



Cross-column prediction of gas-chromatographic retention of polybrominated diphenyl ethers



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ABSTRACT

In this paper, we predict the retention of polybrominated diphenyl ethers (PBDEs) in capillary gas-chromatography (GC) within a useful range of separation conditions. In a first stage of this study, quantitative structure–retention relationships (QSRRs) of PBDEs in six stationary phases with different polarity are established. The single-column QSRR models are generated using the retention data of 126 PBDE congeners by multilinear regression (MLR) coupled to genetic algorithm variable selection applied to a large set of theoretical molecular descriptors of different classes. A quite accurate fitting of experimental retentions is obtained for each of the six GC columns adopting five molecular descriptors. In a further step of this work six molecular descriptors were extracted within the set of molecular descriptors (17 variables) involved in the various single-column QSRRs. The selected molecular descriptors are combined with observed retentions of ten representative PBDEs, adopted as descriptors of the GC system. These quantities are considered as the independent variables of a multiple-column retention model able to simultaneously relate GC retention to PBDE molecular structure and kind of column. The quantitative structure/column–retention relationship is established using a multi-layer artificial neural network (ANN) as regression tool. To optimise the ANN model, a validation set is generated by selecting two out of the six calibration columns. Splitting of columns between training and validation sets, as well as selection of PBDE congeners to be used as column descriptors, is performed with the help of a principal component analysis on the retention data. Cross-column predictive performance of the final model is tested on a large external set consisting of retention data of 180 PBDEs collected in four separation conditions different from those considered in model calibration (different columns and/or temperature program).

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1. Introduction

Polybrominated diphenyl ethers (PBDEs) have been extensively used as flame retardants since the 70s of the last century, after banning of polychlorinated and polybrominated biphenyls [1–4]. They are added to plastics and textiles in a wide range of consumer goods (such as electric and electronic devices, automobile parts, carpeting and furniture) to prevent or retard fire diffusion. Since PBDEs are generally not covalently bound to materials, they can be released by volatilisation into environment during manufacturing, using, disposal or recycling of treated products. Owing to persistence and tendency to bioaccumulation, PBDEs are ubiquitous in environmental compartments and biota, and can exhibit carcinogenic and endocrine disrupting toxicity [5–8]. For these reasons, PBDEs are now included in the list of emerging contaminants and the number of investigations dealing with their analytical

determination in abiotic and biotic matrices has rapidly increased in the last decade [4]. Similar to polychlorinated biphenyls (PCBs), PBDEs theoretically consist of 209 congeners differing in the number and position of bromine atoms in the molecule. Although technical mixtures are constituted by a relatively small number of highly brominated PBDEs (generally, penta-, octa- or deca-BDEs), many less brominated congeners can be found in environmental and human samples, as a consequence of various chemical and biological debromination processes.

Gas-chromatography (GC) coupled to mass spectrometry or electron capture detection is the most suitable technique for monitoring of PBDEs [4,9,10], but progress of GC analysis for this class of contaminants has been severely hindered by lacking of analytical standards. To overcome this limitation, the quantitative structure–retention relationship (QSRR) method has been considered to predict the retention time of PBDE congeners for which no standards were currently available. In this perspective, Rayne and Ikononou [11] applied for the first time a QSRR model developed with 46 PBDEs to deduce retention of the remaining 163 congeners. Later, when larger GC retention databases became

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available [12,13], reliability and accuracy of QSRR predictive methods was evaluated on a greater number of PBDE congeners and for various different separation conditions [12,14–17]. Although a QSRR established for a representative PBDE subset can be usefully applied to predict retention of the remaining congeners, no information on the separation conditions is explicitly incorporated into the model. Therefore, a QSRR calibrated for a given separation configuration (stationary phase, temperature program, kind and flow of gas carrier, etc.) cannot be transferred to external conditions. A simple approach [13,14], based on the development of regression equations of observed retentions collected in different stationary phases and/or different operational conditions, was considered to transfer PBDE retention data within pairs of GC systems. This method, which requires experimental determination of retention for a suitable number of representative PBDE congeners in both GC systems to properly define the empirical (generally a 3rd order polynomial) relationship, seems adequate to transfer retention data within similar columns. However, inversion of the elution order of predicted retentions was observed for different stationary phases or when the temperature rate program is changed for a same column [13]. Based on chemical similarity between PBDEs and PCBs, it was also attempted [12,14] to correlate retentions of these two classes of compounds, but this approach provided unsatisfactory results especially in polar stationary phases.

Previously, we built by artificial neural network (ANN) regression a multi-column retention model able to accurately predict GC behaviour of PCBs within a useful range of separation conditions [18]. In this model, a set of molecular descriptors for PCBs identified by QSRR modelling of a number of calibration columns were combined with retentions of selected congeners able to represent the stationary phase/temperature program. The advantage of this approach is two-fold: first, any external GC system can be empirically characterised using a relatively small set of retention data. Moreover, as the model, apart from column characteristics, incorporates also the effect of molecular structure, even retention behaviour of previously unseen analytes can be predicted in any column and/or separation condition. Recently, a similar approach was also applied to high-performance liquid chromatography with promising results [19]. In this paper, the above predictive method is used to model GC retention of PBDEs. In spite of structural similarity of PCBs and PBDEs, it must be remarked that the retention data available for PBDEs refer to a relatively small range of stationary phase/temperature program as compared with the large GC literature available for PCBs. Therefore, the aim of this investigation, apart from exploring the generality of the multi-column approach, is also evaluation of its predictive performance under less favourable calibration conditions.

2. Method

2.1. Data set

In this paper, we analyse the PBDE retentions taken from two different databases available in the literature. The first one [12] consists of relative retention times (RRTs) of 126 congeners on seven GC capillary columns with different polarity (DB-1, DB-5, HT-5, DB-17, DB-XLB, HT-8 and CP-Sil 19). The second one [13], which is to our knowledge the database with the largest number of congeners to date, consists of RRTs of 180 PBDEs collected on four different GC operating conditions using two common stationary phases of different dimensions: RTx-1614 (with lengths 15 and 30 m) and DB-5MS (with lengths 30 and 60 m). The column CP-Sil 19 of the first database, which exhibits a more polar stationary phase (14% cyanopropyl-phenyl, 86% dimethyl polysiloxane), was not considered in this investigation. Elimination of this column

Table 1
Most relevant characteristics of GC capillary columns and temperature programs used to collect the PBDE retention data analysed in this work.

Column	Stationary phase	Dimension (m × mm × μm)	Initial T (°C)	Hold (min)	1st rate (°C/min)	1st break (°C)	2nd rate (°C/min)	Final T (°C)	Hold (min)	Refs.
DB-1	100% methylpolysiloxane	30 × 0.25 × 0.25	90	2	30	200	1.5	325	1	[12]
DB-5	5% phenyl-methylpolysiloxane	30 × 0.25 × 0.25	90	2	30	200	1.5	325	7	[12]
HT-5	5% phenyl-methylpolysiloxane (carborane)	30 × 0.25 × 0.10	90	2	30	200	1.5	325	7	[12]
DB-17	50% phenyl-methylpolysiloxane	30 × 0.25 × 0.10	90	2	30	200	1.5	325	30	[12]
DB-XLB	-	30 × 0.25 × 0.50	90	2	30	200	1.5	325	30	[12]
HT-8	8% phenyl-methylpolysiloxane (carborane)	25 × 0.22 × 0.25	90	2	30	200	1.5	325	50	[12]
RTx-1614 (30 m)	5% phenyl-methylpolysiloxane	30 × 0.25 × 0.10	90	3	10	140	2	300	15	[13]
RTx-1614 (15 m)	5% phenyl-methylpolysiloxane	15 × 0.25 × 0.10	90	3	10	140	5	300	15	[13]
DB-5MS (30 m)	Phenyl arylene polymer virtually equivalent to a 5%-phenyl-methylpolysiloxane	30 × 0.25 × 0.25	90	3	10	140	2	300	35	[13]
DB-5MS (60 m)	Phenyl arylene polymer virtually equivalent to a 5%-phenyl-methylpolysiloxane	60 × 0.25 × 0.25	90	3	10	140	2	300	90	[13]

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