

REPORT ON CITING REFERENCES OF THE PUBLISHED ARTICLES**ARTICLE I**

Title: *Retention of ionisable compounds on high-performance liquid chromatography - XV. Estimation of the pH variation of aqueous buffers with the change of the acetonitrile fraction of the mobile phase.*

Author(s): Xavier Subirats, Elisabeth Bosch and Martí Rosés.

(Departament de Química Analítica, Universitat de Barcelona)

Source: JOURNAL OF CHROMATOGRAPHY A 1059 (1-2): 33-42 DEC 3 2004

Document Type: Article

Publisher: ELSEVIER SCIENCE BV, PO BOX 211, 1000 AE AMSTERDAM, NETHERLANDS

IDS Number: 875HY

ISSN: 0021-9673

DOI: 10.1016/j.chroma.2004.09.085

Citing references (13):

Title: *Effects of trifluoroacetic acid concentrations in mobile phases on HPLC retention of zwitterionic and weakly basic triazole derivatives.*

Author(s): Kailin Guan and David C. Palmer.

(Johnson & Johnson Pharmaceutical Research and Development, LLC, Raritan, New Jersey, USA)

Source: JOURNAL OF LIQUID CHROMATOGRAPHY & RELATED TECHNOLOGIES 29 (3): 415-430 2006

Document Type: Article

Abstract: Minor changes in the concentration of trifluoroacetic acid (TFA), a popular acidic HPLC mobile phase modifier, resulted in dramatic affects on hydrophobic retention. Two 1,2,4-triazole carboxylic acids and the corresponding decarboxylated 1,2,4-triazoles were chromatographed using a reversed-phase column with 0.01% to 0.4% TFA in the mobile phases. Retention time shifts and reversed elution orders were observed. At low TFA concentrations, the decarboxylated 1,2,4-triazoles eluted earlier, whereas at high TFA concentrations the two 1,2,4-triazole carboxylic acids eluted earlier. An increased capacity factor, when TFA concentrations exceeded 0.05%, exhibited an increased hydrophobicity as a result of TFA-associated chaotropic effects. Formic acid, acetic acid, or phosphoric acid were not as effective as TFA and attenuated the retention shifts significantly such that the reversed order of elution was no longer observed. The use of a combination of TFA and triethylamine (TEA) generated similar chromatographic profiles to those obtained when TFA was used alone. In conclusion, ideal HPLC separations of zwitterionic and weakly basic compounds could sometimes be obtained simply by optimizing TFA concentration in mobile phases.

Publisher: TAYLOR & FRANCIS INC, 325 CHESTNUT ST, SUITE 800, PHILADELPHIA, PA 19106 USA

IDS Number: 007SR

ISSN: 1082-6076

DOI: 10.1080/10826070500452077

Title: *Automation of pH optimization experiments during LC development.*

Author(s): E. Loeser, S. Babiak, P. Zhu, G. Yowell, M. Konigsberger and P. Drumm.
(Chemical and Analytical Development, Novartis Pharmaceuticals, East Hanover, NJ, USA)
Source: CHROMATOGRAPHIA 63 (7-8): 345-351 APR 2006

Document Type: Article

Abstract: The selection of an optimal mobile phase pH under solvent gradient conditions is experimentally challenging. Although quaternary pumps are widely available, they are often used in binary mode to run simple solvent gradients with one pH-adjusted buffer at a time. A more effective use of quaternary pumps is to deliver two different aqueous buffer components (A and B) in a constant proportion to simulate a single, premixed buffer component, while simultaneously producing a solvent gradient by increasing the organic solvent component (S). This approach largely automates the pH optimization experiments. A more detailed investigation of pH effects becomes possible with less time and effort. Once a suitable pH has been identified, the same separation can be reproduced by a simpler binary gradient method which is more suitable for routine work. This study demonstrates the feasibility of this approach both theoretically and through actual.

Publisher: VIEWEG, ABRAHAM-LINCOLN-STRASSE 46, POSTFACH 15 47, D-65005 WIESBADEN, GERMANY

IDS Number: 040AP

ISSN: 0009-5893

DOI: 10.1365/s10337-006-0759-0

Title: *Retention of ionisable compounds on high-performance liquid chromatography XVI. Estimation of retention with acetonitrile/water mobile phases from aqueous buffer pH and analyte pK_a.*

Author(s): Xavier Subirats, Elisabeth Bosch and Martí Rosés.
(Departament de Química Analítica, Universitat de Barcelona)

Source: JOURNAL OF CHROMATOGRAPHY A 1121 (2): 170-177 JUL 21 2006

Document Type: Article

Abstract: In agreement with our previous studies and those of other authors, it is shown that much better fits of retention time as a function of pH are obtained for acid-base analytes when pH is measured in the mobile phase, than when pH is measured in the aqueous buffer when buffers of different nature are used. However, in some instances it may be more practical to measure the pH in the aqueous buffer before addition of the organic modifier. Thus, an open methodology is presented that allows prediction of chromatographic retention of acid-base analytes from the pH measured in the aqueous buffer. The model presented estimates the pH of the buffer and the pK_a of the analyte in a particular acetonitrile/water mobile phase from the pH and pK_a values in water. The retention of the analyte can be easily estimated, at a buffer pH close to the solute pK_a, from these values and from the retentions of the pure acidic and basic forms of the analyte. Since in many instances, the analyte pK_a values in water are not known, the methodology has been also tested by using Internet software, at reach of many chemists, which calculates analyte pK_a values from chemical structure. The approach is successfully tested for some pharmaceutical drugs.

Publisher: ELSEVIER SCIENCE BV, PO BOX 211, 1000 AE AMSTERDAM, NETHERLANDS.

IDS Number: 062RZ

ISSN: 0021-9673

DOI: 10.1016/j.chroma.2006.03.126

Title: *Effect of the density of the C-18 surface coverage on the adsorption mechanism of a cationic compound and on the silanol activity of the stationary phase in reversed phase liquid chromatography.*

Author(s): Fabrice Gritti^a and Georges Guiochon^b.

(^aDepartment of Chemistry, University of Tennessee, Knoxville, TN 37996-1600, USA;

^bDivision of Chemical Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6120, USA)

Source: JOURNAL OF CHROMATOGRAPHY A 1132 (1-2): 51-66 NOV 3 2006

Document Type: Article

Abstract: RPLC columns with different surface coverages (a C-1 endcapped column with a bonding density of 3.92 $\mu\text{mol}/\text{m}^2$) and four C-18-bonded, endcapped columns, with octadecyl chain densities of 0.42, 1.01, 2.03, and 3.15 $\mu\text{mol}/\text{m}^2$) were used to investigate the effects of the density of the surface coverage of RPLC columns on the adsorption mechanism of a cationic compound, amitriptyline chloride, and on the silanol activity of these columns. The mobile phases used were acetonitrile-water (30/70, v/v) solutions, buffered at either pH 2.7 or pH 6.9. At pH 2.7, the residual silanol groups are not ionized. At pH 6.9, some of these groups are ionized and these surface anions can strongly interact with the cationic compound. The adsorption isotherms were measured by frontal analysis (FA) at pH 2.7 and by frontal analysis by characteristic points (FACP) at pH 6.9, because the very high retention observed at neutral pH made FA measurements excessively long and poorly accurate. The adsorption energy distributions (AEDs) were calculated when possible, according to the expectation-maximization (EM) algorithm. A bimodal and a trimodal energy distribution were found for all the columns at pH 2.7 and 6.9, respectively. The third site measured at pH 6.9 was attributed to the strong ion-exchange interactions between the ionized silanol groups and the amitriptylinium cation. The contribution of the ionized silanol groups to the overall retention is maximum for the phases with intermediary bonding densities (1.01 and 2.03 $\mu\text{mol}/\text{m}^2$). The peak tailing is most pronounced for the lowest (C-1 column) and the highest (3.15 $\mu\text{mol}/\text{m}^2$) surface coverages.

Publisher: ELSEVIER SCIENCE BV, PO BOX 211, 1000 AE AMSTERDAM, NETHERLANDS.

IDS Number: 098QR

ISSN: 0021-9673

DOI: 10.1016/j.chroma.2006.07.002

Title: *Liquid chromatography coupled to mass spectrometry. Implementation of chemometric optimization and selected applications.*

Author(s): My Moberg.

(Faculty of Science and Technology, University of Uppsala, Sweden)

Source: Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology. 2006.

Document Type: Doctoral dissertation.

Publisher: Acta Universitatis Upsaliensis. Uppsala, Sweden.

ISBN: 91-554-6612-5

ISSN: 1651-6214

Title: *Chromatographic behaviour of peptides on a mixed-mode stationary phase with an embedded charged group by capillary electrochromatography and high-performance liquid chromatography.*

Author(s): F. Progent^a, M. Taverna^a, A. Banco^b, A. Tchaplà^b, C. Smadja^a.

(^aUniv. Paris-Sud, JE 2495, Protéines et Nanotechnologies en Sciences Séparatives, F-92296 Châtenay-Malabry Cedex, France; ^bUniv. Paris-Sud, EA 4041, Groupe de Chimie Analytique de Paris-Sud, F-91400 Orsay, France)

Source: JOURNAL OF CHROMATOGRAPHY A 1136 (2): 221-225 DEC 15 2006

Document Type: Article

Abstract: Retention behaviour of biological peptides was investigated on a stationary phase bearing an embedded quaternary ammonium group in a C21 alkyl chain by both high-performance liquid chromatography (HPLC) and capillary electrochromatography (CEC). In HPLC experiments, variation of acetonitrile (ACN) content in the mobile phase showed that peptides are mainly separated by RP mechanism. The weak or negative retention factors observed as compared to C18 silica stationary phase suggested the involvement of an electrostatic repulsion phenomenon in acidic conditions. Comparison of HPLC and CEC studies indicated that (i) ion-exclusion phenomenon is more pronounced in HPLC and (ii) higher ACN percentage in mobile phase induce for some peptides an increase of retention in CEC, pointing out the existence of mechanisms of retention other than partitioning mainly involved in chromatographic process. This comparative study demonstrated the critical role of electric field on peptide retention in CEC and supports the solvation model of hydrolytic pillow proposed by Szumski and Buszewski for CEC using mixed mode stationary phase in CEC. (c) 2006 Elsevier B.V. All rights reserved.

Publisher: ELSEVIER SCIENCE BV, PO BOX 211, 1000 AE AMSTERDAM, NETHERLANDS

IDS Number: 116GW

ISSN: 0021-9673

DOI: 10.1016/j.chroma.2006.09.095

Title: *Retention of ionisable compounds on high-performance liquid chromatography XVII. Estimation of the pH variation of aqueous buffers with the change of the methanol fraction of the mobile phase.*

Author(s): Xavier Subirats, Elisabeth Bosch and Martí Rosés.

(Departament de Química Analítica, Universitat de Barcelona)

Source: JOURNAL OF CHROMATOGRAPHY A 1138 (1-2): 203-215 JAN 5 2007

Document Type: Article

Abstract: The use of methanol-aqueous buffer mobile phases in HPLC is a common election when performing chromatographic separations of ionisable analytes. The addition of methanol to the aqueous buffer to prepare such a mobile phase changes the buffer capacity and the pH of the solution. In the present work, the variation of these buffer properties is studied for acetic acid-acetate, phosphoric acid-dihydrogenphosphate-hydrogenphosphate, citric acid-dihydrogencitrate-hydrogencitrate-citrate, and ammonium-ammonia buffers. It is well established that the pH change of the buffers depends on the initial concentration and aqueous pH of the buffer, on the percentage of methanol added, and on the particular buffer used. The proposed equations allow the pH estimation of methanol-water buffered mobile phases up to 80% in volume of organic modifier from initial aqueous buffer pH and buffer concentration (before adding methanol) between 0.001 and 0.01 mol L⁻¹. From both the estimated pH values of the mobile phase and the estimated pK(a) of the ionisable analytes, it is possible to predict the degree of ionisation of the analytes and therefore, the interpretation

of acid-base analytes behaviour in a particular methanol-water buffered mobile phase. (c) 2006 Elsevier B.V. All rights reserved.

Publisher: ELSEVIER SCIENCE BV, PO BOX 211, 1000 AE AMSTERDAM, NETHERLANDS

IDS Number: 126DQ

ISSN: 0021-9673

DOI: 10.1016/j.chroma.2006.10.087

Title: *Influence of the ionic strength of mobile phase on peak shape of antibiotics in RP-HPLC.*

Author(s): Liu, H.^a, Wang, H.-W.^b, Ding, J.-Y.^a, Qiu, S.-L.^a

(^aShanghai Institute for Food and Drug Control, Shanghai 200233; ^bNational Engineering Research Center for Urban Pollution Control, Tongji University, Shanghai 200092)

Source: Chinese Journal of Antibiotics 32 (1), pp. 25-32 2007

Document Type: Article

Abstract: The ionic strength of mobile phase can significantly affect the peak shape of ionogenic compounds such as antibiotics in reversed-phase high performance liquid chromatography (RP-HPLC). The influence may be attributed to overloading of ionogenic analytes in lower ionic strength mobile phase. In such phase, peak becomes increasingly right-angled triangle in shape with increasing sample load together with increasing peak width and tailing. The retention time of the high-concentration front decreases with increasing sample load, while the end of the peak tail has a constant retention time, equal to the symmetrical analytical peak. Due to considerably worse peak shapes, poorer resolution between the main component and its related substances might be observed. With the optimal buffer and the increase of ionic strength, significant improvement in peak shape of antibiotics could be achieved and consequently a decrease in the tailing factor, an increase in the apparent column efficiency as well as an efficient resolution were obtained.

Publisher: Sheng Chengdu Shi: "Zhongguo kang sheng su za zhi" bian ji bu

IDS Number: -

ISSN: 1001-8689

Title: *CEC separation of heterocyclic amines using methacrylate monolithic columns.*

Author(s): Elena Barceló Barrachina, Encarnación Moyano, Lluís Puignou, Maria Teresa Galceran.

(Departament de Química Analítica, Universitat de Barcelona)

Source: ELECTROPHORESIS 28 (11): 1704-1713 JUN 2007

Document Type: Article

Abstract: Two methacrylate-based monolithic columns, one with a negatively charged group (sulfonic group) and another with a new monomer N,N-dimethylamino ethyl acrylate (DMAEA), were prepared and tested for the separation of basic compounds by CEC. This new monolithic stationary phase was prepared by the in situ polymerization of DMAEA with butyl methacrylate and ethylene dimethacrylate, using a ternary porogenic solvent consisting of water, 1-propanol and 1,4-butanediol. The performance of this column was evaluated by means of the analysis of a family of heterocyclic amines. Separation conditions such as pH, amount of organic modifier, ionic strength and elution mode (normal or counterdirectional flow) were studied. At the optimal running electrolyte composition, and using the counterdirectional mode, symmetrical electrochromatographic peaks were obtained, with the number of theoretical plates up to 30 000 and a good resolution between closely related peaks. The 2-acrylamido-2-methyl-1-propane-sulfonic acid column was used for CEC-MS, taking advantage of the compatibility of its elution mode (normal flow) with the MS coupling.

Publisher: WILEY-V C H VERLAG GMBH; PO BOX 10 11 61, D-69451 WEINHEIM, GERMANY

IDS Number: 179HH

ISSN: 0173-0835

DOI: 10.1002/elps.200600356

Title: *Stationary phase characterization and method development.*

Author(s): Uwe D. Neue.

(Waters Corporation, Milford, MA, USA)

Source: JOURNAL OF SEPARATION SCIENCE 30 (11): 1611-1627 JUL 2007

Document Type: Article

Abstract: The properties of stationary phases and their characterization methods are reviewed. New and significant developments have occurred in the last few years, and new methods for stationary phase characterization have become available. The characterization methods are discussed, and the differences between the different methods are pointed out. In addition, method development approaches are reviewed, with special emphasis on recent developments that employ multiple parameters in parallel. Also, the renewed interest of temperature as a tool in method development is surveyed.

Publisher: WILEY-V C H VERLAG GMBH; PO BOX 10 11 61, D-69451 WEINHEIM, GERMANY

IDS Number: 194RI

ISSN: 1615-9306

DOI: 10.1002/jssc.200700082

Title: *On the effect of organic solvent composition on the pH of buffered HPLC mobile phases and the pK_a of analytes.*

Author(s): Xavier Subirats, Martí Rosés and Elisabeth Bosch.

Source: SEPARATION AND PURIFICATION REVIEWS 36: 231-255 2007

Document Type: Article

Abstract: A review about the analyte pK_a and buffer pH variations in RP-HPLC mobile phases with the changes in the organic modifier content (acetonitrile or methanol) is presented. A model to accurately predict the pH of particular mobile phases for several commonly used buffers (acetic, citric and phosphoric acid and ammonia systems) in acetonitrile-water and methanol-water mixtures is described. Linear relationships are also presented for several families of acid-base compounds (aromatic and aliphatic carboxylic acids, phenols, amines and pyridines) to estimate pK_a values of analytes in methanol-water and acetonitrile-water from their corresponding aqueous pK_a . From both, the estimated pH of the mobile phase and the estimated pK_a of acid-base analytes, it is possible to predict their degree of ionisation and, therefore, the analyte chromatographic retention.

Publisher: 325 CHESTNUT ST, SUITE 800, PHILADELPHIA, PA 19106

IDS Number: -

ISSN: -

DOI: 10.1080/15422110701539129

Title: *Effect of temperature on the chromatographic retention of ionizable compounds. III. Modeling retention of pharmaceuticals as a function of eluent pH and column temperature in RPLC.*

Author(s): Leonardo G. Gagliardi^a, Cecilia B. Castells^a, Clara Ràfols^b, Martí Rosés^b, Elisabeth Bosch^b.

(^aUniv Nacl La Plata, Div Quim Analit, Fac Ciencias Exactas, RA-1900 La Plata, Argentina;
^bUniv Barcelona, Fac Quim, Dept Quim Analit, Barcelona, Spain)

Source: JOURNAL OF SEPARATION SCIENCE 31 (6-7): 969-980 APR 2008

Document Type: Article

Abstract: We propose a general simple equation for accurately predicting the retention factors of ionizable compounds upon simultaneous changes in mobile phase pH and column temperature at a given hydroorganic solvent composition. Only four independent experiments provide the input data: retention factors measured in two pH buffered mobile phases at extreme acidic and basic pH values (e.g., at least +/- 2 pH units far from the analyte pK(a)) and at two column temperatures. The equations, derived from the basic thermodynamics of the acid-base equilibria, additionally require the knowledge of the solute pK(a) and enthalpies of acid-base dissociation of both the solute and the buffer components in the hydroorganic solvent mixture. The performance of the predictive model is corroborated with the comparison between theoretical and experimental retention factors of several weak acids and bases of important pharmacological activity, in mobile phases containing different buffer solutions prepared in 25% w/w ACN in water and at several temperatures.

Publisher: WILEY-V C H VERLAG GMBH; PO BOX 10 11 61, D-69451 WEINHEIM, GERMANY

IDS Number: 297JU

ISSN: 1615-9306

DOI: 10.1002/jssc.200700491

Title: *Stability-indicating hydrophilic interaction liquid chromatography method for highly polar and basic compounds.*

Author(s): Min Liu, Emily X. Chen, Ruthie Ji, David Semin.

(Amgen Inc, 1 Amgen Ctr Dr,B25-2-A, Thousand Oaks, CA 91320 USA)

Source: JOURNAL OF CHROMATOGRAPHY A 1188 (2): 255-263 APR 25 2008

Document Type: Article

Abstract: A hydrophilic interaction liquid chromatography (HILIC) method was developed for the analysis of very polar and basic 4-(aminomethyl)pyridine (4-AMP) and its related compounds. Separation parameters such as stationary phase, buffer pH, buffer ionic strength, organic modifier, and column temperature were evaluated. The retention mechanisms were explored through the evaluation of the common chromatographic parameters in the method development. The data indicated the existence of surface adsorption phenomena for 4-AMP and its positional isomers (2-AMP, 3-AMP). For two degradants, different retention mechanisms might be involved when compared to 4-AMP. The selectivity of two critical pairs 3-/4-AMP isomer and Degradant-1/-2 diastereomer changed through isoelution temperature with reversal of elution order. The validation results indicated that the HILIC method is a sensitive, reproducible, and robust method suitable for the analysis of 4-AMP and its related compounds.

Publisher: ELSEVIER SCIENCE BV; PO BOX 211, 1000 AE AMSTERDAM, NETHERLANDS

IDS Number: 296RW

ISSN: 0021-9673

DOI: 10.1016/j.chroma.2008.02.071

ARTICLE II

Title: *Retention of ionisable compounds on high-performance liquid chromatography XVI. Estimation of retention with acetonitrile/water mobile phases from aqueous buffer pH and analyte pK_a.*

Author(s): Xavier Subirats, Elisabeth Bosch and Martí Rosés.

(Departament de Química Analítica, Universitat de Barcelona)

Source: JOURNAL OF CHROMATOGRAPHY A 1121 (2): 170-177 JUL 21 2006

Document Type: Article

Publisher: ELSEVIER SCIENCE BV, PO BOX 211, 1000 AE AMSTERDAM, NETHERLANDS

IDS Number: 062RZ

ISSN: 0021-9673

DOI: 10.1016/j.chroma.2006.03.126

Citing references (6):

Title: *Retention of ionisable compounds on high-performance liquid chromatography XVII. Estimation of the pH variation of aqueous buffers with the change of the methanol fraction of the mobile phase.*

Author(s): Xavier Subirats, Elisabeth Bosch and Martí Rosés.

(Departament de Química Analítica, Universitat de Barcelona)

Source: JOURNAL OF CHROMATOGRAPHY A 1138 (1-2): 203-215 JAN 5 2007

Document Type: Article

Abstract: The use of methanol-aqueous buffer mobile phases in HPLC is a common election when performing chromatographic separations of ionisable analytes. The addition of methanol to the aqueous buffer to prepare such a mobile phase changes the buffer capacity and the pH of the solution. In the present work, the variation of these buffer properties is studied for acetic acid-acetate, phosphoric acid-dihydrogenphosphate-hydrogenphosphate, citric acid-dihydrogencitrate-hydrogencitrate-citrate, and ammonium-ammonia buffers. It is well established that the pH change of the buffers depends on the initial concentration and aqueous pH of the buffer, on the percentage of methanol added, and on the particular buffer used. The proposed equations allow the pH estimation of methanol-water buffered mobile phases up to 80% in volume of organic modifier from initial aqueous buffer pH and buffer concentration (before adding methanol) between 0.001 and 0.01 mol L⁻¹. From both the estimated pH values of the mobile phase and the estimated pK(a) of the ionisable analytes, it is possible to predict the degree of ionisation of the analytes and therefore, the interpretation of acid-base analytes behaviour in a particular methanol-water buffered mobile phase. (c) 2006 Elsevier B.V. All rights reserved.

Publisher: ELSEVIER SCIENCE BV, PO BOX 211, 1000 AE AMSTERDAM, NETHERLANDS

IDS Number: 126DQ

ISSN: 0021-9673

DOI: 10.1016/j.chroma.2006.10.087

Title: *Pharmaceuticals and related drugs.*

Author(s): Gilpin, R. K., Gilpin, C. S.

(Brehm Research Laboratory, University Park, Wright State University, Fairborn, Ohio 45324-2031)

Source: ANALYTICAL CHEMISTRY 79 (12): 4275-4293 JUN 15 2007

Document Type: Review

Publisher: AMER CHEMICAL SOC, 1155 16TH ST, NW, WASHINGTON, DC 20036
USA

Subject Category: Chemistry, Analytical

IDS Number: 178JK

ISSN: 0003-2700

DOI: 10.1021/ac070708x S0003-2700(07)00708-1

Title: *Effects of elevated temperature and mobile phase composition on a novel C-18 silica column.*

Author(s): J. Andreas Lippert^a, Todd M. Johnson^a, Jarem B. Lloyd^a, Jared P. Smith^a, Bryce T. Johnson^a, Jason Furlow^a, Angela Proctor^a, Stephanie J. Marin^b.

(^aDepartment of Chemistry, Weber State University, University Circle, Ogden, UT, USA;

^bARUP Laboratories, Salt Lake City, UT, USA)

Source: JOURNAL OF SEPARATION SCIENCE 30 (8): 1141-1149 MAY 2007

Document Type: Article

Abstract: A novel polydentate C, silica column was evaluated at an elevated temperature under acidic, basic, and neutral mobile phase conditions using ACN and methanol as the mobile phase organic modifier. The temperature range was 40-200 degrees C. The mobile phase compositions were from 0 to 80% organic-aqueous v/v and the mobile phase pH levels were between 2 and 12. The maximum operating temperature of the column was affected by the amount and type of organic modifier used in the mobile phase. Under neutral conditions, the column showed good column thermal stability at temperatures ranging between 120 and 200 degrees C in methanol-water and ACN-water solvent systems. At pH 2 and 3, the column performed well up to about 160 degrees C at two fixed ACN-buffer compositions. Under basic conditions at elevated temperatures, the column material deteriorated more quickly, but still remained stable up to 100 degrees C at pH 9 and 60 degrees C at pH 10. The results of this study indicate that this novel C-18 silica-based column represents a significant advancement in RPLC column technology with enhanced thermal and pH stability when compared to traditional bonded phase silica columns.

Publisher: WILEY-V C H VERLAG GMBH, PO BOX 10 11 61, D-69451 WEINHEIM, GERMANY

Subject Category: Chemistry, Analytical

IDS Number: 176TZ

ISSN: 1615-9306

DOI: 10.1002/jssc.200600525

Title: *Stationary phase characterization and method development.*

Author(s): Uwe D. Neue.

(Waters Corporation, Milford, MA, USA)

Source: JOURNAL OF SEPARATION SCIENCE 30 (11): 1611-1627 JUL 2007

Document Type: Article

Abstract: The properties of stationary phases and their characterization methods are reviewed. New and significant developments have occurred in the last few years, and new methods for stationary phase characterization have become available. The characterization methods are discussed, and the differences between the different methods are pointed out. In addition, method development approaches are reviewed, with special emphasis on recent developments that employ multiple parameters in parallel. Also, the renewed interest of temperature as a tool in method development is surveyed.

Publisher: WILEY-V C H VERLAG GMBH; PO BOX 10 11 61, D-69451 WEINHEIM, GERMANY

IDS Number: 194RI

ISSN: 1615-9306

DOI: 10.1002/jssc.200700082

Title: *On the effect of organic solvent composition on the pH of buffered HPLC mobile phases and the pK_a of analytes.*

Author(s): Xavier Subirats, Martí Rosés and Elisabeth Bosch.

Source: SEPARATION AND PURIFICATION REVIEWS 36: 231-255 2007

Document Type: Article

Abstract: A review about the analyte pK_a and buffer pH variations in RP-HPLC mobile phases with the changes in the organic modifier content (acetonitrile or methanol) is presented. A model to accurately predict the pH of particular mobile phases for several commonly used buffers (acetic, citric and phosphoric acid and ammonia systems) in acetonitrile-water and methanol-water mixtures is described. Linear relationships are also presented for several families of acid-base compounds (aromatic and aliphatic carboxylic acids, phenols, amines and pyridines) to estimate pK_a values of analytes in methanol-water and acetonitrile-water from their corresponding aqueous pK_a . From both, the estimated pH of the mobile phase and the estimated pK_a of acid-base analytes, it is possible to predict their degree of ionisation and, therefore, the analyte chromatographic retention.

Publisher: 325 CHESTNUT ST, SUITE 800, PHILADELPHIA, PA 19106

IDS Number: -

ISSN: -

DOI: 10.1080/15422110701539129

Title: *Stability-indicating hydrophilic interaction liquid chromatography method for highly polar and basic compounds.*

Author(s): Min Liu, Emily X. Chen, Ruthie Ji, David Semin.

(Amgen Inc, 1 Amgen Ctr Dr, B25-2-A, Thousand Oaks, CA 91320 USA)

Source: JOURNAL OF CHROMATOGRAPHY A 1188 (2): 255-263 APR 25 2008

Document Type: Article

Abstract: A hydrophilic interaction liquid chromatography (HILIC) method was developed for the analysis of very polar and basic 4-(aminomethyl)pyridine (4-AMP) and its related compounds. Separation parameters such as stationary phase, buffer pH, buffer ionic strength, organic modifier, and column temperature were evaluated. The retention mechanisms were explored through the evaluation of the common chromatographic parameters in the method development. The data indicated the existence of surface adsorption phenomena for 4-AMP and its positional isomers (2-AMP, 3-AMP). For two degradants, different retention mechanisms might be involved when compared to 4-AMP. The selectivity of two critical pairs 3-/4-AMP isomer and Degradant-1/-2 diastereomer changed through isoelution temperature with reversal of elution order. The validation results indicated that the HILIC method is a sensitive, reproducible, and robust method suitable for the analysis of 4-AMP and its related compounds.

Publisher: ELSEVIER SCIENCE BV; PO BOX 211, 1000 AE AMSTERDAM, NETHERLANDS

IDS Number: 296RW

ISSN: 0021-9673

DOI: 10.1016/j.chroma.2008.02.071

ARTICLE III

Title: *Retention of ionisable compounds on high-performance liquid chromatography XVII. Estimation of the pH variation of aqueous buffers with the change of the methanol fraction of the mobile phase.*

Author(s): Xavier Subirats, Elisabeth Bosch and Martí Rosés.

(Departament de Química Analítica, Universitat de Barcelona)

Source: JOURNAL OF CHROMATOGRAPHY A 1138 (1-2): 203-215 JAN 5 2007

Document Type: Article

Publisher: ELSEVIER SCIENCE BV, PO BOX 211, 1000 AE AMSTERDAM, NETHERLANDS

IDS Number: 126DQ

ISSN: 0021-9673

DOI: 10.1016/j.chroma.2006.10.087

Citing references (4):

Title: *QSRR: Quantitative structure-(chromatographic) retention relationships.*

Author(s): Kaliszan, R.

(Department of Biopharmaceutics and Pharmacodynamics, Medical University of Gdańsk, Gen. J. Hallera 107, 80416 Gdańsk, Poland)

Source: Chemical Reviews Volume 107, Issue 7, July 2007, Pages 3212-3246

Document Type: Review

Abstract: The quantitative structure-retention relationships are the most widely manifestations of linear free-energy relationships and the most often reported results of chemometric data processing. In addition, performance in QSSR verifies well the reliability of the numerous proposed chemometric methods as well as structural descriptors of chemical compounds. Its potential for identification of chromatographed analytes must be recognized. Intermolecular interactions determining separations on specific stationary phases may be identified and quantitatively compared. Chromatographically derived lipophilicity parameters to pharmacokinetic properties facilitates selecting those drugs candidates. Development of QSSR studies not only enlarge the areas of applications but also increase understanding of chemistry.

Publisher: American Chemical Society

IDS Number: -

ISSN: 0009-2665

DOI: 10.1021/cr068412z

Title: *Stationary phase characterization and method development.*

Author(s): Uwe D. Neue.

(Waters Corporation, Milford, MA, USA)

Source: JOURNAL OF SEPARATION SCIENCE 30 (11): 1611-1627 JUL 2007

Document Type: Article

Abstract: The properties of stationary phases and their characterization methods are reviewed. New and significant developments have occurred in the last few years, and new methods for stationary phase characterization have become available. The characterization methods are discussed, and the differences between the different methods are pointed out. In addition, method development approaches are reviewed, with special emphasis on recent developments that employ multiple parameters in parallel. Also, the renewed interest of temperature as a tool in method development is surveyed.

Publisher: WILEY-V C H VERLAG GMBH; PO BOX 10 11 61, D-69451 WEINHEIM, GERMANY

IDS Number: 194RI

ISSN: 1615-9306

DOI: 10.1002/jssc.200700082

Title: *On the effect of organic solvent composition on the pH of buffered HPLC mobile phases and the pK_a of analytes.*

Author(s): Xavier Subirats, Martí Rosés and Elisabeth Bosch.

Source: SEPARATION AND PURIFICATION REVIEWS 36: 231-255 2007

Document Type: Article

Abstract: A review about the analyte pK_a and buffer pH variations in RP-HPLC mobile phases with the changes in the organic modifier content (acetonitrile or methanol) is presented. A model to accurately predict the pH of particular mobile phases for several commonly used buffers (acetic, citric and phosphoric acid and ammonia systems) in acetonitrile-water and methanol-water mixtures is described. Linear relationships are also presented for several families of acid-base compounds (aromatic and aliphatic carboxylic acids, phenols, amines and pyridines) to estimate pK_a values of analytes in methanol-water and acetonitrile-water from their corresponding aqueous pK_a . From both, the estimated pH of the mobile phase and the estimated pK_a of acid-base analytes, it is possible to predict their degree of ionisation and, therefore, the analyte chromatographic retention.

Publisher: 325 CHESTNUT ST, SUITE 800, PHILADELPHIA, PA 19106

IDS Number: -

ISSN: -

DOI: 10.1080/15422110701539129

Title: *Electrostatic repulsion hydrophilic interaction chromatography for isocratic separation of charged solutes and selective isolation of phosphopeptides.*

Author(s): Andrew J. Alpert

(PolyLC Inc, 9151 Rumsey Rd, Ste 180, Columbia, MD 21045 USA)

Source: ANALYTICAL CHEMISTRY 80 (1): 62-76 JAN 1 2008

Document Type: Article

Abstract: If an ion-exchange column is eluted with a predominantly organic mobile phase, then solutes can be retained through hydrophilic interaction even if they have the same charge as the stationary phase. This combination is termed electrostatic repulsion-hydrophilic interaction chromatography (ERLIC). With mixtures of solutes that differ greatly in charge, repulsion effects can be exploited to selectively antagonize the retention of the solutes that normally would be the best retained. This permits the isocratic resolution of mixtures that normally require gradients, including peptides, amino acids, and nucleotides. ERLIC affords convenient separations of highly charged peptides that cannot readily be resolved by other means. In addition, phosphopeptides can be isolated selectively from a tryptic digest.

Publisher: AMER CHEMICAL SOC, 1155 16TH ST, NW, WASHINGTON, DC 20036 USA

IDS Number: 246SH

ISSN: 0003-2700

DOI: 10.1021/ac070997p

ARTICLE IV

Title: *On the effect of organic solvent composition on the pH of buffered HPLC mobile phases and the pK_a of analytes.*

Author(s): Xavier Subirats, Martí Rosés and Elisabeth Bosch.

Source: SEPARATION AND PURIFICATION REVIEWS 36: 231-255 2007

Document Type: Article

Publisher: 325 CHESTNUT ST, SUITE 800, PHILADELPHIA, PA 19106

IDS Number: -

ISSN: -

DOI: 10.1080/15422110701539129

Citing references (1):

Title: *Determination of the chromatographic hydrophobicity index for ionisable solutes.*

Author(s): Elisabet Fuguet, Clara Ràfols, Elisabeth Bosch and Martí Rosés.

(Departament de Química Analítica, Universitat de Barcelona)

Source: JOURNAL OF CHROMATOGRAPHY A 1173 (1-2): 110-119

Document Type: Article

Abstract: A model that relates the chromatographic hydrophobicity index (CHI) to the pH of the mobile phase has been tested in two of the most common high-performance liquid chromatography (HPLC) solvents: methanol and acetonitrile. A set of eight monoprotic acids and nine monoprotic bases of different chemical nature (phenols, benzoic acids, anilines, and pyridine) have been selected for the validation. The variation of CHI values with the pH of the mobile phase shows a good fit to the model for almost all compounds, regardless of their nature, and similar CHI values of the neutral form of the substances are obtained in both organic modifiers. On the contrary, higher differences are observed for the ionic form of the test solutes. The values of the other parameters obtained with the model (s, pK_a) are discussed according to the nature of the compounds, and the variation of solvent pH and compounds pK_a along the gradient elution.

Publisher: ELSEVIER SCIENCE BV, PO BOX 211, 1000 AE AMSTERDAM, NETHERLANDS

IDS Number: 238HZ

ISSN: 0021-9673

DOI: 10.1016/j.chroma.2007.10.012

ARTICLE V

Title: *Nitromethane as solvent in capillary electrophoresis.*

Author(s): Xavier Subirats^{a,b}, Simo P. Porras^c, Martí Rosés^a and Erns Kenndler^b.

(^aInstitute for Analytical Chemistry, University of Vienna, Währingerstrasse 38, A-1090 Vienna, Austria; ^bDepartament de Química Analítica, Universitat de Barcelona, Diagonal 647, E-08028 Barcelona, Spain; ^cLaboratory of Analytical Chemistry, Department of Chemistry, P.O. Box 55, FIN-00014, University of Helsinki, Finland)

Source: JOURNAL OF CHROMATOGRAPHY A 1079 (1-2): 246-253 JUN 24 2005

Document Type: Article

Publisher: ELSEVIER SCIENCE BV, PO BOX 211, 1000 AE AMSTERDAM, NETHERLANDS.

IDS Number: 941QB

ISSN: 0021-9673

DOI: 10.1016/j.chroma.2005.02.072

Citing references (12):

Title: *Comparison of methanol and acetonitrile as solvents for the separation of sertindole and its major metabolites by capillary zone electrophoresis.*

Author(s): X. Subirats^{a,b}, S. Reinstadler^{b,c}, S.P. Porras^d, M.A. Raggi^c and E. Kenndler^a.

(^aInstitute for Analytical Chemistry, University of Vienna, Vienna, Austria; ^bDepartment of Analytical Chemistry, University of Barcelona, Barcelona, Spain; ^cFaculty of Pharmaceutical Sciences, University of Bologna, Bologna, Italy; ^dLaboratory of Analytical Chemistry, Department of Chemistry, University of Helsinki, Helsinki, Finland)

Source: ELECTROPHORESIS 26 (17): 3315-3324 SEP 2005

Document Type: Article

Abstract: Sertindole (1-[2-[4-[5-chloro-1-(4-fluorophenyl)-1H-indol-3-yl]-1-piperidinyl]ethyl]-2-imidazolidinone), an atypical antipsychotic drug, was separated by capillary electrophoresis from its two main metabolites norsertindole and dehydrosertindole. The low solubility of the analytes in water (octanol-water partition coefficient is about 105) is overcome by the use of methanol (MeOH) and acetonitrile (ACN) as solvents for the background electrolyte (BGE). Mobilities were measured in BGEs with defined pH in a broad range. It was found that in MeOH the mobility of the analytes is mainly governed by acid-base equilibria, whereas in ACN other reactions like ion pairing and homoconjugation play a pronounced role and lead to a complex pattern of the mobility as function of the pH. However, separation can be obtained in less than 10 min in both solvent systems.

Publisher: WILEY-V C H VERLAG GMBH, PO BOX 10 11 61, D-69451 WEINHEIM, GERMANY

IDS Number: 965RI

ISSN: 0173-0835

DOI: 10.1002/elps.200500056

Title: *Capillary electrophoresis in N,N-dimethylformamide.*

Author(s): Simo P. Porras and Ernst Kenndler.

(Institute for Analytical Chemistry, University of Vienna, Vienna, Austria)

Source: ELECTROPHORESIS 26 (17): 3279-3291 SEP 2005

Document Type: Article

Abstract: *N,N*-Dimethylformamide (DMF) is a dipolar protophilic solvent with physicochemical properties that makes it suitable as solvent for capillary electrophoresis

(CE). It is prerequisite for the proper application of CE to adjust and to change the pH of the background electrolyte (BGE) in a defined manner. This was done in the present work using benzoic acid-benzoate by selecting different concentration ratios of acid and salt, and calculating the theoretical pH from the activity-corrected Henderson-Hasselbalch equation. The mobilities of the analytes (chloro- and nitro-substituted phenolates) were found to follow reasonably well the typical sigmoid mobility versus pH curve as predicted by theory. The actual mobilities and $pK(a)$ values (at 25 degrees C) of the analytes were derived from these curves. pK_a values were in the range of 11.1-11.7, being thus 3-4.4 units higher than in water. This pK_a shift is caused by the destabilization of the analyte anion and the better stability (solubility) of the molecular analyte acid in DMF, which overcome the higher basicity of DMF compared to water. Absolute mobilities were calculated from the actual mobilities; they were between $32 \times 10(-9)$ and $42 \times 10(-9)$ $m^2/V \times s$. Slight deviations of the measured mobilities from the theoretical mobility versus pH curve were discussed on the bases of ion pairing and heteroconjugation and homoconjugation of either buffer components or buffer components and analytes. Heteroconjugation was used as a mechanism for the electrically driven separation of neutral analyte molecules in a BGE where salicylate acted as complex forming ion. Rough estimation of the complexation constants for the phenolic analytes gave values in the range of 100-200 L/mol. Addition of water to the solvent decreased the effect of heteroconjugation, but it was still present up to the surprisingly high concentration of 20% water. Electrophoretically relevant parameters like ionic mobilities and pK_a values, and conjugation and ion pairing are dependent on the water content of the solvent. The water uptake of DMF was measured when exposed to humidity of ambient air. The resulted behavior of the water uptake was found rather similar to that for acetonitrile and methanol.

Publisher: WILEY-V C H VERLAG GMBH, PO BOX 10 11 61, D-69451 WEINHEIM, GERMANY

IDS Number: 965RI

ISSN: 0173-0835

DOI: 10.1002/elps.200500088

Title: *Are the asserted advantages of organic solvents in capillary electrophoresis real? A critical discussion.*

Author(s): Simo P. Porras^a and Ernst Kenndler^b.

(^aLaboratory of Analytical Chemistry, Department of Chemistry, University of Helsinki, Finland; ^bInstitute for Analytical Chemistry, University of Vienna, Vienna, Austria)

Source: ELECTROPHORESIS 26 (17): 3203-3220 SEP 2005

Document Type: Article

Abstract: Background electrolytes (BGEs) prepared in pure organic solvents are common alternatives to aqueous BGEs in capillary electrophoresis. Several general advantages of organic solvents over water have been asserted in the literature, namely (i) organic solvents increase the separation selectivity; (ii) organic solvents increase the separation efficiency; (iii) high separation voltages and/or high BGE ionic strengths can be used in organic solvents due to lower electric current compared to water. Related assumptions are that (iv) due to higher field strengths applicable in organic solvents the analysis time is shorter than in aqueous BGEs, and (v) the solubility and/or stability of components (either analytes or BGE chemicals) is higher/better in organic solvents. In the present work, these asserted advantages were critically evaluated based on the physical principles of ion transport and zone dispersion in solution. The result was that many of the above-mentioned general advantages are overestimated or even inexistent; often they have no fundamental basis.

Publisher: WILEY-V C H VERLAG GMBH, PO BOX 10 11 61, D-69451 WEINHEIM, GERMANY

IDS Number: 965RI
ISSN: 0173-0835
DOI: 10.1002/elps.200500311

Title: *Theoretical and empirical approaches to express the mobility of small ions in capillary electrophoresis.*

Author(s): Abolghasem Jouyban^a and Ernst Kenndler^b.

(^aFaculty of Pharmacy, Tabriz University of Medical Sciences, Tabriz, Iran; ^bDepartment for Analytical Chemistry, University of Vienna, Vienna, Austria)

Source: ELECTROPHORESIS 27 (5-6): 992-1005 MAR 2006

Document Type: Article

Abstract: A discussion is given about the concepts of the ion mobility, the analyte property which governs migration and thus separation selectivity in CE. It deals with small organic and inorganic ions, not with charged polymers or large particles like colloids. The discussion is directed to two main concepts. (i) The first is based on physico-chemistry of ion conductance in solution, and distinguishes three types of mobility. The absolute mobility is the limiting mobility at zero ionic strength; it depends on the solvent and the temperature. It is obtained by extrapolation of the actual mobilities, those of the fully charged particles at finite ion concentration. The observed reduction of the absolute mobility with ionic concentration is related to an ion cloud, and is formulated by the established theories of ion conductance. It explains the actual mobility as function of (beside other factors) the ionic strength, the viscosity and relative permittivity of the solvent, the temperature, the relaxation time of solvent polarisation and the distance of closest approach between ion and counterion. The effective mobility, finally, is the mobility when association and dissociation equilibria play a role. Most important are acid-base reactions, but complexation, ion pairing and homo- and heteroconjugation were considered as well. (ii) The second approach treats mobility data with different mathematical methods, and formulates their dependence on variables like solvent composition with appropriate algorithms. These empirical methods mainly include least squares and neural network-based methods. The least square methods ranges from the simplest model, which uses only the molecular weight of the analyte, to more complicated model requiring three-dimensional structural descriptors of the solutes. Neural networks have been applied to model the mobility using different input variables and various architectures. Work comparing the accuracy of least squares and neural network methods was discussed; the results showed that the neural network method leads to a more accurate mobility calculation. However, the least squares methods could give some information to the factors affecting the mobility of the analytes. The resulting methods allow the prediction of mobilities under different experimental conditions with certain accuracy. It has been shown that using such models, it is possible to predict mobility of analytes after training the models by a minimum number of data to speed up the method development stage.

Publisher: WILEY-V C H VERLAG GMBH, PO BOX 10 11 61, D-69451 WEINHEIM, GERMANY

IDS Number: 028TO
ISSN: 0173-0835
DOI: 10.1002/elps.200500696

Title: *Capillary zone electrophoresis of some extremely weak bases in acetonitrile.***Author(s):** Simo P. Porras.

(Laboratory of Analytical Chemistry, Department of Chemistry, University of Helsinki, Helsinki, Finland)

Source: ANALYTICAL CHEMISTRY 78 (14): 5061-5067 JUL 15 2006**Document Type:** Article

Abstract: In water capillary zone electrophoresis cannot be used to investigate basic compounds, which are so weak that their pK_a (HB^+) values are less than zero. In acetonitrile the basic strength of such compounds is increased by many orders of magnitude. Accordingly, several extremely weak bases are protonated at low pH in acetonitrile, thus, allowing their investigation by CZE. In this work the CZE separation of thioacetamide, acetamide, thiourea, benzamide, and 4-nitrobenzamide as well as that of *N*-methylformamide, *N*, *N*-dimethylformamide, formamide, and dimethyl sulfoxide is demonstrated in acetonitrile using 10 mmol/L perchloric acid as an electrolyte. The effect of BGE additives, like water and acetic acid, on the CZE performance is discussed. The problem of finding a suitable electroosmotic flow marker at low pH in acetonitrile is addressed, and nitromethane is shown to be a proper marker compound under such extreme conditions. This work demonstrates how organic solvents can enlarge the field of application of CZE.

Publisher: AMER CHEMICAL SOC, 1155 16TH ST, NW, WASHINGTON, DC 20036 USA**IDS Number:** 063KS**ISSN:** 0003-2700**DOI:** 10.1021/ac060243v S0003-2700(06)00243-5**Title:** *Recent applications of conductivity detection in capillary and chip electrophoresis.***Author(s):** Veronika Šolínová and Václav Kašička.

(Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Prague, Czech Republic)

Source: JOURNAL OF SEPARATION SCIENCE 29 (12): 1743-1762 AUG 2006**Document Type:** Review

Abstract: The review provides a comprehensive survey of the recent applications of contact and contactless conductivity detection in capillary electrophoretic and chip electrophoretic analyses of a broad scale of compounds, from low-molecular-mass highly mobile small inorganic and organic ions, via medium-molecular-mass peptides and oligo- and polynucleotides up to high-molecular-mass biopolymers, proteins and nucleic acids fragments. The review presents also the recent developments in the construction of different types of conductivity detectors (detectors with galvanic contact of the sensing electrodes with the BGE and sample components, contactless conductivity detectors with capacitively coupled tubular and semitubular electrodes and combined conductivity/optical detectors) applied in the capillary electromigration methods performed in classical fused silica, polytetrafluorethylene, and polyetheretherketone capillaries or on glass and polymethylmethacrylate microchips. In addition, the principle and theoretical bases of conductivity detection in capillary electromigration techniques, zone electrophoresis, ITP, micellar EKC, and electrochromatography are briefly described.

Publisher: WILEY-V C H VERLAG GMBH, PO BOX 10 11 61, D-69451 WEINHEIM, GERMANY**IDS Number:** 080WH**ISSN:** 1615-9306**DOI:** 10.1002/jssc.200600167

Title: *Chiral separation of amines by non-aqueous capillary electrophoresis using low molecular weight selectors.*

Author(s): Ylva Hedeland.

(Faculty of Pharmacy, University of Uppsala, Sweden)

Source: Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Pharmacy. 2006.

Document Type: Doctoral dissertation.

Publisher: Acta Universitatis Upsaliensis. Uppsala, Sweden.

ISBN: 91-554-6524-2

ISSN: 1651-6192

Title: *Simultaneous contactless conductivity detection and UV detection for the study of separation of tamsulosin enantiomers in discontinuous electrolyte systems by CE.*

Author(s): Jan Petr, Vítězslav Maier, Jana Horáková and Juraj Ševčík.

(Department of Analytical Chemistry, Palacký University, Olomouc, Czech Republic)

Source: ELECTROPHORESIS 27 (23): 4735-4745 DEC 2006

Document Type: Article

Abstract: This work shows the potential of using discontinuous electrolyte systems for the separation of tamsulosin enantiomers by CE. Sulfated P-cyclodextrin was used as a chiral selector. In acidic electrolytes, sulfated P-cyclodextrin migrates as an anion and the analyte (tamsulosin) migrates as a cation. Due to this, four experimental arrangements were proposed. These arrangements differ in composition of electrolytes in the inlet compartment, in the capillary and in the outlet compartment. The separation of tamsulosin enantiomers in acetate buffers with sodium and Tris counterions was studied. Simultaneous contactless conductivity detection and UV detection were used for the study of the separation mechanism in these systems. Mobilities of sulfated beta-cyclodextrin were used for the calculation of the time when the analyte migrates through the BGE zone with the selector. The simulation program Simul 4.0 was used for the calculations of the concentration profiles of the electrolyte components dependent on the time of the separation. The mechanism of enantioseparation in these arrangements was suggested.

Publisher: WILEY-V C H VERLAG GMBH, PO BOX 10 11 61, D-69451 WEINHEIM, GERMANY

IDS Number: 117WC

ISSN: 0173-0835

DOI: 10.1002/elps.200600063

Title: *Nitromethane (MeNO₂).*

Author(s): Devi, Prarthana.

(Medicinal Chemistry Division, Regional Research Laboratory, Jorhat 785006, Assam, India)

Source: SYNLETT (7): 1174-1175 APR 24 2007

Document Type: Editorial Material

Abstract: (A) The catalytic enantioselective Henry reaction of α -keto esters with NM affords β -nitro- α -hydroxy esters.⁹ The reaction proceeds via a 1,2-addition reaction and the product can be converted into β -amino acids. (Chemical Equation Presented) (B) The efficacy of NM has been extended to the base-catalyzed solid-phase condensation of steroidal, alicyclic or aromatic β -formyl enamides under microwave irradiation. ¹⁰ Boruah and co-workers found a new application of the Henry reaction and provided a route for facile, one-pot combinatorial synthesis of annelated pyridines. (Chemical Equation Presented) (C) NM reacts with N-sulfinylimines in the presence of NaOH to produce nitroamines in a highly diastereoselective manner.¹¹ In the presence of TBAF, the reaction rates are strongly increased and the

stereoselectivity is inverted. This approach offers enantiomerically pure β -nitroamines, which have been hardly accessible by azaHenry reactions so far. (Chemical Equation Presented) (D) α,α -Dipeptides are valuable synthetic intermediates and biologically active compounds. Recently, Petrini and Seri¹² have utilized NM in a two-step synthesis of α,α -dipeptide from α -amido sulfone. The procedure involves the nitromethylation of 1 followed by Nef conversion of the nitro group to furnish product 2. (Chemical Equation Presented) (E) NM undergoes an enantioselective Michael addition with 1-(2-alkenoyl)-3,5-dimethyl pyrazoles by a catalytic double activation method using chiral Lewis acid and achiral amine catalyst to give 1-(3-substituted 4-nitrobutanoyl)-3,5-dimethyl pyrazole in high yields.¹³ This method has been successfully employed for the total synthesis of the antidepressant (R)-rolipram (1). (Chemical Equation Presented) (F) A three-component Michael addition reaction of NM with two unsymmetrical α,β -unsaturated carbonyl compounds in the presence of base provides a convenient one-pot synthesis of 1,7-dicarbonyl compounds. ¹⁴ 1,7-Dicarbonyl compounds are initial starting materials for the synthesis of enantiomerically pure alcohols, which are useful building blocks for natural product synthesis. (Chemical Equation Presented) (G) Under solvent-free conditions, γ -nitroacetamido ester can be obtained via Michael addition from the commercial acetamido acrylate and NM.¹⁵ The product is a versatile precursor for the preparation of α -amino acids.

Publisher: GEORG THIEME VERLAG KG, RUDIGERSTR 14, D-70469 STUTTGART, GERMANY

IDS Number: 165MY

ISSN: 0936-5214

DOI: 10.1055/s-2007-977417

Title: *Electromigration of a heteroconjugated imidazole-acetate complex in ACN.*

Author(s): Simo P. Porras, Matti Jussila.

(Department of Chemistry, University of Helsinki, FIN-00014 Helsinki, Finland)

Source: ELECTROPHORESIS 28 (20): 3590-3599 OCT 2007

Document Type: Article

Abstract: ACN is an extremely poor hydrogen bond donor and therefore the anions dissolved in it are Revised May 4, 2007 solvated mainly by other hydrogen bond donors (e.g. uncharged acids) possibly present in Accepted May 4, 2007 the solution. Under properly selected experimental conditions stabilization via hydrogen bonding can be used for separation in CE as has been demonstrated for uncharged acids by several authors. Electromigration based on heteroconjugation can be of importance, e.g. when aqueous separation medium cannot be used due to stability reasons. It also allows CE to be used as a tool for solution chemistry measurements, if the required physicochemical properties of the studied system are known or they can be predicted with sufficient accuracy by existing theories. In the present work we showed that also an uncharged base can stabilize an anion via hydrogen bonding in ACN. In the setup imidazole was chosen as a model base and acetate ion as complexing anion in equimolar ! acetic acid-acetate buffer. The resulted hydrogen-bonded imidazole-acetate complex (i.e. heteroconjugate) possesses a charge and can thus migrate in CE. It was shown that the studied complexation in ACN is sensitive to competition by other hydrogen bond donors such as water and methanol. On the other hand, acetone, which is a poor hydrogen bond donor, did not have much effect on the complexation. To take the effect of ionic strength on mobility into account, mobilities of the imidazole-acetate complex measured at various ionic strengths were corrected to zero ionic strength by the aid of conductivity equation. A fit of the 1:1 binding isotherm to the ionic strength corrected mobility versus acetate concentration data led to rather good correlation. However, x-reciprocal linear transformation of the binding isotherm showed nonlinearity which could be partly explained by

homoconjugation of acetic acid and acetate ion. Since the homoconjugation constant for acetic acid under present experimental conditions was not available, theoretical simulations were used to demonstrate the effects of homoconjugation. The possibility of multiple complexation of imidazole was discussed as well.

Publisher: WILEY-VCH VERLAG GMBH, PO BOX 10 11 61, D-69451 WEINHEIM, GERMANY

IDS Number: 227LB

ISSN: 0173-0835

DOI: 10.1002/elps.200700291

Title: *Nonaqueous CE using contactless conductivity detection and ionic liquids as BGEs in ACN.*

Author(s): Maria Borissova, Jelena Gorbatsova, Arkadi Ebber, Mihkel Kaljurand, Mihkel Koel, Merike Vaher.

(Tallinn Univ Technol, Dept Chem, Akadeemia Tee 15, EE-12618 Tallinn, Estonia)

Source: ELECTROPHORESIS 28 (20): 3600-3605 OCT 2007

Document Type: Article

Abstract: N,N'-Alkylmethylimidazolium cations have been separated in NACE when one of the N,N'-dialkylimidazolium salts (ionic liquids (ILs)) was used as an electrolyte additive to the organic solvent separation medium. The separated species were 1-methyl-, 1-ethyl-, 1-butyl-, 1-octyl-, 1-decyl-3-methylimidazolium and N-butyl-3-methylpyridinium cations and BGE composed of 1-ethyl-3-methylimidazolium ethylsulfate or 1-butyl-3-methylimidazolium trifluoroacetate [BMIm][FACo] (A6; B2) diluted in ACN. It was demonstrated that contactless conductivity detection (CCD) may be applied to monitoring the separation process in nonaqueous separation media, allowing to use the UV light-absorbing imidazolium-based electrolyte additives. There could be marked three concentration regions of added ILs; at first ionic strength of BGE below 1-2 mM, and then the actual electrophoretic mobility of analytes rises from 0. At concentrations above 1-2 mM, the added IL facilitated separation. In concentration region of 1-20 mM, the actual electrophoretic mobility of analyzed imidazolium cations was increasing with decrease in separation medium ionic strength. At higher concentrations of BGE (above 30 mM), the conductivity of the separation media became too high for this detector. Some organic dyes were also successfully separated and detected by contactless conductivity detector in a 20 mM A6 separation electrolyte in ACN.

Publisher: WILEY-VCH VERLAG GMBH; PO BOX 10 11 61, D-69451 WEINHEIM, GERMANY

IDS Number: 227LB

ISSN: 0173-0835

DOI: 10.1002/elps.200700067

Title: *A review of the recent achievements in capacitively coupled contactless conductivity detection.*

Author(s): Pavel Kubáň^a, Peter C. Hauser^b.

(^aInstitute of Analytical Chemistry, Academy of Sciences of the Czech Republic, Veveří 97, 60200 Brno, Czech Republic; ^bDepartment of Chemistry, University of Basel, Spitalstrasse 51, 4004 Basel, Switzerland)

Source: ANALYTICA CHIMICA ACTA 607 (1): 15-29 2008

Document Type: Review

Abstract: Capacitively coupled contactless conductivity detection (CID) in the axial electrode configuration was introduced in 1998 as a quantification method for capillary electrophoresis. Its universality allows the detection of small inorganic ions as well as organic

and biochemical species. Due to its robustness, minimal maintenance demands and low cost the popularity of this detector has been steadily growing. Applications have recently also been extended to other analytical methods such as ion chromatography, high-performance liquid chromatography and flow-injection analysis. (CD)-D-4 has also found use for detection on electrophoresis based lab-on-chip devices. Theoretical aspects of (CD)-D-4 in both the capillary and microchip electrophoresis format have been comprehensively investigated. Commercial devices are now available and the method can be considered a mature detection technique. In this article, the achievements in CID for the time period between September 2004 and August 2007 are reviewed. (c) 2007 Elsevier B.V. All rights reserved. **Publisher:** ELSEVIER SCIENCE BV, PO BOX 211, 1000 AE AMSTERDAM, NETHERLANDS.

IDS Number: 257YA

ISSN: 0003-2670

DOI: 10.1016/j.aca.2007.11.045

ARTICLE VI

Title: *Comparison of methanol and acetonitrile as solvents for the separation of sertindole and its major metabolites by capillary zone electrophoresis.*

Author(s): X. Subirats, S. Reinstadler, S.P. Porras, M.A. Raggi and E. Kenndler.

Source: ELECTROPHORESIS 26 (17): 3315-3324 SEP 2005

Document Type: Article

Publisher: WILEY-V C H VERLAG GMBH, PO BOX 10 11 61, D-69451 WEINHEIM, GERMANY

IDS Number: 965RI

ISSN: 0173-0835

DOI: 10.1002/elps.200500056

Citing references (8):

Title: *Are the asserted advantages of organic solvents in capillary electrophoresis real? A critical discussion.*

Author(s): Simo P. Porras^a and Ernst Kenndler^b.

(^aLaboratory of Analytical Chemistry, Department of Chemistry, University of Helsinki, Finland; ^bInstitute for Analytical Chemistry, University of Vienna, Vienna, Austria)

Source: ELECTROPHORESIS 26 (17): 3203-3220 SEP 2005

Document Type: Article

Abstract: Background electrolytes (BGEs) prepared in pure organic solvents are common alternatives to aqueous BGEs in capillary electrophoresis. Several general advantages of organic solvents over water have been asserted in the literature, namely (i) organic solvents increase the separation selectivity; (ii) organic solvents increase the separation efficiency; (iii) high separation voltages and/or high BGE ionic strengths can be used in organic solvents due to lower electric current compared to water. Related assumptions are that (iv) due to higher field strengths applicable in organic solvents the analysis time is shorter than in aqueous BGEs, and (v) the solubility and/or stability of components (either analytes or BGE chemicals) is higher/better in organic solvents. In the present work, these asserted advantages were critically evaluated based on the physical principles of ion transport and zone dispersion in solution. The result was that many of the above-mentioned general advantages are overestimated or even inexistent; often they have no fundamental basis.

Publisher: WILEY-V C H VERLAG GMBH, PO BOX 10 11 61, D-69451 WEINHEIM, GERMANY

IDS Number: 965RI

ISSN: 0173-0835

DOI: 10.1002/elps.200500311

Title: *Capillary zone electrophoresis of some extremely weak bases in acetonitrile.*

Author(s): Simo P. Porras.

(Laboratory of Analytical Chemistry, Department of Chemistry, University of Helsinki, Helsinki, Finland)

Source: ANALYTICAL CHEMISTRY 78 (14): 5061-5067 JUL 15 2006

Document Type: Article

Abstract: In water capillary zone electrophoresis cannot be used to investigate basic compounds, which are so weak that their pK_a (HB^+) values are less than zero. In acetonitrile the basic strength of such compounds is increased by many orders of magnitude. Accordingly, several extremely weak bases are protonated at low pH in acetonitrile, thus, allowing their

investigation by CZE. In this work the CZE separation of thioacetamide, acetamide, thiourea, benzamide, and 4-nitrobenzamide as well as that of *N*-methylformamide, *N,N*-dimethylformamide, formamide, and dimethyl sulfoxide is demonstrated in acetonitrile using 10 mmol/L perchloric acid as an electrolyte. The effect of BGE additives, like water and acetic acid, on the CZE performance is discussed. The problem of finding a suitable electroosmotic flow marker at low pH in acetonitrile is addressed, and nitromethane is shown to be a proper marker compound under such extreme conditions. This work demonstrates how organic solvents can enlarge the field of application of CZE.

Publisher: AMER CHEMICAL SOC, 1155 16TH ST, NW, WASHINGTON, DC 20036 USA

IDS Number: 063KS

ISSN: 0003-2700

DOI: 10.1021/ac060243v S0003-2700(06)00243-5

Title: *Mobile phase effects on retention on a new butylimidazolium-based high-performance liquid chromatographic stationary phase.*

Author(s): Yaqin Sun and Apryll M. Stalcup.

(Department of Chemistry, University of Cincinnati, Cincinnati, OH, USA)

Source: JOURNAL OF CHROMATOGRAPHY A 1126 (1-2): 276-282 SEP 8 2006

Document Type: Article

Abstract: A new HPLC stationary phase based on *n*-butylimidazolium bromide has been characterized by a linear solvation energy relationship (LSER) approach in the binary acetonitrile/water mobile phases. The retention properties of the stationary phase were systematically evaluated in terms of intermolecular interactions between 28 test solutes and the stationary phase. The results and further comparisons with conventional reversed phase system confirm that retention properties are similar to phenyl phases in acetonitrile/water mixtures. The results obtained with acetonitrile/water mixtures are also compared with results obtained using methanol/water mixtures. (c) 2006 Elsevier B.V. All rights reserved.

Publisher: ELSEVIER SCIENCE BV, PO BOX 211, 1000 AE AMSTERDAM, NETHERLANDS

IDS Number: 082KJ

ISSN: 0021-9673

DOI: 10.1016/j.chroma.2006.06.092

Title: *Nonaqueous capillary electrophoresis in pharmaceutical analysis.*

Author(s): Laurent Geiser and Jean-Luc Veuthey.

(Laboratory of Analytical Pharmaceutical Chemistry, School of Pharmaceutical Sciences, University of Geneva, University of Lausanne, Geneva, Switzerland)

Source: ELECTROPHORESIS 28 (1-2): 45-57 JAN 2007

Document Type: Article

Abstract: This review presents different solvents and electrolytes commonly used as BGEs in NACE for the analysis of pharmaceutical compounds. Most NACE applications carried out since 1998 for the analysis of compounds of pharmaceutical interest are presented in four tables: (i) analysis of drugs and related substances, (ii) analysis of chiral substances, (iii) analysis of phytochemical extracts and (iv) analysis of drugs in biological fluids. These selected examples are used to illustrate the interest in NACE versus conventional aqueous CE.

Publisher: WILEY-V C H VERLAG GMBH, PO BOX 10 11 61, D-69451 WEINHEIM, GERMANY

IDS Number: 137HA

ISSN: 0173-0835

DOI: 10.1002/elps.200600265

Title: *Separation and determination of in vitro oxidized phospholipids by capillary zone electrophoresis.*

Author(s): Yu-Ling Ho, Jing-Huei Chiu, Chung-Yu Wu, Mine-Yine Liu.

(Department of Chemistry, National Changhua University of Education, Changhua 50058, Taiwan)

Source: ANALYTICAL BIOCHEMISTRY 367 (2): 210-218 AUG 15 2007

Document Type: Article

Abstract: A simple capillary zone electrophoresis (CZE) method was used to determine in vitro oxidized phosphatidyl choline (ox-PC). To optimize the capillary electrophoresis (CE) conditions, organic buffer additives, buffer ionic strength, buffer pH, and applied voltage were examined. The optimal CE separation buffer chosen was an aqueous-organic solvent system containing 10% sodium phosphate buffer (5 mM, pH 7.40), 80% methanol, and 10% acetonitrile. One major peak with a small shoulder was found for phosphatidyl choline (PC), whereas one major peak and a complex region containing several lower-mobility peaks were found for ox-PC. The lower-mobility species of ox-PC has high levels of conjugated dienes characterized by strong absorbance at 234 nm. The electropherograms of PC and ox-PC were significantly different and highly reproducible. The intensities of lower-mobility species decreased significantly when the antioxidant vitamin C concentration was increased from 6 to 600 μ M. This study provides a simple CZE method to differentiate in vitro oxidized from nonoxidized PC molecular species

Publisher: ACADEMIC PRESS INC ELSEVIER SCIENCE; 525 B ST, STE 1900, SAN DIEGO, CA 92101-4495 USA

IDS Number: 192JU

ISSN: 0003-2697

DOI: 10.1016/j.ab.2007.04.022

Title: *Capillary electrophoresis in pharmaceutical analysis: A survey on recent applications.*

Author(s): Leena Suntornsuk.

(Mahidol Univ, Fac Pharm, 447 Sri Ayudhya Rd, Bangkok 10400, Thailand)

Source: JOURNAL OF CHROMATOGRAPHIC SCIENCE 45 (9): 559-577 OCT 2007

Document Type: Review

Abstract: -

Publisher: PRESTON PUBL INC, 7800 MERRIMAC AVE PO BOX 48312, NILES, IL 60648 USA

IDS Number: 218QV

ISSN: 0021-9665

DOI:

Title: *CE at the omics level: Towards systems biology - An update*

Author(s): Eun Joo Song, Sheikh Md. Enayetul Babar, Eulsik Oh, Md. Nabiul Hasan, Hye-Min Hong, Young Sook Yoo.

(Korea Inst Sci & Technol, Life Sci Res Div, Bioanal & Biotransformat Res Ctr, POB 131, Seoul, South Korea)

Source: ELECTROPHORESIS 29 (1): 129-142 JAN 2008

Document Type: Review

Abstract: This review provides an updated overview of recent developments and applications of CE based on previously published reports in the field of omic research. The increased

number of published articles on omics shows that the field is growing and attracting the attention of many life science researchers. Due to developments in the omics sciences, many researchers have been studying systems biology, in which biological events in organisms are systematically interpreted through the combination of complex measurements from various methods resulting in high-throughput data. Given the challenges of such complex forms of analysis, CE is a strong candidate for generating omics data useful for acquiring the qualitative and quantitative knowledge necessary for systems-level investigation. By emphasizing CE for systems biology, this review will discuss and focus on the applicability of CE to systems-based analytical data at the genomic, transcriptomic, proteomic, and metabolomic levels from 2005 to the present.

Publisher: WILEY-V C H VERLAG GMBH, PO BOX 10 11 61, D-69451 WEINHEIM, GERMANY

IDS Number: 257VJ

ISSN: 0173-0835

DOI: 10.1002/elps.200700467

Title: *Analysis of the recent antipsychotic aripiprazole in human plasma by capillary electrophoresis and high-performance liquid chromatography with diode array detection.*

Author(s): Alessandro Musenga; Maria Addolorata Saracino; Domenico Spinelli; Egon Rizzato; Giancarlo Boncompagni; Ernst Kenndler; Maria Augusta Raggi.

(Univ Bologna, Dept Pharmaceut Sci, I-40126 Bologna, Italy; Univ Bologna, Dept Organ Chem A Mangini, I-40126 Bologna, Italy; Univ Vienna, Inst Analyt Chem, A-1090 Vienna, Austria)

Source: ANALYTICA CHIMICA ACTA 612 (2): 204-211 APR 2008

Document Type: Article

Abstract: Two methods, based on the use of capillary electrophoresis (CE) and high-performance liquid chromatography (HPLC), respectively, were developed for the analysis of the atypical antipsychotic aripiprazole in plasma of schizophrenic patients for therapeutic drug monitoring purposes. Good analytical performances were obtained with the CE method, using uncoated fused silica capillaries and a background electrolyte composed of 50 mM phosphate buffer at pH 2.5. With 20 kV voltage, aripiprazole was detectable at 214 nm within 5 min. The second analytical method, based on HPLC with diode array detection, employed a C8 reversed-phase column and a mixture of a 12.5 mM phosphate buffer, pH 3.5, containing triethylamine and acetonitrile as the mobile phase. Aripiprazole was detected at 254 nm and a complete chromatographic run lasted about 10 min. For both analytical methods loxapine was used as the internal standard and the same plasma sample pretreatment by means of solid-phase extraction on cyano cartridges was carried out, with extraction yield values always higher than 91.3%. Linear responses for aripiprazole were obtained between 70 and 700 ng mL⁻¹ and precision assays (expressed as relative standard deviation values) were lower than 7.0%. After validation, both methods were successfully applied to human plasma samples drawn from schizophrenic patients undergoing therapy with Abilify (R) tablets. Accuracy was satisfactory, with recovery value higher than 91.0%.

Publisher: ELSEVIER SCIENCE BV; PO BOX 211, 1000 AE AMSTERDAM, NETHERLANDS

IDS Number: 289IX

ISSN: 0003-2670

DOI: -