INTERLABORATORY COMPARISON ON SHORT CHAIN CHLORINATED PARAFFIN USING A CANDIDATE REFERENCE MATERIAL AS STANDARDS FOR QUANTIFICATION: PRELIMINARY FINDINGS

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Introduction

Chlorinated paraffins (CPs) are one of the primary industrial chemicals[1,2] which became recently famous worldwide. CPs have been extensively used as commercial materials for metalworking fluids, flame retardants, and so. Among CPs, short-chain chlorinated paraffins (SCCPs) composed of 10–13 carbon numbers have been learnt to be persistent and long-range transport[1-3]. Newly, therefore, SCCPs have been registered as listed chemicals under Annex A of the Stockholm Convention on Persistent Organic Pollutants (POPs); thus, environmental monitoring and risk assessments have been performed.

CPs are alkanes substituted to chlorines; they have been known to be the presence of innumerable isomers. Based on the assumption that no more than one chlorine atom binds to any carbon atom, there are theoretically 6,304 positional isomers[4]. Due to large number of SCCP isomers, reliable measurements of SCCP are a big challenge, whereas measurements of SCCP have been applicable to both of gas and liquid chromatography such as gas chromatography-mass spectrometry (GC/MS) with chemical ionization (CI)[5] and liquid chromatography-mass spectrometry (LC/MS) with atmospheric pressure chemical ionization (APCI)[6]. On the other hand, a verification between the results obtained by above methods was frequently difficult because of no reliable methods with reference materials. Then, some interlaboratory comparisons on SCCP were performed worldwide[7,8]. However, a reliability of these results obtained from interlaboratory comparisons on SCCP was poorer than that on dioxins and PCBs until now. For the results from our previous study, it was indicated that the results reported by participants became equivalent by using as common standards for quantification[9].

Therefore, the second interlaboratory comparison was performed using a candidate reference material of SCCPs as standards for quantification in this study. Similar to the first comparison, this second interlaboratory comparison also 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 second interlaboratory comparison are described here.

Materials and methods

Interlaboratory comparison samples

As far as we know, there are no useful reference materials for an evaluation of SCCP profiles, so a candidate reference material for our interlaboratory comparison was prepared[9]. Briefly, the candidate reference material used in this study was prepared using a mixture of alkanes (decane, undecane, dodecane, tridecane = 1:3:3:2 mass ratios) as the starting material. The degree of chlorination of this candidate reference material was approximately 55 %. Moreover, this candidate reference material was clearly specified the composition ratios of carbon and chlorine homologues as SCCP profiles. Separately, a measurement sample with the different degree of chlorination was also prepared as well as this candidate reference material.

Protocol of interlaboratory comparison

Candidate reference material and measurement sample prepared as mentioned above were distributed to participants without dilution because participants could make sample solutions with arbitrary preparation concentration using desired solvents. Basically, participants reported the results of quantifications of each homologue using a candidate reference material.

Measurement conditions reported by participants

Sixteen participants reported the results obtained from SCCP measurements. The analytical instruments used were as follows: orbitrap MS, time-of-flight MS (TOFMS), quadrupole MS, and flame ionization detection (FID) for the GC; TOFMS, tandem mass spectrometry (MS/MS), and MS for the LC. The quadrupole MS, MS/MS, and MS were categorized into general performance (Table 1). The ionization methods used were as follows: the electron impact ionization (EI), negative CI (NCI), and appropriate combinations of EI and NCI methods according to the number of chlorines for the GC; electrospray ionization (ESI) and APCI for the LC. One of the participants used APGC (atmospheric pressure gas chromatography) equipped with TOFMS. Among participants, one laboratory reported only total SCCP concentration due to the use of GC-FID, other three laboratories reported the relative results. Additionally, other one laboratory reported the results without the use of a candidate reference material. Namely, the results of total concentration reported from 15 laboratories were used, the homologue profiles reported from 14 laboratories were applied to comparisons in this study.

Results and discussion

Total SCCP concentration

At first, in term of absolute values, total SCCP concentrations were compared. As a result, the reported concentration ranged from 0.23 to 1.40 g/g (average, 0.67 g/g; median, 0.64 g/g). This range seemed to be due to the inconsistency of reported homologues. Next, because several participants did not report tetrachlorinated paraffins, comparisons were made using the results of pentachlorinated to nonachlorinated paraffins to simplify the match-up among participants that reported the concentrations. Since the degree of chlorination of the measurement sample was approximately 45%, tetrachlorinated paraffins were the main component in this study. Therefore, comparisons using the results of pentachlorinated to nonachlorinated paraffins were useful for minimizing this range. In this manner, a concentration range of 0.23–1.06 g/g (average, 0.41 g/g; median, 0.36 g/g) was achieved. The coefficient of variation (CV) of 15 laboratories was approximately 46 %, which was confirmed to be equivalent to that of other recent interlaboratory comparisons[10-12]. In case of a rejection of the result from Lab 15, a concentration range was revised to 0.23–0.58 g/g (average, 0.37 g/g; median, 0.36 g/g), and the CV became approximately 22%. These statistical analysis results seemed to improve the measurement of SCCPs by using a candidate reference material despite interlaboratory comparison including GC and LC instruments in combination with several specification of mass spectrometry. Moreover, there were no significant differences between the results from GC/MS series (average, 0.36 g/g; median, 0.34 g/g) and LC/MS series (average, 0.38 g/g; median, 0.38 g/g) when tetrachlorinated paraffins were excluded. Namely, the results at fewer differences in this study might be reliable because the technical mixture was the measurement sample. Furthermore, it might become easier to find the participant having measurement errors by using such interlaboratory comparison with a candidate reference material.

Concerning the results of the comparison between high- (high-resolution such as orbitrap, TOF) and general performance MS, the least variation was observed in high performance MS (from 0.23 g/g to 0.42 g/g) relative to general performance MS (from 0.27 g/g to 0.58 g/g). In the measurement sample of this interlaboratory comparison, the difference between the high- and general performance MS was relatively small, so it is urgently necessary to evaluate the results of SCCP measurement using a general performance MS on the matrix sample. Because the CVs calculated from previous interlaboratory comparisons used the matrix samples were still large, it become important to verify the potential of application to general performance MS on SCCP measurement.

Table 1. Summary of measurement conditions and of SCCP concentrations (g/g) reported by participants.

| MS performance	Lab No. (Instrument)	Homologue				Total SCCP	
		Carbon number 10	Carbon number 11	Carbon number 12	Carbon number 13	Reported	Unified
General	1 (GC)	-	-	-	-	1.15	-
General	2 (GC)	0.06	0.19	0.19	0.14	0.58	0.58
General	3 (GC)	0.04	0.17	0.15	0.09	0.44	0.27
General	4 (GC)	0.07	0.23	0.24	0.11	0.65	0.33
General	5 (GC)	0.01	0.05	0.29	0.03	0.38	0.38
High	6 (GC)	0.07	0.26	0.30	0.18	0.81	0.36
High	7 (GC)	0.01	0.04	0.09	0.08	0.23	0.23
High	8-1 (GC)	0.05	0.24	0.28	0.15	0.72	0.35
High	8-2 (GC)	0.01	0.09	0.13	0.11	0.33	0.33
High	9 (GC)	-	-	-	-	-	-
High	10 (LC)	-	-	-	-	-	-
High	8-3 (LC)	0.02	0.10	0.16	0.15	0.42	0.42
High	11-1 (LC)	0.06	0.23	0.30	0.21	0.79	0.37
General	11-2 (LC)	0.06	0.23	0.31	0.20	0.79	0.37
General	12 (LC)	0.05	0.20	0.23	0.14	0.62	0.36
General	13 (LC)	-	-	-	-	-	-
General	14 (LC)	0.05	0.22	0.32	0.20	0.80	0.39
General	15 (LC)	0.17	0.36	0.46	0.41	1.40	1.06
High	16 (APGC)	-	-	-	-	-	-

Homologue profiles

Figure 1 shows carbon homologue profiles. These results were almost in agreement except for those of Lab 5. This result supported the mass ratio (1: 3: 3: 2) of the mixture of alkanes, which was the starting material for synthesis.

After excluding the results of tetrachlorinated paraffins among the participants, the carbon homologue profiles were in good agreement (Figure 2). In other words, the results obtained from multiple analytical instruments such as GC and LC in combination with several ionization methods could be corrected using a candidate reference material for quantification whose the composition ratios of carbon and chlorine homologues was specified in advance. Notably, our results for carbon homologues in this interlaboratory comparison indicated less variation for each carbon homologues in comparison with some previous publications related to technical mixtures and reference standards[12,13]. It was concluded that this was due to the candidate reference material used in this study being unified and having the composition ratios of carbon and chlorine homologues stated properly. As our results, not only the total SCCP concentrations but also the carbon homologue profiles were comparable, unlike in the case of some previous publications. Additionally, the results of carbon homologue profiles obtained individually with GC/MS and LC/MS series agreed well (except for those of Lab 5).

As expected, the results from high performance MS (Labs 6 to 11-1) had less variations relative to general performance MS.
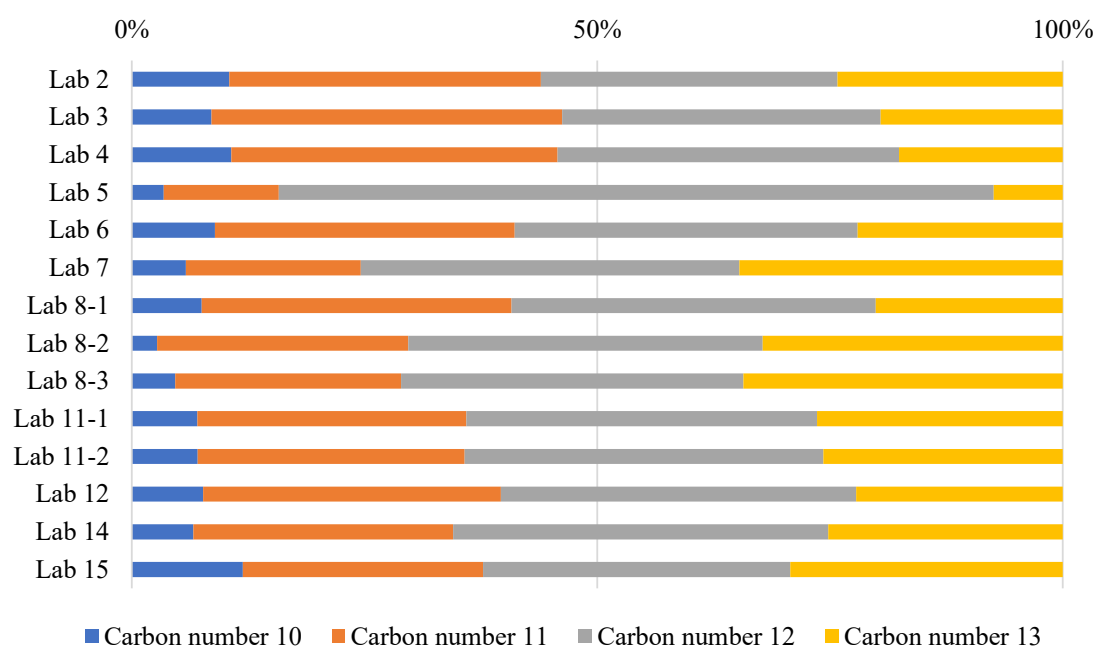
Figure 1. Relative profiles of carbon homologues reported by participants.
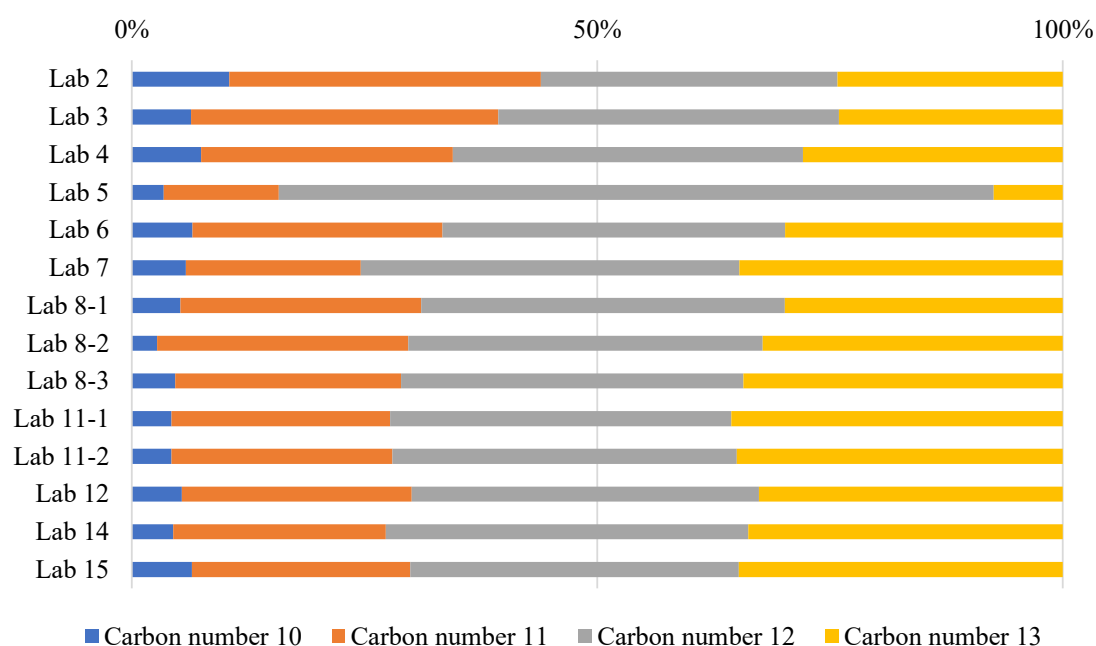
Figure 2. Relative profiles of carbon homologues unified using pentachlorinated to nonochlorinated paraffins.

For the results of chlorine homologue profiles, similar to the carbon homologue profiles, we compared the results of pentachlorinated to nonachlorinated paraffins from C10 to C13 reported by all the participants to simplify the match-up among the reported data. Unlike carbon homologues, the results of a few participants were inconsistent (data not shown). Large variations were found in laboratories used general performance GC/MS with the NCI method; thus, this might be attributed to analytical conditions. NCI method has easily detectable SCCP isomers with high chlorination, and this characteristic could be regarded as the cause of large variations[14,15]. On the other hand, one laboratory used general performance GC/MS with the NCI method reported comparable profiles. It seems to need the further investigation regarding measurement conditions on SCCPs. In case of chlorine homologues, some variation found even when using high-performance MS.

As a result of this second interlaboratory comparison on SCCP measurement using a candidate reference meterial, it became clear that using the composition ratios of carbon and chlorine homologues specified, regardless of the analytical instruments, the total concentrations and homologue profiles (especially for carbon homologues) could be evaluated among the participants. Therefore, it is considered that a development of this candidate reference material as standards for quantification was one of the means to solve the critical problems of SCCP measurement. It was also clarified that the results obtained from high performance MS such as TOFMS had less variations than those from general performance MS owing to sufficient separation of the analytes.

References
1. Bayen S, Obbard JP, Thomas GO (2006) *Environ Int*. 32(7): 915-929.
2. Glüge J, Wang Z, Bogdal C, et al. (2016) *Sci Total Environ*. 573(15): 1132-1146.
3. Wei GL, Liang XL, Li DQ, et al. (2016) *Environ. Int*. 92-93: 373-387.
4. Tomy GT, Stern GA, Muir DCG, et al. (1997) *Anal Chem*. 69(14): 2762-2771.
5. Geiß S, Schneider M, Donnevert G, et al. (2012) *Accredit Qual Assur*. 17(1): 15-25.
6. Bogdal C, Alsberg T, Diefenbacher PS, et al. (2015) *Anal Chem*. 87(5): 2852-2860.
7. Pellizzato F, Ricci M, Held A, et al. (2009) *Trar Trends Anal Chem*. 28(8): 1029-1035.
8. van Mourik LM, van der Veen I, Crum S, et al. (2018) *Trac Trends Anal Chem*. 102(1): 32-40.
9. Hanari N, Nakano T (2019) *Organohalogen Compd*. 81: 340-343.
10. Stevenson G, Yates A, Gillett R, et al. (2011) *Organohalogen Compd*. 73, 1367-1369.
11. van der Veen I, Crum S, de Boer J (2014) *QUASIMEME Report R-14/18*.
12. van Mourik LM, van der Veen I, Crum S, et al. (2018) *Trac Trends Anal Chem*. 102, 32-40.
13. Reth M, Ciric A, Christensen GN, et al. (2006) *Sci Total Environ*. 367(1): 252-260.
14. Yuan B, Bogdal C, Berger U, et al. (2017) *Environ Sci Technol*. 51(18): 10633-10641.
15. Meziere M, Kratschmer K, Perkons I, et al. (2020) *J Am Soc Mass Spectrom*. 31(9): 1885-1895.