SIMPLIFIED ANALYTICAL METHODS FOR COMMERCIAL MIXTURES OF SHORT-CHAIN CHLORINATED PARAFFINS

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Introduction

Short-chain chlorinated paraffins (SCCPs) are complex technical mixtures of chlorinated contaminants with linear carbon chain lengths from 10 to 13 and a content of chlorine greater than 48% of weight. At present, SCCP production is estimated to be at more than 165,000 t/year globally ¹, and commercial mixtures of SCCPs are used for plasticizers, flame retardants in rubber, plastics, paints, textiles, and lubricants in metalworking fluids ². SCCPs were classified as persistent organic pollutants (POPs) under the Stockholm Convention (Annex A) in 2017, and were identified as Class I specified chemical substances in the Japan Chemical Substance Control Law in October 2018, indicating that a proper detoxification process for SCCPs is required. However, because SCCPs have many homologs and isomers, it is difficult to separate them into individual homologs and isomers using general analytical methods.

Moreover, the standard materials used for quantification of SCCPs are also limited. Thus, decomposition methods and chemical analysis methods for calculating the destruction efficiency for SCCPs are being developed. Because conventional methods target the low concentration SCCPs in the environmental matrices, a high sample volume and complex pretreatment processes are needed before instrumental analysis. For analyzing high SCCP-containing samples, such as commercial mixtures and decomposed compounds, we need to develop a proper analytical method for highly concentrated samples.

Many previous environmental SCCPs studies utilized gas chromatography (GC)–negative chemical ionization (NCI)–magnetic sector mass spectrometry (HRMS) ³, liquid chromatography (LC)–atmospheric pressure chemical ionization (APCI)–quadrupole time of flight MS (QToF–MS) ⁴, GC–triple quadrupole MS (QqQ–MS) ⁵, GC–ToFMS ⁶ and GC and LC–Orbitrap-MS ⁷⁻⁸. Although these instruments can provide a high sensitivity and selectivity, the instrumentation is expensive for conducting routine analyses, and their operation requires specialized technical skills. GC–quadrupole MS with negative ion chemical ionization (GC–NICI–qMS) has been used to analyze SCCPs in various environmental matrices ⁹, and GC-qMS is one of the most commonly used analytical techniques.

To calculate the destruction efficiency for the decomposition process of SCCPs, a rapid screening method using a widely used instrument is required. In this study, we determined the rapid analysis method for a commercial mixture of SCCPs and their decomposition products using GC–NICI–qMS.

Materials and methods

Sulfuric acid (H₂SO₄), n-hexane, nonane, and silica gel (Wako-gel S1) were purchased from Wako Pure Chemical Industries (Tokyo, Japan). A commercial mixture of SCCPs (52# China, containing 58% of SCCPs) was used for identification, quantification, and measuring the sample. This sample was provided by Kyoto University. After the sample was dissolved in 3 mL n-hexane, it was passed through a glass column packed with 500 mg of 44% H₂SO₄ silica gel and concentrated to near dryness. Treated samples were dissolved in nonane to use the standard calibration solution (4 points, five analyses for each concentration, 5.8–58 ppm of total SCCP conversion).

SCCP analysis was performed on a JMS-Q1500GC (JEOL Ltd., Tokyo, Japan) qMS equipped with an Agilent 7890B GC (Agilent Technologies Inc., Tokyo, Japan) and a CTC PAL RTC autosampler (CTC Analytics AG., Zwingen, Switzerland). GC separation was achieved using an HP5-MSUI fused-silica capillary column (20 m × 0.18 mm ID × 0.18 µm film, Agilent Technologies Inc., Tokyo, Japan). The injector was held at 280 °C and operated in the pulsed splitless mode with a 1.0 µL injection volume. The column oven temperature program for the analysis of the PCB congeners was maintained at 130 °C for 1 min, heated to 180 °C at a rate of 40 °C min⁻¹, heated to 300 °C at a rate of 5.5 °C min⁻¹, and maintained at 300 °C for 5 min. Helium (purity: >99.99995) at a column flow rate of 0.9 mL min⁻¹ (constant flow rate) was used as the reagent gas for the NICI source. The ionizing energy and ion source temperature were set to 150 eV and 200 °C, respectively. The identification and quantification of the target SCCPs were achieved in selected ion monitoring (SIM) mode with the NICI–MS detector. The SIM settings of the GC–NICI–qMS were following a previous study ¹⁰. Procedural blanks were

processed in parallel for every five samples to check for interference or contamination by solvents and glassware.

The JMS-1500GC was operated using JEOL msPrimo[™] software. Analyzed data were converted to the NetCDF (Analytical Instrument Association: AIA format) file structure. Automated peak detection, peak matching, and data preprocessing were performed by R ver 3.5.1 and R package XCMS.

Method quantitation limits (MQLs) were defined as ten times the standard deviation (SD) of a low concentration sample (5.8 ppm of total SCCP conversion of the standard calibration solution) (n = 5).

Results and discussion:

Based on the measurement, nine types of SCCPs were detected from all calibration standard solution samples (Figure 1). Detected compounds are summarized in Table 2 and 3. A linear

| Parameter | Condition |
|------------------|--|
| System | Agilent 7890B + JMS-Q1500GC + CTC PAL RTC autosampler |
| Column | HP-5MSUI (20 m × 0.18 mm ID × 0.18 μ m film) |
| Oven program | 130 °C (1 min) - 40 °C /min - 180 °C - 5.5 °C /min - 300 °C |
| Flow rate | 0.9 mL/min (He: Constant flow rate) |
| Ion source temp. | 200 °C |
| Ionization mode | NICI (150 eV) |
| Reagent gas | Methane |
| Detection mode | SIM |
| Injector temp. | 280 °C |
| Injector vol. | 1.0 μl |
| Injection mode | Pulsed splitless |

Table.1 Parameter settings of GC-NICI-qMS

relationship between spiked amounts and peak areas could be obtained for the calibration standard solution sample ($R^2 = 0.974-0.982$), and in this study, the quadratic curve was better fit than the linear curve for all detected SCCPs (Figure 2). The cause of non-linearity was unknown; however, matrix effects and/or systematic errors caused by the superposition of ions of different compositions and the same nominal mass were involved in the non-linearity of the calibration curve. For future method improvement, using internal standards to correct the preprocessing loss may be useful.



Figure 1 Gas chromatography-mass spectrometry (GC-MS) total ion chromatograms (TIC) of SCCPs mixture (5.8-58ppm)

Figure 2 Standard calibration curve for quantification of individual SCCPs

The relative standard deviations (RSDs) of repeated injections (n = 5) for each concentration level (spiked at 5.8, 12, 29 and 58 ppm of the total SCCP conversion solution) were 2.9–4.0%, 3.2–5.0%, 1.1–2.5%, and 2.3–3.3%, respectively (Table 2), indicating each RSD value was stable. The MQLs of the nine types of SCCPs for the total SCCP conversion was calculated five times in a repeated analysis of low concentration samples and determined to be 1.67–2.35 ppm (Table 3). Additionally, we investigated the MQL of individual m/z values of the SCCPs. These values were calculated from analyzed values from the GC–ToFMS (Cl₅) and GC–Orbitrap–MS (Cl₆₋₈). The MQL of the nine-individual m/z values for the SCCPs were in the range of 0.027–0.35 ppm (Table 3). These MQLs are comparable from previously reported GC–NCI–QToF–MS, and LC–APCI–QToF–MS but higher than those from GC–HRMS and LC and GC–Orbitrap–MS³⁻⁸ (Table 4).

The destruction efficiency of chemical substances required by the technical guidelines of the Basel Convention is 99.999% (5.8 ppm in this commercial mixture) ¹¹, indicating that the MQL achieved via this analytical method (approximately 2 ppm) was sufficient for the requirements of the technical guidelines. Moreover, using a maximum value for the MQL in the individual m/z values of SCCPs (in this study: 0.35 ppm) instead of the MQL of the total SCCP, MQL values become lower. However, considering the dilution/pretreatment at the time of analysis of actual decomposed samples, a lower limit of quantitation of approximately one digit is expected in the future.

Conclusions

A simplified analytical method for SCCPs in a commercial mixture was demonstrated. This method provides sufficient sensitivity for the technical guidelines of the Basel Convention using a widely used instrument. However, in the future, optimization of the pretreatment process and instrumental parameters will be needed to analyze the decomposition products of the SCCPs.

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| Compositional formula | m/z | 5.8 ppm | 12 ppm | 29 ppm | 58 ppm |
|-----------------------|-------|---------|--------|--------|--------|
| $C_{10}H_{17}Cl_5$ | 279.0 | 2.9 | 3.5 | 1.6 | 2.3 |
| $C_{11}H_{19}Cl_5$ | 293.0 | 3.5 | 3.2 | 2.0 | 2.7 |
| $C_{10}H_{16}Cl_6$ | 312.9 | 3.0 | 3.2 | 1.7 | 3.2 |
| $C_{11}H_{18}Cl_6$ | 327.0 | 4.0 | 4.0 | 1.1 | 3.0 |
| $C_{12}H_{20}Cl_6$ | 341.0 | 3.4 | 4.1 | 1.7 | 3.2 |
| $C_{10}H_{15}Cl_{7}$ | 346.9 | 3.5 | 3.8 | 1.9 | 3.1 |
| $C_{11}H_{17}Cl_7$ | 360.9 | 3.8 | 4.2 | 2.1 | 3.3 |
| $C_{12}H_{19}Cl_7$ | 374.9 | 3.7 | 4.6 | 2.5 | 2.7 |
| $C_{12}H_{18}Cl_{8}$ | 408.9 | 3.3 | 5.3 | 2.2 | 2.8 |

Table. 2 Detected SCCPs and their relative standard deviations (RSDs) of repeated injections (n = 5) for each concentration level

Table. 3 Method quantification limits (MQL) of the detected SCCPs

| Compositional formula | MQL- \sum SCCPs (ppm) ¹ | MQL-indvidual (ppm) ² |
|-----------------------|--------------------------------------|----------------------------------|
| $C_{10}H_{17}Cl_5$ | 1.67 | 0.075 |
| $C_{11}H_{19}Cl_5$ | 2.01 | 0.35 |
| $C_{10}H_{16}Cl_6$ | 1.71 | 0.053 |
| $C_{11}H_{18}Cl_6$ | 2.34 | 0.19 |
| $C_{12}H_{20}Cl_6$ | 2.00 | 0.17 |
| $C_{10}H_{15}Cl_7$ | 2.01 | 0.027 |
| $C_{11}H_{17}Cl_7$ | 2.23 | 0.14 |
| $C_{12}H_{19}Cl_7$ | 2.15 | 0.22 |
| $C_{12}H_{18}Cl_8$ | 1.90 | 0.085 |

¹ Based on the total SCCP conversion of the technical mixture (58%) ² Based on the analytical value of the individual m/z of SCCPs (analyzed by GC–Orbitrap–MS)

| | This study | GC-HRMS ¹ | GC-NCI-QToFMS ¹ | GC-Orbitrap-MS ¹ |
|--------------------------------------|-------------------------------------|--|---|---|
| MQL (ppb) | 27-350 | 0.50-58 | 2.5-40 | 0.10-6.7 |
| Target SCCPs (Individual) | Individual SCCPs (C10-13, Cl5-9) | C10-13, Cl5-9 | C10-13, Cl5-9 | C10-13, Cl5-9 |
| References | | 3 | 6 | 7 |
| | | | | |
| | | | | |
| | This study (| GC-APCI-QToFMS ¹ | GC-NCI-QToFMS ¹ | LC-Orbitrap-MS ¹ |
| MQL (ppb) | This study (1700 | GC-APCI-QToFMS ¹ 330-3300 | GC-NCI-QToFMS ¹ 79-270 | LC-Orbitrap-MS ¹ 13-90 |
| MQL (ppb) Target SCCPs (Total) | This study (1700 Total SCCPs | GC-APCI-QToFMS ¹ 330-3300 49, 60, 70%Cl | GC-NCI-QToFMS ¹ 79-270 52, 56, 63%Cl | LC-Orbitrap-MS ¹ 13-90 52, 56, 63%Cl |

Table. 4 Comparisons of method quantification limits (MQL) with other published methods (ppb)

¹ Based on 3.3 times the instrumental detection limit