

Determination of short chain chlorinated paraffins (SCCPs) in commercial chlorinated paraffins (CPs) products using comprehensive two-dimensional gas chromatography coupled with tandem mass spectrometry

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Introduction

Chlorinated paraffins (CPs) are known as a group of synthetic chlorinated *n*-alkanes. They are widely used in industries related to metalworking fluids, sealants, rubbers, textiles and so on [1]. According to the carbon chain length, CPs are divided into short chain chlorinated paraffins (SCCPs; C₁₀-C₁₃), medium chain chlorinated paraffins (MCCPs; C₁₄-C₁₇), and long chain chlorinated paraffins (LCCPs; C₁₈-C₃₀) [1]. SCCPs received more attention because of their persistence, bioaccumulation, potential for long-range environmental transport and toxicity [1]. Stockholm Convention has listed SCCPs as the candidate persistent organic pollutants (POPs) [2].

CPs production is rising in China year by year [3]. The contribution of SCCPs among CPs products is unclear [4]. It is necessary to clarify the SCCPs concentration levels in Chinese commercial CPs products.

For the instrumental analysis of SCCPs, one-dimensional gas chromatography is commonly used for separation, and low resolution mass spectrometry in selected ion monitoring (SIM) mode is widely used as the detector [3]. However, one-dimensional gas chromatography coupled with low resolution mass spectrometry has the disadvantage on SCCPs and MCCPs separation since some of the congeners those share the similar quantitative or qualitative ions have the overlapped retention times [5]. Comprehensive two-dimensional gas chromatography (abbreviated to GC×GC hereinafter) is a promising tool for better analyzing SCCPs.

In this study, an analytical method using GC×GC coupled with triple quadrupoles tandem mass spectrometry (GC×GC-QQQMS) on the quantification of SCCPs was developed. The SCCPs concentrations in Chinese commercial CPs products were measured. Moreover, the SCCPs congeners' relative contributions of above samples were also described.

Materials and methods

The SCCPs measurement was performed on comprehensive two-dimensional gas chromatography couples with triple quadrupole mass spectrometry (GC×GCMS-TQ8040; Shimadzu, Kyoto, Japan). GC×GC thermal modulator

(Zoex Corp., Houston, TX, USA) was fitted to GC instrument. The capillary column set was the combination of one non-polar column and one moderately polar column. The first column was a 15 m InertCap 5MS/Sil fused silica capillary column (0.25 mm i.d., 0.1 μm thickness of 5% phenyl and 95% polysilphenylene-siloxane film; GL Sciences Inc., Tokyo, Japan). The second column was a 2.5 m BPX-50 fused silica capillary column (0.1 mm i.d., 0.1 μm thickness of 50% phenyl polysilphenylene-siloxane film; SGE Analytical Science, Melbourne, Australia). Negative chemical ionization (NCI) was used as ionization source for SCCPs measurement. It has an advantage of enhancing the sensitivity of dominant fragment ions since little ion fragmentation could occur in NCI source [6]. Methane was the reagent gas. In SIM mode, a pair of ions including one quantitative ion and one qualitative ion were selected for 24 SCCPs congeners as well as the ISTD. Two-dimensional data processing was conducted using ChromSquare Ver. 2.2 (Shimadzu, Kyoto, Japan).

Three SCCPs mixtures (C10-C13 containing different chlorine contents of 51.5%, 55.5%, and 63%; 100 ng/ μL solutions in cyclohexane; 100% pure) were purchased from Dr. Ehrenstorfer (Augsburg, Germany). The ^{13}C labeled 1,5,5,6,6,10-hexachlorodecane used as an internal standard (ISTD) was purchased from Cambridge Isotope Laboratories (Andover, USA). The commercial CPs products were bought from three industries. In factory A CPs products are classified according to chlorination degree. Samples noted as CP-42, CP-52, and CP-70 indicate the approximate chlorine content of 42%, 52%, and 70% by weight. On the samples CP-B and CP-C collected from factory B and C, respectively, neither chlorination degree nor carbon chain length is labeled. CPs products were dissolved into cyclohexane and diluted into certain concentrations. After that CPs solutions were mixed with ISTD before measurements.

Results and discussion

Two-dimensional gas chromatogram of the mixture of SCCPs standards with ISTD under the optimal analytical condition was shown in Figure 1. 4 Events were divided according to carbon chain lengths in order to clearly integrate peak volume of every congener. In each carbon chain length group, the congener with less chlorine substitution eluted earlier in both 1st column and 2nd column. 24 congeners could be separated clearly in the two-dimensional gas chromatogram.

A quantification method using the calibration between total response factor (RF) and chlorine (Cl) content was developed by Reth et al. (2005) and widely used in SCCPs quantification [7]. The calculations of both RF and Cl content are based on the integrated peak volumes of quantitative ions of 24 congeners. RF-Cl content calibration curves of thirteen chlorine content levels of SCCPs standards were established. Unlike the previous researches, there were two linear correlations obtained in different Cl content ranges. The first calibration ranged between Cl content of 0.585 and 0.636. Total response factor was well calibrated with Cl content ($R^2 = 0.9544$) with the equation of RF

= $212.92 \times (\text{Cl content}) - 122.14$. The second calibration was obtained in the range of 0.635-0.651 of Cl content. The calibration equation was $\text{RF} = 1395.1 \times (\text{Cl content}) - 872.59$ with R^2 of 0.9736. These two calibration curves were used in the quantification of SCCPs in CPs products.

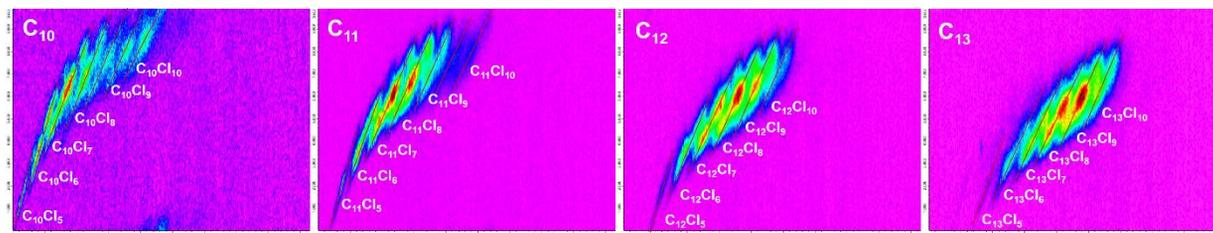


Figure 1 2D chromatogram of SCCPs standards and ISTD.

To calculate 24 congeners' relative concentration, Tomy et al. (1997) presented a method by using the SIM signals of selected quantitative ions [8]. This method is based on the assumption that the adjusted ion signals are proportional to the chlorine atom number in a parent molecule, as well as its molar concentration. The adjusted ion signals were calculated from the integrated peak volumes of the quantitative ions divided by the fractional abundance of the quantitative ions. The fractional abundance data were referred from data monitoring by GCxGC-TOF-MS [5].

The SCCPs relative concentrations in CPs (w/w) were 1.60%, 66.22%, and 0.16% in CP-42, CP-52, and CP-70, respectively. CP-52 consisted most amount of SCCPs. While, the very small shares of SCCPs in CP-42 and CP-70 could be neglected. The congener relative concentrations of CP-52 were shown in Figure 2. C_{13}Cl_7 and C_{13}Cl_8 took shares of 26.7% and 22.5% among SCCPs, respectively (Figure 2). While, in CP-42 C_{13}Cl_7 and C_{13}Cl_8 contributed 24% and 21.8% among SCCPs, respectively. In CP-70, $\text{C}_{12}\text{Cl}_{10}$ was the dominant congener with a share of 39.6% (Figures are not shown). Gao et al. (2012) determined that SCCPs mass fractions were 3.7%, 24.9%, and 0.5%, respectively, in CP-42, CP-52, and CP-70 [9]. C10 group showed highest contribution in those CPs products [9]. Therefore, SCCPs concentration and each congeners' contribution in CPs products varied within the same chlorine content products. We could deduce that carbon chain length contribution in paraffins, which are the materials to produce CPs, were different. There are factories producing CPs without a certain requirement of chlorine content. CP-B consisted 73.7% of SCCPs, while there was 43.9% of CP-C contributed by SCCPs. It suggested that CPs products produced by various factories could have a wide range of SCCPs proportions. This difference was also supposed to be determined by the carbon chain length distribution in paraffins.

In order to collect sufficient information of SCCPs pollution from CPs products, determining the SCCPs

concentration in CPs products is necessary. It is also recommended to make a clear regulation on the carbon chain length distribution in paraffins to control the SCCPs pollution.

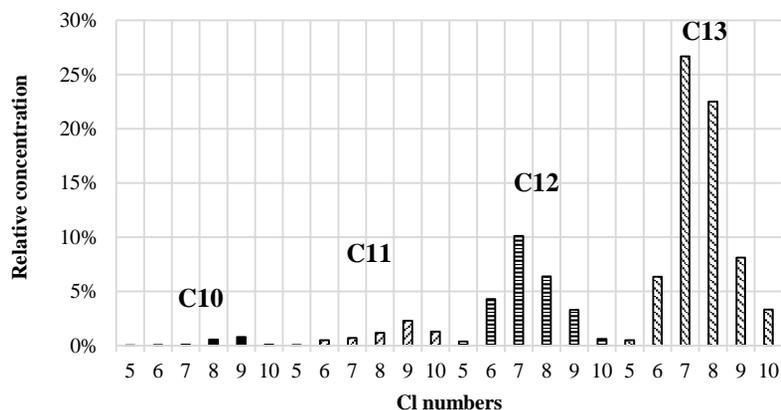


Figure 2 Congener relative concentrations in CP-52.

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