

Chemometric studies of retention in capillary gas chromatographic separation of hydrocarbons in coupled columns

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Received 7 October 2004; received in revised form 19 January 2005; accepted 25 January 2005

Abstract

This paper describes how different multivariate analysis and classification methods can be used, to characterize the gas chromatographic separation of complex hydrocarbon mixtures in three columns coupled in series. Principal component analysis (PCA), correspondence factor analysis (CFA), and hierarchical ascending classification (HAC) were used as potential tools for evaluating the experiments on single columns and on column series. It has been demonstrated that: (1) multivariate analysis with PCA and CFA offers a powerful strategy to search for the main factors influencing the separation of hydrocarbons without a priori knowledge of the key factors of the separation. (2) With CFA the contribution of retention due to vapour pressure can be minimized. The use of retention indices, which use the *n*-alkanes as reference compounds, also helps to decrease the dominant focus on vapour pressure in favor of the more selectivity-based interaction forces. (3) CFA helps to analyze the degree of relevance of the chosen experimental design to the most important factors, controlling chromatographic selectivity.

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Keywords: Chemometrics; Data evaluation; Multivariate techniques; Capillary gas chromatography; Three columns coupled in series; Multicomponent hydrocarbon separation

1. Introduction

The main task for the separation of complex mixtures by capillary gas chromatography (CGC) is to find the optimum separation system selectivity. The selectivity of a gas chromatographic separation can be modified by temperature, the stationary phase polarity or by a combination of both [1]. Mixed stationary phases have been proposed in order to develop optimized stationary phase selectivity, initially. However, the final selectivity of mixed stationary phases often do not result from a linear combination of the pure stationary phases due to their mutual physicochemical interactions [2]. This explains why the use of serially coupled columns has

been envisaged more successfully [3]. The selectivity of a column series at isothermal conditions can in general be tuned by variation of the lengths of the coupled columns or by control of the carrier gas flow rates in individual columns. Several papers were published dealing with the theory and practice of gas-chromatographic analysis on two-column systems [4–14]. The use of more than two columns may, however, enlarge the experimental dimensions in which the selectivity may be tuned. A theory and its experimental verification have been published for the separation of a complex mixture of hydrocarbons on a gas chromatographic system consisting of three different capillary columns [15].

In gas chromatography, retention is a phenomenon that depends dominantly on solute-stationary phase interactions. For the successful treatment of retention data for a complex mixture, various chemometric techniques can be used

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[16,17]. These methods allow the simultaneous evaluation a relatively large amount of data, greatly facilitating the clarification of both practical and theoretical problems. These chemometric procedures have already been extensively employed in chromatography for: (1) identification of the basic factors influencing retention and separation, (2) comparison of various stationary and mobile phases, (3) assessment of the relationship between molecular structure and retention behavior (quantitative structure–retention relationship, QSRR) and (4) elucidation of correlations between retention behavior and biological activity [18–21].

As each chemometric procedure generally highlights only one, or only a few features of the chromatographic problem under analysis, the concurrent application of more than one technique is more the rule than the exception [18,21].

The aim of the present paper is to show how different multivariate analysis and classification methods can be used, to characterize the gas chromatographic separation of complex mixtures of hydrocarbons in three columns coupled in series. Principal component analysis (PCA), correspondence factor analysis (CFA), and hierarchical ascending classification (HAC) were used as potential tools for evaluating the experiments on single columns and on column series.

2. Experimental

Three columns with different polarities were used:

- A. SE 30, 30 m × 0.32 mm × 0.25 μm (from Machery-Nagel, Germany);
- B. SE 54, 25 m × 0.25 mm × 0.25 μm (from RIC, Belgium);
- C. Nucol (bonded polyethyleneglycol, SUPELCO, Bellefonte, USA), 15 m × 0.25 mm × 0.25 μm (from Supelco, USA).

The columns were coupled in series by press-fit connectors. The HP 5890 A (Hewlett-Packard, Avondale, USA) gas chromatograph with split injector and FID was used for all measurements.

The inlet carrier gas pressure was measured by an additional U-manometer with an accuracy of 100 Pa. An aneroid manometer was used to measure the outlet pressure with an accuracy of 10 Pa.

The chromatograms were evaluated by HP 3365 ChemStation software (Hewlett-Packard, Avondale, USA).

Hydrogen was used as a carrier gas. The oven temperature was 60 °C.

The characterization of the sample constituents and their corresponding retention times on the three single columns A, B and C and four different column series ABC, CBA, BCA and ACB is listed in Table 1.

The retention factors and retention indices have chiefly been processed for calculations. Retention factors (k_i) of each hydrocarbon (i) were calculated from corresponding reten-

tion times (t_R) listed in Table 1 using the equation:

$$k_i = \frac{t_{R,i} - t_M}{t_M}$$

where t_M is a corresponding retention time of methane.

Retention indices (I_i) of each hydrocarbon (i) were calculated from corresponding retention times (t_R) listed in Table 1 using the equation:

$$I_i = 100z + 100 \frac{\ln(t'_{R,i}/t'_{R,z})}{\ln(t'_{R,z}/t'_{R,z+1})}$$

where t'_R is adjusted retention time ($t'_R = t_R - t_M$) and z denotes number of carbon atoms in a n -alkane elutes before considered hydrocarbon (i). The retention times of the n -alkanes and other hydrocarbons should increase in the order: $t_{R,z+1} > t_{R,i} > t_{R,z}$.

2.1. Chemometrics methods

For the calculations of PCA, CFA and HAC the program Statistica 4.3 for Windows was used [22].

3. Results and discussion

3.1. Principal component analysis (PCA) and correspondence factor analysis (CFA)

The hydrocarbons in the used model mixture exhibit only slight differences in chromatographic behaviour both on the individual chromatographic columns as well as the column series. This is why a multivariate analysis was used to detect these small differences.

The retention factors (k_i) and retention indices (I_i) on the column series are expected to be a linear combination of the retention data on single columns [2,3]. As the retention indices for the column series have no direct physical interpretation, we will focus our attention only on the retention indices for the three uncoupled columns. Therefore the calculations were performed using two data matrices. The first matrix containing retention factors was of size 51 × 7, which includes all 51 sample constituents on seven different columns (A, B and C) or column series (ABC, ACB, BCA and CBA). The second matrix containing retention indices was of size 51 × 3 (all 51 sample constituents on three different columns A, B and C). Both for the retention factors and the retention indices PCA and CFA were performed.

The PCA map of retention factors is shown in Fig. 1, which corresponds to the first factorial plan defined by the two main factorial axes. Only these two main factorial axes are significant. This implies that only two interaction mechanisms influence the separation. The variation along the first principal component is related the variation of vapour pressure of the compounds, it takes into account 97.3% of the variance, i.e. of the information content. The second main

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