ANALYSIS OF SHORT CHAIN CHLORINATED PARAFFINS (SCCPs) USING HIGH RESOLUTION MASS SPECTROMETRY AND NEGATIVE CHEMICAL IONISATION (NCI GC-HRMS)

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Introduction

The purpose of this research was to develop and demonstrate a sensitive and selective analytical method for short-chain chlorinated paraffins in environmental samples. The work utilisedisobutane as a stable negative chemical ionisation (NCI) reagent gas. The separation of gas chromatography coupled to the exceptional selectivity and sensitivity of NCI HRMS are presented as a technique sufficient for the instrumental analysis of SCCPs. The Thermo Scientific™ DFS™ high resolution mass spectrometer was able to demonstrate proof of principle that it has the necessary sensitivity, selectivity, and repeatability for the analysis of SCCPs in environmental samples.

Chlorinated paraffins (aka. polychlorinated alkanes, PCAs, CPs) have been produced since the 1930s for use as additives in lubricants and cutting fluids as well as flame retardants in plastics and sealants. Chlorinated paraffins are manufactured by the chlorination of specified normal paraffin fractions (straight-chain hydrocarbons) obtained from petroleum refining.

Commercial chlorinated paraffins are not single compounds, but are highly complex mixtures, each containing several homologous n-alkanes corresponding to their manufacture from n-paraffin fractions with numerous degrees of chlorination.Chlorinated paraffins are characterised to a first approximation by the carbon-chain length range of their n-alkanes and by the chlorine content of the product. Chlorinated paraffins are divided into three groups:

1. **Short-chain chlorinated paraffins**(SCCPs or sPCAs) comprising 10 to 13 carbon atoms and various degrees of chlorine content, giving theoretically millions of individual analyte permutations.
2. **Medium-chain chlorinated paraffins**(MCCPs or mPCAs) comprising 14 to 17 carbon atoms
3. **Long-chain chlorinated paraffins** (LCCPs) with more than 18 or more carbon atoms.

SCCPs remain a high production volume chemical with over 600,000 tons produced in 2007[1]. However, they have been detected in almost every compartment of the environment with SCCPs readily undergoing long range transport[4]. Consequently, SCCPs are currently listed as a class of compounds to be considered for listing under Article 8 of the UNEP Stockholm Convention[2]. In 2001, the Europe Union listed short-chain CPs (SCCPs) as priority hazardous substances[3]. The complexity of SCCP mixtures makes the analysis of SCCPs troublesome:

- SCCPs have complex chromatograms due to high number of homologues
- SCCPs readily fragment in a mass spectrometer source creating significant interferences.
- Complex chromatograms make resolving of nominally isobaric interferences impossible my LRMS.
- MS/MS techniques are of little added value to remove interferences due to the exceptionally high level of fragmentation of SCCPs

This challenge has resulted in significant spread of inter-laboratory trial results ; with concentrations varying by over two orders of magnitude in some studies[1].

This has resulted in scientists calling for the use of HRMS methods as a gold standard benchmark for the analysis of SCCPs[1]. We present an instrumental analysis method for the analysis of SCCPs using NCI GC-HRMS.

Materials and methods
Sample extracts and standards were provided ready prepared by Environment Canada, Burlington ON, Canada:

1. A standard of a SCCP $C_{10}H_{17}Cl_5$– "CP3"
2. A mixture of SCCPs C10-13 55.5% Cl in cyclohexane
3. Extracted matrix samples containing C13 mirex as an internal standard.

A Thermo Scientific Trace 1310 GC fitted with a split/splitless 'instant connect' injector module, was interfaced to a Thermo Scientific DFS high resolution mass spectrometer and a Thermo Scientific TriPlus RSH auto-sampler.

Gas Chromatography:

- GC Column: Trace Gold TR-5MS (PN: 260F047P) 30m x 0.25mm, 0.1 μm film
- GC Liner: Single taper splitless (PN: 453A1345)
- Injector temp.: 220 °C
- Splitless time: 3 minutes
- Transfer line: 220 °C
- Column Flow: 1 $mLmin^{-1}$, constant flow

Mass Spectrometry:

Electron capture negative chemical ionisation was used to analyse SCCPs.

- EC NCI Buffer Gas: Isobutane and ammonia
- Source Pressure: $6x10^{-4}$mBar
- Electron engery: 90 eV
- Emission current: 0.3 mA
- Ion source temp.: 80-95 °C
- Scan Multiple Ion Detection (MID)

Data Analysis:

The DFS was operated using Thermo Scientific Xcalibur ™ 2.2 software. Data were analysis using Xcalibur and Thermo Scientific TargetQuan 3.

Results
Electron capture negative chemical ionisation as a technique is comparatively sensitive to ion source conditions. Ion source temperature, nature of buffer gas, amount of sample and source contaminations play important roles in achieving stable analysis.

Several gases were trialled to achieve stable conditions; ammonia and isobutane were found to give acceptable results. The combination of isobutane with a lowered ion source temperature was found to be most robust and sensitive. The low source temperature was found to be critical. Isobutane had a cooling effect on the source, giving increased sensitivity. When the source heated above 110-120 °C sensitivity rapidly deteriorated. Source condition and cleanliness is critical to robust EC NCI. Despite its reputation as a 'dirty' gas; isobutane, was most robust allowing long sequences of sample extracts without significant loss in performance. Source contamination from isobutane was not noticeably different from other gases trialled.

Figure 1. **MID chromatogram of SCCP standard: CP3, 20 pg on column**

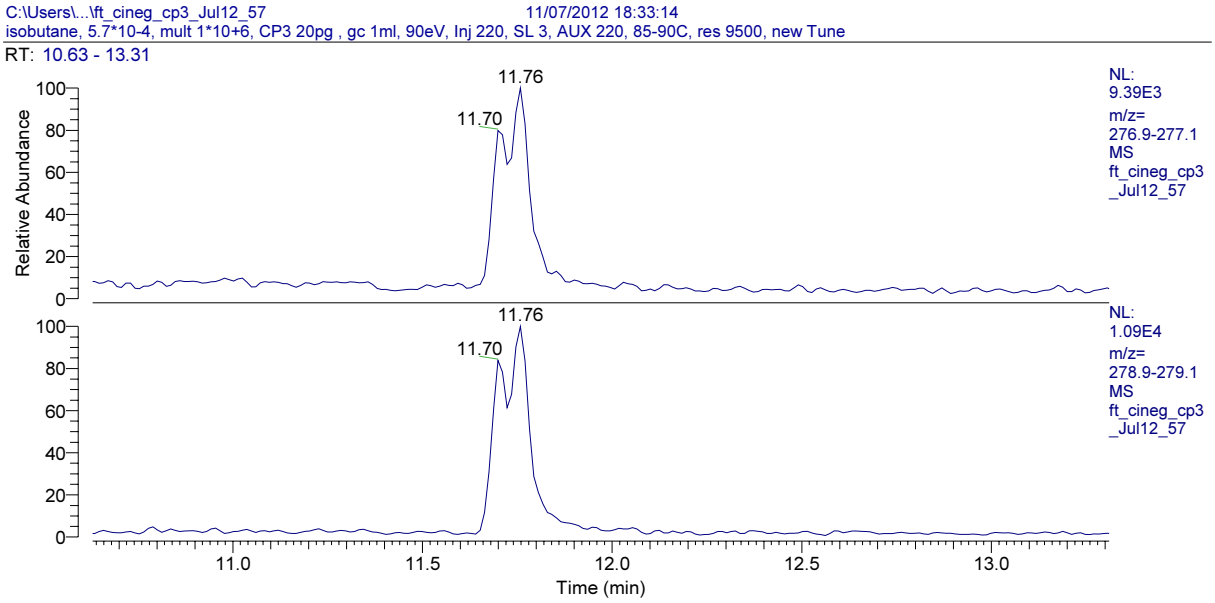
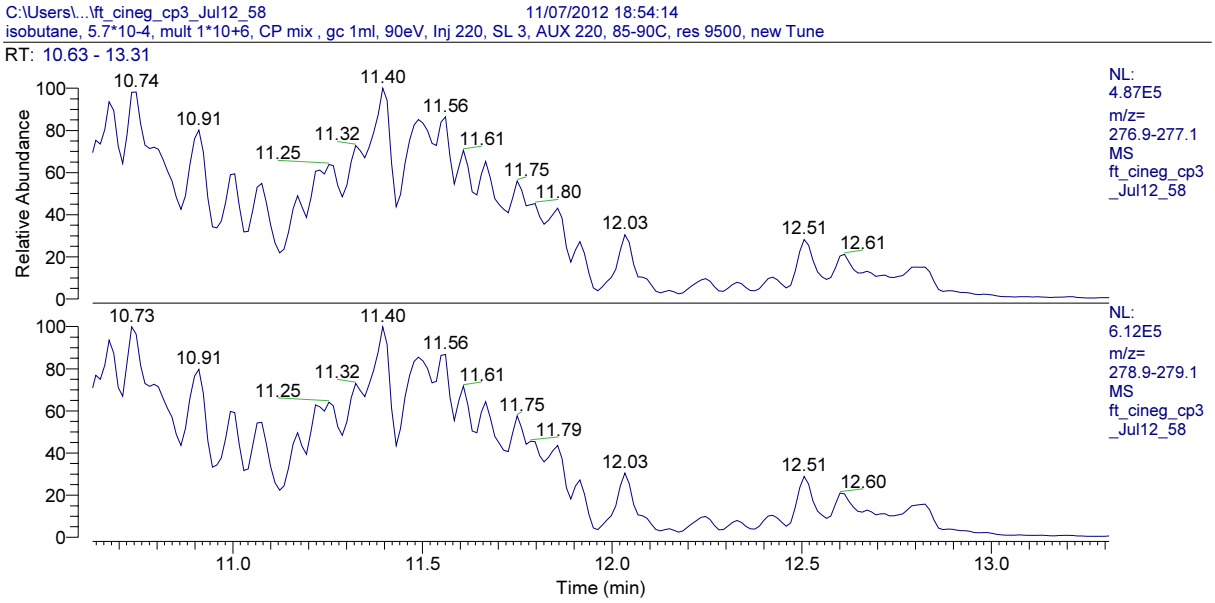


Figure 2. **MID chromatogram of SCCP mixture, $C_{10\text{-}13}$ 55.5% Cl**



Analytical standards were analysed bracketing matrix samples in sequences of 30 sample injections with a stable response throughout. Detection limits were approximately 2 pg on column. There were no significant matrix interferences observed.

Results and discussion

In conclusion:

- An analytical method for analysis of SCCPs was developed and demonstrated as fit for purpose.
- Negative chemical ionisation using iso-butane as a reagent gas has been demonstrated as a suitably robust and sensitive technique for the analysis of SCCPs.
- The additional sensitivity and selectivity of the Thermo Scientific DFS GC-HRMS serve to remove nominally isobaric interferences that are observed using low resolution techniques; resulting in clean chromatograms.

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