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Journal of Food Composition and Analysis 18 (2005) 345–357

JOURNAL OF FOOD COMPOSITION AND ANALYSIS

www.elsevier.com/locate/jfca

Original Article

A practical, theory-supported approach of linear temperature programmed gas chromatographic retention indices used in the recognition experiments of Hungarian food specialities, called "*Hungarics*"

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Received 2 April 2003; received in revised form 8 December 2003; accepted 11 February 2004

Abstract

An evidence in the form of a short deduction applying few thermodynamic and mathematic simplifications and inaccuracy is given for the elution behaviour of homologous series members (e.g., *n*-hydrocarbons) under isotherm and linear temperature programmed gas chromatographic conditions. Experimental proof is presented to support the statements of the theoretical implication. A precise and uniformly applicable PTRI measurement process is described by using two model solutions that make the results proper for generalization. The capability of the aroma-spectra method of solving identification and recognition tasks is demonstrated.

Keywords: Kováts index system; *L*inear *t*emperature *p*rogrammed *g*as *c*hromatographic *r*etention *i*ndex (PTRI in brief) measurement; Relative aromagrams, i.e., aroma-spectra; Determination of samples origin

1. Introduction

In the early years of gas chromatography, the almost unsolvable problem of retention time fluctuation obstructing the smooth inter-laboratory identification of the analytes (relying on the retention data obtained by other research groups) occurred mostly as a consequence of limited repeatability and reproducibility of the chromatographic runs. A sufficient, practical solution of the problem could be achieved when Ervin Kováts (1958) recognized that under isotherm

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0889-1575/$ - see front matter © 2004 Published by Elsevier Inc.
doi:10.1016/j.jfca.2004.02.014

conditions the elution of the members of homologous series (e.g., *n*-alkanes, fatty acid ethyl esters, etc.) obeys power functions mathematically. Consequently, the logarithmized retention data, precisely the logarithmic reduced retention volume (lg V'_R) or time (lg t'_R), define straight lines as a the function of carbon number. The disadvantage of isotherm chromatographic work has been eliminated by Van den Dool and Kratz (1963) when they introduced a new generalized equation for linear temperature programmed gas chromatographic runs based on the equidistant elution of *n*-alkanes following each other, as can be seen in Fig. 1.

Theoretical gas chromatographers who minded losing the molecule-structural information hidden with the Kováts Indices refused to use the new identification possibility that was soon forgotten for its poor reproducibility. Without arguing over the structural characterization strength of Kováts Indices, our research group thinks that this kind of retention data handling should be considered much more as a practical approach of the identification problem than a theoretical one that is based on the physico-chemical character of the analyte molecules. Eventually the retention behaviour originates and can be deduced from molecule-structural and sorption interaction features, but its manifestation through the Clausius–Clapeyron law and heterogeneous partition equilibrium makes the phenomenon debatable and uneasy to control by theoretical tools. In our opinion the extremely high reproducibility of the Kováts Indices is the primary consequence of the logarithmization mathematical step that ceases the deviation of the retention data and not of the thermodynamic features lying in the physico-chemical depth.

Besides elaborating new methods and equipment in the sampling of the volatile compounds (Ishihara and Honma, 1992) and opening new fields in the investigation of the essential oil components (Mateo et al., 1997), the development of gas chromatography ensured surprising possibilities. The advent of fused silica capillary chromatography and later that of the *e*lectronic *p*ressure/flow *c*ontrol (EPC) brought about an unexpected and incredible improvement in the reproducibility of retention data and created the possibility of rediscovering (Bicchi et al., 1999) and using the *l*inear *t*emperature *p*rogrammed *g*as *c*hromatographic *r*etention *i*ndex (LTPGCRI, that is PTRI in brief) measurements for the practical solution of identification tasks.

The present study gives a short thermodynamic proof of the retention behaviour of homologous series' members. Furthermore, it reports on the experience gathered in an 8-year span of scent and fragrance recognition investigation conducted in the field of Hungarian food product specialities (e.g., Muscat ottonel wine, Kovács et al., 1999; Red paprika spice powder, Kocsis et al., 2002; Kocsis et al., 2003). These products are called by a collective noun "Hungarics".

2. Theoretical

The gas chromatographic elution behaviour of the members of homologous series (e.g., *n*-alkanes, fatty acid ethyl esters, etc.) can be described by the experience and practice proved equation valid under isotherm running conditions:

$$t'_R = K \cdot a^i, \tag{1}$$

where t'_R is the reduced retention time of the members of the series, "K" and "a" are constants depending on the features of the measuring system and compounds, and "i" is the carbon number