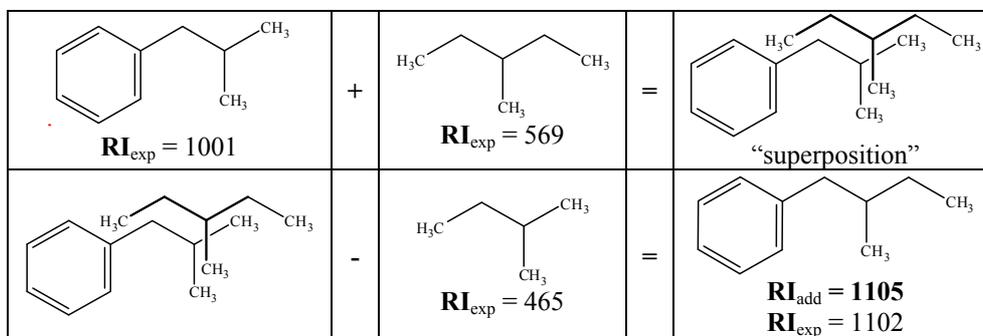
## Revealing the structures of isomeric alkyl arenes using additive evaluation of gas chromatographic retention indices

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There are many cases in analytical practice when we have to identify compounds with similar mass spectra in complex mixtures. Particularly, revealing the structures of isomeric products of Friedel-Crafts reaction, namely the alkylation of arenes, cannot be based on their mass spectra solely. Isolation and purification of each product of alkylation for its identification seems to be highly time- and money-consuming work. So far as the differences between mass spectra of isomeric alkyl arenes can be negligible, interpretation of data should be started with GC retention indices (**RI**) of products. If these data are unknown for estimated reaction products, evaluated values can be used instead of experimental.

This method of RI prediction is the simplest one; we can consider it with the example of RI calculation for (2-methylbutyl)benzene. We should assemble the “superposition” (see Scheme) of required structures (2-methylpropylbenzene and 3-methylhexane) and then subtract the molecule including the “duplicated” fragments (2-methylbutane). The simple arithmetic calculations provide to estimated **RI** value ( $1001 + 569 - 465 = 1105$ ). The experimental RI value for this compound is 1102.



**RI<sub>add</sub>** – the additively evaluated value

**RI<sub>exp</sub>** – one of the values from NIST/EPA/NIH (2005) database.

Formally schemes of such design don't imply pre-calculation of any increments. The average deviation of calculated and experimental RI's values within the series of alkyl arenes is 11 i.u., which is comparable with interlaboratory **RI** reproducibility. It shows that additive RI estimation is efficient in evaluation of structures of products of organic reactions, when both substrates and reagents are known.

The application of this approach for products of alkylation of alkyl arenes by alcohols is considered.

### **Automatic interpretation of gc-ms data in toxicological screening**

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One of the main problems in analytical toxicology is the identification of components of multicomponent mixtures of volatile organic compounds (VOC). For this purpose GC-MS is an indispensable technique. The chromatograms of biological samples contain a lot of peaks of background compounds which are often hardly distinguishable from the peaks of target compounds. The list of probable contaminants includes hundreds of compounds, which makes manual identification time- and labor-consuming. Automated GCMS data interpretation allows higher sample throughput. The software for automated interpretation of GC-MS data (AMDIS) was developed by the US National Institute of Standards and Technologies. It allows identification of components of complex mixtures even in the case of incomplete chromatographic resolution. However, the AMDIS with on-line large-volume nonspecific MS databases is unsuitable for toxicological screening. We performed a series of experiments and obtained evidence showing that the AMDIS in an open version (with on-line NIST 05 MS library) fails to identify components of model VOC mixtures, which could be readily identified by manual interpretation. This problem raised the necessity of creating domestic MS libraries compatible with the AMDIS software. However, the use in analysis of samples from complex matrices (like a corps material) was observed false-positive identification of light alcohols, ketones and aldehydes. False answers were rejected by help of gas chromatographic retention indices interpretation. So it became evident that concurrent interpretation of GC retention and MS data is necessary for unambiguous identification. Reference values for VOC retention indices and mass spectra were obtained experimentally.

With the using of references and own experimental data we create the list of 2252 compounds, including industrial and domestic poisons, toxic admixtures of alcohol, drugs, stimulants, products of toxic compounds decomposition, background components of urine, saliva and blood. A mixture of 180 components of various chemical origin was analyzed with GC-MS, and mass spectra and retention indices obtained were assembled in database. It was shown experimentally that automated identification with domestic database was done without false negative and positive results. Automated GC-MS data interpretation in analysis of natural (including high salted) water, synthetic urine and other samples spiked with VOCs was more efficient in comparison with manual data interpretation.

12.

**Application of gas chromatography in a comparative study of biomass, lignite and hard coal steam gasification**

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An increasing world's energy demand and environmental concerns related to GHG emissions as well as depleting fossil fuel resources and unstable prices of crude oil and natural gas cause a renewed interest in utilization of renewable energy sources, in particularly biomass.

In the paper a comparative study of steam gasification of biomass, lignite and hard coal, in a laboratory scale fixed bed reactor at the temperature of 700<sup>0</sup>C are presented. The effectiveness of steam gasification of biomass, lignite and hard coal samples, in terms of flows and composition of the main gaseous products and carbon conversion were studied. The procedure and results of fuels' chars reactivity testing in the process with a use of gas chromatography as well as the results of experimental data analysis with chemometric methods. The highest reactivity  $R_{50}$  and  $R_{max}$  were observed for biomass samples. A negative correlation between chars reactivities and heat of combustion, calorific value, carbon, nitrogen and fixed carbon content in a sample, total synthesis gas yield and CO content in synthesis gas were also observed. As it was expected synthesis gas produced in the process of biomass steam gasification was characterized by relatively lower calorific values when compared to gas produced through steam gasification of lignite and hard coal. It suggests that biomass gasification should be treated not as an alternative but as a complement for lignite and hard coal gasification.

**TLC densitometric investigation of the degradation of 4-chlorophenol using advanced oxidation processes (AOPs)**

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Chlorophenoles are contaminants with toxicity for humans and animals. They are non biodegradable and their removal is difficult. Advanced oxidation processes (AOPs) are one of alternatives for water treatment standard techniques. These processes completely degrade chlorophenoles to carbon (IV) - oxide or to biodegradable and less toxic intermediers.

In this work degradation was performed with AOPs using non-thermal plasma reactor based on coaxial dielectric barrier discharge. Three different sets of conditions for degradation of 4-chlorophenol was examined using falling film dielectric barrier discharge (DBD) reactor: DBD, DBD/H<sub>2</sub>O<sub>2</sub> and DBD/Fe<sup>2+</sup>. Degradation of 4-chlorophenol was monitored using thin-layer chromatographic method with densitometric detection (Camag TLC Scanner 3). RP18 silica plates were used with acetone-water-triethylamine 60:38:2 (v/v) as mobile phase. Scanning and densitometric analysis was performed at 240 nm.

## **Determination of ethyl 2-cyanoacrylate in workplace air\***

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Ethyl 2-cyanoacrylate (ECA,  $C_6H_7NO_2$ , CAS No. 7085-85-0) is a clear, colourless liquid with a strong, acrid odour. It reacts readily with water to form a solid polymer. It is soluble in methyl ethyl ketone, toluene, acetone, *N,N*-dimethylformamide, and nitromethane. Contact with alcohols, amines, or water may cause polymerization.

Various homologues of cyanoacrylate (CA) adhesive have been studied and used, including methyl- (MCA), ethyl- (ECA), isobutyl-, isohexyl-, and octyl-CA. The cyanoacrylates are used as adhesives both domestically and in a wide range of industrial environments — e.g., the manufacture of lampshades, plastics, electronics, scientific instruments, shoes and jewellery. The other known application of MCA and ECA is also visualization of fingerprints for criminal investigations.

The main health effects that have been observed to date in relation to occupational exposure to ECA are eye and respiratory tract irritation. Based on the harmfulness of ethyl 2-cyanoacrylate the exposure limit values: NDS-MAC (TWA) of  $1 \text{ mg/m}^3$  were proposed by the Interdepartmental Commission for Maximum Admissible Concentrations Intensities.

The determination method is based on the adsorption of ethyl 2-cyanoacrylate vapours on phosphoric acid-treated XAD-7 sampling tubes (80/40 mg sections), desorption with 2 ml of 0,2% (v/v) phosphoric acid in acetonitrile and high performance liquid chromatographic (HPLC/UV) analysis of the resulting solution. This method makes it possible to separate the ethyl 2-cyanoacrylate in the presence of methyl 2-cyanoacrylate. Calibration was carried out with standard solutions of ethyl 2-cyanoacrylate, using the following conditions: measurement range from 0,1 to  $2,5 \text{ mg m}^{-3}$ , for determination of 12 l air volume, 20  $\mu\text{l}$  injected sample. This method was fully validated.

### **Acknowledgement**

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**GC/MS analysis of some dialkyl esters of 1,2-cyklohexanedicarboxylic acid**E. Dziwiński<sup>1</sup>, A. Tasarska<sup>2</sup>, J. Lach<sup>1</sup><sup>1</sup>*Institute of Heavy Organic Synthesis „Blachownia”, Kędzierzyn-Koźle, Poland,*<sup>2</sup>*Institute of Chemistry, Opole University, Opole, Poland*

Dialkyl phthalates are used very often as the plasticizers of the different polymers. Because this type of compounds is recognized as the potential cancerogenes, they should be replaced by other types of compounds such as dialkyl esters of 1,2-cyclohexanedicarboxylic acid. The synthesis of these new plasticizers is based on the high pressure hydrogenation reaction of the appropriate dialkyl phthalates in the presence of catalyst.

The aim of our study was the application of gas chromatography – mass spectrometry (GC/MS) method to the identification of the hydrogenation products of di-n- and iso- butyl and octyl phthalates. The identification of these products was done in two ways:

- by exact measurement of retention times or relative retention times of the compounds analyzed and determination for them chromatographic retention arithmetic or Kovat's indices. The determined values of indices are very helpful, especially in the GC analyses of their isomers.

and/or

- by registration during GC/MS analysis and detailed interpretation the mass spectra of the individual esters. The general feature of mass fragmentation of dialkyl esters of 1,2-cyclohexanedicarboxylic acid is the presence in their mass spectra the most intense and characteristic peak at  $m/z$  155 corresponding to the ion with protonated 1,2-cyclohexanedicarboxylic acid anhydride structure, similarly as in the case of mass spectra of dialkyl phthalic acid esters where peak at  $m/z$  149 corresponds to the ion with protonated phthalic acid anhydride is present.

The application of the GC/MS method is very useful in qualitative and quantitative analyses both dialkyl esters of 1,2-cyclohexanedicarboxylic acid and dialkyl esters of phthalic acid occurring in the complex mixtures.

## Determination of aziridine in workplace air by hplc method

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Aziridine (ethyleneimine) is a colourless oily liquid with an intense odour of ammonia. Aziridine is an intermediate and monomer in the preparation of cationic polymers, such as polyaziridine. This polymer are used for improvement of wet strength of paper, in rocket and jet fuels, lubricants, as flocculating agents and in protective coatings, in textile finishing and for adhesives, polymer stabilizers, and surfactants. Occupational exposure to aziridine may occur in its production and in the preparation of polyaziridine polymers. The substance can be absorbed into the body by inhalation of its vapour, through the skin and by ingestion.

Aziridine is possibly carcinogenic and mutagenic to humans. It may cause heritable genetic damage to human germ cells.

The Interdepartmental Commission for Maximum Admissible Concentrations and Intensities in Poland established the NDS-MAC (TWA)<sup>1)</sup> value of 0,62 mg/m<sup>3</sup> for aziridine.

Determination of a worker's exposure to airborne aziridine is made using a XAD-2 resin tube (100/50 mg sections) coated with 1-naphthylisothiocyanate. The aziridine derivative formed was subsequently desorbed with acetonitrile and analysed by high performance liquid chromatography using a diode array detector. The working range for a 12-L air sample is 0,062 to 1,24 mg/m<sup>3</sup>.

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<sup>1)</sup> Maximum Admissible Concentrations

**BioArena – non analytical application of planar chromatography**

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BioArena is a system, which integrates the modern technique and biological results of bioautography with layer liquid chromatography, suitable for investigating biochemical interactions. It has proved to be very effective way for examining the mechanism of toxicity of substances. Planar chromatography is a suitable technique for studying both the hydrophobicity and biological activity of new substances.

In our investigations a group of fourteen newly synthesized organic compounds has been investigated. The substances have potentially high bioactivity and they may be regarded as herbicides for use in agriculture. The lipophilicity of the test substances has been described by two indices – the retention in water,  $\log k_w$ , calculated from chromatographic data obtained by RP TLC on RP-18 as stationary phase with buffer–methanol mixtures as mobile phases, and  $\log P$  parameters calculated from molecular structures. The mechanism of action of the substances tested was examined in BioArena system. We reported practical determination of the crucial role of HCHO in the mechanism of action of new compounds. In the studies we observed a decrease of toxicity against *Pseudomonas savastanoi* pv. *phaseolicola* when HCHO molecules were eliminated by use of HCHO-capturing molecules, i.e. L-arginine and reduced glutathione and an increase in toxicity when  $\text{Cu}^{+2}$  ions, formaldehyde promoters, were added to the system.

The results obtained with BioArena as a complex separation and detection system support earlier observations that formaldehyde and its reaction products play a special and crucial role in the effects of antibiotic in general. Planar liquid chromatographic technique seems to be suitable for studying both the hydrophobicity and biological activity of new potential pesticides.

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**A comparison of the essential oil fingerprints derived from selected sage (*Salvia*) species with use of thin-layer chromatography directly and indirectly coupled with mass spectrometry**

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The low-temperature analysis of essential oils derived from plants by means of TLC is a relatively novel approach to investigating these volatile compounds [1-3], and it challenges the long established approaches of the first choice, most of them based on the use of gas chromatography.

The low-temperature TLC analysis and fingerprinting of essential oils derived from various different sage (*Salvia*) species has already been presented in our papers [4,5].

In this study, we compare the performance of the TLC-MS system described in paper [5] (and used to obtain TLC/mass spectrometric fingerprints of essential oils derived from the different sage species) with performance of the new TLC-LC-MS separation/fingerprinting strategy. With use of this novel approach, preliminary low-temperature fractionation of the essential oils derived from the different sage species is followed by the high-performance liquid chromatographic separation and fingerprinting of individual fractions with use of the LC-MS system. Abundant chromatographic evidence is provided and relevant practical conclusions are drawn.

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**A comparison of the phenolic compound fingerprints derived from selected sage (*Salvia*) species with use of thin-layer chromatography directly and indirectly coupled with mass spectrometry**

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In our earlier studies [1-4], we presented the results of investigations focused on a comparison of phenolic compounds and essential oils originating from twenty different sage (*Salvia*) species by means of fingerprints obtained by TLC/densitometry, HPLC/DAD, and HPLC/ELSD. In paper [4], a comparative analysis of chromatographic fingerprints recorded for the different sage (*Salvia*) species with use of chemometrics was also given.

In this study, we compare fingerprinting performance of the TLC-MS system earlier described in paper [5] with the performance of the new TLC-LC-MS separation combined with fingerprinting. With use of this new approach, the preliminary TLC fractionation of phenolic acids and flavonoids derived from the several sage species is followed by the high-performance liquid chromatographic separation and fingerprinting of individual fractions with use of the LC-MS system. In that way, multidimensional fingerprints are obtained, with an enhanced content of analytical information. Abundant chromatographic evidence is provided and relevant conclusions are drawn.

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