A New Analytical Method for Chlorinated Paraffins Using Bromide-Anion Attachment Atmospheric Pressure Chemical Ionization Mass Spectrometry

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Introduction

Chlorinated paraffins (CPs) pose a considerable risk to humans and the environment. Despite the recent addition of short-chain CPs ($C_{10\text{-}13}$, SCCPs) to the Stockholm Convention on persistent organic pollutants (POPs), medium- ($C_{14\text{-}17}$, MCCPs) and long-chain CPs ($C_{18\text{-}}$, LCCPs) continue to be manufactured in increasing quantities. Global occurrence of SCCPs, MCCPs, and LCCPs in various environmental matrices has been reported recently, including soil,[1] sediments,[2] wildlife,[3, 4] and human samples.[5-8] Monitoring the impact of CP regulation and shifts in manufacturing necessitates analytical approaches which are sensitive, precise, accurate, and robust.

Commonly, simultaneous analysis of SCCPs, MCCPs, and LCCPs is carried out using chloride-anion attachment atmospheric pressure chemical ionization mass spectrometry (Cl-APCI-MS) with chloroform or dichloromethane.[9, 10] However, accurate measurement of CPs using this approach requires either an ultrahigh resolution mass spectrometer (e.g. Orbitrap[11]) or deconvolution of overlapped mass spectra to resolve the chloride adduct ions $[M+Cl]^-$ from their decomposition ions (e.g. $[M+Cl-x HCl]^-$, where $x \geq 1$).[12] In the present work a new analytical technique using bromide-anion attachment (Br-) APCI-MS is introduced wherein hetero-halogen ions (i.e. $[M+Br]^-$) are produced and easily resolved using a moderate resolution MS (e.g. QTOF). The method improves sensitivity and selectivity relative to traditional methods, and offers significantly faster analysis.

Materials and methods

Development and validation of our new Br-APCI-MS method is presented in detail in Yuan et al. (2018).[13] Here we provide a brief outline.

Chemicals and environmental samples: Fragmentation of CPs was investigated with a CP congener mixture standard 'MIX-2' consisting of five chlorinated *n*-decane congeners with known positions of substituted chlorines (Dr. Ehrenstorfer GmbH, Augsburg, Germany), two commercial SCCP mixtures, one commercial MCCP mixture, and one commercial LCCP mixture. CPs in six biota samples and five sediment samples were quantified. Single chain length standards from C_{10} to C_{13} were used for quantifying individual SCCP congener groups. Five commercial MCCP mixtures and six commercial LCCP mixtures were used for quantifying MCCPs and LCCPs, respectively.

Instrumental analysis: The samples dissolved in cyclohexane were directly injected into an APCI-QTOF-MS (QTOF Premier, Waters, Manchester, UK) operated in full scan (*m/z* 300 – 1040), negative ion mode at a resolution of 9000-10000. The mobile phase was hexane. A solution of bromoform or dibromomethane in hexane was introduced into the mobile phase between the injector and the ion source. For individual congener groups (C_nCl_m, where n=10-30, m=3-12), the two most abundant *m/z* signals of their $[M+Br]^-$ were extracted from the mass spectra for quantification.

Quantification procedure: SCCPs in biota and sediment samples were quantified using a C_nCl_m-response-factor (RF) algorithm[12] and commercial mixtures of single-chain-length SCCPs. Due to lack of single-chain-length

commercial mixtures, MCCPs and LCCPs in these samples were quantified using a C_nCl_m-pattern-reconstruction algorithm developed by Bogdal et al.[9] and commercial mixtures of MCCPs/LCCPs.

Results and discussion:
Performance of Br- versus Cl-APCI-MS: The Br-APCI-MS method produced nearly exclusive $[M+Br]^-$ adduct ions for individual C_nCl_m. Other adducts such as $[M+Br-HCl]^-$ or $[M+Br-HBr]^-$ were not observed. This means that individual C_nCl_m can be resolved with only a moderately high resolution MS such as the QTOF MS used here. In contrast, Cl-APCI-MS produced $[M+Cl]^-$ ions for C_nCl_m which overlapped with $[M+Cl-HCl]^-$ ions produced from C_nCl_{m+1}. As a result of this overlap, signals for C_nCl_m measured by Cl-APCI-MS were overestimated up to 39% in this work, and such overestimation can be even higher.[14] To resolve such an overlap requires a mass overlap deconvolution step for hundreds of C_nCl_m. Hence the absence of this tedious step is a major advantage of the Br-APCI-MS method. Moreover, since the second half of 2017, several studies have reported the occurrence of chlorinated olefins (COs),[15] unsaturated by-products[11] or degradation products of CPs.[16] The presence of COs confounds CP analysis using traditional Cl-APCI-MS and cannot be resolved. The method presented here provides a possible solution to this problem. Furthermore, instrumental responses in the new method were greater than those of the Cl-anion attachment method, resulting in lower LODs for most CPs by an average of 2-fold relative to the Cl-anion attachment method.

Analysis of environmental samples: The new method was applied to quantifying CPs in biota and sediment samples. C_nCl_m patterns of CPs in herring fillet, blue mussels, and Swedish sediment are shown in Figure 1. The total concentrations of CPs in fish and mussels ranged from 540 to 3600 ng/g lipid weight. SCCPs and MCCPs accounted for 14-60% and 36-86% of total CPs, respectively, while LCCPs were present in all samples. In sediment samples from Sweden, total CP concentrations generally decreased from 374 to 47 ng/g dry sediment between 1985 and 2016. LCCPs predominated in all sediment samples, accounting for 56-87% of total CPs. CP concentrations quantified using Br-APCI-MS were 55%-163% of the concentrations determined by Cl-APCI-MS method, demonstrating reasonable consistency of the methods.

Alternative to bromoform: While bromoform is more toxic than chloroform and dichloromethane (occupational exposure limits of 0.5, 2, and 25 ppm respectively).[17] However, the use of halogenated solvent was reduced from 10% (v/v) of dichloromethane[9] or 30% of chloroform[10] to 2% of bromoform in the mobile phase. Thus we contend that the risks for human health are not significantly increased using the current method. To further reduce the potential health impacts of using these reagents, we also tested dibromomethane instead of bromoform to enhance formation of bromide anions, considering that dibromomethane has a moderate occupational exposure limit (5 ppm). Only 3% dibromomethane was required, making this reagent a good alternative to bromoform. Nevertheless, lab procedures involving any of these solvents should follow strict safety procedures, including the use of appropriate personal protective equipment in order to minimize exposure.

Characterizing the potential environmental and human health risks of CPs necessitates a rapid and reliable analytical technique. The newly developed Br-APCI-MS method presented here is easy to implement and has many advantages over conventional measurements by Cl-APCI-MS, including improved selectivity and sensitivity.

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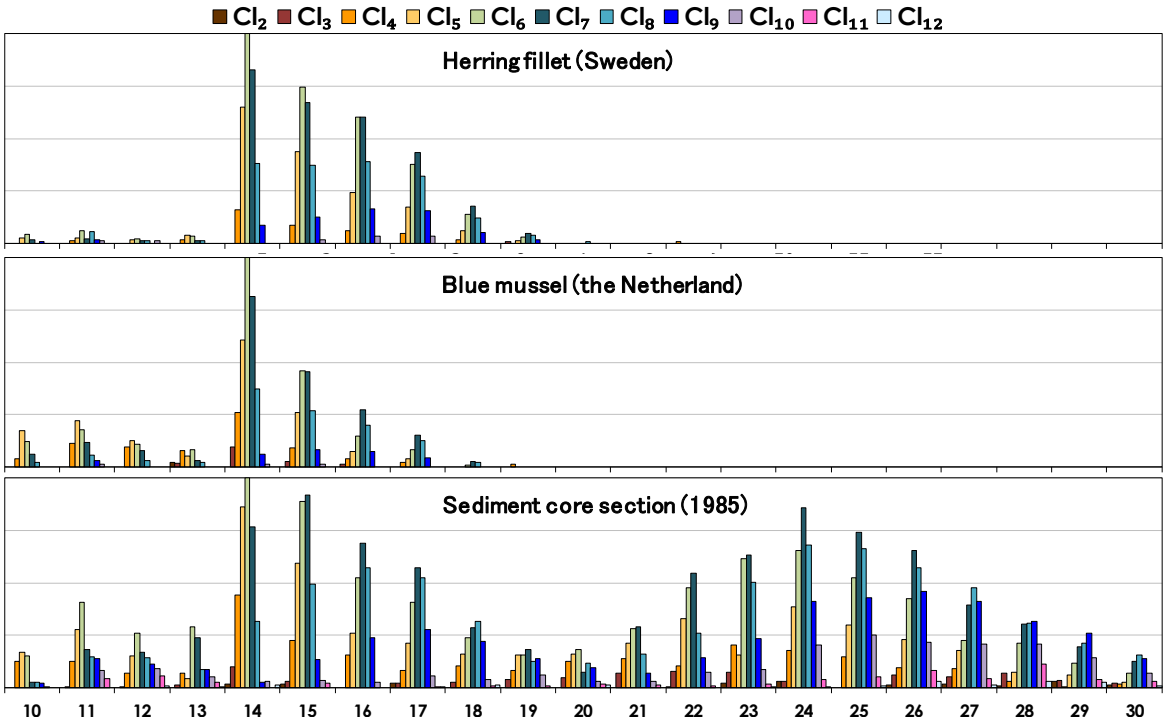

Figure 1. C_nCl_m patterns in the environmental samples. X-axis represents carbon chain lengths. Y-axis represents relative abundances of individual congener groups.

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