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Abstract

Title	Retention Behavior of Pyrazines in Reversed-Phase High Performance Liquid Chromatography

(800 words)

Flavor is one of the most important constituents in cocoa products such as chocolates. The quantity of pyrazines in cocoa beans is important in the production of the cocoa products such as chocolate, because the content is one of the key parameters to produce a desirable taste of these food products.

In this thesis, retention behavior of several pyrazines and its derivatives in reversed-phase liquid chromatography (RPLC) is described. When the column temperature was changed with the acetonitrile and the methanol were used as the mobile phase component, a different retention behavior for pyrazines were observed.

In Chapter 1, general introduction of this thesis including the aims and scope of the study is described along with the background of this work. Development of prediction models using MLR and ANN that could accurately describe the retention behavior of a group of pyrazine and alkylpyrazines in RPLC are described in Chapter 2. A better understanding of the mechanisms that govern the retention of solutes in chromatographic system remains as a major goal in separation science. For this perspective, the quantitative structure-retention relationships (QSRR) method became a popular tool for investigating the retention mechanism. In this chapter, retention prediction models based on MLR and ANN were developed to describe and predict the retention behavior of pyrazines under reversed-phase conditions using ODS as the stationary phase. MLR-derived models showed that the retention of the analytes can be attributed to the effect of the organic modifier in the mobile phase (ACN or MeOH) and log P of the analytes. A comparison between the MLR and the ANN models revealed that the predictive ability of the trained ANN was better than that of MLR especially when applied to the ACN data set. The derived models can be used as tools for method development and optimization for the analysis of pyrazines and related compounds.

In Chapter 3, retention behaviors of pyrazine and alkylpyrazines in RPLC were examined, and an abnormal retention behavior in RPLC of pyrazines was found. About the change in the retention behavior, various factors such as the entropy changes could be considered. In this work, it was shown that alkyl pyrazines tend to be in the stationary phase when the column temperature is elevated with ACN-based mobile phase solvent. In terms of the dependence of the retention on the content of organic solvent in the mobile phase at constant temperature, all the pyrazines showed a normal behavior, as found in most RPLC conditions. The results suggest that more efficient separation of pyrazines could be developed by tuning up both the mobile phase composition and the column temperature, although further theoretical studies should be made to interpret the abnormal dependence of the pyrazines' retention on the column temperature with ACN/water as the mobile phase solvent.

To make clear this phenomenon, the temperature effect on the retention of diazines, consisted of pyrazines, pyridazines, pyrimidines and their derivatives, in RPLC was further studied at various column temperatures in Chapter 4. For comparison, the retention behavior of pyrazole, imidazole and their methyl derivatives was also studied. From the RPLC separation of various nitrogen-containing heterocyclic compounds performed at different temperatures and with mobile phase conditions, an abnormal temperature effects on retention of diazines (pyrazines, pyridazines and pyrimidines), that is, the retention of these analytes were increased when the column temperature was elevated, was confirmed with the mobile phases consisting of ACN and water. The enthalpy of solute transfer from mobile phase to stationary phase were calculated from van't Hoff plots, and enthalpy-entropy compensation effects were observed for diazines with ACN/water as the mobile phase.

Finally, the over-all conclusion of this thesis is summarized in Chapter 5.