

Conversion Method for GC Retention Times of PCB Congeners

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1. Introduction

Polychlorinated biphenyl (PCB) is one of the most widespread persistent organic pollutants. PCB theoretically consists of 209 congeners, of which around 150 have been reported at significant levels in environment and technical PCB mixtures. Recently, a comprehensive, quantitative and congener-specific (CQCS) analysis becomes in great demand since transport mechanisms, accumulation and degradation are congener-dependent¹. In the CQCS PCB analysis, each congener is separated by high-resolution gas chromatography (HRGC) and detected by an electron capture detector (ECD) or a mass spectrometer (MS). An important process in the analysis is the identification of each congener through GC retention. All 209 pure congener standards are now commercially available, but they are still expensive and cannot be utilized in all analytical laboratories. Recently, complete retention database on 27 HRGC systems using 20 stationary phases were reported by Frame² and are promised to greatly advance the CQCS PCB analysis.

There are so many congeners in PCB that analytical processes of acquired chromatograms are labor-intensive and time-consuming. Thus, a fully automatic quantitation including the congener identification is desirable in analytical laboratories where many environmental samples are routinely quantified. The automatic identification based on the retention requires precise retention times of the GC system in an analytical laboratory, since all peaks arisen from congeners should be individually quantified if they elute separately. Even if the same kind of stationary column is used, GC condition employed may be different from ones used in literatures, such as column dimensions, temperature programs, flow rate and injection mode. These cause retention differences from literature values in greater than a full width at half height (FWHH), of which accuracy is required in the identification of just resolved adjacent peaks. In this paper, we propose a new method to convert retention data in literatures to ones in a specific analytical laboratory with high accuracy. The converted retention times can be used for the automatic congener identification process³.

2. Experimental

Kanechlor mixture (GL Siences Inc.) was measured by JMS-GCmate mass spectrometer (JEOL Ltd. Japan) connected with Model 6890 gas chromatograph (Hewlett-Packard). GC columns used was HT-8 (SGE) with 30 m long, 0.22 mm i.d. and 0.25 μ m film thickness. GC was operated in pulsed splitless mode with flow rate 1 ml/min and with Helium as carrier gas. The oven temperature was programmed in the condition proposed by the literature¹; 80°C for 2 min, 30°C/min to 170°C and 3°C/min to 320°C. Temperatures of injection and detection are 300°C and 280°C, respectively. MS was operated in the selected ion monitoring (SIM) mode.

3. Results and Discussion

On the same kind of stationary column, retention differences of congeners between different GC systems are dependent on column dimensions (length, internal diameter, film thickness), temperature programs, carrier gas, flow rate and injection mode. These characterize a specific GC system and can be called an instrument function. The retention differences are therefore reflected from the difference between the instrument function of each GC system. If the instrument function difference is evaluated, the retention data in one GC system can be converted to ones in another GC system. This relationship is expressed as follows.

$$Tm_i = F(To_i) + E_i$$

In this equation, Tm_i is a congener retention time in a target GC system of an analytical laboratory and To_i is a congener retention time in a literature. F is an instrument function difference between two GC systems and is called a conversion function in this work. E_i is an error arisen in retention measurements or retention not covered with the conversion function. As an instrument function is expected to vary smoothly in increase of retention time, the conversion function is also to be a smoothly curved function and can be expressed by a polynomial function. The conversion function can be derived from some Tm_i 's of congeners measured in the target GC system. With F obtained and To_i 's of all 209 congener, Tm_i 's not measurable in the target GC system can be predicted by the equation

$$Tc_i = F(To_i)$$

where Tc_i is a calculated retention time.

We applied the algorithm described above to HT-8 GC column, which was proposed for the single column/MS detection strategy of the CQCS PCB analysis^{1,4}. We measured a technical PCB mixture (Kanechlor) with the same temperature program described in the literature². The differences were column length (30 m in this work vs. 50 m in the literature), flow rate (constant flow vs. constant pressure), injection mode (pulsed splitless vs. split) and detector (MS vs. ECD). The congener concentrations of technical mixture were exactly measured by Frame⁵ and were categorized into three classes: congeners above 1.0 Wt% are called major congeners, between 0.05 and 1.0 Wt% are minor congeners and below 0.05 Wt% are trace or undetectable congeners. Measured SIM chromatograms showed typical peak patterns due to dominant major congeners, whose peaks were easily identified by referring to a literature⁶. The retention times of 61 major congeners and 47 minor congeners with relatively strong intensities from dichlorobiphenyls to octachlorobiphenyls were used in this experiment. As major congeners are widely disperse in all retention time range of PCB congeners, they were used to obtain the conversion function. Retention times of minor congeners were not included in the calculation of the conversion function and were used as the validation purpose of this study.

As shown in Figure 1(a), T_{m_i} 's measured in our GC system are highly correlated with T_{o_i}

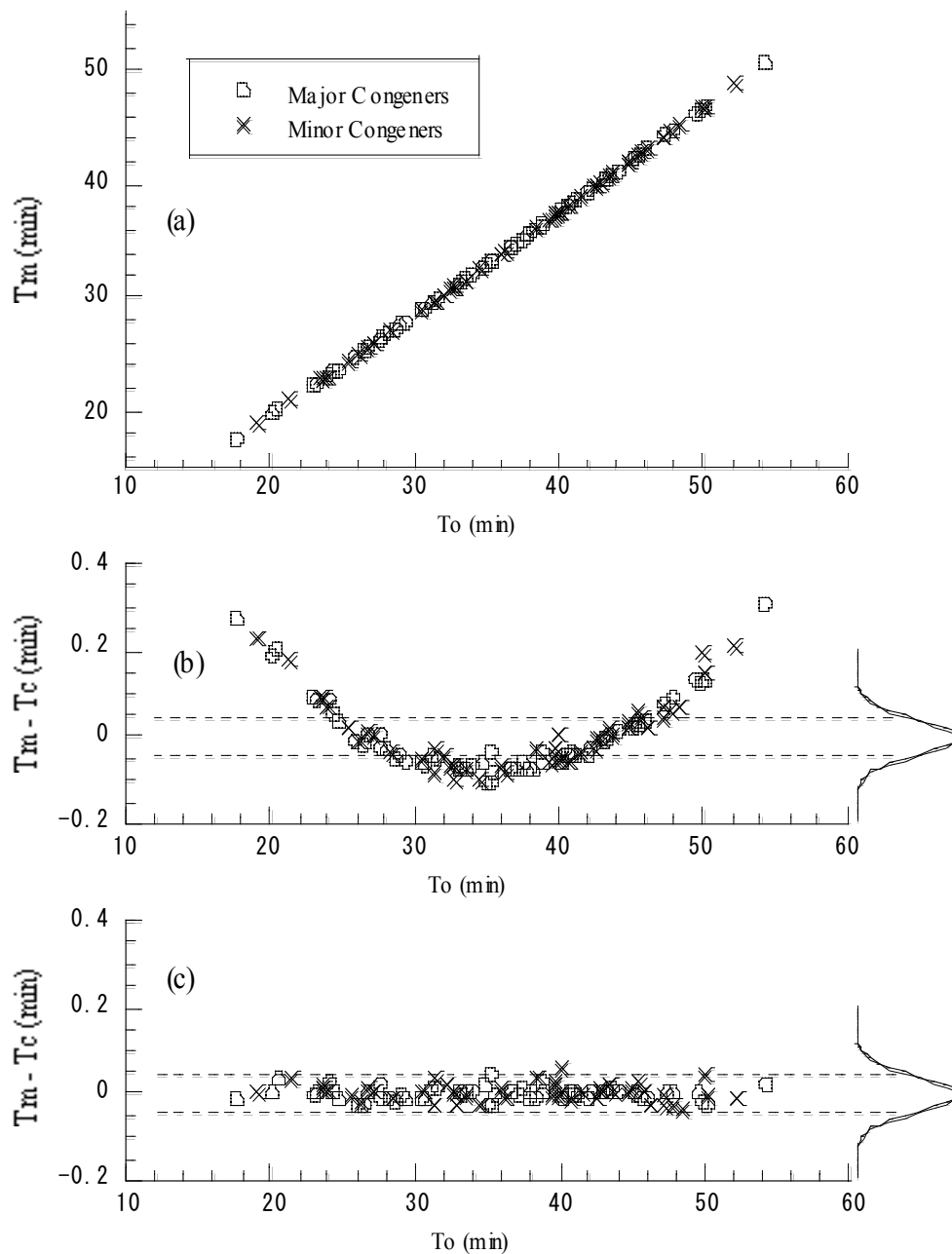


Figure 1. (a) Plot of T_m vs T_o .

(b) Residual plot of linear conversion function.

reported by Frame.² However, when the conversion function F is assumed to be linear, the residuals E_i 's ($= Tm_i - Tc_i$) shown in Figure 1(b) exhibit systematic errors, which are smoothly changed in To_i . Thus, we used a higher order polynomial as the conversion function. The residuals shown in Figure 1(c) are the result of a cubic function. The residuals are randomly located around zero without any systematic errors and disperse almost within the peak FWHH whose width is indicated with horizontal broken lines in Figure 1(b) and (c). Major and minor congeners are shown as circle and cross markers, respectively, in Figure 1. No apparent differences are found in two kind of congeners: The residual dispersion of minor congeners is identical to the one of major congeners. This implies that the conversion function can be derived from major congeners of technical mixture.

4. Conclusion

The calculated retention times with the prediction ability within peak FWHH enable the identification process of the CQCS PCB analysis to be automated by a computer. The residual plot is also valuable for the validation of congener identification. A large deviation from the calculated retention time reveals misidentification of PCB congener. Moreover, the proposed method can deal with non-technical mixture congeners derived from processes such as dechlorination of commercial products, although it employs not expensive pure standards but technical PCB mixture readily available,

Some congeners exhibited slightly larger deviations when GC temperature programs were changed.² Further experimental investigation of this aspect, in the spirit of the present study, is in progress.

5. Acknowledgements

The authors thank Mr.Sugita of Japan Quality Assurance Organization, Dr.Nakano of Hyogo Prefectural Institute of Environmental Science and Dr. Noma of Hiroshima Prefectural Health and Environment Center for their helpful comments.

6. References

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