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QUANTIFIYING SHORT-CHAIN CHLORINATED PARAFFIN CONGENER GROUPS BY MASS SPECTRA DECONVOLUTION AND RESPONSE FACTOR CALCULATION IN ATMOSPHERIC PRESSURE CHEMICAL IONIZATION HIGH RESOLUTION MASS SPECTROMETRY

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Introduction

Chlorinated paraffins (CPs) are straight-chain alkanes with various chlorine contents. They are commonly used as lubricants, plasticizers, flame retardants and metal cutting fluids. Carbon chain length within the range of 10-13, 14-17 and 18-30 are often defined as short-chain (SCCPs), medium-chain (MCCPs) and long-chain CPs (LCCPs), respectively. The physical and chemical properties of CPs vary with their carbon chain length, and so does the toxicity.[1] SCCPs are toxic to many aquatic organisms, and are potential carcinogens.[2] In 2006 the Persistent Organic Pollutants (POPs) Review Committee of the Stockholm Convention had listed SCCPs as POP candidates.[3]

CPs are complex chemical mixtures with tens of thousands of congeners. CP congeners with an identical number of chlorines for a given alkane chain length are usually referred to as a "congener group", which has a defined molecular formula of C_nCl_m. The identification of CP congener groups relies on detection of pseudo-molecular ions by soft ionization mass spectrometry, but interferences between CPs lead to overlapping mass spectra. In a recent study, we demonstrated that CP congener groups could be resolved by deconvolving soft ionization mass spectra of CPs, which is a prerequisite for accurate congener group quantification.[4] To extend the method to quantitative analysis of individual congener groups in complex samples, response factors (RFs) for each congener group are required.

Here we report a mathematical method for obtaining RFs of CP congener groups from measurements using atmospheric pressure chemical ionization quadrupole-time-of-flight mass spectrometry (APCI-QTOF-MS). The RF of each CnClm is calculated from selected CP chain length standards, so that each CnClm in a sample can be quantified by the corresponding RF.

Materials and Methods

Materials: Pesticide grade cyclohexane, dichloromethane (DCM) and n-hexane were obtained from Merck (Darmstadt, Germany). Chain length standards (4 C_{10}, 4 C_{11}, 5 C_{12} and 4 C_{13}, 10 ng μL^{-1} in cyclohexane) and SCCP reference standards ($C_{10\text{-}13}$, chlorine contents 51.5 %Cl, 55.5 %Cl and 63.0 %Cl, 100 ng μL^{-1} in cyclohexane) were purchased from Ehrenstorfer GmbH (Augsburg, Germany). Eleven SCCP technical products, the chlorine contents of which lie between 49 %Cl and 71 %Cl, were diluted to 50 – 100 ng/μL for method validation. α-Hexabromocyclododecane (HBCD) was used as volumetric standard.

Spiked Environmental Sample Extracts: The clean-up procedure was based on Jansson et al. and Chen et al.[5, 6] Six fish and sediment extracts, which did not contain detectable levels of SCCPs, were pretreated using gel permeation chromatography and a multi-layered column containing silica of different acidities. Known amounts of SCCP reference standards were spiked before instrumental analysis.

Instrumental Analysis: The direct injection full scan method (scan range m/z 250 – 1000) using APCI-QTOF-MS (QTOF Premier, Waters, Manchester, UK) described previously[7] was used with several adjustments. The collision energy was optimized by the approach that we recently introduced[4] to 0.7 V, the cone voltage to 20 V, and the source temperature to 100 °C. The observed resolution was >9000.

Data Acquisition and Mass Spectra Deconvolution: Mass spectral data were acquired and the overlapping ions were deconvolved using the processing approach described in our previous work.[4] Full scan mass spectra from two background areas before and after the peak of the SCCPs were subtracted from the SCCP spectra. The instrument responses of $[M + Cl]^-$ of $C_nCl_2 – C_nCl_{n+2}$ in APCI-MS were deconvolved from the mass spectra.

Response Factor Calculation: Fig.1 presents the general procedure for calculation of the average RF of CP congener group. The RF of a CP congener group is calculated by dividing the instrument response by the injection amount. Instrument responses of individual congener groups were deconvolved from the mass spectra of chain length standards. Theoretical abundances of CP congener groups have been found to follow a Gaussian curve in CP mixture standards,[8] which therefore can be expressed using a Gaussian distribution equation (eq.1). In eq.1, $\%Cl_i$ is the chlorine content of the chain length standard i, and σ_i is the standard deviation describing how close the congener groups are clustered. x_m is the chlorine content of C_nCl_m. σ_i is the only unknown variable to be calculated.

Following steps 1 to 3 (Fig.1), The RF of the same congener group was calculated from a series of chain length standards (C_{10} chain length standards are shown in Fig.1 as an illustration). The differences were minimized by optimizing σi of each chain length standard. Thereafter the optimized σ_i was used to calculate the average RF of each CP congener group in the chain length standard i.The average coefficient of variation is 14% between RFs (C_nCl_m) in individual chain length standards.

Results and Discussion

Response Factors of CP Congener Groups: Calculated RFs of SCCP congener groups are shown in Fig.2, after normalizing to the RF of $C_{13}Cl_2$. For congener groups of a certain carbon chain length, the RFs generally increase first and then decrease with an increasing number of substituent chlorines.

Analytical Method Performance: Total SCCP concentrations can be quantified by applying the calculated RFs. Accuracies for SCCP reference standards, technical products and spiked environmental extracts were 102% - 105%, 86% - 118% and 77% - 98%, respectively.

CP chlorine contents were calculated by the RFs of congener groups as well. The calculated chlorine contents of 3 SCCP reference standards and 11 technical products were nearly identical to the %Cl provided by the manufacturers (Fig.3). E.g., the chlorine content of SCCP 63.0 %Cl reference standard is calculated to 62.9 – 63.2 %Cl (n = 6), compared to 60.5 %Cl, 60.9 %Cl and 66.2 %Cl measured by other methods.[9-11] Absolute deviations for spiked environmental extracts range from -0.5 %Cl to 0.4 %Cl.

Conclusions: This work is a significant step forward for our earlier study on CP mass spectra deconvolution. We describe a method to calculate the RFs of CP congener groups from measurements of CP standards that enables SCCP quantification in environmental samples. The method is expected to also be effective for analysis of longer chain CPs if suitable chain length standards are available. The method is likely also applicable to other soft ionization mass spectrometric techniques. The method we present here could play a key role in respond to the urgent need for more accurate quantification of CPs in environmental samples and technical products.

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$$f_i(C_nCl_m|x_m,\sigma_i) = \frac{1}{\sigma_i\sqrt{2\pi}} e^{-\frac{(x_m-\%Cl_i)^2}{2{\sigma_i}^2}} \quad \text{(eq.1)}$$

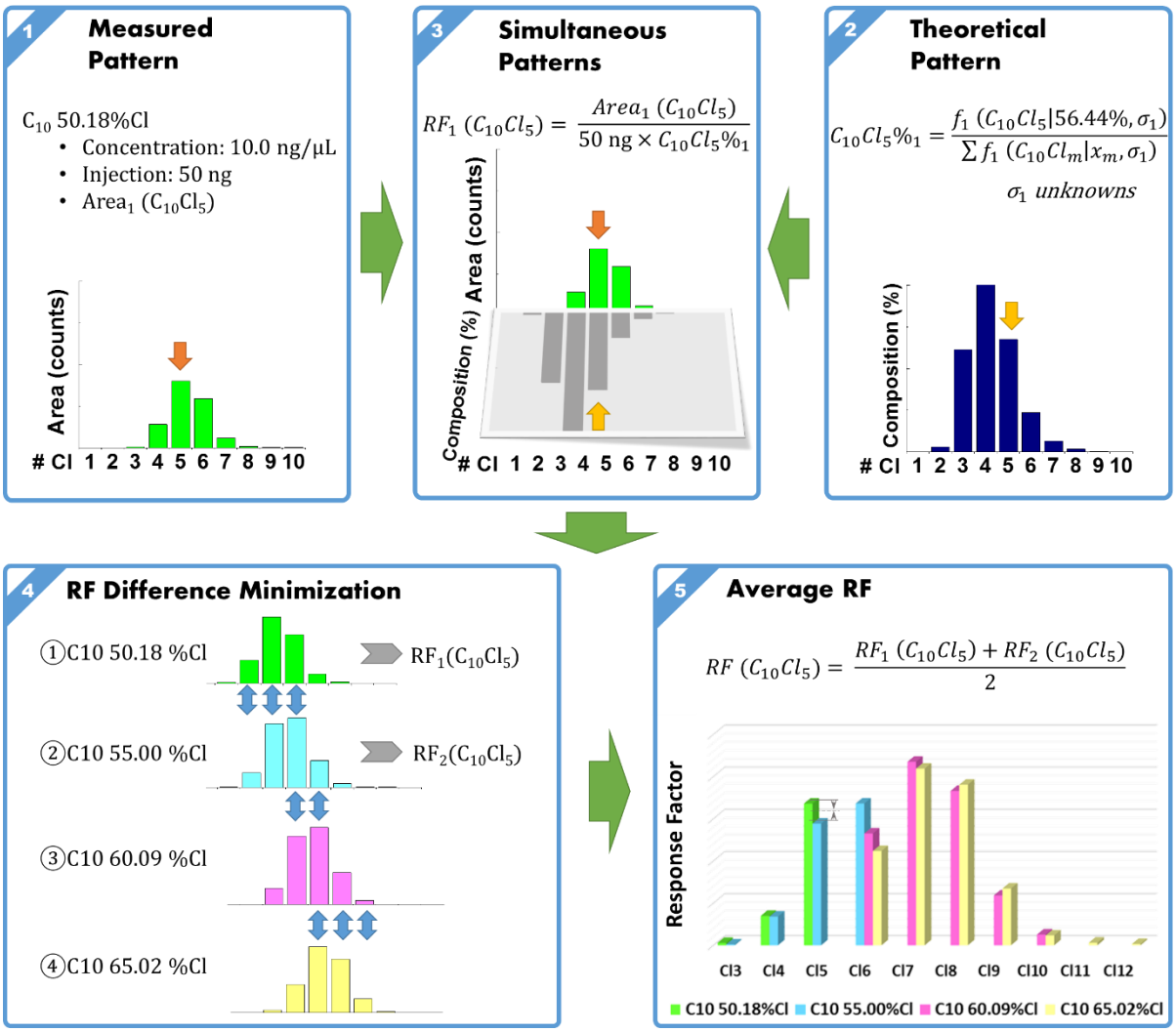

Fig.1 Flowchart summary of C_{10} response factor (RF) calculation

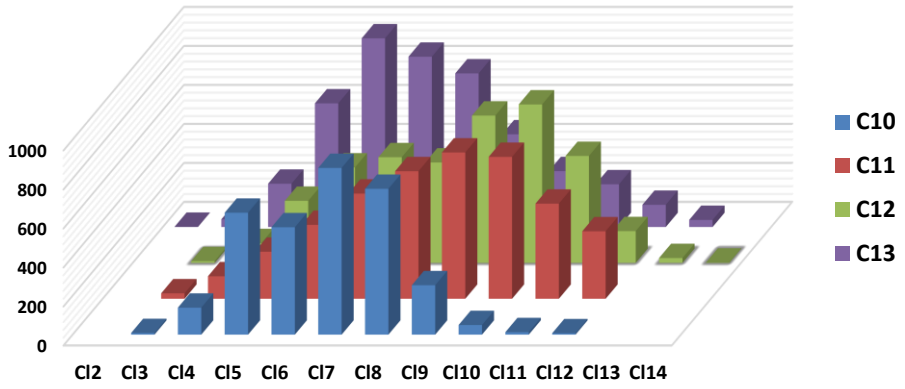

Fig.2 Calculated RFs of SCCP congener groups normalized to the RF of $C_{13}Cl_2$

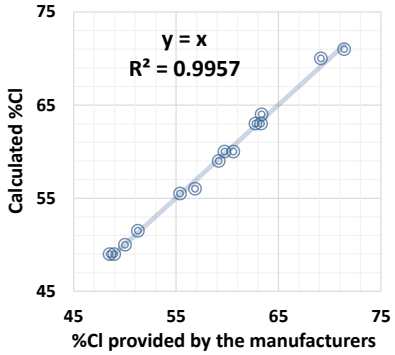

Fig.3 Correlation between calculated %Cl and the %Cl provided by the manufacturers.