Calculation of gas chromatographic retention indices of PCBs using non n-alkanes as reference standards and mathematical relationships between physicochemical properties and GC-RIs of PCBs

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Introduction

Direct determinations of physicochemical properties of persistent organic pollutants (POPs) such as PCBs are time-consuming, extremely laborious and also costly. There are many alternative methods to estimate physicochemical properties of POPs, including chromatographic methods based on mathematical relationships between the retention values and physicochemical properties. *n*-alkanes are usually used to calculate retention values, that is, retention indices (RI). The *n*-alkanes are only suitable as reference compounds when non-specific detection such as flame ionization (FID) or mass spectrometry (MSD) is used. However, as the high-sensitivity analysis of PCBs requires the use of specific detectors such as the electron capture detector (ECD) where the response of *n*-alkanes is negligible, an alternative reference of ECD-detectable compounds is desirable[1].

In this study, alternative reference standards to be applied on GC/ECD are proposed, and physicochemical properties of PCBs are predicted using GC-RIs method of PCBs calculated on GC system. Finally, predicted results in this paper are compared to those predicted by other alternative methods.

Materials and Methods

First, the retention indices of PCBs were calculated using *n*-alkanes (number of carbon atom 14 to 29) on GC/MSD system (HP6890GC/HP5973MSD) and their selected physicochemical properties were estimated. A DB-5 column (30m×0.25 ×0.25 , J&W Scientific) and the following oven temperature program was used: 70 ℃ (4min), 5 ℃/min, 300 ℃ (5min). Helium was used as the carrier gas with a flow rate of 1.0mL/min and measurements were conducted in selected ion monitoring (SIM) mode.

Secondly, to investigate the reproducibility of retention index system by alternative reference standards, retention indices of PCBs were determinated on GC/ECD system using five different oven temperatures. PCB -1, 14, 25, 72, 113, 161, 181, 199 and 206 were used as alternative reference standards instead of *n*-alkanes. These PCBs congeners showed the best linearity in the graph between retention time and the number of chlorine atoms of PCBs under the condition of various oven condition. The number of chlorine atoms in these PCBs molecules is 1,2,3,4,5,6,7,8 and 9, respectively.

A Shimadzu GC/ECD2010 and a DB -5 column (60m ×0.25 ×0.25 , J&W Scientific) were used. Injector and detector temperature were maintained at 270 ℃ and 310 ℃, respectively. Nitrogen was used as the carrier gas with a flow rate of 1.0 mL/min.

To investigate the reproducibility of retention index system, five different oven conditions were used and as follows: run 1 (200 ℃ (2min), 1 ℃/min, 285 ℃ (1min)), run 2 (180 ℃ (2min), 1 ℃/min, 285 ℃ (1min)), run 3 (140 ℃ (2min), 1 ℃/min, 285 ℃(1min)), run 4 (140 ℃ (2min), 2 ℃/min, 285 ℃ (10min)), and run 5 (140 ℃ (2min), 3 ℃/min, 285 ℃ (60min)).

PCBs standards (method 1668 congener set, 209 chlorinated biphenyl congeners by HRGC/HRMS) and *n*-alkanes standards (multi-state hydrocarbon window defining standards, normal C_8-C_{40} hydrocarbons) were purchased from

AccuStandard.

The data cited to establish mathematical relationship between physicochemical properties and retention indices of PCBs are from Harner and Bidleman [2] for octanol-air partitioning coefficient (log K_{OA}) and Mackay et al. [3] for aqueous solubility (-log S_W) and octanol-water partitioning coefficient (log K_{OW}).

Results and Discussion

Retention indices of PCBs for each of the five temperature programmed oven conditions were calculated using the equation proposed by van den Dool and Kratz[4].

$$RI = 100n + 100 \cdot \frac{R_X - R_n}{R_{n+1} - R_n}$$

where R_x is the retention time of the PCB of interest, and R_n and R_{n+1} are the retention times of the *n*-alkanes or the reference PCBs bracketing the PCB of interest, with carbon or chlorine number n and n+1, respectively.

Retention indices calculated using a series of alternative reference standards under the condition of five different oven temperature showed good precision with variation ranging from 0.03 % to 2.33 % RSD (relative standard deviation). The graph of retention indices calculated using *n*-alkanes and PCB reference standards is shown in Fig. 1. The coefficient of determination R^2 (0.9977, n = 199) at the 0.01% level of significance indicates the stability of retention index system by the numbers of chlorine atoms in the alternative reference standards instead of those of carbon atoms in the *n*-alkanes.

The following mathematical relationships between selected physicochemical properties reported in the literature (Harner and Bidleman[2] for log K_{OA} and Mackay et al.[3] for -log S_W & log K_{OW}) and GC-RIs of PCBs calculated using *n*-alkanes were established: log K_{OA} = 0.0042 × RI + 0.3943 (R^2 is 0.9750, n = 19), log K_{OW} = 0.0025 × RI + 1.0106 (R^2 is 0.8699, n = 49), and -log S_W = 0.0028 × RI + 0.7489 (R^2 is 0.8000, n = 45). log K_{OA}, -log S_W and log K_{OW} of PCBs using these established mathematical relationships were predicted and compared with those predicted by other methods. The coefficients of determination, R^2, between log K_{OA}, log K_{OW} and -log S_W predicted by GC-RIs method and those predicted by other methods (QSPR method [5] and multicolumn method[6] for log K_{OA} and QSPR method[7] for log K_{OW} and -log S_W) were 0.9390 (n = 209), 0.9869 (n =103), 0.9258 (n = 209) and 0.9226 (n = 209), respectively.

The mathematical relationships established between selected physicochemical properties reported in the literature (same as above) and the average value of GC-RIs of PCBs calculated on GC/ECD system using PCB reference standards under the condition of five different oven temperature were as follows: log K_{OA} = 0.0063 × RI + 6.2512 (R^2 is 0.9790, n = 19), log K_{OW} = 0.0038 × RI + 4.4345 (R^2 is 0.8778, n = 47), and -log S_W = 0.0047 × RI + 4.5119 (R^2 is 0.8226, n = 42). log K_{OA}, -log S_W and log K_{OW} of PCBs using these established mathematical relationships were predicted.

Finally, comparisons of log K_{OA} and log K_{OW} values predicted using PCB reference standards with those predicted by the multicolumn[6] and QSPR methods[5,7] are shown in Figs. 2, 3 and 4. Coefficients of determination between results in this study and those of other methods are greater than 0.91.

The mean differences between the estimates by this method and that of other methods is 0.267 and 0.148 log units for log K_{OA}, 0.160 and 0.690 log units for log K_{OW} and -log S_W, respectively.

These results indicate that PCBs can be used as reference standards instead of *n*-alkanes to calculate the GC-RIs of PCBs when a detector with a negligible response for *n*-alkanes is applied. They further suggest that regressions with GC-RIs can be used to predict the physicochemical properties of PCBs.

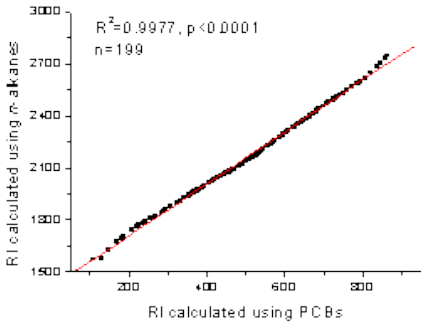

Fig. 1 Comparison of RI calculated using *n*-alkanes and PCBs

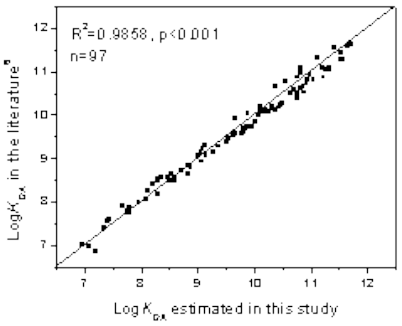

Fig. 2 Comparison of Log K_{OA} by multicolumn method and by this study

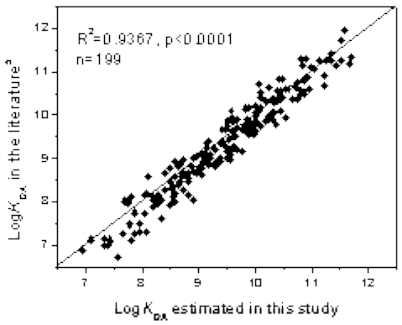

Fig. 3 Comparison of Log K_{OA} by QSPR method and by this study

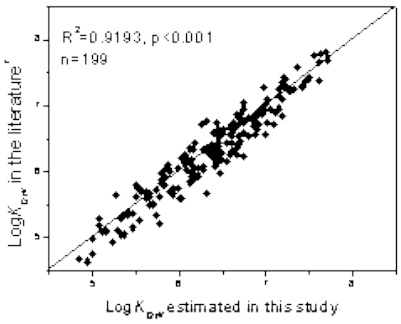

Fig. 4 Comparison of Log K_{OW} by QSPR method and by this study

This chromatographic method established using PCBs as reference standards in the present study might be applied to predict the physicochemical properties of chemical such as polybrominated biphenyls(PBBs) and polybrominateddiphenyl ethers(PBDEs) having the similar structure to PCBs.

Acknowledgement

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