



# Characterization of 1,3-alternate calix[4]arene-silica bonded stationary phases and their comparison to selected commercial columns by using principal component analysis

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## ABSTRACT

Twelve calix[4]arene stationary phases in 1,3-alternate conformation, synthesized in the authors' laboratory, were characterized in terms of their surface coverage, hydrophobic selectivity, aromatic selectivity, shape selectivity, hydrogen bonding capacity and ion-exchange capacity. The set of tests commonly used for evaluation of commercially available stationary phases was applied to assess fundamental chromatographic properties of the calixarene phases. The new calixarene phases were compared to each other, to Caltrex and LiChrosorb C-18 columns. Principal component analysis has been used to provide comparison between 1,3-alternate calix[4]arene phases and commercially available phenyl, fluorophenyl and fluoroalkyl columns.

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## 1. Introduction

The continuous efforts to synthesize the “universal and unfailing” HPLC stationary phase with excellent chemical stability, improved selectivity and efficiency have increased significantly in recent years. Among many different types of HPLC phases, working in different separation modes, the reversed phases play presently a dominant role [1] and a number of RP columns differing in ligand types and the way these are bonded to the solid support is commercially available. Apart from classical reversed phase columns, calixarene stationary phases have lately attracted the attention of many researchers and the potential of this class of macrocyclic compounds for HPLC applications has been shown [2,3]. The modifications of calixarene molecules influencing their chromatographic properties include: conformations in which they are blocked, the type of functional groups and substituents present at their upper and lower rims, the calixarene ring-size, and the type of spacer fixing the macrocycles to the solid support. The calixarene supramolecular host molecules in a cone and 1,3-alternate conformation, bonded to the silica gel, form inclusion complexes with the analytes and possess unique chromatographic properties [4–12]. In this paper we characterize twelve novel calix[4]arene stationary

phases in 1,3-alternate conformation in terms of surface coverage, hydrophobic and shape selectivity as well as hydrogen bonding and ion-exchange capacity. The Tanaka characterization protocol, which is a well-established, still favored by many academic groups approach, was used to characterize fundamental chromatographic descriptors of calixarene phases [13–17]. Based on this protocol it is possible to compare the new type of calixarene columns to the great number of other RP-phases, characterized by other research groups. Although this test was originally developed for *n*-alkyl based RP columns, it may also be applicable to other phase types [18,19]. In order to assess the aromatic selectivity of these phases, we have additionally used the approach proposed by Horak and Lindner [18]. They have suggested that the retention ratio of the Tanaka test solutes (*n*-pentylbenzene/*o*-terphenyl) may provide an indication of the capacity of the phase to undergo aromatic interactions with aromatic analytes. The calixarene phases were compared to each other, to Caltrex columns possessing calixarene molecules in cone conformations and to LiChrosorb C-18 phase. Additionally, principal component analysis has been used to explore the differences and similarities between 1,3-alternate calix[4]arene phases and selected commercially available RP columns. From among great number of RP stationary phases, we choose phenyl, fluorophenyl as well as fluoroalkyl columns with chemical structures resembling the building blocks of the calixarene phases.

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