

POSTER SESSION II

THURSDAY, JUNE 6th, 2013

CHAIRPERSONS:

Eveline De Mey and Łukasz Cieřła

1.

Chemometric comparison of the retention of 35 model compounds in HPLC gradient conditions with four columns and two gradient modifiers

Ewelina Bartuzi, Łukasz Komsta

*Department of Medicinal Chemistry, Faculty of Pharmacy
Medical University of Lublin, Jaczewskiego 4, 20-090 Lublin, Poland*

This study is a HPLC continuation of our earlier TLC studies. We have performed chemometric interpretation of 35 simple compounds in different TLC conditions and investigated the best ways to determine lipophilicity: on the RP18 plates¹, silica plates² and cyanopropyl plates³. The compounds were also subjected to an additional study about a closer look of extrapolation ways and averaging methods⁴. The current study is done with the same compounds on an unified HPLC system. We have used four columns LiChroCart 125 mm (C18, C18 endcapped, CN and DIOL) with two modifiers: acetonitrile and methanol. Each system was run in an unified gradient along 20 minutes with linear increasing modifier concentration in water from 10 to 90 %. Flow was set to 1 ml/min.

It can be shown, that the longest retention times were obtained with C18 encapped and methanol, whereas the shortest ones were noticed with DIOL column and acetonitrile. In general, the retention times are multicollinear (intercorrelated); two of compounds (antraquinone and 8-hydroxyquinoline) were outliers in DIOL systems (a very long retention time). PCA analysis on the retention time matrix explained 85.9% of total variance in PC1, 10.9% in PC2. However, PC2 information was related only to difference of the two outlying substances. When the two outliers are removed, PC1 explained 97.3% of variance, and PC2 1.3%. First PC represented an average retention, second PC represented differences in retention. It can be concluded, that differences on retention can be modelled as one main trend: some compounds have CN and DIOL retention times simultaneously increased, with parallel decrease of the retention in C18 endcapped column with methanol as the modifier.

Robust correlations between Log P and retention times were in range from 0.51 to 0.86, the best correlation was obtained on C18 non-endcapped column with methanol as a modifier.

-
- 1 J. Pharm. Biomed. Anal. 2010, 53, 4, 911-918
 - 2 J. Planar Chromatogr. 2012, 25, 1, 5-9
 - 3 J. Planar Chromatogr. 2012, 25, 5, 471-474
 - 4 Acta Chromatogr., in press

2.

STRUCTURE ACTIVITY RELATIONSHIP OF THIOSEMICARBAZONE DERIVATIVES

J. Bogocz, J. Polański

Department of Organic Chemistry, Institute of Chemistry,
University of Silesia, Katowice, Poland. jbogocz@us.edu.pl

Abstract: Structure-Activity Relationship is an approach designed to find relationship between chemical structure and biological activity of studied compounds. It is the concept of linking chemical structure to a chemical property or biological activity.

Thiosemicarbazones (TSC) are a class of compounds exhibiting a broad range of biological activity such as: anticancer, antibacterial, antiviral and antiparasitic. An increasing number of publications devoted to TSCs indicated the growing interest in this group of compounds. In this study we performed a query of chemical databases in a search for (Q)SAR that could explain the molecular basis of the TSC activity. The maximum common substructure and ADMET properties was used as molecular descriptor in our analyses.

Reference:

- Keiser MJ.** 2009. Predicting new molecular targets for known drugs. *Nature* 462: 175–181.
- Beraldo H., Gambino, D.** 2004. The wide pharmacological versatility of semicarbazones, thiosemicarbazones and their metal complexes. *Medicinal Chemistry* 4: 31-39.

3.

Application of TLC and HPLC to quantification of protoporphyrin IX, Zn-protoporphyrin IX, and hemin in Parma ham

Hannelore De Maere^{1,3}, Marlena Jaros², Marta Dziewięcka², Ilse Fraeye¹, Mieczysław Sajewicz², Hubert Paelinck¹, Teresa Kowalska²

¹Research Group for Technology and Quality of Animal Products, KaHo Sint-Lieven, Ghent, Belgium

²Department of General Chemistry, Institute of Chemistry, Katowice, Poland

³Food Quality Laboratory, ISA, Lille-Cedex, France

Porphyrins are naturally occurring organic heterocycles, which play an important role in metabolism of living organisms. All compounds which belong to this group can structurally be derived from the simplest porphyrin, known as porphin. The molecule of each porphyrin is built of four pyrrole rings coupled together with methane bridges (=CH-)⁵. Due to that, all these molecules are flat, stable, strongly coloured, and prompt to form complexes with metal ions. Porphyrins absorb light and have characteristic absorption spectra both in the visible and ultraviolet wavelength range⁶.

This study is devoted to quantification of three porphyrins, i.e., protoporphyrin IX, Zn-protoporphyrin IX, and hemin in Parma ham by means of thin-layer chromatography (TLC) and high-performance liquid chromatography (HPLC).

Protoporphyrin IX plays a specific role among all tetrapyrroles, as it is a kind of a template for a wide variety of naturally occurring compounds, e.g., for the investigated Zn-protoporphyrin IX and hemin. All these compounds affect the colour properties of meat, and moreover, Zn-protoporphyrin IX contributes to the formation of a characteristic stable red colour of Parma ham⁷.

Sample of Parma ham was pre-treated for the TLC and HPLC analyses, following the available data from the literature, with minor modifications of our own only³. The calibration curves for protoporphyrin IX, Zn-protoporphyrin IX, and hemin were elaborated both with aid of TLC and HPLC.

Thin-layer chromatographic analysis was carried out under the following working conditions: The ready-made chromatographic glass plates were pre-coated with RP-18 stationary phase and methanol was used as mobile phase. Development of the chromatograms was carried out to the distance of 15 cm in the normal chromatographic chambers after Stahl. After the development and drying, the chromatograms were first visually inspected in UV light and then densitometrically scanned.

High-performance liquid chromatographic analysis was performed with use of the C18 type stationary phase, in the isocratic mode with use of the following mobile phase: A + B, 9:1 (v/v). A: MeOH + DCM, 9:1 (v/v); B: H₂O + CH₃COOH, 97:3 (v/v). The assumed mobile phase flow rate was 0.8 mL min⁻¹.

Upon the results obtained, the adequate conclusions were drawn.

⁵ M. Biesaga, K. Pyrzyńska, M. Trojanowicz, *Porphyryns in analytical chemistry. A review*; Talanta 51, **2000**, 209-224.

⁶ I. Żak, *Porfiryny i pochodne*, W: I. Żak (red.). Chemia medyczna; ŚLAM, Katowice, **2001**, 298-299.

⁷ J. Wakamatsu, H. Odagiri, T. Nishimura, A. Hattori, *Quantitative determination of Zn protoporphyrin IX, heme and protoporphyrin IX in Parma ham by HPLC*; Meat Science 82, **2009**, 139-142.

4.

Principal Component Analysis and Hierarchical Clustering Analysis as novel approach for study bioactivity of α -adrenergic and imidazoline receptors ligands

Slavica Filipić (a), Katarina Nikolic (a), Adam Smoliński (b), and Danica Agbaba (a)

- (a) Institute of Pharmaceutical Chemistry, Faculty of Pharmacy, University of Belgrade, Vojvode Stepe 450, PO Box 146, 11000 Belgrade, Serbia,
knikolic@pharmacy.bg.ac.rs
- (b) Central Mining Institute, Department of Energy Saving and Air Protection, Plac Gwarków 1, 40-166 Katowice, Poland

Abstract

Pharmacological profile of 29 drugs, α -adrenergic/imidazoline receptors ligands and related compounds, were studied by Principal Component Analysis (PCA) and Hierarchical Clustering Analysis (HCA). Chromatographic retention parameters (logK_w at pH 4.4, *S* at pH 4.4, logK_w at pH 7.4, *S* at pH 7.4, logK_w at pH 9.1, and *S* at pH 9.1), capillary electrophoresis migration parameters (μ_{eff} at pH 4.4, μ_{eff} at pH 7.4, and μ_{eff} at pH 9.1), and computed molecular descriptors [1-6] of the 29 ligands were used as variables in the chemometric clustering approach. The PCA and HCA of the 29 drugs in the space of the 34 descriptors provided clustering of the compounds in terms of studied descriptors. The final analysis of the HCA dendrogram, sorted according to the Ward linkage method with the data color map, provided additional sub-clustering of the formed HCA sub-clusters and allowed specific grouping of the examined drugs with the highest agreement with their activities on α -adrenergic and imidazoline receptors and with their pharmacological and side effects. The presented chemometric approach could be used as simple and reliable tool for initial investigation of pharmacological activities of novel α -adrenergic and imidazoline receptors ligands.

References

1. Becke A.D., Density-functional thermochemistry. III. The role of exact exchange, J. Chem. Phys. , 1993, 98, 5648-5652,
2. Lee C.; Yang W.; Parr R.G.; Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. Phys. Rev. B Condens. Matter. 1988, 37, 785-789.
3. Gaussian 98 (Revision A.7), M. J. Frisch at al., Gaussian, Inc., Pittsburgh PA, 1998.
4. ChemAxon Marvin 5.5.1.0 program, Budapest, Hungary, 2011.
www.chemaxon.com/products.html
5. CS Chem3D Ultra 7.0, Cambridge Soft Corporation, (Property Picker ActiveX Control), 100 Cambridge Park Dr. Cambridge, MA 02140-2317 U.S.A., 2001.
<http://www.cambridgesoft.com/>
6. Dragon 6, TALETE srl, Via V. Pisani, 13 - 20124 Milano – Italy. <http://www.talete.mi.it>

5.

GAS CHROMATOGRAPHY COMBINED WITH MASS SPECTROMETRY AS A TOOL FOR FOOD QUALITY

CONTROL

JADWIGA GABOR, MARTA ŁĘŻNIAK, SYLWIA GOLBA
TOMASZ FLAK, ANDRZEJ SWINAREW*

¹ *University of Silesia, Institute of Materials Science,*
*ul. Bankowa 14, 40-007 Katowice, * andrzej.swinarew@us.edu.pl*

Keywords: gas chromatography, quality control, mass spectrometry.

Quality control for different kind of beer presented on the market were performed using a gas chromatograph Shimadzu GCMSQP2010 Plus, with a capillary column ZB5 MSi 30 m length and a diameter 0.25 mm, with film thickness 0.25 μ and installed precolumn 5 m length. Injector temperature was set to 250 °C, column temperature was changed in the range from 100 °C (1 min isothermal) to 250 °C at the rate of 25 °C/min, transfer line temperature was equal to 250 °C. Identification of compounds was based on comparative analysis of the spectra obtained from a library of mass spectra JWS (John Wiley and Sons), and then by comparing the mass spectra and retention times of test compounds and standards.

The analysis was performed using an internal standard method with caffeine as a reference compound. Samples were degassed and mixed in a 1:1 ratio with the standard solution.

Quality control was performed due to determine the amount of propylene glycol in beer. The amount of propylene glycol was in the range from 4 to 67 mg/dm³

6.

GPC AS A TOOL FOR ANIONIC POLYMERIZATION OF PROPYLENE OXIDE CONTROL

SYLWIA GOLBA¹, JADWIGA GABOR¹, MARTA ŁEŻNIAK¹,
TOMASZ FLAK¹, BEATA SWINAREW², ANDRZEJ SWINAREW^{1,*}

¹ *University of Silesia, Institute of Materials Science,*

*ul. Bankowa 14, 40-007 Katowice, * andrzej.swinarew@us.edu.pl*

² *Institute for Engineering of Polymer Materials and Dyes, Paint and Plastics Department,
44-100 Gliwice, Poland*

Keywords: size exclusion chromatography (SEC), mass spectrometry, MALDI TOF.

In novel chemical laboratory there is a lot of techniques to analyze material during the synthesis process. Each of these techniques can measure different properties. Sometimes it is necessary to confirm results or combine them. But only all techniques together are able to well describe analyzed material.

This work is an attempt to describe polymers and control the polymerization process in real-time using three analytical methods mainly GPC because of its simplicity and TTL properties. Every of analyzed materials are typical for industry. For all polymers were used matrix-assisted laser desorption/ionization time of flight (MALDI TOF) supported with gas chromatography combined with mass spectrometry (GC-MS) as a reference technique.

7.

Determination flavonols and phenolic acids in *Andrographis paniculata* and dietary supplements

J. Kadłubowska, A. Filipiak-Szok*, M. Kurzawa, E. Szłyk

Nicolaus Copernicus University, Faculty of Chemistry,
Chair of Analytical Chemistry and Applied Spectroscopy,
Gagarin 7 St., 87-100 Toruń, Poland
*E-mail: ania_f@doktorant.umk.pl

Andrographis paniculata (AP) annual shrub (family *Acanthaceae*, literally "king of bitters" or known as an Ayurveda herb *Kalamegha*) grows abundantly in India, Sri Lanka, Taiwan, China and Thailand. The aerial parts of the plant (leaves, roots and stems) are used for extraction of the active phytochemicals. *Andrographis paniculata* Nees is used for several applications in traditional Chinese medicine to treat many diseases and infections. In Europe is a component of dietary supplements.

In the present work, a method involving water-bath extraction (with ethanol or water), HPLC – RP- C18 column chromatography with photodiode array detection was developed for determining the level of quercetin derivatives (e.g., quercitrin, hyperoside, rutin, and keampherol) and derivatives of benzoic and cinamic acids (gallic, caffeic, chlorogenic, ferulic, p-hydroxybenzoic acid) in *Andrographis paniculata* and dietary supplements containing AP. The impact of hydrolysis digestion was also tested.

The HPLC -PDA system was applied. Phenolic acids were detected at two wavelengths: 254 and 325 nm, using a 45-min program, while flavonols were identified at 360 nm, in 50-min gradient program. Analyses were carried out on Discovery RP-C₁₈ column (5 μm particle size, 150×4,6 mm, SUPELCO), maintained at 30°C. Mobile phase for phenolic acids was A: 2% acetic acid and phase B: methanol, whereas for flavonols was A: isopropanol-water (95:5 v/v) and B: isopropanol-water-THF (50:40:10 v/v). The rate-flow was 1 ml/min in both programs. The total amount of studied flavonols and phenolic acids was compared with total content of polyphenols using Folin-Ciocalteu's method.

Research was funded by „CHEMO-KOP – Rozwój nowoczesnych studiów CHEMICZNYCH II stopnia w Uniwersytecie Mikołaja KOPernika dla zwiększenia liczby absolwentów kierunków o szczególnym znaczeniu dla gospodarki” realizowany w ramach Poddziałania 4.1.2 Programu Operacyjnego Kapitał Ludzki – grant nr 23/2012.

8.

Investigation of cyclohexene oxidation mechanism over nanogold catalyst using NMR and GC-MS methods.

Maciej Kapkowski¹, Piotr Bartczak^{1,2}, Jarosław Polański

¹University of Silesia in Katowice, Institute of Chemistry, Department of Organic Chemistry, Poland

²JARS Research Center LLC., 05-070 Sulejówek, 11 Listopada Street

Abstract

Gold nanoparticles catalyze a wide range of the oxidation reactions.¹ Simple hydrocarbons, due to their structural minimalism are excellent model objects, which provides to obtain useful oxidation model, given the importance of such conversion currently we are still looking the new catalysts which will be more efficient in this type of reactions. One of the first alkene oxidised over Au/C or Bi-Au/C was cyclohexene reacted with tert-butyl hydroperoxide (TBHP) in 1,2,3,5-tetramethylbenzene.²

The aim of this study was to optimize the conditions of the selective oxidation of cyclohexene using nanogold catalysts of varying Au percent (0.1%, 1.0%, 5.0%, 10.0%) on a matrix of SiO₂, using 30% aqueous hydrogen peroxide solution (H₂O₂). The optimization of the oxidation process involved: the percentage of gold, temperature and reaction times.

Literature:

1 Y. Zhang, X. Cui, F. Shi, Y. Deng, *Chem. Rev.*, 2011, DOI:10.2011/CR200260m.

2 M. D. Hughes, Y. -J. Xu, P. Jenkins, P. McMorn, P. Landon, D. I. Enache, A. F. Carley, G. A. Attard, G. J. Hutchings, F. King, E. H. Stitt, P. Johnston, K. Griffin, C. J. Kiely, *Nature*, 2005, **437**, 1132.

Correspondence address: kapkowski.maciej@vp.pl

²Author received a grant for the project *DoktoRIS - Scholarship program for innovative Silesia* co-financed by the European Union in the framework of the ESF

Determination of purine alkaloids in some Asiatic plants

D. Kasiorkiewicz, A. Filipiak-Szok*, M. Kurzawa, E. Szłyk

Nicolaus Copernicus University, Faculty of Chemistry,
Chair of Analytical Chemistry and Applied Spectroscopy,
Gagarin 7 St., 87-100 Toruń, Poland
*E-mail: ania_f@doktorant.umk.pl

Alkaloids usually have strong, sometimes toxic physiological effects on the human body. Many toxic alkaloids respectively served in low doses are an effective drug for various diseases and conditions (such as morphine, codeine or quinine). Many alkaloids are also components of stimulants (caffeine, theobromine, nicotine). Purine alkaloids, such as caffeine, theobromine and theophylline were detected and analyzed in some Asiatic plants (*Cola accuminata*, *Embllica officinalis*, *Andrographis paniculata*, *Puearia lobata* and *Garcinia cambogia*). Alkaloids were also identified in tea and coffee samples.

In the present work, HPLC-PDA method is developed for determining the level of purine alkaloids. The HPLC system equipped with auto sampler and photodiode array, SHIMADZU (Kyoto, Japan) was applied. Analyses were carried out on Discovery RP-C₁₈ column (5 µm particle size, 150×4,6 mm, SUPELCO), maintained at 25°C. The impact of extraction method (SPE, ultrasonic, water-bath), solvent (methanol, ethanol, water, chloroform, and sodium carbonate), pH, procedure and various extraction conditions (time and temperature) were tested. The optimal conditions were ultrasonic extraction at pH=9.0 (sodium carbonate and methanol, 2:3, v/v), then extracts were shared in two fraction. One was at SPE, second was shaking with chloroform. These two fractions were evaporated, the residue dissolved in methanol and analyzed by HPLC-PDA method. The recovery for caffeine standard was 101.23%, while for theophylline 91.05%. The developed method was validated for specificity, repeatability, recovery and accuracy.

Application of Analysis of Variance to different forms of HPLC-UV/VIS data

Małgorzata Kazura¹, Piotr Zerzucha¹, Beata Walczak¹, Dalene de Beer², Elizabeth Joubert^{2, 3}, Alexandra E. Schulze², Theresa Beelders², André J. de Villiers⁴

¹Institute of Chemistry, The University of Silesia, Katowice, Poland

²Post-Harvest and Wine Technology Division, Agricultural Research Council (ARC), Stellenbosch, South Africa

³Department of Food Science, Stellenbosch University, Matieland (Stellenbosch), South Africa

⁴Department of Chemistry and Polymer Science, Stellenbosch University, Matieland (Stellenbosch), South Africa

Nowadays, hyphenated chromatographic techniques are standard analytical tools to solve complex analytical problems. The power of combining separation techniques with multivariate detection methods (usually spectroscopic techniques) has been demonstrated over the years for both quantitative and qualitative analysis of unknown compounds in complex natural extracts. Chromatography produces pure or nearly pure fractions of chemical components of the studied mixture and multivariate detection methods produces selective information for identification using standards or library spectra [1]. Hyphenated techniques are often the methods of choice in order to obtain fingerprints of complex mixtures, such as blood or urine samples, herbal extracts, etc. where the goal is to find differences among samples and to identify components responsible for these differences. These techniques are known to provide a huge amount of data, since each sample is characterized by a two-way data table [2]. Having at our disposal the HPLC-UV/VIS data (signals registered for rooibos tea samples), we can build different forms of data representation for the set of m samples. These can be: a collection of two dimensional individual signals, mean chromatograms, and a peak table. All of these forms require intensive signal preprocessing, prior to data analysis. In our study we propose a new form of data representation well suited for chromatographic data originating from multi-channel detection, namely inbound-pairwise representation. The biggest advantage is that any kind of chemometric analysis can be performed directly for hyphenated chromatographic data, because the proposed approach (inbound-pairwise representation), eliminates the need for time consuming warping of the studied signals and allows elimination of all problems associated with the peak correspondence. In our study Analysis of Variance was performed for all those different forms of a studied data set.

References:

- [1] K.N. Patel, J.K. Patel, M.P. Patel, G.C. Rajput, H.A. Patel, *Pharm. Methods*, 1(2010) 2.
- [2] M. Daszykowski, R. Danielsson, B. Walczak, *J. Chromatogr. A*, 1192 (2008) 157.

Multivariate curie resolution In thin layer chromatography

Mariola Kobyłka, Łukasz Komsta

*Department of Medicinal Chemistry, Faculty of Pharmacy
Medical University of Lublin, Jaczewskiego 4, 20-090 Lublin, Poland*

It was recently proven by us, that the most popular spot purity approach in TLC, based on correlation of spectra measured in three places of the spot, cannot detect even large amount of contamination in certain cases⁸. These results should be taken seriously, as common spectral similarity between drugs and impurities can additionally increase the risk of presence of unnoticed inhomogeneities.

The chemometric techniques are very helpful in testing for homogeneity. The main difference between HPLC and TLC is the nonlinearity of detector response and this was the subject of our second recent study⁹, where we tested chemometric approaches of peak purity testing. It was concluded, that the simplest recommended method could be visual inspection of Principal Component Analysis (PCA) scores, as this method is most sensitive to inhomogeneity in the case of nonlinearity, spectral similarity and high overlap.

If the inhomogeneity is detected inside the spot, an average analyst wants then to obtain spectral profiles, estimated by the application of curve resolution methods. These methods try to find bilinear decomposition of spot matrix with one important constraint: spectral and concentration profiles must be nonnegative. This is the last part of our study and the subject of current poster. It discusses usefulness of self modelling multivariate curve resolution (nonnegative matrix factorization) as a chemometric tool for analysis of inhomogeneous spots captured by densitometer in multivariate way. Two examples are analyzed: a spot of decomposed aspirin with comparative spot of pure salicylic acid, and spots of overlapped ciprofibrate and clofibric acid.

In general, this approach works well in the case of TLC and the algorithm finds reliable spectral and concentration profiles, even with high overlap and spectral similarity. Nonlinearity does not affect this algorithm in visible manner.

8 M. Kobyłka, Ł. Komsta, *Acta Chromatographica* 24(2012)3, 433–444.

9 Ł. Komsta, M. Kobyłka, *J. Chrom. Sci.* doi:10.1093/chromsci/bms154

12.

The Investigation of the Sonogashira coupling in a heterogeneous system using chromatographic techniques.

M. Korzec¹, P. Bartczak^{1,2}, J. Polański¹

¹ University of Silesia, Institute of Chemistry, Department of Organic Chemistry

² JARS Research Centre Sp. z o. o., 05-070 Sulejówek, 11 Listopada Street

Sonogashira Coupling is used to form the C-C bonds between atoms of various hybridizations. Currently, most of the reactions are carried out in homogeneous systems using palladium catalysts such as: Pd(PPh₃)₂Cl₂, supported by a various compounds of copper(I), Ag₂O, silver or other. The Mechanism of Sonogashira coupling is not clearly understood.

In our work we used a novel heterogeneous catalysts in Sonogashira coupling. We revealed that, the whole system is influenced by temperature, time and the amount of phosphine. Various chromatographic methods were used for the purpose of this study. This includes: TLC, HPLC and HPLC-ESI-MS. These techniques provide qualitative and quantitative specification of the reaction products. Based on our studies and results we hypothesized that in the Sonogashira coupling a couple of products appeared, which depends on conditions such as: temperature, time and the amount of phosphine.

Literature:

R. Chinchilla, C Najera "The Sonogashira Reaction: A Booming Methodology in Synthetic Organic Chemistry". Spain : American Chemical Society, 2007, 107.

K. Sonogashira. "Development of PD-CU catalyzed cross-coupling of terminal acetylenes with sp²-carbon halides". Japan : Journal of Organo metallic Chemistry, 2001. 663.

Correspondence address: korzec@autograf.pl

² Author received a grant for the project DoktoRIS - Scholarship program for Innovative Silesia co-financed by the European Union in the framework of the ESF

13.

Comparative analysis of diesel oil samples of different origin based on chromatographic fingerprints

B. Krakowska^a, M. Daszykowski^a, I. Grabowski^b, G. Zaleszczyk^b, M. Sznajder^b

^a*Institute of Chemistry, The University of Silesia, 9 Szkolna Street, 40-006 Katowice, Poland*

^b*Customs Chamber of Customs Laboratory in Biala Podlaska
21 Celnikow Polskich Street, 21-500 Biala Podlaska, Poland*

Diesel oil is a very popular fuel used for transport purposes. It is a mixture of hydrocarbons refined from petroleum and contains additives modifying physico-chemical properties. To ensure certain quality of diesel fuel a constant monitoring of its chemical composition is required. Gas chromatography (GC) is one of the most popular techniques used for this purpose. It has a potential to separate and quantify chemical components. Gas chromatography aims to describe a sample by its chromatographic profile regarded as a fingerprint. However, the comparative analysis of chromatographic fingerprints requires application of advanced chemometric techniques.

In this work chromatographic fingerprints of diesel oils differed with respect to geographical location were characterized using gas chromatography with the flame ionization detection, GC-FID. Prior to analysis raw chromatograms were baseline corrected with the penalized asymmetric least squares approach (P-ALS) [1]. Then, correlation optimized warping (COW) [2] was used to correct misalignment of chromatographic peaks. Preprocessed fingerprints were a subject to further comparative analysis.

In order to visualize the differences between diesel oil samples principal component analysis (PCA) [3] was used. This exploration method allows distinguishing two groups of samples. It is possible to conclude the observed groups differ in content of fatty acid methyl esters, FAME. It is important to stress that preprocessing of chemometric fingerprints is an important step in comparative analysis and can greatly influence its results and conclusions.

Literatura

[1] P. H. C. Eilers, *Anal. Chem.*, 2003, 75, 3631-3636

[2] N. Nielsen, J. Carstensen, J. Smedsgaard, *J. Chromatogr. A*, 1998, 805, 17

S. Wold, K. Esbensen, P. Geladi, *Chemom. Intell. Lab. Syst.*, 1987, 2, 37-52

Ustawa z dnia 27 maja 2011r. o zmianie ustawy o systemie monitorowania i kontrolowania jakości paliw oraz innych ustaw [Act amending the act on the system for monitoring and controlling the quality of fuels and other acts], (Dz.U. 2011 nr 153 poz. 902)

[3]

[4]

14.

Estimation of linear isotherm model parameters in Supercritical Fluid Chromatography (SFC)

Marek Leśko^a, Donald P. Poe^b, Krzysztof Kaczmarek^a

a) Department of Chemical and Process Engineering, Rzeszow University of Technology, 35-959 Rzeszow, Poland

b) Department of Chemistry and Biochemistry, University of Minnesota Duluth, Duluth, MN 7 55812 USA.

ABSTRACT

Supercritical fluid chromatography is one of the most attractive separation methods among chromatographic techniques. The use of mainly the carbon dioxide as mobile phase which is environmentally friendly, nontoxic, non-flammable, inexpensive makes SFC forward – looking separation technique. This is also consistent with so called “green chemistry” which is currently preferred in industrial applications. Moreover, industrial laboratories require faster and more efficient separation techniques such as SFC which allow achieve shorter retention times than HPLC ever shorter than in Ultra - High Performance Liquid Chromatography. Because of this advantages SFC is still develop.

Mathematical modelling of the chromatography process requires knowledge of the isotherm model. Therefore a necessary step in numerical calculations is estimation of isotherm model parameters. In this study the inverse method has been successfully used to estimation of linear isotherm model parameters in SFC. Estimation was done directly on the base of retention times of experimental profiles obtained in SFC by inverse method which minimize difference between calculated and experimental retention times. Experimental data were obtained for alkylbenzenes. The mobile phase was carbon dioxide-methanol, 95/5% v/v. The 250 mm x 4.6 mm i.d. column packed with 5 – micron Luna C18 particles was used. Separation was done for outlet pressure from 100 bar to 150 bar in different sets of experimental conditions: (1) column is operated under convective air; (2) column is operated in still air conditions. To estimate five parameters of linear isotherm model five experimental data were chosen which were obtained for column operated in still air conditions where radial gradients of temperature can be neglected. The estimation method was validated by comparing the appropriate experimental data with calculated on the basis of a mathematical model and estimated parameters of linear isotherm model. It was achieved good agreement.

15.

ANALYSIS OF SELECTED NON-STEROIDAL ANTI- INFLAMMATORY DRUGS FOR ANIMALS USING
THE CHROMATOGRAPHIC TECHNIQUES.

MARTA ŁEŻNIAK, JADWIGA GABOR, SYLWIA GOLBA
TOMASZ FLAK, ANDRZEJ SWINAREW*

¹ *University of Silesia, [Insitute of Materials Science](#),
ul. Bankowa 14, 40-007 Katowice, * andrzej.swinarew@us.edu.pl*

Non-steroidal anti-inflammatory drugs for small animals are used to control the pain and inflammation associated with osteoarthritis in pets. From the wide range, were selected four examples of anti- inflammatory drugs and were compared with standards (sample 1-4). In the present study the HPLC technique was used as the tool for analysis of active substance and cover of the analgesics pill as well as the quality of active substance control. The analgesics were respectably separated by the use of HPLC column Pinnacle DB PAH Dimensions: 50mm x 2.1mm ID Particle Size: 1.9µm Pore Size: 140Å, temp.: 30°C sample eluent: ACN/MeOH, conc from.: 20µg/mL each component inj. vol.: 5µL, mobile Phase A: water B: MeOH/ACN. Flow: 0,2-0,9mL/min. The chosen UHPLC system was equipped with micro-mixer, DAD and FLD detectors. For better identification and system efficiency determination the active compounds from each medicament were determined by the use of GC/MS system. Several chemicals were chosen for analysis, in the group were selected respectably: sample 1 - carprofen, sample 2 - tolfenamic acid, sample 3 - meloxicam, sample 4 – robenacoxib.

16.

STABILITY OF LIPOPHILIC VITAMINS IN FODDER PREMIXES

Joanna Maćkowiak^{1,2}, Adam Voelkel¹, Zuzanna Okulus¹

¹Poznań University of Technology, Institute of Chemical Technology and Engineering, Poznań, Poland

²Cargill (Poland) Inc., Department Kiszkowo, Poland

Spectrophotometric and chromatographic method were applied in the examination of the stability of selected lipophilic vitamins, i.e. vitamin A and vitamin E. These were used in the form of their acetates what ensures their higher stability in the final product. However, the storage of the products, e.g. fodder premixes, is accompanied by the significant decrease of the content of both vitamins what results in the decrease of products quality. The series of fodder premixes of different composition were examined both standard procedures. Fourier transform infrared spectroscopy (FTIR), high performance liquid chromatography (HPLC) and MS-ESI techniques were also used in the examination of the products after prolonged storage time. The results of the experiments allowed to present the preliminary conclusions concerning the magnitude and the factors influencing the vitamins degradation.

17.

TLC determination of tiapride hydrochloride and its impurities in pharmaceuticals

Katarina Ranković, Slavica Filipić, Katarina Nikolić, Danica Agbaba*

Department of Pharmaceutical Chemistry, Faculty of Pharmacy, University of Belgrade, Vojvode Stepe 450, Belgrade, Serbia

Tiapride (N-[2-(diethylamino)ethyl]-2-methoxy-5-(methylsulfonyl)benzamide) hydrochloride) is a substituted benzamide with the D₂/D₃ dopamine receptor antagonist activity and it belongs to the atypical antipsychotics with general properties similar to those of sulpiride.

Hydrolysis under the forced acidic and basic conditions leads to the hydrolysis of the amide bond to give 2-methoxy-5-methylsulphonylbenzoic acid (impurity I) and to the cleavage of the methoxy group (which is a vinylogous ester and therefore activated to hydrolytic cleavage by the virtue of being *ortho* to the ester functionality and *para* to the sulphone), to yield N-(2-diethylaminoethyl)-2-hydroxy-5-methylsulphonylbenzamide (impurity II). Also, tiapride can be oxidized under relatively drastic conditions to give N-oxide, i.e., N-(2-diethylaminoethyl)-2-methoxy-5-methylsulphonylbenzamide-N'-oxide (impurity III).

A simple, rapid, accurate and precise HPTLC method is presented for simultaneous determination of tiapride hydrochloride and its three degradation impurities (I, II, and III), which have to be monitored in pharmaceutical dosage forms according to the manufacturer requirements of 0.2 %. Analysis of tiapride hydrochloride and impurities I, II, and III, was performed on silica gel 60 F₂₅₄ HPTLC plates using methylene chloride-methanol-concentrated ammonia, 9:1.6:0.1 (v/v) as mobile phase. Detection was performed at 240 nm. All validation requirements, specificity, linearity ($r \geq 0.997$), recovery (95.08 %-100.39 %), limit of quantification (0.1-0.2 %), and robustness were examined and fulfilled, and the proposed method can be successfully applied for the quality control analysis of commercially available tablets and injections.

Determination of water-soluble vitamins in European and Asiatic spices

M. Smolińska, A. Filipiak-Szok*, M. Kurzawa, E. Szłyk

Nicolaus Copernicus University, Faculty of Chemistry,
Chair of Analytical Chemistry and Applied Spectroscopy,
Gagarin 7 St., 87-100 Toruń, Poland

*E-mail: ania_f@doktorant.umk.pl

Vitamins are a broad group of organic compounds that are minor, but essential, constituents of food required for normal growth, self-maintenance, and functioning of human and animal bodies. These compounds can be classified in two main groups – water-soluble and fat-soluble vitamins. Because of the critical role of vitamins in nutrition and their relative instability, qualitative and quantitative analyses are important issues and a challenging task for food manufacturers.

In the present work, a method involving water-bath extraction, SPE (Bakerbond C₁₈ (500-mg) cartridges) and HPLC – RP- C18 column chromatography with photodiode array detection is developed for determining the level of vitamins (e.g. ascorbic acid, folic acid, thiamine (vitamin B₁), D-biotin (vitamin B₇), niacinamide (vitamin B₃), calcium D-Pantothenate (vitamin B₅), pyridoxine hydrochloride (vitamin B₆), folic acid, and riboflavin (vitamin B₂) in European (pepper, basil, curcuma, thyme, cinnamon and ginger) and Asiatic spices (*Ocimum sanctum*, *Curcuma longa*, Ceylon cinnamon, Ginger root). The impact of procedure and various extraction conditions were tested.

The HPLC-PDA system was applied. Analyses were carried out on Discovery RP-C₁₈ column (5 µm particle size, 150×4,6 mm, SUPELCO), maintained at 35°C. Mobile phase was A: 0.1 M KH₂PO₄ (pH 7.0) and B: methanol, in ratio 90:10 at isocratic condition. The rate-flow was 0.7 ml/min. Identification of compounds was achieved by comparing their retention times and UV spectra with those of standards stored in a data bank. The accuracy of the method was tested by measuring average recovery; values ranged between 97.65 and 99.40%.

Chemometric approach to lipophilicity of selected cosmetic raw materials

Anna W. Sobańska, Elżbieta Brzezińska

Zakład Chemii Analitycznej
Katedra Chemii Medycznej
Uniwersytet Medyczny w Łodzi
ul. Muszyńskiego 1 Łódź
anna.sobanska@umed.lodz.pl

Retention parameters R_f and R_m were obtained for 16 cosmetic raw materials by thin-layer chromatography on RP-18 stationary phase using water-organic modifier (acetone, methanol, dioxane, acetonitrile, dimethylformamide or tetrahydrofurane) binary mixtures as mobile phases. First principal components (PC1) were calculated for R_f and R_m values obtained for each organic modifier used throughout this study and correlated with lipophilicities calculated *via* different methods (ALOGPs, AClogP, ABlogP, milogP, ALOGP, MLOGP, KOWWIN, XLOGP2, XLOGP3, ACDLab) and with experimental $\log P_{o/w}$ found for 9 out of 16 investigated compounds. Analysis of correlations of PC1 calculated for R_f and R_m values revealed significant differences between the organic modifiers investigated with respect to chromatographic estimation of lipophilicity of studied compounds.

Acknowledgements

This work was supported by an internal grant from the Medical University of Lodz, Poland (no. 503(3-016-03)503-01).

Thanks are due to Merck and BASF for free samples of sunscreens used through this investigation.

20.

Single chromatographic run approach to lipophilicity of selected cosmetic raw materials

Anna W. Sobańska, Elżbieta Brzezińska

Zakład Chemii Analitycznej
Katedra Chemii Medycznej
Uniwersytet Medyczny w Łodzi
ul. Muszyńskiego 1 Łódź
anna.sobanska@umed.lodz.pl

Retardation factors R_f were obtained for 22 cosmetic raw materials by thin-layer chromatography on RP-18 stationary phase using water-organic modifier (acetone, methanol, dioxane, acetonitrile, dimethylformamide or tetrahydrofurane) binary mixtures as mobile phases. R_m values were calculated for different concentrations of organic modifiers (60, 70, 80 and 90 % v/v) in mobile phase and correlated with lipophilicities obtained *via* different theoretical methods (ALOGPs, AClogP, ABlogP, milogP, ALOGP, MLOGP, KOWWIN, XLOGP2, XLOGP3, ACDLab) and with experimental $\log P_{o/w}$ found for 9 out of 22 investigated compounds. Analysis of correlations of R_m values with calculated and experimental $\log P$ values suggested that R_m values obtained for a single chromatographic run may be an interesting alternative to R_m^0 (retention factor extrapolated to zero concentration of an organic modifier) for compounds of moderate lipophilicity ($0 < \log P < 6$).

Acknowledgements

This work was supported by an internal grant from the Medical University of Lodz, Poland (no. 503(3-016-03)503-01).

Thanks are due to Merck and BASF for free samples of sunscreens used through this investigation.