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A retention index system for comprehensive two-dimensional gas chromatography using polyethylene glycols

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ABSTRACT

The characterization and identification of compounds in complex real-world samples is quite difficult and new concepts and workflows are highly desirable. Retention indices (RIs) are widely used in gas chromatography (GC) to support the identification of unknown compounds. Several attempts have been made to introduce a similar concept for the second dimension in comprehensive two-dimensional (2D) GC (GC × GC) but, an easily applicable and robust system remains elusive.

In the present study, a new RI system for GC × GC was developed. Polyethylene glycols (PEGs) were used in combination with a simple linear regression, with *n*-alkanes as reference points for virtually unretained compounds and PEG homologs as reference compounds for second-dimension RIs (PEG-²*I*). The *n*-alkanes were assigned a PEG-²*I* of zero and the distance between consecutive PEG homologs from PEG-2 (diethylene glycol) and higher were assigned a PEG-²*I* value of 10. We used ethylene glycol and PEG-2 through PEG-10 as reference compounds, thereby covering a PEG-²*I* range from 20.0 for ethylene glycol, over 50.0 for diethylene glycol (PEG-2) to 130.0 for decaethylene glycol (PEG-10); additional PEGs can be added to cover a wider polarity range. The PEG-²*I* system was initially evaluated using a 30 m × 0.25 mm non-polar (5% phenyl, 0.25 μm film thickness) first-dimension column and a 1.6 m × 0.18 mm polar (50% phenyl, 0.18 μm film thickness) second-dimension column. This system was validated for use with non-polar first-dimension columns and a semi-polar (50% phenyl) second-dimension column, and exhibited robustness to changes in the carrier gas flow velocity, oven temperature ramping rate, and secondary oven temperature offset. An average relative standard deviation of 2.7%, equal to a 95% confidence interval of 0.76 PEG-²*I* units, was obtained for the PEG-²*I* values of 72 environmental pollutants. Additionally, the system was found to be applicable over a wide range of boiling points (in the current case, from *n*-heptane to *n*-dotriacontane (C₇–C₃₂)) and can be used with various column dimensions. Changing the second-dimension column to either a narrower 0.1 mm column or a wider 0.25 mm column, yielded similar 95%-percentiles to that of the 0.18 mm column, differing by only 0.05 and 0.03 PEG-²*I* units, respectively. Moreover, methods for improving the system were suggested.

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1. Introduction

The possibilities for identifying unknown organic compounds have improved significantly with the introduction of retention indices (RI) in gas chromatography (GC). In 1958, Kováts [1] introduced a relationship between the elution time of a compound and the elution of *n*-alkanes as the basis for RIs associated with isothermal one-dimensional GC. This work has been cited more than 1000 times in the last fifty years [2], and several subsequent studies have proposed other RI calculation methods or modifications to the

original relationship. For example van den Dool and Kratz [3] generated alkane or linear retention indices (LRIs) by adapting Kováts' indices for linear oven temperature programming. Similarly Lee et al. [4] introduced another RI concept, i.e. the Lee index, which uses polycyclic aromatic hydrocarbons (PAHs) as retention markers (naphthalene, phenanthrene, chrysene, and picene) for the analysis and indexing of polycyclic aromatic compounds (PACs).

The invention of comprehensive 2D GC (GC × GC) by Phillips and Liu in 1991 [5] has yielded considerable improvement in the characterization of complex samples [6]. Most of the early studies employing GC × GC have focused on the analysis of petrochemical samples [7,8]. However, GC × GC is applicable to many other complex sample matrices, e.g., sediment [9], air [10], food extracts [11], and biological samples [12,13]. This technique is

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Table 1
Experimental settings for testing robustness of the proposed new retention index system.

Carrier gas flow (mL/min)	Oven ramping rate (°C/min)	2nd oven offset (°C)	Modulation (sec)	Repetitions
0.8	3	20	9	2
0.8	3	40	6	2
0.8	5	40	6	2
0.8	5	20	6	2
0.8	4	30	6	2
1.25	3	20	6	2
1.25	3	40	6	2
1.25	5	40	6	2
1.25	5	20	6	2
1.25	4	30	6	2
1	4	40	6	2
1	4	20	9	2
1	3	30	9	2
1	5	30	6	2
1	4	30	6	5

particularly well-suited for complex sample characterization and analysis, including non-target analysis [6,14–16] and biomarker identification [17]. Nevertheless, the generation and use of both first-dimension (1D ; nomenclature after Schoenmakers et al. [18]) and second-dimension (2D) RIs (I) is highly desirable.

The development and implementation of a robust RI system for the 2D in GC \times GC have, however, proven difficult. In GC, injection of a mixture of n -alkanes, or related homologous series of compounds, results in a set of equidistant peaks, because all homologs interact with the GC stationary phase in the same manner. In addition, each CH_2 -unit accounts for the same incremental contribution to the vapor pressure of the compounds. Finding RI reference compounds that, in the same manner, produce equidistant peaks in the 2D space have proven challenging. Therefore, iso-volatility curves or iso-volatility plots have been used to generate I values similar to the Kováts indices [19–24].

Most methods use continuous or repeated injection of reference compounds, usually n -alkanes [19,20,25] or fatty acid methyl esters (FAME) [21], for the creation of “iso-volatility” curves within the $2D$ separation space. The second retention time (2t_R) of the injected component decreases exponentially with increasing temperature and the 2I value is obtained via interpolation (or sometimes extrapolation) between successive alkane lines in the pseudo-isothermal 2D analysis. This method is complex, requires attention to the details of the experiment, valid only for compounds with boiling points within a certain range [19,26], and has poor precision [27]. Several of these drawbacks were overcome via modifications [21,26,28], but application of the method remains complex. Therefore, the 2D space is typically framed by injecting suitable n -alkanes or FAMEs, deriving an equivalent 2I space, and predicting the 2I values of solutes found within the calibrated GC \times GC space in subsequent sample analyses. However, this approach is vulnerable to (among others) experimental-system variations and matrix effects.

A more theoretical approach, compared with this method, was presented by Dorman et al. [24]. They calculated thermodynamic RIs, which were obtained through enthalpy and entropy data and used for predicting the $2D$ elution of analytes from the Grob mix. Arey et al. [29] used stationary phase-gas phase equilibrium partition coefficients to calculate 2D RIs, which were then used to estimate the physico-chemical properties (e.g., aqueous solubility and air-water partition coefficients) needed to predict environmental partitioning. Similarly, Antle et al. calculated 2I similar to the Lee RIs and estimated physical properties using the iso-volatility curves of two- to five-ring PAHs to assess the environmental impact on the weathering of coal tar [30].

The present study was aimed at providing a new RI system for the most widely used GC \times GC setup, i.e., an apolar \times polar column set [31], which may be applied across a wide range of

analyte boiling points and with any column dimensions and GC program settings (e.g., carrier gas flow or oven temperature ramping rate). The new system is based on the co-injection of samples and polyethylene glycol (PEG) and n -alkane reference standards, which results in both first-dimension LRIs and second-dimension PEG RIs (PEG- 2I) for all analytes. The size and polarity of the PEGs increase with increasing number of CH_2CH_2O units and, hence, their chromatographic peaks become distributed along the diagonal of the GC \times GC plane, rendering them well-suited for use as retention reference compounds. The repeatability and robustness of the system have been systematically evaluated, pros and cons discussed, and improvements (e.g., expansion of the applicability domain) proposed.

2. Material and methods

The goal of this work was to introduce a new RI system for GC \times GC using polyethylene glycols as retention markers. The RIs of 72 compounds were calculated using the work flow presented in Section 3.4 and the results for different settings and columns were compared.

2.1. Material

PEGs were purchased from Sigma Aldrich (mono till hexa and octa; Steinheim, Germany) and Tokyo Chemical Industry Co., Ltd. (hepta, nona and deca; Zwijndrecht, Belgium). An aliphatic alcohol mix (C_2 – C_8) and an n -alkane standard (C_7 – C_{40}) were obtained from Chiron AS (Trondheim, Norway) and Sigma Aldrich (Supelco, Bellefonte, PA, USA), respectively. The 8270 MegaMix[®] standard (hereafter, referred to as MegaMix) was purchased from RESTEK (Bellefonte, PA, USA). This standard consisted of 76 structurally diverse compounds, 72 of which could be analyzed (see Table 4 in the results section for compound list). Dichloromethane (DCM; 99.99%) was obtained from Fisher Scientific (Loughborough, UK).

2.2. Methods

A mixture consisting of the MegaMix, PEGs, alkanes, and the aliphatic alcohol mix was prepared in DCM. All analyses were performed on an Agilent Technologies 6890 gas chromatograph (Palo Alto, CA, USA) coupled to a Pegasus 4D time-of-flight mass spectrometer (TOF MS; Leco Corp., St. Joseph, MI, USA). A secondary oven and a quad-jet dual stage modulator were built into the main GC oven. The split/splitless injector was operated in splitless mode at a temperature of 280 °C. Data were acquired and processed using the Chroma-TOF software (version 4.50; LECO Corp.). The 2t_R is assigned to each peak, by the software, based on the most abundant

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