

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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