

PRELIMINARY RESULTS OF INTERLABORATORY COMPARISON ON SHORT CHAIN CHLORINATED PARAFFIN IN TECHNICAL FORMULATION PREPARED AS CANDIDATE REFERENCE MATERIAL

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Introduction

Chlorinated paraffins (CPs) are primary industrial chemicals¹ which became globally popular. CPs have been mainly used in some industrial applications such as the flame retardants, plasticizers, metalworking fluids, and so. There are over 200 different technical formulations produced by numerous companies, and marketed under different trade names². Among CPs, short chain chlorinated paraffin (SCCP) has also been known to be persistent and long-range transport. Because of huge usage of the technical CP formulations and of leakages of them from the polymeric materials, SCCP was widely diffused as environmental contaminants and has been reported in polymeric materials, water, and biological samples worldwide^{1,3-6}. Moreover, SCCP is registered as listed chemicals under Annex A of the Stockholm Convention on Persistent Organic Pollutants (POPs). CPs are chlorinated linear chain alkanes, and SCCP comprising 10 to 13 carbon atoms is one of the three groups divided based on the number of carbon atoms. Based on the assumption that no more than one chlorine atom binds to any carbon atom, there are theoretically 6,304 positional isomers⁷. Due to large number of SCCP isomers, a reliable determination of SCCP is a big challenge, whereas measurements of SCCP were applicable to both of gas and liquid chromatographys such as gas chromatography-mass spectrometry (GC/MS) and chemical ionization (CI)⁸, and liquid chromatography-mass spectrometry (LC/MS) and atmospheric pressure chemical ionization (APCI)⁹. On the other hand, a verification between results obtained by above methods was frequently difficult because of no reliable methods with reference materials. Then, some interlaboratory trials on SCCP were performed worldwide¹⁰⁻¹¹. However, a reliability of these results obtained from interlaboratory trials on SCCP was poorer than that on dioxins and PCBs until now.

In this study, technical SCCP formulation was prepared as a candidate reference material, and then this technical SCCP formulation was used for interlaboratory comparison as a sample distributed. This interlaboratory comparison focused on measurements of SCCP using GC/MS and LC/MS without clean-up process on sample matrix only because of simplifying evaluation of methods. Preliminary results obtained from this interlaboratory comparison were described here.

Materials and methods

Interlaboratory comparison samples

As far as we know, there are no useful reference materials for an evaluation of SCCP composition, so a candidate reference material for this interlaboratory comparison was prepared in this study. The SCCP was prepared by reacting pure gaseous chlorine with the starting paraffins (C10 to C13) at temperatures between 70 °C and 80 °C¹². A mass of each starting paraffin was weighed by balance, and then each starting paraffin was mixed well. The reaction was terminated by stopping the chlorine flow once the required degree of chlorination (approximately 55 %) was reached. The end point was assessed by calculation of viscosity based on the mass. The product was then blown with nitrogen gas to remove any unreacted chlorine and residual HCl. The final product was obtained by pressure filtration as a candidate reference material.

Protocol of interlaboratory comparison

Technical SCCP formulation prepared as mentioned above was distributed to participants without dilution using a solvent because participants could make sample solutions with arbitrary preparation concentration using desired solvents. Basically, participants reported the data based on the peak area percentage relative to total peak area on each congener in order to compare between GC/MS and LC/MS.

Measurement condition reported by participants

Six participants reported the results obtained from SCCP measurements. Summary of measurement conditions used by participants is shown in Table 1. Time-of-flight mass spectrometry (TOFMS) was the main instrument in this study. Measurement conditions were categorized as follow: two GC/TOFMS and combination with negative-ion CI and electron impact ionization (EI+), two LC/MS and APCI-, one LC/TOFMS and APCI-, one LC/TOFMS and electrospray ionization (ESI-). For ionization on GC/TOFMS, its method was used the two ionizations quite differently with the increase of the chlorine number. For assessment of data obtained from

LC/MS, the peak area percentage relative to total peak area was translated based on isotope abundance ratio because of low resolution mass spectrometry compared with TOFMS. Additionally, Dr. Ehrenstorfer standard (DES), which was decided congener ratio among three participants, was used for quantification in participants using a TOFMS, and one remained participant using a TOFMS used slightly different from congener ratio decided by three participants¹³.

Table 1: Summary of measurement condition on participants

Participant	Measured congener	Ionization method	Peak area percentage	Quantification
A: GC/TOFMS	Cl ₅ to Cl ₉	EI+ (low chlorinated paraffins) CI- (highly chlorinated paraffins)	○	○
B: GC/TOFMS	Cl ₃ to Cl ₉	EI+ (low chlorinated paraffins) CI- (highly chlorinated paraffins)	○	○
C: LC/TOFMS	Cl ₄ to Cl ₁₀	ESI-	○	○*
D: LC/TOFMS	Cl ₄ to Cl ₉	APCI-	○	○
E: LC/MS	Cl ₁ to Cl ₁₀	APCI-	○ (after translation based on isotope abundance ratio)	-
F: LC/MS	Cl ₁ to Cl ₁₀	APCI-	○(after translation based on isotope abundance ratio)	-

*Slightly different congener ratio was used for quantification compared with other three participants.

Results and discussion:

Peak area percentage relative to total peak area

At first, results based on peak area percentage relative to total peak area reported by six participants were compared (Figure 1). Obviously, relative congener profiles of carbon numbers 10 to 13 were divided into two groups of GC and LC (except participant E). Among SCCP, carbon numbers 10 and 11, which was relatively higher volatile compounds in this study, accounted for approximately 40 % in the total on results from GC/TOFMS. On the other hand, carbon numbers 12 and 13, which was relatively lower volatile compounds, accounted for approximately 70 % in the total on results from LC/(TOF)MS except participant E. This result suggested the reflection of the relationship between volatility of compounds and characteristic of chromatographs.

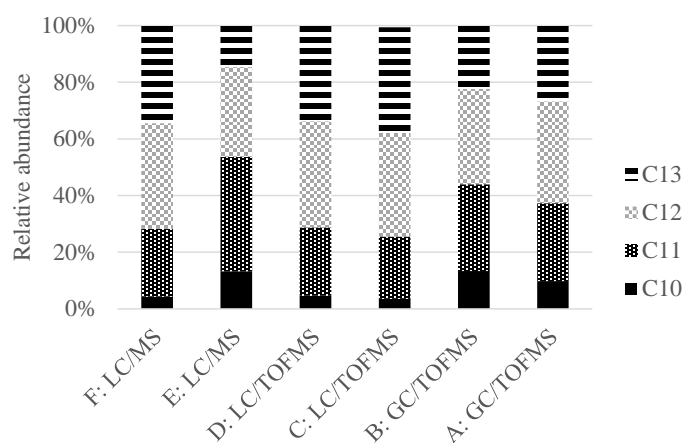


Figure 1: Relative congener profiles of carbon numbers 10 to 13 based on peak area percentage relative to total peak area

Next, congener profile of carbon number 12 focused on because of the main congener in data reported. Relative congener profiles of chlorine numbers 5 to 9 in carbon number 12 based on peak area percentage relative to total peak area are shown in Figure 2. Congeners of chlorine numbers 5 to 9 were target compounds in all the participants. As similar to the results from relative congener profiles of carbon numbers 10 to 13, relative congener profiles of chlorine numbers 5 to 9 in carbon number 12 were divided into two groups of GC and LC. Among carbon number 12, chlorine numbers 7 to 9 accounted for approximately 60 % in the total on results from GC/TOFMS. On the other hand, chlorine numbers 5 and 6 accounted for approximately 70 % in the total

on results from LC/(TOF)MS. This result suggested that the chlorine in targets on GC measurements (negative chemical ionization) had an advantage for ionization especially for highly chlorinated compounds.

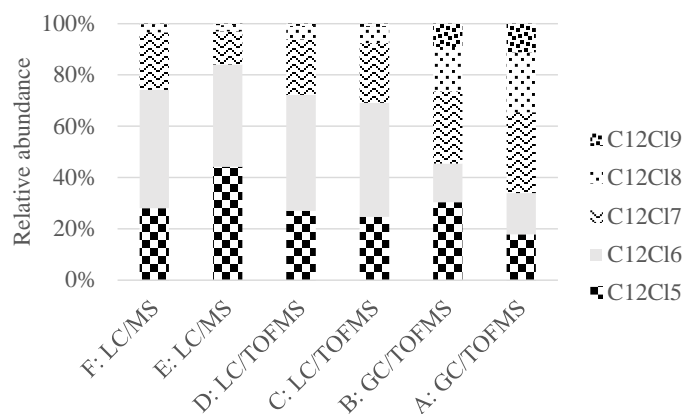


Figure 2: Relative congener profiles of chlorine numbers 5 to 9 in carbon number 12 based on peak area percentage relative to total peak area

Quantification using a commercial standard

By obtaining the results based on quantification using a commercial standard (DES), relative congener profiles could be compared except the data obtained from LC/MS in this study. Relative congener profiles of carbon numbers 10 to 13 based on quantification using DES are shown in Figure 3. Interestingly, relative congener profiles arising from the results based on quantification using the DES were comparable. A slight different profile was observed in the results obtained from participant C because participant C used slightly different from congener ratio decided by three participants for quantification.

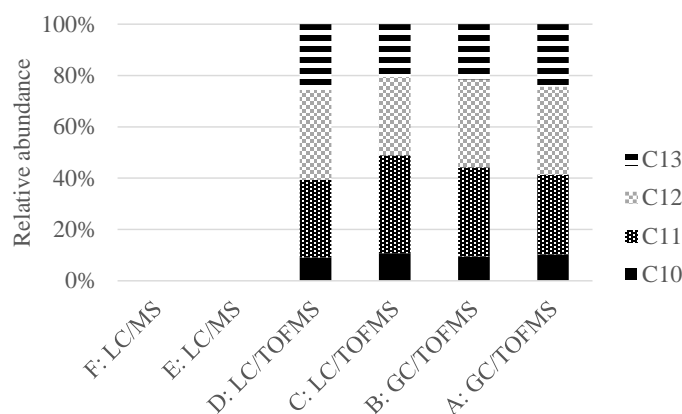


Figure 3: Relative congener profiles of carbon numbers 10 to 13 based on quantification using a commercial standard

Next, relative congener profiles of chlorine numbers 5 to 9 in carbon number 12 based on quantification using DES are shown in Figure 4. As similar to the results from relative congener profiles of carbon numbers 10 to 13, relative congener profiles arising from the results based on quantification using the DES were comparable despite of including slightly different from congener ratio for quantification. These results suggested that the method based on TOFMS was becoming available¹⁴.

As these results, for SCCP measurements in this interlaboratory comparison, an obvious bias was found between GC and LC in case of comparison using peak area percentage relative to total peak area. On the other hand, comparable data on SCCP profiles were obtained between GC and LC in case of quantification using the DES of which congener ratio was decided before this interlaboratory comparison.

In this study, total concentration of SCCP was not considered yet because an understanding of the characteristics between GC and LC using this prepared sample focused on. Researchers organized four interlaboratory studies reported that analytical performance improved on the last round for the test solution¹¹. Also, we have known that methods for the determination of CPs need further harmonization and validation¹⁴. Near future, we are going to

perform second interlaboratory comparison with this candidate reference material as calibrants, and will improve not only quantification standards but also measurement methods.

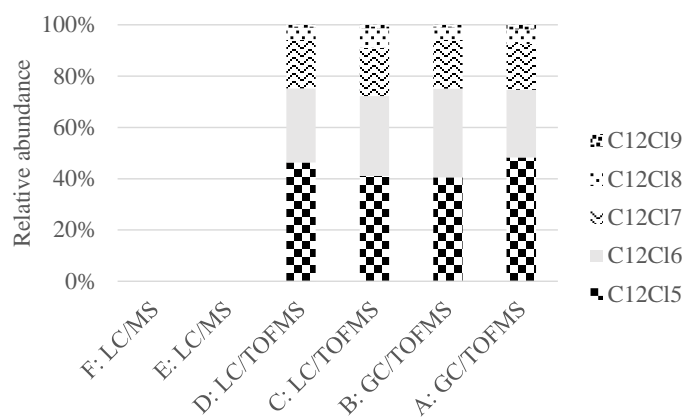


Figure 4: Relative congener profiles of chlorine numbers 5 to 9 in carbon number 12 based on quantification using a commercial standard

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