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Quantification of short- and medium-chain chlorinated paraffins in environmental samples by gas chromatography quadrupole time-of-flight mass spectrometry

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ABSTRACT

Chlorinated paraffins (CPs) are technical products produced and used in bulk for a number of purposes. However, the analysis of CPs is challenging, as they are complex mixtures of compounds and isomers. We herein report the development of an analytical method for the analysis of short-chain CPs (SCCPs) and medium-chain CPs (MCCPs) using quadrupole time-of-flight high-resolution mass spectrometry (GC-NCI-qTOF-HRMS). This method employs gas chromatography with a chemical ionization source working in negative mode. The linear relationship between chlorination and the CP total response factors was applied to quantify the CP content and the congener group distribution patterns. In a single injection, 24 SCCP formula groups and 24 MCCP formula groups were quantified. Extraction of accurate masses using qTOF-HRMS allowed the SCCPs and MCCPs to be distinguished, with interference from other chemicals (e.g., PCBs) being largely avoided. The SCCP and MCCP detection limits were 24–81 ng/mL and 27–170 ng/mL, respectively. Comparison of the obtained results with analytical results from gas chromatography coupled with electron capture negative ionization low-resolution mass spectrometry (GC-ECNI-LRMS) indicate that the developed technique is a more accurate and convenient method for the analysis of CPs in samples from a range of matrices.

1. Introduction

Chlorinated paraffins (CPs), also known as polychlorinated *n*-alkanes, are semi-volatile chemicals (SVOCs) [1,2], which have been used in large amounts in various commercial products for several decades [1,3]. The commercial CP mixtures can be divided into three categories, namely short-chain chlorinated paraffins (SCCPs) C_{10}–C_{13}, medium-chain chlorinated paraffins (MCCPs) C_{14}–C_{17}, and long-chain chlorinated paraffins (LCCPs) C > 17. SCCPs in particular have drawn significant attention due to their high toxicity [2]; however, as MCCPs and SCCPs coexist in the environment, and MCCPs can be transformed into SCCPs via environmental processes such as combustion, the issue of MCCP analysis should also be addressed.

The quantification of CPs in environmental samples is challenging [4] due to the high complexity of the industrial mixtures and self-interference among the CPs. A number of different methods have been developed to date for the determination of SCCPs and MCCPs in a range of environmental matrices. Tomy et al. applied electron capture negative ionization high-resolution mass spectrometry (ECNI-HRMS) for the analysis of MCCPs and SCCPs [5,6]. This technique is well-suited to routine analyses, and has been employed in our laboratory [7]. Recently, two-dimensional gas-chromatography (GC × GC) methods have also been applied to separate SCCPs [8,9], as have mathematical methods such as principal component analyses (PCA) and multiple linear regression [10–12]. Alternative methods include the determination of SCCPs by short-column GC/ECNI-MS [13], carbon skeleton reaction gas chromatography [14], and on-line dechlorination–hydrogenation of chlorinated paraffin mixtures using GC and GC/MS [15,16]. However, these methods present several challenges such as high cost and the risk of interference between other chlorinated pollutants and CPs with the same nominal mass. Recently, Bogdal

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et al. developed a novel technique based on the chlorine-enhanced atmospheric pressure chemical ionization (APCI) method, using a quadrupole time-of-flight high-resolution mass spectrometry (APCI-qTOF-HRMS) system for fast quantification of CPs in environmental samples [17]. However, this direct injection method is problematic due to the requirement for rigorous clean-up procedures.

Interference related to mass overlap between SCCP and MCCP congeners must also be addressed, and fragmentation patterns should be studied to allow more accurate quantification of CPs. With these challenges in mind, we herein report the development of a novel analytical approach based on the GC-NCI-qTOF-HRMS system to simultaneously analyze SCCPs and MCCPs in a single injection. High-resolution GC-qTOF was employed to directly quantify SCCPs and to avoid possible interference by MCCPs in environmental samples. Twenty-four different SCCP formula groups (C_{10}–C_{13} with 5–10 chlorine atoms) and 24 MCCP formula groups (C_{14}–C_{17} with 5–10 chlorine atoms) were analyzed by extracting accurate masses. CPs bearing fewer chlorine atoms and shorter chain lengths were also studied. Finally, samples from a range of environmental matrices were analyzed using the developed method.

2. Materials and methods

2.1. Standards and reagents

Pesticide analytical grade solvents were purchased from J.T. Baker (Phillipsburg, NJ, USA). Solutions of the SCCP mixtures (100 ng/μL, C_{10}–C_{13} with 51%, 55.5%, and 63% chlorination, 100% purity) and MCCP mixtures (100 ng/μL, C_{14}–C_{17} with 42%, 52%, and 57% chlorination, 100% purity) in cyclohexane and ε-hexachlorocyclohexane (ε-HCH, solution in cyclohexane, 10 ng/μL, 99.9% purity) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). 1,5,5,6,6,10-Hexachlorodecane ($^{13}C_{10}$-, 100 ng/μL solution in cyclohexane, ≥98% purity) and 1,5,5,6,6,10-hexachlorodecane (unlabeled, 100 ng/μL in cyclohexane, ≥98% purity) were purchased from Cambridge Isotope Laboratories (Andover, USA). 2,5,6,9-Tetrachlorodecane (10 ng/μL in cyclohexane, 98.3% purity) and 1,2,9,10-tetrachlorodecane (10 ng/μL in cyclohexane, 99.3% purity) were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Solutions of 1,1,1,3,9,11,11,11-octachloroundecane (100 ng/μL in cyclohexane, >98% purity) and 1,1,1,3,10,12,12,12-octachlorododecane (100 ng/μL in cyclohexane, 97.7% purity) were obtained from Chiron AS, Stiklestadveien, Norway.

2.2. Sample preparation

To test the performance of the NCI-qTOF-HRMS method, samples from several environmental matrices were analyzed for both SCCPs and MCCPs. The detailed information of these samples is provided in Supplementary material section Sample Collection and Preparation.

Air samples were obtained using a passive air sampler (Xpress-Application Developer, XAD). Organic film samples were collected from dichloromethane-wetted Kimwipes© after wiping a window surface. Food samples were purchased from several well-known fast food outlets. The industrial CP products were kindly provided by manufacturers. Sample pretreatment was based on our previously reported method [18,19] with some minor modifications. Briefly, frozen dried samples (1 g) were mixed with diatomaceous earth (5 g) and spiked with the $^{13}C_{10}$-1,5,5,6,6,10-hexachlorodecane surrogate standard (10 ng) prior to accelerated solvent extraction (ASE). The extract was concentrated to approximately 1 mL by rotary evaporation. The extract was then cleaned and fractionated on a 1.5 cm silica-Florisil® composite column packed with Florisil® (3 g), neutral silica gel (2 g), acidic silica gel (5 g, 30%), and anhydrous sodium sulfate (4 g) (packed from bottom to top). The column was conditioned with *n*-hexane (50 mL), and the sample was eluted with *n*-hexane (40 mL) (fraction 1 contained polychlorinated biphenyls and toxaphenes), followed by dichloromethane (50 mL) and *n*-hexane (50 mL) (fraction 2 contained CPs and HCHs). The second fraction was concentrated to approximately 2 mL by rotary evaporation and further concentrated to close to dryness under a gentle stream of N_2. The fraction was then reconstituted in cyclohexane (200 μL). Prior to MS analysis, a ε-HCH (10 ng) was added as recovery standard to determine the sample recoveries. Instrumental blanks were composed of pure cyclohexane. No CPs were observed following injection of the blanks.

2.3. Instrumentation

An Agilent 7200 GC–QTOF mass spectrometer (Agilent Technologies, Santa Clara, USA) operated in negative chemical ionization (NCI) mode and controlled by MassHunter Acquisition B.07 was used in this study. The GC system was equipped with a DB-5MS Ultra Inert 30 m (0.25 mm i.d., 0.25 μm thick) capillary column. The GC oven temperature was programmed to begin at 100 °C (held for 1 min), followed by an increase to 160 °C at a rate of 5 °C/min (held for 2 min), then an increase to 310 °C at 30 °C/min (held for 12 min). Splitless injections (2 μL) were carried out at 280 °C using ultrapure helium as the carrier gas at a flow rate of 1.0 mL/min. The auxiliary heating and ion source temperatures were set at 280 °C and 150 °C, respectively. A solvent delay of 5 min was used to prevent damage in the ion source filament. QTOF MS was operated at 5 spectra/s in the *m*/*z* range 50–600, with a resolution of approximately 15,000 at *m*/*z* 300–600. Mass spectrometry grade PFTBA (perfluorotri-*n*-butylamine) was used for the daily mass calibration. MassHunter Quantitative Analysis B.07 and MassHunter Qualitative Analysis B.07 were applied for data treatment. The workflow for the chlorination response factor-based quantification method is described in Fig. S1.

When analyzing CPs, it is necessary to distinguish between different congener groups, as they generate a series of ions in the *m*/*z* range 300–600. In our previously reported GC-ECNI-LRMS method [18,19], to minimize interference from other CPs (e.g., SCCPs or MCCPs), we carefully determined the retention time range for each congener group and calculated the quantitative and qualitative ion ratios based on the chromatographic and mass spectrometric results. The integration range of the quantitative ion was set by comparison of the peak cluster shape between the quantitative ion and the qualitative ion, which should be within the range of the corresponding standard retention times. We also consulted the work of Reth and Oehme [7] to calculate the quantitative and qualitative ion ratios of each congener in the SCCP and MCCP standards and in the samples employed herein. The congener ratios between the standards and the real samples were compared. Where the obtained ratio fell into the range of the MCCP standard, it was concluded that SCCP congener quantification suffered from interference from the MCCPs. Thus, the integration range end point should be modified according to the starting retention time of the corresponding MCCP congener. Indeed, the quantification method developed herein further reduced interference from the MCCPs [14]. For example, the $C_{11}H_{16}Cl_8$ formula group in the SCCP standards gave a quantification ion to qualification ion response ratio of 1.20, while in the MCCP standards, the $C_{16}H_{28}Cl_6$ formula group response ratio was 1.00. A ratio of ≥1.20 indicated that the total response was generated by the $C_{11}H_{16}Cl_8$ formula group; while a ratio of ≤1.00 indicated