

ASMS 2015

TP 113

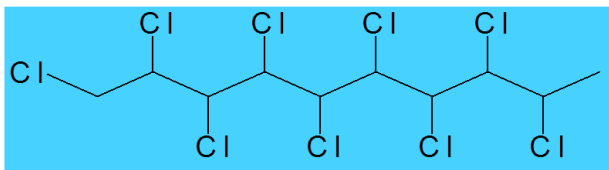
A New Approach to the
Analysis of Chlorinated
Paraffins by GC/Q-TOF

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 paraffins 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 N₂ 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

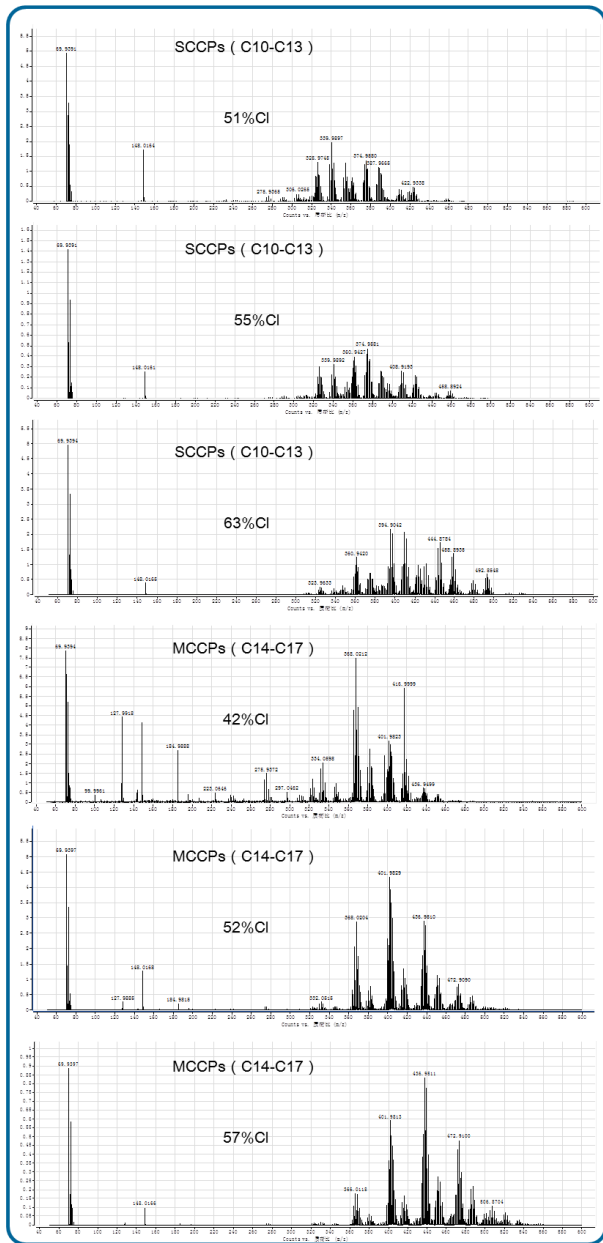
Pesticide analysis grade solvents were purchased from J.T.Baker (Phillipsburg, NJ, USA). SCCP mixtures (C10–C13 51 %, 55.5 %, and 63 % chlorination), MCCP mixtures (C14-C17 42%, 52%, 57% chlorination) 100 µg/mL solution in cyclohexane (Dr.Ehrenstorfer, Augsburg, Germany) ε - hexachlorocyclohexane (ε-HCH, 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



Results and Discussion

Linear ranges of SCCPs and MCCPs

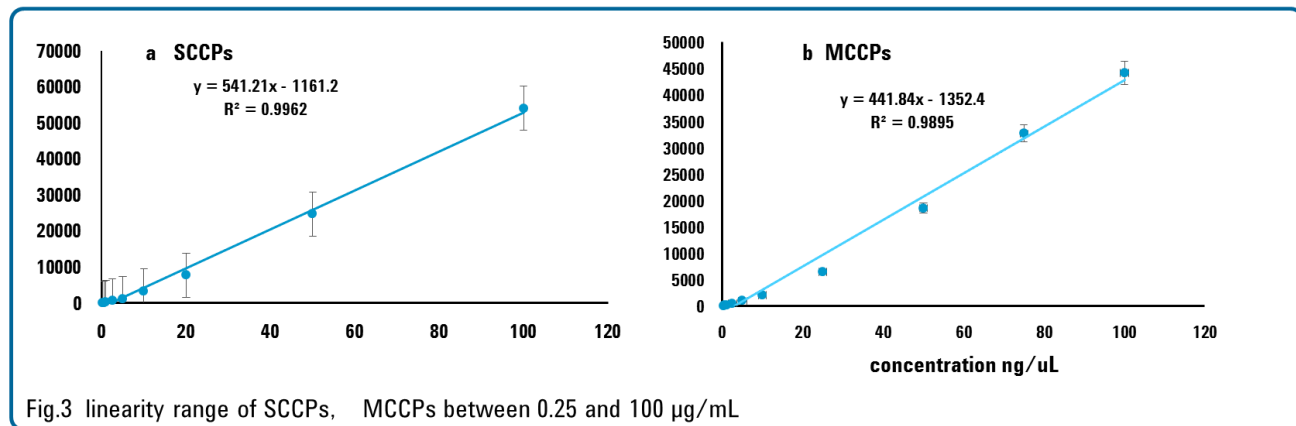
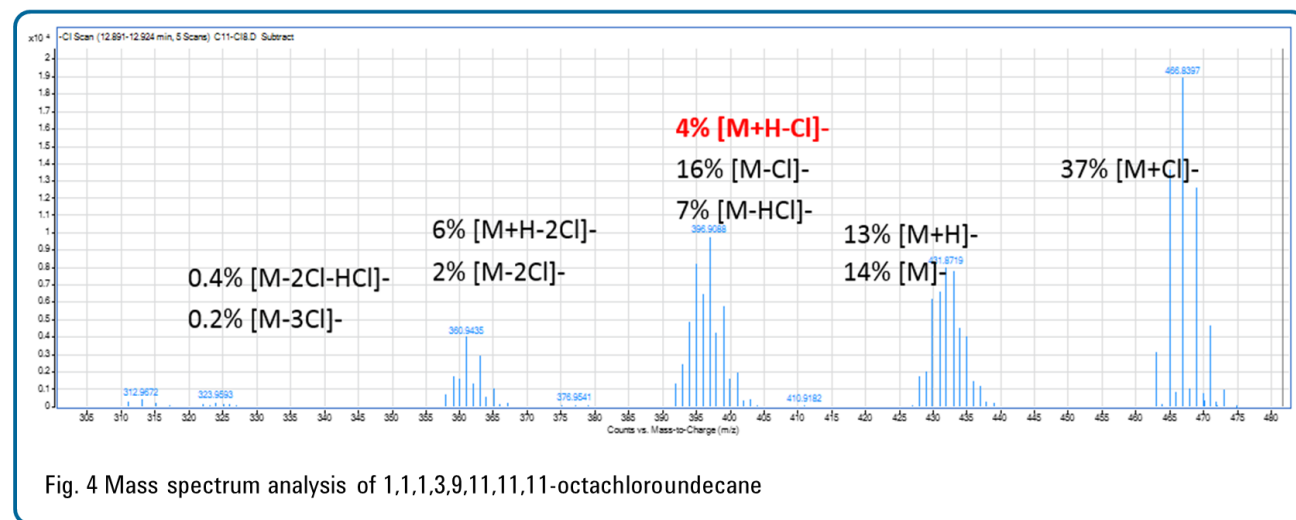


Fig. 3 shows the linear ranges of the NCI-TOF-HRMS response for SCCPs and MCCPs based on weighted linear regressions for the reference standards SCCPs (C10-13, 55.5% chlorine content) and MCCPs mixtures (C14-17, 52.0% chlorine content).



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 $[M+Cl]^-$ generated from $C_{11}Cl_6$ $[M-2Cl]^-$ generated from $C_{11}Cl_9$ will all interfere with the quantitative ion of $C_{11}Cl_8$. 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 paraffins (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.