

EVALUATION AND VALIDATION OF A HYDRODECHLORINATION METHOD FOR THE DETERMINATION OF CHLORINATED PARAFFINS

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Abstract

An analytical method to determine short chain (C_{10} - C_{13}) and medium chain (C_{14} - C_{17}) chlorinated paraffins (CPs) in leachates was evaluated and validated. CPs in samples were extracted with DCM, fractionated on florisil column, dechlorinated to *n*-alkanes with Pd catalyst and analyzed by gas chromatography – low resolution mass spectrometry (GC-LRMS). Good recovery, precision and sensitivity were achieved for leachate samples spiked with technical mixture of CPs. Method detection limits (MDL) determined from the low level samples were between 0.05 and 0.22 pg/mL for C_{10} to C_{17} , or 0.5 and 0.4 pg/mL for the total short chain and medium chain paraffins respectively. The precisions for the medium level sample were 13 and 15% at 95% confidence level for short chain and medium chain respectively. Recoveries of 95 to 102% were achieved at both CP levels. This simple and practical method can be adopted as a routine method by environmental labs for the routine monitoring of CPs in environmental samples.

Introduction

Commercially produced polychlorinated alkanes or chlorinated paraffins (CPs) are complex mixtures of short chain (C_{10} - C_{13}), medium chain (C_{14} - C_{17}) and long chain (C_{20} - C_{30}) CPs with chlorine content from 30 to 70% by mass. The first major commercial use was as extreme pressure additives in lubricants in 1932.¹ They were also used in large scale as flame retardants for canvas and other textiles during the second world war.² The application of CPs was later expanded for use as additives in vinyl plastic, paints, rubbers, adhesives and sealants.³ The world production of CPs around 1990 was about 300 kilo-tonnes per year.^{4,5} The production of CPs in Canada in 2000 was 8.5 kilo-tonnes. An additional 1.8 kilo-tonnes was imported.⁶

Environment Canada's assessment report of Priority Substances List 1 released in 1993 identified sufficient data to conclude that short chain chlorinated paraffins (SCCPs) are toxic to human health as defined in Paragraph 11© of the Canadian Environmental Protection Act (CEPA) 1988. The medium chain (MCSPs) and long chain (LCSPs), however, were not considered as toxic due to insufficient data that was available at that time. About 10 years later, the follow-up report on PSL1 Substances released in 2003 proposed that there is reason to suspect that MSCPs and LCSPs are toxic to human health as defined in Section 64 (c) of the CEPA, 1999.⁶

The commercial CP products are very complex mixtures because of the large variation of positions for chlorine substitution. The total number of possible congeners for SCCPs is over 6000 and the number is much greater for MSCPs and LCSPs because of more possible substitution positions on longer carbon chains.⁷ As a result, most of the CP congeners in products can not be separated and identified even with the best analytical tools available today. New methodologies have been developed in recent years to improve the accuracy and specificity in the measurement of CPs. To enhance sensitivity and minimize the potential interferences from other persistent organic pollutants, and also to be able to determine individual homologue groups of SCCPs, a high-resolution gas chromatography / electron capture negative ion-high-resolution mass spectrometry (HRGC/ECNI-HRMS) method based on the Kratos Concept HRMS was published in 1997.⁷ However, one of the weakness of this method is that the analytical results are strongly influenced by the chlorine content of the technical standard used for calibration. This was demonstrated by a comparison study that quantified three SCCPs solutions using three reference standards with different chlorine contents.⁸ Results showed that the spiked solvent sample at 1500 ng of SCCPs with 55% Cl content can be quantified as 4300 ng and 413 ng when the calibration standard has 51 and 63% Cl content respectively. A large discrepancy among 7 participating labs was also observed from an inter-laboratory study on the analysis of SCCP

solutions using a similar ECNI-MS method.⁹ Another disadvantage of ECNI-MS is that molecules with less than 5 chlorine atoms are not readily ionized. It was suggested that this problem can be improved by the use of CH₄/CH₂Cl₂-negative ion chemical ionization (NICI)-MS.⁸ However, this technique may not be suitable for dirty samples due to the rapid contamination of the ion source.¹⁰ Another study showed that SCCPs with chlorine atoms less than 5 in water samples can be quantified by using the metastable atom bombardment ionization (MAB)-HRMS.¹¹ In addition to a relatively high uncertainty of the results, these HRMS analytical techniques are both costly and time consuming.

The technique of hydrodechlorination of chlorinated organic compounds using a catalyst was first reported by Thompson et al.¹² This technique was later applied with capillary GC for aromatic organochlorine compounds and polychlorinated alkanes.¹³ CPs were able to be simultaneously dechlorinated and hydrogenated to the corresponding alkanes with a Pd catalyst material in the GC injector.¹⁴ This approach was applied to our study to assess and validate the hydrodechlorination technique for converting the complex mixture of CPs to simple straight chain alkanes for analysis with low-resolution mass spectrometry (LRMS).

Material and Methods

An aliquot of the aqueous sample was extracted three times with dichloromethane (DCM) at ¼ of sample volume in a separatory funnel each time. The combined DCM extract was changed to hexane on a rotary evaporator and concentrated to about 5 ml before the 6 g activated florisil column cleanup. The florisil column was first eluted with 20ml hexane to remove alkanes and other interferences. CPs were eluted with 25 ml of DCM/hexane (1:1). The final volume was made to 100 µL in toluene with the internal standard, cyclododecane at 1 µg/mL.

Preparation of the palladium catalyst is similar to the procedures described elsewhere.¹⁴ Palladium catalyst was prepared by dissolving 8 mg of PdCl₂ in 1 mL hot 5% acetic acid and then mixing with 2 g glass beads (60/80 mesh) which is then dried while stirring in a water steam bath. The pH of the residue was adjusted to 9 by adding 1 mL deionized water and the dropwise addition of ammonia solution. After drying, the catalyst material was washed with cyclohexane and air dried on a glass fibre filter. The GC injector glass liner was filled from the bottom with glass wool (2mm), CaCO₃ (2mm), Pd-catalyst (10mm) and glass wool (2mm). The catalyst is then activated in the GC injector at 300 °C under hydrogen for one hour.

Dechlorinated paraffins were analyzed using Agilent 6890 GC equipped with a DB-5 column (30 m x 0.25 mm, 0.25 µm film) for carbon chains separation, coupled to an Agilent 5973 MSD for *n*-alkane structure identification and quantification.

Results and Discussion

Technical mixture of chlorinated paraffins with carbon chain length from 10 to 13 (Cereclor 60L, 59% chlorine) and 14 to 17 (Cereclor S52, 52% chlorine) were tested for the efficiency of dechlorination. The %dechlorination (or % recovery) was calculated as follows:

$$\%dechlorination = \frac{\sum A_x * 100}{CP_x (1 - DC_x + DC_x / 35.453)}$$

where $\sum A_x$ is the total quantified *n*-alkanes concentration of short or medium chain; CP_x is the concentration of technical mixture of short or medium chain with known % of chlorine; and DC_x the degree of chlorination (e.g., 0.5 for 50% Cl). Results show that the range of dechlorination of both technical mixtures at 10, 20, 50 and 100 µg/mL was between 94 and 107%. The linearity of online dechlorination was demonstrated by drawing a CP_x vs. A_x plot, in which the coefficient of determination (R^2) were greater than 0.994 for all carbon chains (C₁₀ - C₁₇).

The method validation study was performed on a leachate sample collected from a landfill. The background level of CPs in this sample was found to be slightly above the detection limit. Fourteen portions of the 500 mL samples were spiked with technical mixture Hordalub 80 (56% Cl, Hoechst) for SCCP and Cloparin 50 (51% Cl, Caffaro) for MSCP. Each sample was fortified with CPs at 4 pg/mL as the low level or 20 ng/mL as the intermediate level. Samples were extracted with DCM, fractionated on florisil columns, dechlorinated and analyzed on GC-MS as described above. Validation results are summarized in Table 1. Method detection limits (MDL) determined from the low level samples were between 0.05 and 0.22 pg/mL for C₁₀ to C₁₇, or 0.5 and 0.4 pg/mL for the total short chain and medium chain paraffins respectively. The precisions for the medium level sample were 13 and 15% at 95% confidence level for short chain and medium chain respectively. Excellent recoveries (95 to 102%) were achieved at both CP levels. The relatively high standard deviation of heptadecane (C₁₇) observed was due to the tailing of the chromatographic peak. Some improvement in chromatographic conditions would be needed. Another leachate sample collected from an old landfill site closed in 1980 was also analyzed. CP level in this sample was calculated to be 2.56 pg/mL of SCCP and 9.12 pg/mL of MSCP based on the assumption of 50% chlorine. The GC-MS ion chromatogram of this leachate sample is shown in Figure 1.

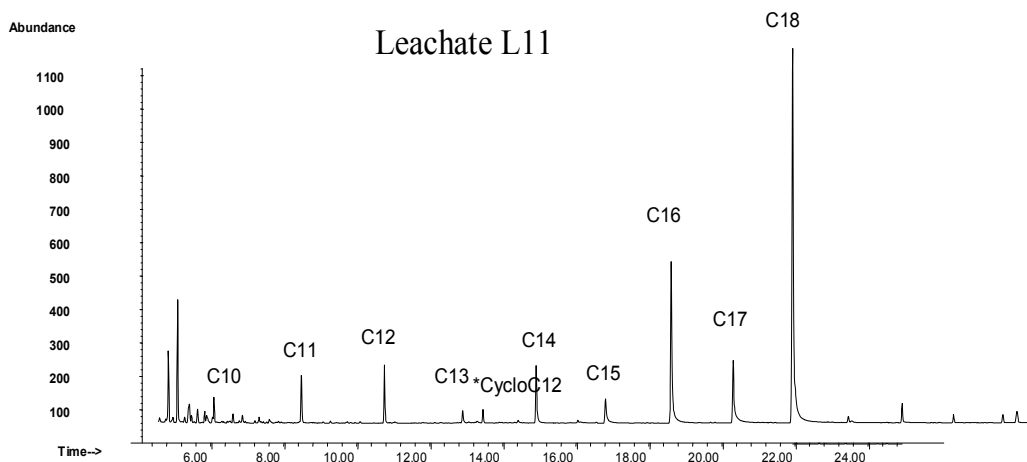
The validation test has demonstrated that this method is able to determine total CPs by quantification of *n*-alkane after the online hydrodechlorination. Any non-chlorinated alkanes, if present in the sample, are expected to be removed by the florisil cleanup before GC-MS analysis. The ability to minimize possible interferences from paraffins containing other halogens, oxygen, sulphur and nitrogen is not known and must be assessed. In conclusion, this method provides very good precision, recovery and sensitivity with acceptable uncertainty for the determination of short chain and medium chain of CPs in liquid samples. This method can be applied routinely by most environmental analytical laboratories at a reasonable cost.

References

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Table 1 Summary of Validation Results

sample size, ml		500	500	500	500	500	500	500	500
number of samples		7	7	7	7	7	7	7	7
CP spiked, µg		2	2	2	2	10	10	10	10
		AVE	SD	RSD	MDL	AVE	SD	RSD	Precision
		pg/mL	pg/mL	%	pg/mL	pg/mL	pg/mL	%	%
Decane	C10	0.174	0.028	16.1	0.053	0.730	0.058	7.9	19
Undecane	C11	0.672	0.116	17.3	0.220	3.126	0.154	4.9	12
Dodecane	C12	0.626	0.094	15.0	0.178	2.910	0.164	5.6	14
Tridecane	C13	0.404	0.032	7.92	0.061	1.962	0.114	5.8	14
total short chain		1.876	0.252	13.4	0.478	8.728	0.458	5.2	13
% recovery		97.43	11.15	11.4		95.71	5.09	5.3	
Tetradecane	C14	0.814	0.072	8.85	0.136	4.376	0.178	4.1	10
Pentadecane	C15	0.460	0.048	10.4	0.091	2.566	0.138	5.4	13
Hexadecane	C16	0.422	0.096	22.7	0.182	1.888	0.122	6.5	16
Heptadecane	C17	0.316	0.050	15.8	0.095	1.544	0.256	16.6	41
total medium chain		2.012	0.190	9.44	0.360	10.37	0.628	6.1	15
% recovery		99.79	9.420	9.44		102.8	6.23	6.1	

**Figure 1 GC-MS Ion Chromatogram of a Leachate Sample**