



Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma



Chlorinated paraffin analysis by gas chromatography Orbitrap high-resolution mass spectrometry: Method performance, investigation of possible interferences and analysis of fish samples

Kerstin Krätschmer^{a,b}, Cristian Cojocariu^c, Alexander Schächtele^b, Rainer Malisch^b, Walter Vetter^{a,*}

^a University of Hohenheim, Institute of Food Chemistry (170b), Garbenstraße 28, 70599 Stuttgart, Germany

^b European Union Reference Laboratory (EU-RL) for PCBs and Dioxins in Feed and Food, Bissierstraße 5, 79114 Freiburg, Germany

^c Thermo Fisher Scientific, Tudor Road, Manor Park, Runcorn, Cheshire WA7 1TA, United Kingdom

ARTICLE INFO

Article history:

Received 22 September 2017

Received in revised form

15 December 2017

Accepted 15 January 2018

Available online xxx

Keywords:

Gas chromatography with Orbitrap mass spectrometry

High resolution

Chlorinated paraffins

Polychlorinated alkanes

Persistent organic pollutants (POPs)

Fish

ABSTRACT

For decades, high quantities of short-chain chlorinated paraffins (SCCP) and medium-chain chlorinated paraffins (MCCP) have been widely used, for instance as plasticizers or flame retardants, leading to global pollution due to unintentional emissions from products or waste. Due to the high complexity of chlorinated paraffins with several thousand congeners there is no consensus on an analytical procedure for SCCPs and MCCPs in food samples. Amongst the multitude of methods currently in use, high-resolution mass spectrometry is particularly valuable for in-depth studies of homologue patterns. Here we analyse SCCPs and MCCPs with gas chromatography coupled to high-resolution Orbitrap mass spectrometry (GC-Orbitrap-HRMS) operated in full-scan acquisition in electron capture negative ion (ECNI) mode at 60,000 and 120,000 resolution (FWHM, m/z 200, equals roughly 30,000 and 60,000 at 5% peak height). Linear dynamic range, selectivity and sensitivity tests confirmed an excellent linearity in a concentration range of 25–15,000 $\text{pg}/\mu\text{L}$ with very low limits of detection (LODs) in the low $\text{pg}/\mu\text{L}$ range. Spiking experiments with high levels of native mono- and di-*ortho*-polychlorinated biphenyls (PCBs) and mixtures of MCCP and SCCP standards did not have a negative impact on isotope ratios of the examined homologues. Besides the $[\text{M}-\text{Cl}]^-$ fragment ions used for quantification, the mass spectra of homologues also featured $[\text{M}-\text{HCl}]^-$ ions whose abundance increased with decreasing chlorination degree. In addition, $[\text{M}-\text{HCl}-\text{Cl}]^-$ ions were detected with a relative abundance of 5–10%. Three salmon (*Salmo salar*) samples farmed in Norway showed a consistent CP homologue pattern which differed both from the CP pattern in a sample from Scottish aquaculture and a wild salmon sample. These measurements produce evidence that discretely different CP patterns may exist in different areas of origin. Our results demonstrate that GC/ECNI-Orbitrap-HRMS is well-suited for the analysis of CPs by overcoming a range of mass interference problems and due to its thus far unmatched sensitivity.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

Chlorinated paraffins (CPs) are industrially produced by the chlorination of mixtures of *n*-alkanes [1]. This results in complex mixtures of a copious amount of constitutional and optical isomers within a wide range of carbon chain lengths and degrees of chlorination [1,2]. CPs are most commonly classified by carbon chain lengths into three groups, i.e. short-chain CPs (SCCPs, $\text{C}_{10}\text{--C}_{13}$), medium-chain CPs (MCCPs, $\text{C}_{14}\text{--C}_{17}$) and long-chain CPs

(LCCPs, $\text{C}_{18}\text{--C}_{30}$) [2]. These three groups are chlorinated to different degrees, so that different products exist for each class, usually consisting of thousands of congeners following the general sum formula $\text{C}_n\text{H}_{2n+n-x}\text{Cl}_x$ [2].

The annual global CP production was estimated at >1.1 million tons/year for 2012 with later data currently being unavailable [3]. This 2012 production volume alone almost equals the total polychlorinated biphenyl (PCB) production volume from 1929 until their global ban [3]. SCCPs have shown persistence [4–8] and are believed to have harmful effects on exposed humans and the environment [9–14]. They have been found in all parts of the food chain as well as urban living environment [15,16] and human milk [14,17]. Therefore, SCCPs were categorised by the Stockholm Con-

* Corresponding author.

E-mail address: walter.vetter@uni-hohenheim.de (W. Vetter).

vention as POPs and added to Annex A of the convention at the Conference of the Parties in April/May 2017 [18,19]. However, phasing out the SCCP production in Europe, the U.S. and Canada in the last decade prior to the Stockholm Convention classification has already prompted a shift towards the use of MCCPs.

CPs analysis is challenging due to the (i) high complexity of technical mixtures, (ii) varied composition of CP in food and environmental samples and (iii) restrictions for only one type of CPs, i.e. SCCPs. This has not only analytical consequences but also effects possible future regulatory efforts: while the Stockholm Convention at the moment only regards SCCPs, low-resolution mass spectrometry (LRMS) or analogue detection methods often report 'SCCP' results that are actually closer to a total CP result. Without further specification of the required analytical instrument or method, it is debatable if regulatory measures set specifically for SCCPs or MCCPs would be conducive to harmonised official controls of CPs. The alternative would be regulating sum parameters like the total CP amount. In addition, SCCPs, MCCPs and other polyhalogenated pollutants show overlapping gas chromatographic (GC, Fig. S1, Supplementary information) and mass ranges [20,21]. To this day there is no consensus on an analytical procedure for SCCPs and MCCPs in food samples, resulting in barely comparable results from a multitude of methods which each face different challenges concerning availability of standards, different response factors and quantification methods in general.

GC with electron-capture negative ion low resolution mass spectrometry (GC/ECNI-LRMS) is the most commonly used method because it provides information regarding the chain length and degree of chlorination of CPs [22–24], which is in contrast to other LRMS or non-mass spectrometry methods that offer a way to screen for CPs in general but are often unable to determine further information [25–30]. Yet, GC/ECNI-LRMS (operated at nominal mass) suffers from unresolvable mass overlaps between homologues with two chlorine atoms and five carbon atoms difference [21]. GC/ECNI-MS spectra of CPs are usually dominated by $[M-Cl]^-$ fragment ions, but other ion species (e.g. $[M]^-$, $[M-HCl]^-$, $[M+Cl]^-$, $[M-H]^-$, and $[M-3Cl]^-$) were detected as well [31–33]. However, quantification of CPs using GC-ECNI-LRMS is usually based on the screening of the two most abundant isotope peaks of the $[M-Cl]^-$ fragment ions of each homologue. These additional fragment ions may interfere with the quantifier and qualifier ions. By taking into account eight carbon chain lengths (C_{10} – C_{17}), each with five to seven degrees of chlorination (for example Cl_5 – Cl_{10} or Cl_6 – Cl_{12}) this necessitates the monitoring of 40–56 SCCP and MCCP homologues and a total of 80–112 m/z values in the range m/z 279–551 ($\Delta = 272$ u, corresponding to $C_{10}H_{17}Cl_5$ – $C_{17}H_{22}Cl_{12}$ in this example) [23]. While some ions are doubly listed different homologues due to very similar exact masses being measured as nominal masses, this is still more than every 4th possible ion in this mass range. Due to restrictions on the maximum possible number of mass transitions monitored in one GC run, such an analytical approach would necessitate several injections per sample. The GC/ECNI-HRMS method presented by Tomy et al. in the late 1990s is able to circumvent the problems of measurements based on nominal mass, but still needs several GC injections per sample for a comprehensive analysis [34,35]. Newer approaches based on high-resolution mass spectrometry (HRMS) like direct injection APCI-qTOF-MS provided full CP analysis in one single run by using the full scan mode instead [36]. In connection to the world-wide ban of SCCPs and prior existing regulations like the limit of 1% by weight SCCP in preparations or 0.15% by weight SCCP in articles according to EU law [37], HRMS instruments like Orbitrap-MS are particularly valuable for analysis and in-depth studies of CP patterns. The method of detection presented in this study assumedly could provide deeper insights into fragmentation and thermal degradation of CPs before and during

analysis [33,38]. However, Orbitrap-MS had not been used yet in combination with GC for the analysis of CPs.

The goal of the present study was the setup of a GC with high-resolution accurate mass Orbitrap-based GC/ECNI-MS method for the analysis of SCCP and MCCPs.

Main focus was put on possible spectrometric interferences between SCCPs and MCCPs as well as with PCBs and partly other POPs using mixtures of CP standards and a mixture of SCCPs, MCCPs and selected PCB congeners. After verifying the suitability of the method with different ion species and combined analyses of CPs and other halogenated compounds, the method was used to analyse CPs in salmon samples.

2. Materials and methods

2.1. Samples and standards

2.1.1. Salmon samples

Frozen and fresh salmon (*Salmo salar*) fillets ($n=6$) from aquaculture in Norway and Scotland as well as wild salmon from the Eastern Pacific/Bering Sea (Table S1, Supplementary information) were acquired in January 2016 as part of the official food control in southern Germany. Samples (aggregate sample ≥ 1 kg, increment samples 200–250 g) were homogenized without skin according to the demands of Annex III of Regulation (EC) 589/2014 for whole fish [39]. Storage of the homogenized samples took place in glass bottles at -25°C which were soaked in alkaline laboratory cleaning agent overnight, washed with distilled water at 80°C , heated to 437°C for 6 h and thoroughly rinsed with n -heptane and dichloromethane and stored sealed with aluminium foil beforehand to avoid procedural contamination with CPs.

2.1.2. CP and PCB standards

Two standard solution mixtures of SCCP (100 mg/L in cyclohexane, C_{10} – C_{13} , 55.5 wt% Cl) and MCCP (100 mg/L in cyclohexane, C_{14} – C_{17} , 42 wt% Cl) were purchased from Dr. Ehrenstorfer (Augsburg, Germany). Solutions of SCCP and MCCP in cyclohexane (0.05 ng/ μL , 0.1 ng/ μL , 0.5 ng/ μL , 1 ng/ μL , 5 ng/ μL , 10 ng/ μL , 15 ng/ μL , respectively) were supplemented with 0.1 ng/ μL 1,5,5,6,6,10- $^{13}\text{C}_{10}$ -hexachlorodecane (Cambridge Isotope Laboratories, Tewksbury, MA, USA) and 0.05 ng/ μL ϵ -hexachlorocyclohexane (ϵ -HCH) (Dr. Ehrenstorfer, Augsburg, Germany) for calibration purposes. Additionally, the CP standard solutions were fortified with a mixture of native mono-*ortho* PCBs and di-*ortho* PCBs in cyclohexane (Cambridge Isotope Laboratories, Tewksbury, MA, USA) at concentrations of 15 ng/ μL –1.5 ng/ μL for individual congeners in a concentration ratio similar to their natural abundance in food samples analysed by EURL for Dioxins and PCBs over the course of ten years (Table S2, Supplementary information).

2.2. Chemicals and solvents

Silica gel 60 (230–400 mesh) and Florisil PR (60–100 mesh) for pesticide analysis as well as sodium sulphate (anhydrous, analytical grade) and concentrated sulphuric acid (analytical grade) were purchased from Carl Roth (Karlsruhe, Germany). Acetone, n -hexane and methanol in residue analysis grade were from LGC Standards (Wesel, Germany). Pre-cleaned, cross-linked polyacrylic acid (90–850 μm) was from Sigma-Aldrich (Saint Louis, MO, USA).

2.3. Salmon sample preparation

Frozen homogenised salmon (*Salmo salar*) fillets ($n=6$) were processed based on the method of Reth et al. [4]: 5 g sample including the internal standard 1,5,5,6,6,10- $^{13}\text{C}_{10}$ -hexachlorodecane was

Download English Version:

<https://daneshyari.com/en/article/7608738>

Download Persian Version:

<https://daneshyari.com/article/7608738>

[Daneshyari.com](https://daneshyari.com)