

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

Roman Kaliszan



Quantitative Structure Chromatographic Retention Relationships:

Quantitative Structure Roman Kaliszan, 1987 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

Principles and Practice of Modern Chromatographic Methods Kevin Robards,Danielle Ryan,2021-12-03 Principles and Practice of Modern Chromatographic Methods Second Edition takes a comprehensive unified approach in its presentation of chromatographic techniques Like the first edition the book provides a scientifically rigid but easy to follow presentation of chromatography concepts that begins with the purpose and intent of chromatographic theory the what and

why that are left out of other books attempting to cover these principles This fully revised second edition brings the content up to date covering recent developments in several new sections and an additional chapter on composite methods New topics include sample profiling sample preparation sustainable green chemistry 2D chromatography miniaturization nano LC HILIC and more Contains thorough chapters that begin with an updated schematic overview and a visual representation of the content Avoids the obfuscation of different terminologies and classification systems that are prevalent in the area such as the relationship between liquid chromatography and column chromatography Provides integrated and comprehensive topic coverage based on chromatographic bibliometrics and survey reports on the relative usage of chromatographic techniques

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 ScholarlyEditions eBook that delivers timely authoritative and comprehensive information about Analysis Measurement Monitoring Imaging and Remote Sensing Technology The editors have built Issues in Analysis Measurement Monitoring Imaging and Remote Sensing Technology 2011 Edition on the vast information databases of ScholarlyNews You can expect the information about Analysis Measurement Monitoring Imaging and Remote Sensing Technology in this eBook to be deeper than what you can access anywhere else as well as consistently reliable authoritative informed and relevant The content of Issues in Analysis Measurement Monitoring Imaging and Remote Sensing Technology 2011 Edition has been produced by the world s leading scientists engineers analysts research institutions and companies All of the content is from peer reviewed sources and all of it is written assembled and edited by the editors at ScholarlyEditions and available exclusively from us You now have a source you can cite with authority confidence and credibility More information is available at <http://www.ScholarlyEditions.com>

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Table of Contents Quantitative Structure Chromatographic Retention Relationships

1. Understanding the eBook Quantitative Structure Chromatographic Retention Relationships
 - The Rise of Digital Reading Quantitative Structure Chromatographic Retention Relationships
 - Advantages of eBooks Over Traditional Books
2. Identifying Quantitative Structure Chromatographic Retention Relationships
 - Exploring Different Genres
 - Considering Fiction vs. Non-Fiction
 - Determining Your Reading Goals
3. Choosing the Right eBook Platform
 - Popular eBook Platforms
 - Features to Look for in an Quantitative Structure Chromatographic Retention Relationships
 - User-Friendly Interface
4. Exploring eBook Recommendations from Quantitative Structure Chromatographic Retention Relationships
 - Personalized Recommendations
 - Quantitative Structure Chromatographic Retention Relationships User Reviews and Ratings
 - Quantitative Structure Chromatographic Retention Relationships and Bestseller Lists
5. Accessing Quantitative Structure Chromatographic Retention Relationships Free and Paid eBooks
 - Quantitative Structure Chromatographic Retention Relationships Public Domain eBooks
 - Quantitative Structure Chromatographic Retention Relationships eBook Subscription Services
 - Quantitative Structure Chromatographic Retention Relationships Budget-Friendly Options

6. Navigating Quantitative Structure Chromatographic Retention Relationships eBook Formats
 - ePub, PDF, MOBI, and More
 - Quantitative Structure Chromatographic Retention Relationships Compatibility with Devices
 - Quantitative Structure Chromatographic Retention Relationships Enhanced eBook Features
7. Enhancing Your Reading Experience
 - Adjustable Fonts and Text Sizes of Quantitative Structure Chromatographic Retention Relationships
 - Highlighting and Note-Taking Quantitative Structure Chromatographic Retention Relationships
 - Interactive Elements Quantitative Structure Chromatographic Retention Relationships
8. Staying Engaged with Quantitative Structure Chromatographic Retention Relationships
 - Joining Online Reading Communities
 - Participating in Virtual Book Clubs
 - Following Authors and Publishers Quantitative Structure Chromatographic Retention Relationships
9. Balancing eBooks and Physical Books Quantitative Structure Chromatographic Retention Relationships
 - Benefits of a Digital Library
 - Creating a Diverse Reading Collection Quantitative Structure Chromatographic Retention Relationships
10. Overcoming Reading Challenges
 - Dealing with Digital Eye Strain
 - Minimizing Distractions
 - Managing Screen Time
11. Cultivating a Reading Routine Quantitative Structure Chromatographic Retention Relationships
 - Setting Reading Goals Quantitative Structure Chromatographic Retention Relationships
 - Carving Out Dedicated Reading Time
12. Sourcing Reliable Information of Quantitative Structure Chromatographic Retention Relationships
 - Fact-Checking eBook Content of Quantitative Structure Chromatographic Retention Relationships
 - Distinguishing Credible Sources
13. Promoting Lifelong Learning
 - Utilizing eBooks for Skill Development
 - Exploring Educational eBooks
14. Embracing eBook Trends
 - Integration of Multimedia Elements

- Interactive and Gamified eBooks

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