Quantitative Structure-Retention Relationships with Model Analytes as a Means of an Objective Evaluation of Chromatographic Columns

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Abstract

The performance of several previously designed model series of test analytes has been tested to characterize in an objective, quantitative manner modern stationary phases for reversed-phase high-performance liquid chromatography (RP-HPLC) using quantitative structure-retention relationships (QSRRs). Three QSRR approaches and three respective series of test analytes recommended for studies of the molecular mechanism of chromatographic retention are employed: the reduced linear solvation energy relationship (LSER)-based model of Abraham, a model employing structural descriptors from molecular modeling, and a model relating retention to the *n*-octanol–water partition coefficient log P. All of the models and test analytes proposed provide reliable QSRR equations. Those equations discriminate in quantitative terms individual columns and chromatographic systems and can be interpreted in straightforward rational chemical categories. In view of QSRRs, the differences in the intermolecular interactions between a given stationary phase and a structurally defined analyte rationalize the observed differences in retention. The QSRR models (previously derived retrospectively) are demonstrated to work well on new sets of RP-HPLC data. At the same time, it has been confirmed that the three test series of analytes have properly been designed and can be recommended for comparative studies of analytical columns. QSRRs once derived on a given column for model analytes can be used to predict the retention of other analytes of a defined structure. That in turn can facilitate the procedure of the rational optimization of chromatographic separations.

Introduction

Quantitative structure–retention relationships (QSRRs) are one of the most extensively studied manifestations of linear free-energy relationships (LFERs). QSRRs are the statistically derived relationships between the chromatographic parameters determined for a representative series of analytes in a given separation system and the quantities (descriptors) accounting for structural differences among the analytes tested (1).

Among the several areas of application of QSRRs (2), a wide interest from analytical chemists has recently developed in the studies on the molecular mechanism of separation operating in individual chromatographic systems both in high-performance liquid chromatography (HPLC) (3,4) and gas chromatography (GC) (5). The QSRR approach has allowed for the rationalization of differences in analyte retention on various stationary phases in terms of intermolecular interactions of a particular class involving the analyte, the stationary phase (zone), and the eluent.

The wide variety of the presently available reversed phase (RP)-HPLC phases differ in the ligand type of support material and the way in which the ligands are immobilized on the matrix. However, the polar and ionic properties of such support materials (such as silica or alumina) are responsible for secondary intermolecular interactions that often determine the unique character of an RP-HPLC phase (6). Numerous stationary phases for HPLC have nominally been identical, suggesting that they show similar chromatographic properties. However, as pointed out more recently by Sandi et al. (7), Barrett et al. (8), Cruz et al. (9), and Carr et al. (10), despite the widespread application of both analytical and preparative RP-HPLC, the underlying principles and molecular mechanism of retention are still subjects of a long-standing study and debate.

The active role in the retention of the stationary phase has long been acknowledged (11–15). The bonded phase is a complicated heterogeneous medium in which chemical composition and configuration vary with the mobile phase composition, the nature of the support, the bonding density of the ligand, and the alkyl ligand chain length (12,16–18).

Quantitative comparisons of stationary phases are difficult because there are no unequivocal quantitative tests (6). Best suited for that purpose might be the analysis of QSRRs. Tan et al. (19) and Abraham et al. (20) found in their QSRR studies that the relative importance of analyte structural descriptors in QSRR equations describing retention does not differ signifi-

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Quantitative Structure Chromatographic Retention Relationships

Łukasz Komsta,Yvan Vander Heyden,Joseph Sherma

Quantitative Structure Chromatographic Retention Relationships:

Quantitative Structure Roman Kaliszan,1987-10-14 The use of computers in numerical characterization of molecular structures has given chemists fundamentally new information on chemical structures leading to major developments in physical analytical and medicinal chemistry This book written by a pioneer in the field extends and updates research on quantitative structure retention relationships QSRR by consolidating and critically reviewing the extensive literature on the subject while providing basic theoretical and practical information required in all investigations involving chromatography analytical chemistry biochemistry and pharmaceutical research Coverage includes detailed discussions of the general theories and mechanisms of chromatographic separations prediction of retention coefficients statistical techniques and formal requirements of QSRR studies specific applications of chromatographic data and much more Also provides several carefully selected figures and tables plus extensive bibliographies **Liquid Chromatography** R. Kaliszan,2013-01-08 In view of linear free energy relationships LFER chromatographic systems are free energy transducers translating differences in the structure of analytes into quantitative differences in physicochemical properties like retention parameters Hence quantitative structure property retention relationships QSP R R bear valuable information on analytes and the separation systems involved We illustrate here what can be achieved from the statistically valid and physically meaningful quantitative structure retention relationships QSRR In particular one can predict retention data confirm identification and optimize conditions of separation of given structurally defined analytes Also QSPR can shed light on the molecular mechanism of separation operating on specific stationary phases Additionally one can assess such properties of drug analytes of pharmacokinetic importance like lipophilicity and acidity Also differences in interactions of xenobiotics with biomacromolecule components of chromatographic systems can conveniently be quantified By means of QSRR the chromatographic behavior of analytes in diverse separation systems can be related to their pharmacological properties

Recent Advances in QSAR Studies Tomasz Puzyn,Jerzy Leszczynski,Mark T. Cronin,2010-01-19 This book presents an interdisciplinary overview on the most recent advances in QSAR studies The first part consists of a comprehensive review of QSAR methodology The second part highlights the interdisciplinary aspects and new areas of QSAR modelling

Chemometrics in Chromatography Łukasz Komsta,Yvan Vander Heyden,Joseph Sherma,2018-02-02 Chemometrics uses advanced mathematical and statistical algorithms to provide maximum chemical information by analyzing chemical data and obtain knowledge of chemical systems Chemometrics significantly extends the possibilities of chromatography and with the technological advances of the personal computer and continuous development of open source software many laboratories are interested in incorporating chemometrics into their chromatographic methods This book is an up to date reference that presents the most important information about each area of chemometrics used in chromatography demonstrating its effective use when applied to a chromatographic separation *Gas Chromatography* Colin Poole,2012-07-26 This title provides comprehensive coverage of modern gas chromatography including theory instrumentation columns and applications addressing the needs of advanced students and professional scientists in industry and government laboratories Chapters are written by recognized experts on each topic Each chapter offers a complete picture with respect to its topic so researchers can move straight to the information they need without reading through a lot of background information Individual chapters written by recognized experts The big picture of gas chromatography from theory to methods to selected applications Provides references to other sources in associated areas of study to facilitate research Gives access to core data for practical work comparison of results and decision making **Handbook of Molecular Descriptors** Roberto Todeschini,Viviana Consonni,2008-07-11 Quantitative studies on structure activity and structure property relationships are powerful tools in directed drug research In recent years various strategies have been developed to characterize and classify structural patterns by means of molecular descriptors It has become possible not only to assess diversities or similarities of structure databases but molecular descriptors also facilitate the identification of potential bioactive molecules from the rapidly increasing number of compound libraries They even allow for a controlled de novo design of new lead structures This is the most comprehensive collection of molecular descriptors and presents a detailed review from the origins of this research field up to present day This practically oriented reference book gives a thorough overview of the different molecular descriptors representations and their corresponding molecular descriptors All descriptors are listed with their definition symbols and labels formulas some numerical examples data and molecular graphs while numerous figures and tables aid comprehension of the definitions Cross references throughout a list of acronyms and notations allow easy access to the information needed to solve a specific research problem Examples of descriptor calculations along with tables of descriptor values for a set of selected reference compounds and an up to date reference list add to the practical value of the book making it an invaluable guide for all those dealing with bioactive molecules as well as for researchers **Molecular Descriptors for Chemoinformatics** Roberto Todeschini,Viviana Consonni,2009-10-30 The number one reference on the topic now contains a wealth of new data The entire relevant literature over the past six years has been painstakingly surveyed resulting in hundreds of new descriptors being added to the list and some 3 000 new references in the bibliography section Volume 1 contains an alphabetical listing of more than 3300 descriptors and related terms for chemoinformatic analysis of chemical compound properties while the second volume lists over 6 000 references selected from 450 journals To make the data even more accessible the introductory section has been completely re written and now contains several walk through reading lists of selected keywords for novice users *Advances in Chromatography* Nelu Grinberg,Eli Grushka,2017-08-15 For more than five decades scientists and researchers have relied on the Advances in Chromatography series for the most up to date information on a wide range of developments in chromatographic methods and applications For Volume 54 the series editors have invited established well known chemists to offer cutting edge reviews of chromatographic methods applied in the life sciences that emphasize the underlying principle of separation science The clear presentation of topics and vivid illustrations for which this series has become known makes the material accessible and engaging to analytical biochemical organic polymer and pharmaceutical chemists at all levels of technical skill Issues in Analysis, Measurement, Monitoring, Imaging, and Remote Sensing Technology: 2011 Edition ,2012-01-09 Issues in Analysis Measurement Monitoring Imaging and Remote Sensing Technology 2011 Edition is a 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authority confidence and credibility More information is available at http www ScholarlyEditions com *Software-assisted Method Development In High Performance Liquid Chromatography* Szabolcs Fekete,Imre Molnar,2018-08-01 The book is a useful contribution in the field of HPLC and may represent a valuable tool for chromatography practitioners in different fields as well as teachers and instructors The 12 chapters provide comprehensive insights of current day retention and resolution modelling in HPLC and its applications for small and large molecule analysis It may be a useful reference for specialists in pharmaceuticals but not limited to It may be a valuable resource to assist scientists involved in method development aiming to achieve the best results with reduced costs time and efforts Analytical and Bioanalytical ChemistryThis handbook gives a general overview of the possibilities in recent developments in chromatographic retention modeling As a result of the latest developments in modeling software several new features are now accessible opening a new level in HPLC method development Many of these current possibilities in software assisted liquid chromatographic method modeling for analytical purposes are presented Several modes of chromatography including Reversed Phase Liquid Chromatography RPLC Ion Exchange Chromatography IEX Hydrophobic Interaction Chromatography HIC and Hydrophilic Interaction Liquid Chromatography HILIC are explained in detail For all these chromatographic modes the most important variables for tuning retention and selectivity are exposed Beside the industrial and practical benefits of retention modeling the possibilities in teaching and education are also illustrated Finally numerous representative industrial examples are shown to highlight the benefits time and cost savings offered by state of the art software assisted HPLC method development **Advances in Chromatography** J. Calvin Giddings,2021-06-23 This book presents the most up to date information on a wide range of developments in chromatographic methods and applications It provides timely cutting edge reviews in the fields of bio analytical organic polymer and pharmaceutical chemistry **Separation Methods in Drug Synthesis and Purification** Klara Valko,2020-06-19 Separation Methods in Drug Synthesis and Purification Second Edition Volume Eight provides an updated on the analytical techniques used in drug synthesis and purification Unlike other books on either separation science or drug synthesis this volume combines the two to explain the basic principles and comparisons of each separation technique New sections to this volume include enantiomer separation using capillary electrophoresis CE and capillary electro chromatography the computer simulation of chromatographic separation for accelerating method development the application of chromatography and capillary electrophoresis used as surrogates for biological processes and new developments in the established techniques of chromatography and preparative methods Features descriptions and applications of all separation methods used in the pharmaceutical industry Written by the leading scientists in their respective fields providing solutions for a wide range of industrial separation problems encountered within the pharmaceutical industry Thoroughly updated with brand new separation science techniques and the latest developments in the established techniques of chromatography **Thin Layer Chromatography in Drug Analysis** Lukasz Komsta,Monika Waksmundzka-Hajnos,Joseph Sherma,2013-12-20 Used routinely in drug control laboratories forensic laboratories and as a research tool thin layer chromatography TLC plays an important role in pharmaceutical drug analyses It requires less complicated or expensive equipment than other techniques and has the ability to be performed under field conditions Filling the need for an up to date **High Performance Liquid Chromatography in Pesticide Residue Analysis** Tomasz Tuzimski,Joseph Sherma,2015-05-20 HPLC is the principal separation technique for identification of the pesticides in environmental samples and for quantitative analysis of analytes At each stage of the HPLC procedure the chromatographer should possess both the practical and theoretical skills required to perform HPLC experiments correctly and to obtain reliable repeatable and r *Molecular Basis of Chromatographic Separation* Esther Forgacs,Tibor Cserhati,1997-07-03 Chromatographic separation is widely used in many scientific disciplines today having an ever increasing number of scientific and technological applications The widespread use of this rapid and powerful technique requires that it be fully understood so that the most suitable may be determined for each possible separation problem in each possible domain of scientific research and technology Molecular Basis of Chromatographic Separation provides complete coverage of the practical and molecular aspects of this popular technique It compiles and evaluates recent results outlines available methods and discusses how to select the best method for a particular application **Encyclopedia of Chromatography** Jack Cazes,2009-10-12 Thoroughly revised and expanded this third edition offers illustrative tables and figures to clarify technical points in the articles and provides a valuable reader friendly reference for all those who employ chromatographic methods for analysis of complex mixtures of substances An authoritative source of information this introductory guide to specific chromatographic techniques and theory discusses the relevant science and technology offering key references for analyzing specific chemicals and applications in industry and focusing on emerging technologies and uses *Monolithic Silicas in Separation Science* Klaus K. Unger,Nobuo Tanaka,Egidijus Machtejevas,2010-11-29 Edited by the experts and pioneers in the field this is the first monograph to cover the topic containing the must have information hitherto only scattered among journals Clearly divided into sections on preparation characterization and modeling and applications this is essential reading for chemists chromatographers analytical chemists biochemists and biologists **Comprehensive Two Dimensional Gas Chromatography** Lourdes Ramos,2009-07-22 The book reviews the basic concepts and highlights the most relevant advances and developments that have taken place in the field of comprehensive two dimensional gas chromatography GC x GC since its introduction in 1991 The several instrumental and technical approaches assayed and developed during these seventeen years and that have contributed to the development of this powerful separation technique and to its increasing application in many areas is explained and comprehensively illustrated through a number of chapters devoted these specific topics More specialized aspects of the technique including theoretical aspects modelization of the chromatographic process software developments and alternative couplings is also covered Finally special attention is paid to data treatment for both qualitative and quantitative analysis This book will be a practical resource that will explain from basic to specialized concepts of GC x GC and will show the current state of the art and discuss future trends of this technique Outlines basic concepts and principles of GCxGC technique for non specialists to apply the technique to their research Provides detailed descriptions of recent technical advances and serves as an instructional guide in latest applications in GCxGC Sets the scene for possible future development and alternative new applications of technique **Selectivity and Detectability Optimizations in HPLC** Satinder Ahuja,1989-06-06 High Performance Liquid Chromatography Edited by Phyllis Brown and Richard Hartwick This contributed volume is designed to consolidate the basic theories of chromatography along with the more exciting developments in the field This monograph addresses some questions that concern researchers in separation science including what is the current state of the art in liquid chromatography has the development of liquid chromatography plateaued if so what new methods will take its place or complement it and if not where will the new frontiers be and what direction will liquid chromatography take 1989 0 471 84506 X 688 pp Quantitative Structure Chromatographic Retention Relationships R Kaliszan Written by a pioneer in the field this book extends and updates research on quantitative structure retention relationships by consolidating and critically reviewing the extensive literature on the subject while also providing the basic theoretical and practical information required in all investigations involving chromatography analytical chemistry biochemistry and pharmaceutical research Among the topics covered are the nature of chromatographic interactions molecular interpretation of distribution processes in chromatography topological indices as retention descriptors and multiparameter structure chromatographic retention relationships 1987 0 471 85983 4 303 pp Detectors for Liquid

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