

Calibrated salvage of gas chromatography capillary column retention indices

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Abstract

A calibration method was developed to generate gas chromatographic retention index offset plots, for the purpose of merging separate temperature-programmed retention index datasets into a unified database. The 8°C/min on OV-1 stationary phase subset of the Sadtler Standard Gas Chromatography Retention Index Library was used as an initial model. This calibration method was applied to three hydrocarbon datasets. Retention index search windows were assigned to each incorporated molecule, derived from the 0.95 prediction bands of the polynomial regression fits to the offset plots.

Keywords: Retention indices; Temperature-programmed retention indices

1. Introduction

Temperature-programmed retention indices (RI) can be highly reproducible on a given capillary column stationary phase if working variables such as carrier flow-rate, film thickness and the linear temperature programming rate are standardised. This has great promise for the identification of unknown eluates. However since most published RI values have not been produced under conditions in which these parameters were strictly comparable, their usefulness for databases remains latent.

It has been shown in Ref. [3] that the retention indices of the 8°C/min on OV-1 stationary phase subset of the excellent Sadtler compilation could be reproduced on a 25-m capillary column by adjusting the program rate to 17°C/min and the helium inlet pressure to 62.5 kPa, i.e., “pseudo-Sadtler” conditions. Using the calibrated correction developed in [3] allowed the successful incorporation of the large Sadtler [1] and Jennings and Shibamoto [2] datasets

into a “pseudo-Sadtler” database, containing both experimentally measured and corrected RI values. Incorporation of any corrected RI value into the “pseudo-Sadtler” database [3] was deemed justifiable, if the calibration derived search window assigned to the corrected RI was narrower than the search window of ± 50 –60 RI units adopted in The International Association of Forensic Toxicologists (TIAFT) compilation [6]. This criterion prevented the incorporation of the entire Pflieger RI collection [7].

In the work presented in Ref. [3], each calibration (offset) plot was created by taking a representative structure subset of the dataset to be incorporated, and applying the “pseudo-Sadtler” conditions to provide RI_{exp} values. The differences (offsets) between the published values ($RI_{Ha-OV101}$, RI_{White} and $RI_{Ha-Ultra1}$) and the RI_{exp} values were then fitted by a second-order polynomial fit to give a predicted offset, and individual search windows could be assigned from the associated 0.95 prediction limits. This predicted

offset was then added to the published RI value to give a corrected RI value. The goal of this study was to apply this methodology developed in [3], to the three smaller RI datasets in [8–10] and if the individual search windows are narrower than ± 50 –60 RI units, to introduce the corrected RI value into the “pseudo-Sadtler” database.

Some comments on these three datasets are merited. The Hayes and Pitzer dataset in [8] has 184 entries with $RI_{\text{Ha-OV101}}$ values ranging from retention index 464.94 to 1682.39. Of these, 176 entries were useable (i.e., with $RI_{\text{Ha-OV101}} > 600$). The 17°C/min GC temperature program prevents reliable RI estimation below 600. Typical structures in [8] include branched alkanes, 1-alkenes, alkylbenzenes, alkylcyclohexanes and alkyl naphthalenes. The White et al. dataset in [9] has 382 entries with RI_{White} values ranging from 100.00 to 1800.00, but only 303 are useable (i.e., excluding *n*-alkane standards and structures with RI values less than 600.00). Typical structures include branched alkanes, branched alkenes, 1-alkenes, alkylbenzenes, alkylcyclohexanes, alkylcyclopentanes, chloroalkanes and alkyl naphthalenes. The Hayes and Pitzer dataset in [10] has 117 entries with $RI_{\text{Ha-Ultra1}}$ ranging from 560.33 to 1769.1; of these 116 were useable (i.e., with $RI_{\text{Ha-Ultra1}} > 600$). Typical structures include branched alkanes, 1-alkenes, alkylbenzenes and alkylcyclohexanes.

2. Experimental

2.1. Calibration

The Base/Neutrals mixture for Environmental Protection Agency method 625 (Sigma part number 38,463-1; 41 structures in total), was injected as in Ref. [3] and the retention indices measured by simple linear interpolation between bracketing *n*-alkanes, using the Van den Dool and Kratz equation [4]. This was used firstly to find the “pseudo-Sadtler” conditions and later acted as a daily control. Of the 41 structures, 29 are reliably in the Sadtler data set. A least squares unweighted fit of these 29 retention indices with the RI_{Sad} values allowed adjustment of the temperature programming and helium flow-rate to find the best alignment i.e. the

“pseudo-Sadtler” conditions. These were a linear temperature programming rate of 17°C/min from 35 to 300°C and a HP 5890A GC column head-pressure of 62.5 kPa helium (=1.5 ml/min at 20°C). The programming rate was used for final fine tuning rather than the gas flow-rate [5].

2.2. Instrumentation

All structures were measured with simultaneous injection of *n*-alkanes standards (C_5 to C_{40} inclusive except C_{39} which was not commercially available). Each structure was measured six times and the average RI determined. A Hewlett-Packard Ultra-1 capillary column (25 m×0.32 mm I.D. and a film thickness of 0.52 μm) was used for consistency with the Sadtler compilations. The column was monitored for performance deterioration as in Ref. [3].

A Finnigan TSQ-70B quadrupole mass spectrometer was used as a GC detector, running in 70 eV electron-impact ionisation mode, coupled with a Hewlett-Packard 5890 series II gas chromatograph. The mass scan, electron multiplier, conversion dynode and the electron current parameters were as in [3]. The GC parameters were identical to those in [3]. Carbagas helium grade “60” was used (rather than the hydrogen carrier gas in the Sadtler database) after having been passed over a drying bed.

Linear and polynomial fits (prediction limits=confidence limits for the prediction of a single *y* point) were made using the non-linear least square regression facility of the technical graphics program ORIGIN (version 3.73; Microcal Software, Northampton, MA, USA).

3. Results and discussion

The initial optimisation experiments to model the Sadtler 8°C/min on OV-1 dataset proved successful. The combination of 62.5 kPa helium head pressure and a 17°C/min programming rate was chosen from linear least-square parameters [3].

When a simple unweighted linear regression of the RI_{exp} versus the RI_{White} values for the same structures was made, an excellent fit was seen, but small localised trends became invisible. Therefore a simple offset plot was used (Fig. 1) and this was fitted

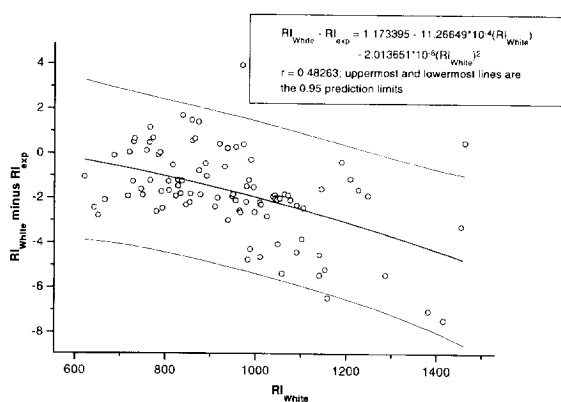


Fig. 1. $RI_{\text{White}} - RI_{\text{exp}}$, versus RI_{White} (96 structures).

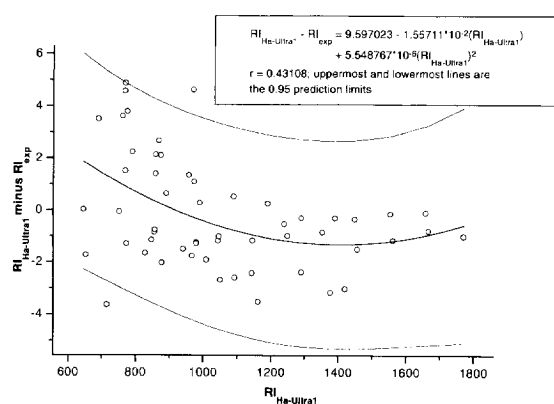


Fig. 3. $RI_{\text{Ha-Ultra}} - RI_{\text{exp}}$, versus $RI_{\text{Ha-Ultra}}$ (55 structures).

unweighted to a second-order polynomial, which then gave a predicted offset across the RI_{White} range from 620.81 to 1460.86 (96 structures). The 0.95 prediction limits, being RI dependent, give a search window for each individual structure incorporated into the “pseudo-Sadtler” database. The narrowest 0.95 prediction limits were ± 3.43 (1-phenylbutane; $RI_{\text{White}} = 1042.19$) and the widest (i.e., “worst case”) 0.95 prediction limits were ± 3.79 (1-chlorododecane; $RI_{\text{White}} = 1460.86$).

A similar approach was tried with the other smaller two datasets [8,10]. Fig. 2 shows the RI offset plot for 89 structures in [8]. An unweighted second-order polynomial fit was used to calculate offsets for these $RI_{\text{Ha-OV101}}$ values. The narrowest 0.95 prediction limits were ± 4.88 (1-phenylpentane; $RI_{\text{Ha-OV101}} = 1141.13$) and the widest 0.95 prediction limits were ± 5.66 (1-phenyldecane; $RI_{\text{Ha-OV101}} =$

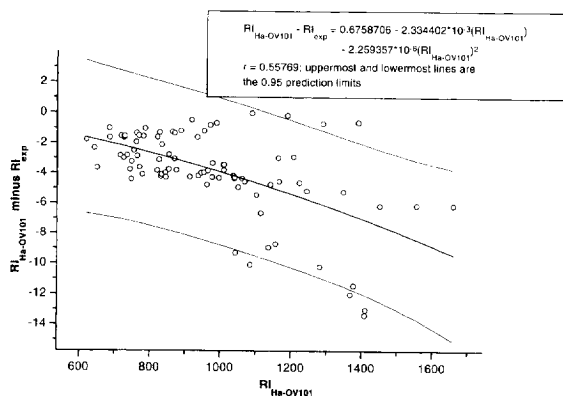


Fig. 2. $RI_{\text{Ha-OV101}} - RI_{\text{exp}}$, versus $RI_{\text{Ha-OV101}}$ (89 structures).

1659.28). Fig. 3 shows the RI offset plot for 55 structures in Ref. [10]. The narrowest 0.95 prediction limits were ± 3.98 (1-dodecene; $RI_{\text{Ha-Ultra}} = 1189.04$) and the widest 0.95 prediction limits were ± 4.52 (1-phenylundecane; $RI_{\text{Ha-Ultra}} = 1769.12$).

The end result of this work was the incorporation of almost all of the RI data contained in Refs. [8–10], into the “pseudo-Sadtler” database even when only interpolatable data from the polynomials fitted to the RI offsets was used. The search windows for all the incorporated RI values are considerably smaller than those of the TIAFT compilation [6]. Generally, the incorporated data from White et al. [9] is the best of the present three datasets and approaches the statistical quality (number of offset points and search window widths) of the 8°C/min on OV-1 subset of the Sadtler Standard Gas Chromatography RI Library [3].

4. Conclusions

This empirical calibration approach allows the salvaging of some capillary column gas chromatography RI compilations by merging them into a “pseudo-Sadtler” database and has the advantage that each incorporated structure is tagged with a statistically derived search window. When identical structures arise in this “pseudo-Sadtler” database then the entry with the larger search window can be deleted and so an avenue exists for continual improvement.

Using this strategy, the capillary column RI database already reported in Ref. [3] was enlarged from 3135 to approximately 3450 entries, again making it the largest as yet reported.

References

- [1] The Sadtler Standard Gas Chromatography Retention Index Library, Sadtler Research Laboratories, Philadelphia, PA, 1984.
- [2] W. Jennings and T. Shibamoto, *Qualitative Analysis of Flavor and Fragrance Volatiles by Glass Capillary Gas Chromatography*, Academic Press, New York, 1980.
- [3] R. Richmond, *J. Chromatogr.*, 724 (1996) 229.
- [4] H. van den Dool and P.D. Kratz, *J. Chromatogr.*, 11 (1963) 463.
- [5] L. Weber, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 9 (1986) 446.
- [6] *Gas Chromatographic Retention Indices of Toxicologically Relevant Substances on Packed or Capillary Columns with Dimethyl Stationary Phase*, VCH, Weinheim, 1992.
- [7] K. Pfeleger, H.H. Maurer and A. Weber, *Mass Spectral and GC Data of Drugs, Poisons, Pesticides, Pollutants and their Metabolites*, 2nd ed., VCH, Weinheim, 1992.
- [8] P.C. Hayes and E.W. Pitzer, *J. Chromatogr.*, 253 (1982) 179.
- [9] C.M. White, J. Hackett, R.R. Anderson, S. Kail and P.S. Spock, *J. High Resolut. Chromatogr.*, 15 (1992) 105.
- [10] P.C. Hayes and E.W. Pitzer, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 8 (1985) 230.