

# Interlaboratory Comparison on Short-chain Chlorinated Paraffins Using a Reference Material as Standards for Quantification: A Simulated Environmental Sample

Nobuyasu Hanari<sup>1</sup>, Takeshi Nakano<sup>2\*</sup>

<sup>1</sup> National Metrology Institute of Japan, National Institute of Advanced Industrial Science and Technology (NMIJ/AIST), 1-1-1 Umezono, Tsukuba 305-8563, Japan

<sup>2</sup> Osaka University, 2-4 Yamadaoka, Suita 565-0871, Japan, ntakeshi@jrl.eng.osaka-u.ac.jp

## 1 Introduction

Chlorinated paraffins (CPs) are one of the primary industrial preparations<sup>1,2</sup> which became well-known recently. CPs have been widely applied to as commercial materials for metalworking fluids, plasticizers of polyvinyl chloride, and so. Among CPs, short-chain chlorinated paraffins (SCCPs) composed of 10–13 carbon numbers have been persistent and long-range transportation ability<sup>1-3</sup>. 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 carefully.

CPs are alkanes substituted to chlorines; they have been known to be the group of innumerable isomers. In case of a basis of the assumption that no more than one chlorine atom binds to any carbon atom, there are theoretically 6,304 positional isomers<sup>4</sup>. Due to huge number of SCCP isomers, a reliable analysis of SCCPs become a big problem. Moreover, SCCP analysis have been applicable to both of gas and liquid chromatography such as gas chromatography-mass spectrometry (GC/MS) and liquid chromatography-mass spectrometry (LC/MS), whereas a verification between the results obtained by above methods was difficult because of no reliable methods with reference materials. Then, results obtained from a variety of analytical methods in interlaboratory comparisons on SCCP analysis were compared worldwide<sup>5,6</sup>. However, a reliability of these results obtained from interlaboratory comparisons on SCCP, though improved, was inferior to that on dioxins and PCBs.

Under such situation, interlaboratory comparison in our previous study was performed. For the first interlaboratory comparison, it was indicated that peak area obtained from equipment depended on instruments such as GC and LC<sup>7,8</sup>. Additionally, the first and second interlaboratory comparisons were performed using a unified standard material of SCCPs as standards for quantification. As a result, it was indicated that the results reported by participants became somewhat equivalent by using as unified standards for quantification<sup>7-10</sup>. Moreover, the first and second interlaboratory comparison focused on SCCP analysis using GC/MS and LC/MS without clean-up process on sample matrix only because of simplifying evaluation of methods. In the third interlaboratory comparison study, a simulated environmental sample containing PCBs and medium chain CPs as interferences was prepared. The aim of this study was to evaluate proper analytical methods to matrix-type samples by analyzing the simulated environmental sample. Also, the point of this study was using a unified material, that is a reference material (RM) of quantification standards. Preliminary results obtained from this third interlaboratory comparison are described here.

## 2 Materials and Methods

**Interlaboratory comparison samples.** The NMIJ RM 4076-a, that is a reference material evaluated SCCP homolog compositional profiles, was used for our interlaboratory comparison<sup>11</sup>. This reference material was diluted in toluene to be 1000 mg/L and used as a quantification standard solution. Separately, a simulated environmental sample spiked with PCBs and MCCPs as interferences was also prepared gravimetrically. Amounts of PCBs and MCCPs were approximately half and 40 times in comparison with SCCP amounts (preparation value, approximately 130 mg/kg), respectively.

**Protocol of interlaboratory comparison.** The quantification standard solution based on the NMIJ RM 4076-a and simulated environmental sample prepared as mentioned above were distributed to participants. Basically, participants reported the results of quantifications by using a concentration and homolog compositional ratios based on the reference material.

### Analytical conditions reported by participants

Fifteen laboratories reported the results obtained from SCCP analysis. Among participants, one laboratory reported only SCCP peak area. The analytical equipment used were as follows: orbitrap MS, time-of-flight MS (TOFMS), and quadrupole MS in the GC-based instruments; TOFMS and tandem mass spectrometry (MS/MS) in the LC-based instruments. The ionization methods used were as follows: the electron ionization (EI), negative chemical ionization (NCI), and appropriate combinations of EI and NCI methods according to the number of chlorines for the GC analysis; electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI) for the LC analysis. Also, some laboratories performed a clean-up process. Analytical condition of laboratories is summarized in Table 1. Namely, the results of total concentration and the homolog profiles reported from 14 laboratories were applied to comparisons in this study without unifying the match-ups among the study's participants that had reported the results of a variety of homolog profiles such as chlorine homologs 4 to 9, or 5 to 8, etc. Furthermore, some results were a volume-based

and were converted to a mass-based using the density of solvent used in final solution. There were some participants reporting multiple results using different analytical conditions such as instruments in this study.

Table 1: Summary of analytical conditions and concentrations (mg/kg) of total short-chain chlorinated paraffins (SCCPs) reported by laboratories

Lab No.	Instrument	Ionization method	Total SCCP
1	GC-QMS	NCI	4.91
2	GC-QMS	NCI	647*
3	GC-QMS	EI	384
4	GC-Orbitrap MS	EI & NCI	167
5	GC-Orbitrap MS	NCI	122
6	GC-TOFMS	EI & NCI	193*
7	GC-TOFMS	EI	127*
8	GC-TOFMS	NCI	154*
9	LC-TOFMS	APCI	129
10	LC-TOFMS	ESI	67.2*
11	LC-TOFMS	ESI	94.8
12	LC-TOFMS	APCI	_*
13	LC-TOFMS	APCI	113
14	LC-MS/MS	ESI	105
15	LC-MS/MS	ESI	113

Single and double asterisks mean the implementation of clean-up process and the reporting of peak area, respectively.

### 3 Results

The results on total SCCP concentration (mg/kg) reported from 14 laboratories are shown in Table 1 and Figure 1. The total SCCP concentrations in this study apparently varied and ranged from 4.91 to 674 mg/kg. The coefficient of variation (CV) of 14 laboratories was approximately 93 %. In case of a rejection of the results from Labs 1-3, the CV became improved to approximately 28%. In other words, almost of results were generally in agreement with the preparation value (approximately 130 mg/kg) of a simulated environmental sample except for these 3 laboratories. This large deviation of these 3 laboratories seemed to be due to the presence of interferences. Because these 3 laboratories used GC-QMS, insufficient separation might be achieved during SCCP analysis. One of these 3 laboratories had performed clean-up process, but it was so far from the preparation value unfortunately. Namely, it was considered that the resolution of instrument was insufficient specification in the QMS, and/or the removal of the interferences was insufficient, even if the clean-up process was performed. The rest of the results (67 to 193 mg/kg) including MS/MS seemed to be in good agreement with the preparation value. Moreover, the results from LC/MS series (average, 104 mg/kg) were found a bit difference compared with the results from GC series except for the results from Labs 1-3 (average, 153 mg/kg). This difference might be attributed to due to the analytical sample, but the details are still unclear.

Surprisingly, the results (105 to 113 mg/kg) obtained from LC-MS/MS without clean-up process were equivalent to the results obtained from the high-resolution instruments. This selected method<sup>12</sup> seemed be because that the resolution of instruments was sufficient to this simulated environmental sample.

#### Carbon chain length and chlorine homolog profiles

Figure 2 shows carbon chain length profiles of SCCPs. These results were almost in agreement even if the results obtained from GC-QMS did not exclude. This result seemed to support comparatively the mass ratio (1: 3: 3: 2) of the mixture of alkanes, which was the starting material for synthesis<sup>11</sup>. In other words, the results obtained from multiple analytical instruments such as GC and LC in combination with several ionization methods might be corrected well using a RM for quantification whose the composition ratios of carbon and chlorine homologues was specified in advance. On the other hand, the results of carbon chain length profiles obtained individually with LC series sufficiently agreed despite of including of TOFMS and MS/MS. The effect of the clean-up process in this study needs the further investigation.

Unlike the carbon chain length profiles, for the results of chlorine homologue profiles it seemed the difficult that we could consider the comparable (data not shown). This was because that the results of a few laboratories including especially for Labs 1-3 were inconsistent obviously. In case of the chlorine homologue profiles, some variations found even when using high-resolution MS. Therefore, it is necessary to continuously investigate these cause.

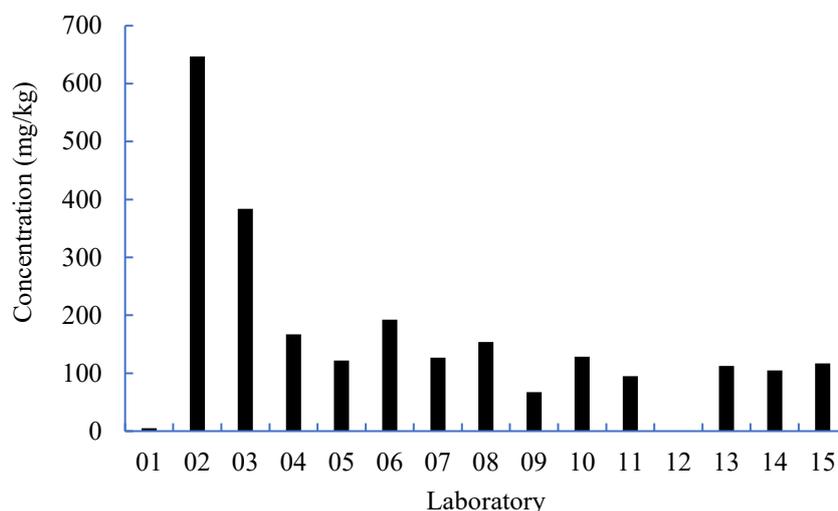


Figure 1: The results of the total short-chain chlorinated paraffin concentrations (mg/kg) reported by laboratories

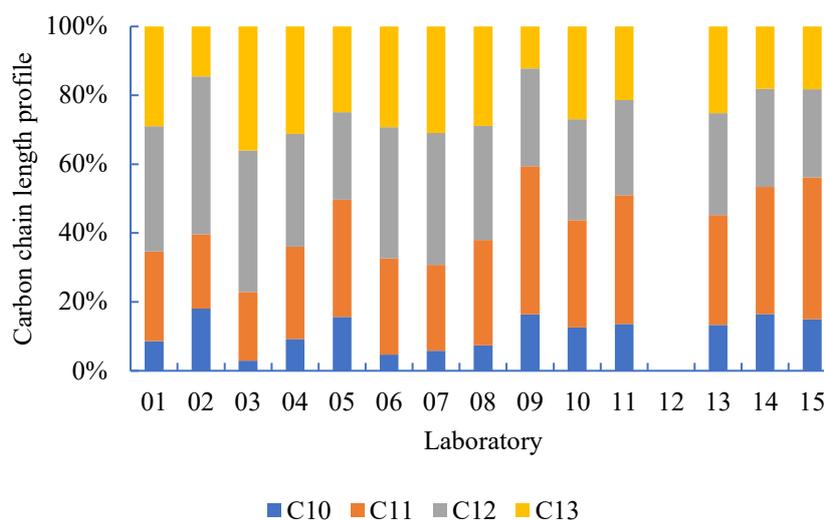


Figure 2: The relative carbon chain length profiles of short-chain chlorinated paraffins reported by laboratories

#### 4 Discussion

The CV of 14 laboratories in this study was equivalent to that was of other interlaboratory comparisons<sup>5,6,13</sup>. Similar to previous publications in the analysis of various matrix-type samples such as extracts, sediments, foods, and spiked samples, the results seemed to improve with each round for our interlaboratory comparison. Also, in this study, to participation of the laboratories using methods based on LC-MS/MS<sup>12</sup> was characteristic due to that GC/MS methods were generally favored in SCCP analysis. Notably, our results for carbon chain length profiles in this interlaboratory comparison indicated less variation compared with previous publication<sup>13</sup> because of use of a unified RM. Namely, as our results, not only the total SCCP concentrations but also the carbon chain length profiles were somewhat comparable, unlike in the case of some previous publications because the unified RM was used as standards for quantification and SCCP with similar homolog compositional ratios to this unified RM was spiked to the simulated environmental sample. Moreover, as in previous publications<sup>6,14,15</sup>, it was observed that the NCI method could cause large variations.

#### 5 Conclusions

For the third interlaboratory comparison on SCCPs, by sharing not only a RM but also homolog compositional ratios of SCCPs in this RM, the results of SCCP concentrations and homolog profiles exhibited less variation despite of the simulated environmental sample containing the interferences. On the other hand, in case of the present of the interferences for SCCP analysis, it was indicated that an application to the high-resolution MS including the LC-MS/MS was required to obtain better results in this study's sample. Therefore, the method based on LC-MS/MS might be able to use as core techniques to propose the reliable methods for matrix analysis. However, it seems to need the further detailed investigation regarding analytical methods on SCCPs.

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## 7 References

1. Bayen S, Obbard JP, Thomas GO, 2006, Chlorinated paraffins: A review of analysis and environmental occurrence. *Environ Int*, 32, 915-929.
2. Glüge J, Wang Z, Bogdal C, Scheringer M, Hungerbühler K, 2016, Global production, use, and emission volumes of short-chain chlorinated paraffins - A minimum scenario. *Sci Total Environ*, 573, 1132-1146.
3. Wei GL, Liang XL, Li DQ, Zhuo MN, Zhang SY, Huang QX, Liao YS, Xie ZY, Guo TL, Yuan ZJ, 2016, Occurrence, fate and ecological risk of chlorinated paraffins in Asia: A review. *Environ Int*, 92-93: 373-387.
4. Tomy GT, Stern GA, Muir DCG, Fisk AT, Cymbalisty CD, Westmore JB, 1997, Quantifying C10–C13 Polychloroalkanes in Environmental Samples by High-Resolution Gas Chromatography/Electron Capture Negative Ion High-Resolution Mass Spectrometry. *Anal Chem*, 69, 2762-2771.
5. Pellizzato F, Ricci M, Held A, Emons H, Bohmer W, Geiss S, Iozza S, Mais S, Petersen M, Lepom P, 2009, Laboratory Intercomparison Study on the Analysis of Short-Chain Chlorinated Paraffins in an Extract of Industrial Soil. *TrAC Trends Anal Chem*, 28, 1029-1035.
6. van Mourik LM, van der Veen I, Crum S, de Boer J, 2018, Developments and interlaboratory study of the analysis of short-chain chlorinated paraffins. *TrAC Trends Anal Chem*, 102, 32-40.
7. Hanari N, Nakano T, 2019, Preliminary results of interlaboratory comparison on short chain chlorinated paraffin in technical formulation prepared as candidate reference material. *Organohalogen Compd*, 81, 340-343.
8. Hanari N, Nakano T, 2020, Elucidation of Affecting Factors in the Analysis of Short-chain Chlorinated Paraffins Using a Candidate Reference Material. *Bunseki Kagaku*, 69, 351-356 (in Japanese).
9. Hanari N, Nakano T, 2021, Interlaboratory comparison on short chain chlorinated paraffin using a candidate reference material as standards for quantification: preliminary finding. *Organohalogen Compd*, accepted.
10. Hanari N, Nakano T, 2022, Comparison of short-chain chlorinated paraffin concentrations and homolog profiles by interlaboratory trial using a candidate reference material. *Chemosphere*, 291, 132783.
11. Hanari N, Orihara Y, Aoyagi Y, 2022, A reference material (NMIJ RM 4076-a) for the determination of short-chain chlorinated paraffins. *Environ Sci Pollut Res*, accepted.
12. Matsukami H, Takemori H, Takasuga T, Kuramochi H, Kajiwara N, 2020, Liquid chromatography–electrospray ionization-tandem mass spectrometry for the determination of short-chain chlorinated paraffins in mixed plastic wastes. *Chemosphere*, 244, 125531.
13. Krätschmer K, Schächtele A, 2019, Interlaboratory studies on chlorinated paraffins: Evaluation of different methods for food matrices. *Chemosphere*, 234, 252-259.
14. Yuan B, Bogdal C, Berger U, MacLeod M, Gebbink WA, Alsberg T, de Wit CA, 2017, Quantifying Short-Chain Chlorinated Paraffin Congener Groups. *Environ Sci Technol*, 51, 10633-10641.
15. Meziere M, Kratschmer K, Perkons I, Zacs D, Marchand P, Dervilly G, Le Bizec B, Schächtele A, Cariou R, Vetter W, 2020, Addressing Main Challenges Regarding Short- and Medium-Chain Chlorinated Paraffin Analysis Using GC/ECNI-MS and LC/ESI-MS Methods. *J Am Soc Mass Spectrom*, 31, 1885-1895.