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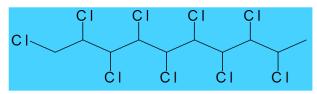
A New Approach to the Analysis of Chlorinated Paraffins by GC/Q-TOF

Wei Gao¹, Yawei Wang¹, Wenwen Wang²; ¹Research Center for Eco-Environmental Sciences, Beijing, China; ²Agilent Technologies Company Limited, Beijing, China

Introduction

Chlorinated paraffins (CPs), also known as polychlorinated n-alkanes have been used in large amounts for decades in commercial products. The commercial CPs mixtures can be divided into different species: short chain chlorinated paraffins (SCCPs) C10-C13, medium chain chlorinated parrifins C14-C17 (MCCP), and long chain chlorinated paraffins C20-C30 (long).CPs mixtures are extremely complex with over 10's of thousands of congeners and isomers, which makes separation by GC very challenging.

NCI-LRMS is well-suited for routine analysis, however it is subject to the interferences and overlap from other polychlorinated pollutants and CPs with the same nominal mass. In addition to the need of optimization on sample extraction and clean-up procedures, the interferences from mass overlap between SCCP and MCCP congeners are also to be addressed. In this study, due to sensitivity and separation challenge, an analytical approach based on NCI-GC-QTOF has been developed.





Experimental

Method

Freeze-dried food samples were extracted with accelerated solvent extraction (ASE). The sample extract was cleaned and fractionated on a 1.5cm i.e. Silica-Florisil composite column packed, from the bottom to top, with 3 g of Florisil, 2 g of neutral silica gel, 5 g of acid silica gel (30%) and 4 g anhydrous sodium sulfate. The column was conditioned with 50 mL of n-hexane and the sample was eluted with 40mL of n-hexane, followed by 50 mL of dichloromethane and 50 mL n-hexane. The second fraction was concentrated to about 2 mL with rotary evaporation and further concentrated to near dryness under a gentle stream of N_2 and then reconstituted in 200µL of cyclohexane. Prior to GC-QTOF analysis, 10 ng ϵ -HCH was added to determine the recoveries.

Standards and reagents

Pesticide analysis grade solvents were purchased from J.T.Baker (Phillipsburg, NJ, USA). SCCP mixtures (C10–C13 51 %, 55.5 %, and 63 % chlorination), MCCP mixtures (C14-C17 42%, 52%, 57% chlorination) 100 μg/mL solution in cyclohexane (Dr.Ehrenstorfer, Augsburg, Germany) ε-hexachlorocyclohexane (ε-HCH, solution in cyclohexane, 10 ng/μL) were purchased from Ehrenstorfer GmbH (Augsburg, Germany), 13C10-trans-chlordane (99%) in n-nonane was supplied by Cambridge Isotope Laboratories (Andover, USA). 1, 5, 5, 6, 6, 10-Hexachlorodecane (13C10)100 μg/mL solution in nonane, 1, 5, 5, 6, 6, 10-Hexachlorodecane (unlabeled) 100 μg/mL in nonane was purchased from Cambridge Isotope Laboratories (Andover, USA)

Instrument conditions

System: Agilent 7200 GC-QTOF

Column: HP-5MS UI (30 m×0.25 mm×0.25 µm)

Column temperature: 100 °C hold 1 min , at 5 °C /min to 160 °C hold 2 min , at 30 °C /min to 310 °C hold 10 min;

Carrier gas: Helium; Flow rate: 1.0mL/min;

Injection port temperature: 280 °C; Injection volume: 1µL; Injection mode: Splitless, purge on after 1.5min

Ion source: NCI

MS Acquisition: Full Scan 50-600m/z; 5Hz

Results and Discussion

Mass spectrum of Chlorinated paraffins

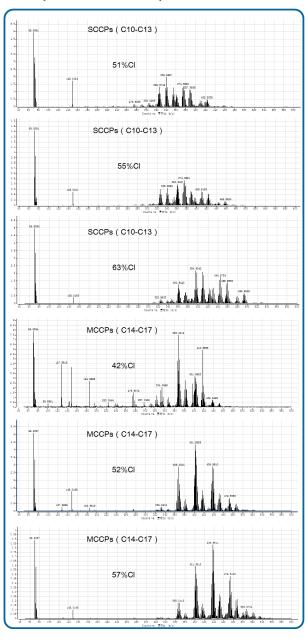


Fig.1 Mass spectra of SCCP 51% CI, SCCP 55% CI, SCCP 63% CI; MCCP 42%CI, MCCP 52% CI and MCCP 57% CI.

Limit of detection

To determine the instrumental limit of detection (LOD) of the NCI-TOF-HRMS system, seven replicate analyses of the technical CP formulations were performed. The LOD was derived from the standard deviation of the signal intensity of the five replicate injections multiplied by the Student's T-value at a 99% confidence level. In vegetable samples, a congener group was defined as detected if both m/z values were detected above their respective LODs and the LOD of the congener group was set equal to the LOD of the least sensitive of the two m/z traces monitored. The LOD for SCCPs, MCCPs was calculated as the sum of the LOD of the corresponding congener groups which were 0.5ng and 0.2ng respectively.

Relationship of response factor and chlorination

We plotted the calculated chlorination of the mixtures of SCCPs and MCCPs standards against response factors and found good linearity between them.

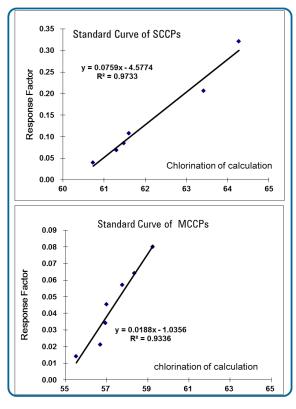


Fig.2 Standard Curve of MCCPs and SCCPs using response factor and chlorination

Results and Discussion

Linear ranges of SCCPs and MCCPs

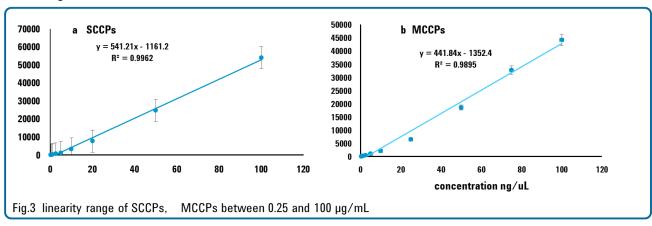
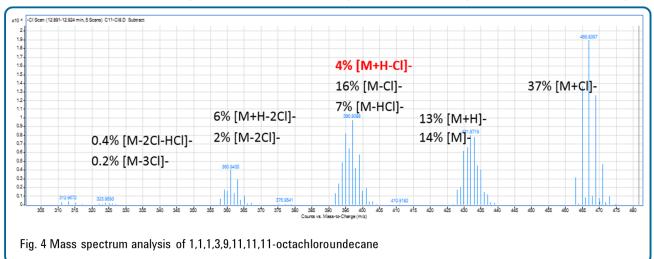


Fig. 3 shows the linear ranges of the NCI-TOF-HRMS response for SCCPs and MCCPs based on weighted linear regressions for the reference standards SCCPs (C10-13, 55.5% chlorine content) and MCCPs mixtures (C14-17, 52.0% chlorine content).



Analyze mass spectrum of single isomers

Fig.4 shows the possible fragmentation patterns of a single isomer 1,1,1,3,9,11,11,11-octachloroundecane, the result suggests that ions such as [M+CI] generated from $C_{11}CI_6$ [M-2CI] generated from $C_{11}CI_9$ will all interfere with the quantitative ion of $C_{11}CI_8$ TOF scan offers information in the full range between 50-600 which enables us to select the suitable ions for qualification and quantification to distinguish different CPs congener groups.

Conclusions

Using accurate mass data operated in TOF mode is a suitable technique for the qualification and quantification of chlorinated parrafins (CPs). Quantitation and confirmation of CPs at trace levels in complex matrices such as vegetables and sediments are achieved by using accurate mass matching in MS, while optimization of GC and MS acquisition parameters and selection of ions. This approach is highly efficient in distinguishing SCCPs from MCCPs in complex environmental sample matrices by exact mass resolution.