Application Note

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Analysis of Short- and Medium-Chain Chlorinated Paraffins in Textiles and Leather Using Triple Quadrupole LC/MS

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Abstract

A comprehensive Agilent 1290 Infinity II LC and Agilent 6470 triple quadrupole LC/MS system (LC/TQ) method was developed for the quantitation of chlorinated paraffins. The method for short-chain chlorinated paraffin (SCCP) and medium-chain chlorinated paraffin (MCCP) content produced more stability and sensitivity for routine consumer testing laboratories. The workflow included sample preparation, chromatographic separation, mass spectrometry (MS) detection, data analysis, and interpretation. The workflow applicability was demonstrated on consumer product samples using an Agilent 1290 Infinity II LC system coupled to an Agilent 6470B triple quadrupole LC/MS.

Introduction

Chlorinated paraffins (CPs) are complex mixtures of chlorinated n-alkanes, usually with 30 to 70% chlorine content by mass. CPs are categorized according to carbon chain length as short-chain (SCCPs, C_{10} to C_{13}), medium-chain (MCCPs, C_{14} to C_{17}), and long-chain (LCCPs, $C_{>17}$). SCCPs and MCCPs are commonly used as flame retardants in textiles, plasticizers in polymers, and finishing agents in leather.[1] In addition, it has been considered to include the short-chain chlorinated paraffins into the list of the Stockholm Convention on Persistent Organic Pollutants (POPs). Therefore, leading apparel and footwear brands have restricted the use of CPs in their production. Meanwhile, the analysis of chlorinated paraffins is challenging. Gas chromatography with negative chemical ionization mass spectrometry (GC-NCI-MS) was known as an appropriate technique for determining SCCPs and MCCPs content in consumer products at many routine testing laboratories.[2,3] However, there are some problems in the quantification of CPs by GC, since GC chromatograms of these complex mixtures typically show overlapping of different chain length and chlorination degrees, and possible interference from presence of sulfochlorinated paraffins and equivalent chain-length chloroalkenes. Also, according to the ISO 18219-1:2021 method, it is acceptable to use liquid chromatography/triple quadrupole mass spectrometry (LC/TQ) as an alternative method to analyze SCCPs and MCCPs in leather. The LC/TQ is expected to get a better result compared to the GC/MS method.[2] The responses of the different chlorination degrees vary in a wide range of samples.[3] Therefore, in this workflow, an LC/TQ was used to develop a comprehensive method including acquisition, data analysis, and sample preparation. The typical samples used mixtures (59% chlorination degree for SCCPs and 55% chlorination degree for MCCPs) to determine the amount of SCCPs and MCCPs in textile and leather articles. The LC/TQ method focuses on giving better resolution and eliminating possible false positives encountered with the GC-NCI-MS method.

Experimental

Chemicals and reagents

All reagents were analytical or HPLC grade. LC/MS-grade methanol (MeOH) and water were supplied by Merck (Darmstadt, Germany). LC/MS grade ammonium acetate was purchased from Sigma-Aldrich. Technical mixture standards of SCCPs (55.5 and 63% Cl) and MCCPs (52 and 57% Cl) were purchased from Dr. Ehrenstorfer (Augsburg, Germany).

Standards and solutions

The SCCPs standard solution 59.25% Cl, 100 mg/L was prepared by mixing 0.5 mL of SCCPs C_{10} to C_{13} 55.5% Cl, 1,000 mg/L with 0.5 mL of SCCPs C_{10} to C_{13} 63% Cl and 1,000 mg/L into a 10 mL volumetric flask. Then, the solution was filled to the mark with methanol.

The MCCPs standard solution 55% Cl, 100 mg/L was prepared by mixing 0.4 mL of MCCPs C_{14} to C_{17} 52% Cl, 1,000 mg/L with 0.6 mL of MCCPs C_{14} to C_{17} 57% Cl, 1,000 mg/L into a 10 mL volumetric flask and then filled up to the mark with methanol. These solutions were used to prepare the 5-point calibration curve (0.5, 0.8, 1.0, 2.0, and 5.0 mg/L)

Sample preparation

The sample preparation was referenced to ISO 18219-1:2021 method[2] with hexane extraction and analysis by LC/TQ.

Figure 1 has a detailed description of the optimized sample preparation procedure used in this study.

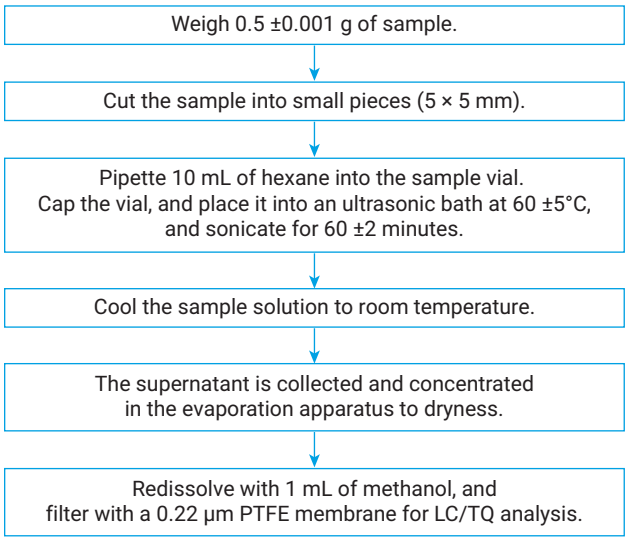

Figure 1. Summary of sample preparation procedure.

Instrument conditions

Chromatographic separation was performed using an Agilent ZORBAX SB-CN column (2.1 × 100 mm, 1.8 µm) installed on an Agilent 1290 Infinity II LC system. An Agilent 6470B triple quadrupole LC/MS with an Agilent Jet Stream (AJS) electrospray ion source was operated in dynamic multiple reaction monitoring (dMRM) mode. All data acquisition and processing were performed using the Agilent MassHunter software. The LC system conditions are listed in Table 1. The LC/TQ parameters are shown in Table 2.

Table 1. LC configuration and parameters.

Parameter	Value
Instruments	Agilent 1290 Infinity II High Speed Pump (G7120A) Agilent 1290 Infinity II Multisampler with multiwash option (G7167B) Agilent 1290 Infinity II Multicolumn Thermostat (G7116B)
Needle Wash	Mode: Multiwash Solvent 1: Acetonitrile:2-propanol (50:50) Solvent 2: Methanol:Water (60:40)
Autosampler Temperature	10 °C
Injection Volume	5 µL
Analytical Column	RRHD SB-CN, 2.1 × 100 mm, 1.8 µm UHPLC Grd, SB-CN, 2.1 mm, 1.8 µm
Column Temperature	30 °C
Mobile Phase A	5 mM ammonium acetate in water
Mobile Phase B	5 mM ammonium acetate in MeOH
Flow Rate Gradient	0.3 mL/min
Gradient	Time (min) A (%) B (%) Flow (mL/min) 0 40 60 0.3 8 1 99 0.3 14 1 99 0.3 14.1 40 60 0.3 18 40 60 0.3
Stop Time	18 min

Table 2. MS Parameters

Parameter	Value
Ionization Source	Agilent Jet Stream electrospray ionization (AJS ESI)
Ionization Mode	Negative
Scan Type	dMRM
Cycle Time	500 ms
MS1/MS2 Resolution	Unit
Gas Temperature	150 °C
Gas Flow	10 L/min
Nebulizer	40 psi
Sheath Gas Temperature	150 °C
Sheath Gas Flow	10 L/min
Capillary Voltage	3,500(–) V

Dynamic multiple reaction monitoring (dMRM) mode was used for data acquisition, with acquisition windows and dwell times adjusted to obtain at least 10 data points for each peak as well as for maximum sensitivity. Table 3 gives a complete list of the analyte retention times and MRM transitions.

Table 3. MRM parameters.

Compounds	Precursor Ion	Product Ion	Ret Time (min)	Fragmentor (V)	CE (V)	Cell Accelerator Voltage (V)
CP10-4	337	59	6.45	85	38	4
CP10-4	339	59	6.45	85	25	4
CP10-5	373	59	4.47	85	21	4
CP10-5	371	59	4.47	85	25	4
CP10-6	407	347	4.71	85	5	4
CP10-6	405	345	4.71	85	5	4
CP10-7	443	59	4.9	85	33	4
CP10-7	441	381	4.9	85	10	4
CP10-8	475	415	5.64	90	10	4
CP10-8	475	59	5.64	90	12	4
CP11-5	387	59	4.86	90	25	4
CP11-5	385	59	4.86	90	38	4
CP11-6	421	361	5.09	90	10	4
CP11-6	419	359	5.09	90	10	4
CP11-7	459	459	5.32	90	1	4
CP11-7	457	457	5.32	90	1	4
CP11-7	455	395	5.32	90	5	4
CP11-7	453	393	5.32	90	5	4
CP11-8	491	431	5.58	90	5	4
CP11-8	489	429	5.58	90	5	4
CP11-9	525	465	5.8	85	10	4
CP11-9	523	463	5.8	85	10	4
CP12-10	573	513	6.5	90	5	4
CP12-10	571	511	6.5	90	5	4
CP12-4	367	59	4.97	90	21	4
CP12-4	365	59	4.97	90	13	4
CP12-5	401	59	5.19	90	21	4
CP12-5	399	59	5.19	90	17	4
CP12-6	435	375	5.41	90	4	4
CP12-6	433	373	5.41	90	4	4
CP12-7	469	409	5.62	90	4	4
CP12-7	469	59	5.62	90	30	4
CP12-7	467	407	5.62	90	4	4
CP12-8	505	445	5.85	90	4	4
CP12-8	505	59	5.85	100	30	4
CP12-8	503	443	5.85	90	4	4
CP12-9	539	479	6.07	90	4	4
CP12-9	537	477	6.07	90	4	4

Compounds	Precursor Ion	Product Ion	Ret Time (min)	Fragmentor (V)	CE (V)	Cell Accelerator Voltage (V)
CP13-10	589	589	6.52	90	1	4
CP13-10	587	587	6.52	90	1	4
CP13-10	587	527	6.52	90	4	4
CP13-5	415	59	5.52	90	21	4
CP13-5	413	59	5.52	90	13	4
CP13-6	449	389	5.7	90	4	4
CP13-6	447	387	5.7	90	4	4
CP13-7	483	423	5.9	90	4	4
CP13-7	481	421	5.9	90	4	4
CP13-8	519	459	6.12	90	4	4
CP13-8	517	457	6.12	90	4	4
CP13-9	553	493	6.3	90	4	4
CP13-9	551	491	6.3	90	4	4
CP14-10	603	543	6.73	110	5	4
CP14-10	601	541	6.73	110	5	4
CP14-4	395	59	5.67	70	30	4
CP14-4	393	59	5.67	70	30	4
CP14-5	429	59	5.81	100	21	4
CP14-5	427	59	5.81	100	25	4
CP14-6	463	59	5.99	95	29	4
CP14-6	461	59	5.99	95	25	4
CP14-7	497	437	6.18	95	5	4
CP14-7	495	435	6.18	95	5	4
CP14-8	533	473	6.36	100	5	4
CP14-8	531	471	6.36	100	5	4
CP14-9	567	507	6.54	95	5	4
CP14-9	565	505	6.54	95	5	4
CP15-10	615	555	6.95	100	9	4
CP15-10	613	553	6.95	100	5	4
CP15-5	443	59	6.07	75	25	4
CP15-5	441	59	6.07	75	21	4
CP15-6	477	477	6.254	110	1	4

Compounds	Precursor Ion	Product Ion	Ret Time (min)	Fragmentor (V)	CE (V)	Cell Accelerator Voltage (V)
CP15-6	477	59	6.254	110	21	4
CP15-6	475	59	6.254	110	25	4
CP15-7	511	451	6.41	100	5	4
CP15-7	511	59	6.41	100	30	4
CP15-7	509	59	6.41	100	30	4
CP15-8	547	487	6.58	90	5	4
CP15-8	545	485	6.58	90	5	4
CP15-9	581	521	6.77	90	5	4
CP15-9	579	519	6.77	90	5	4
CP16-10	629	569	7.1	90	9	4
CP16-10	627	567	7.1	90	9	4
CP16-6	493	59	6.489	95	17	4
CP16-6	491	59	6.489	95	13	4
CP16-7	525	465	6.622	100	5	4
CP16-7	523	463	6.622	100	5	4
CP16-8	561	501	6.79	100	5	4
CP16-8	559	499	6.79	100	5	4
CP16-9	595	535	6.95	100	5	4
CP16-9	593	533	6.95	100	9	4
CP17-5	469	469	5.994	90	1	4
CP17-5	467	407	5.994	90	4	4
CP17-5	467	59	5.994	90	30	4
CP17-6	503	443	6.14	90	4	4
CP17-6	503	59	6.14	100	29	4
CP17-7	539	479	6.4	100	5	4
CP17-7	537	477	6.4	100	5	4
CP17-7	537	59	6.4	100	30	4
CP17-8	575	515	6.975	95	9	4
CP17-8	573	513	6.975	95	9	4
CP17-9	609	549	7.12	90	9	4
CP17-9	607	547	7.12	90	9	4

Results and discussion

LC/TQ method development

MS conditions

A major part of this work was the development of dynamic MRM transitions of individual compounds in SCCP and MCCP mixtures. For each compound, MRM transitions, as well as fragmentor voltages and collision energies were optimized using Agilent MassHunter Optimizer software. Other general parameters such as gas temperature, gas flow, nebulizer pressure, sheath gas temperature, sheath gas flow, and capillary voltage also have a strong influence on the signal of each MCCP and SCCP congener. Therefore, these parameters were carefully optimized with source optimization software. Finally, the optimized values of MS parameters are presented in Tables 1 and 2. Each congener of MCCPs and SCCPs was monitored by two MRM transitions. The structures of MCCP and SCCP congeners are not capable of accepting protons, so they are monitored in negative mode.

LC conditions

The LC conditions play an important role in separating the MCCP and SCCP congeners as well as having a great influence on the sensitivity of the method. Enhanced parent ion formation directly influenced peak shape, indirectly affected dwell time, and affected peak data points.

So LC parameters such as solvent mobile phase, gradient program, and the chromatographic column were optimized cautiously. Since each congener of MCCPs and SCCPs tends to form the parent ion as an adduct $[M+CH_3COO]^-$, the mobile phase of methanol and water containing 5 mM ammonium acetate was used to enhance the sensitivity of the method. The two Agilent chromatographic columns including ZORBAX RRHD SB-CN column (100 mm × 2.1 mm, 1.8 µm) and ZORBAX RRHD Eclipse Plus C18 column (50 mm × 2.1 mm, 1.8 µm) were used to evaluate the separation of MCCP and SCCP congeners. The ZORBAX RRHD SB-CN column was chosen because it showed better performance with superior separation ability and peak shape (Figures 2 and 3). The optimal LC gradient program is presented in Table 1.

To ensure the robustness of system operation, the multiple needle wash mode was used with solvent 1 as the strong solvent and solvent 2 as the initial mobile phase ratio. An inline filter was also attached before the guard column to protect the guard column and the analytical column. After blow drying, sample extract was redissolved with methanol to ensure complete dissolution of MCCPs and SCCPs. However, the initial LC gradient was 60% methanol only, so multiple wash modes and inline filters were utilized to prevent precipitation from matrix components. Preventing precipitation eliminated clogging in the needle seat and the analytical column.

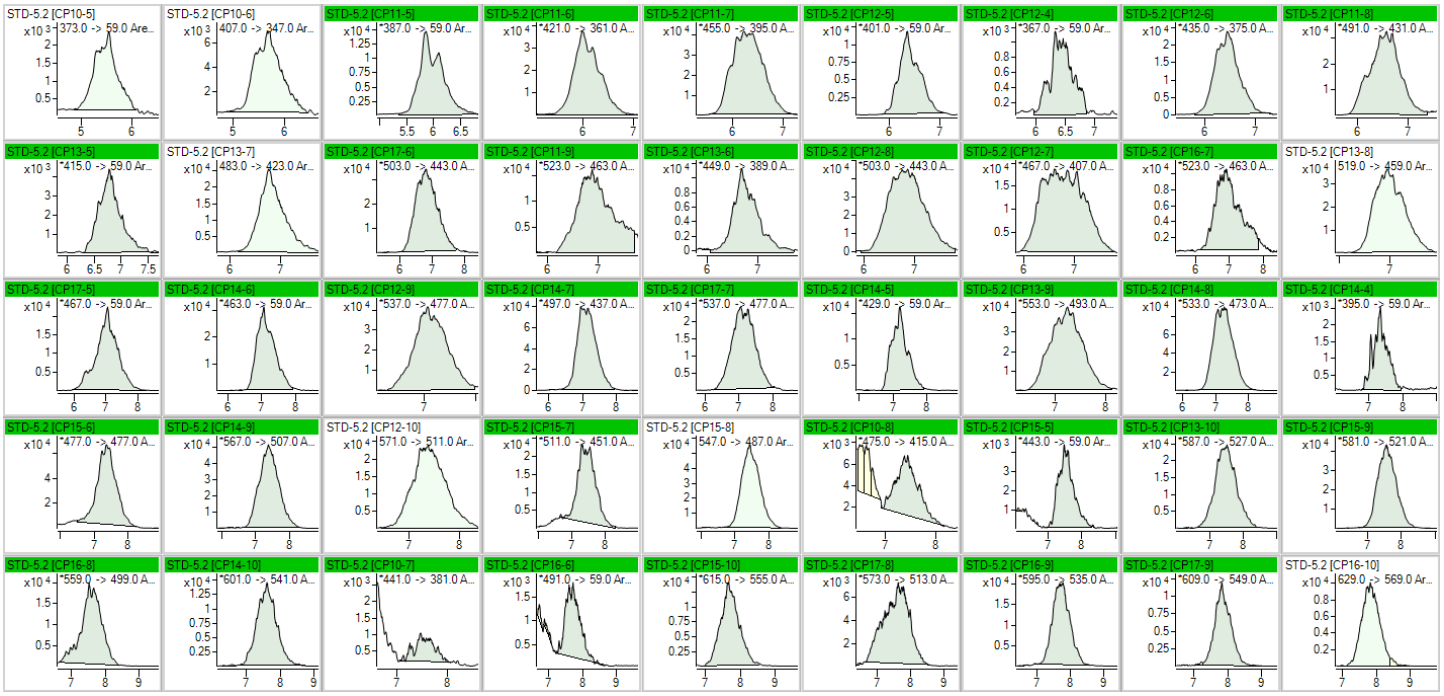

Figure 2. Chromatograms of MCCP and SCCP congeners at 5 mg/L of ΣMCCPs and ΣSCCPs using ZORBAX Eclipse Plus RRHD C18 column.

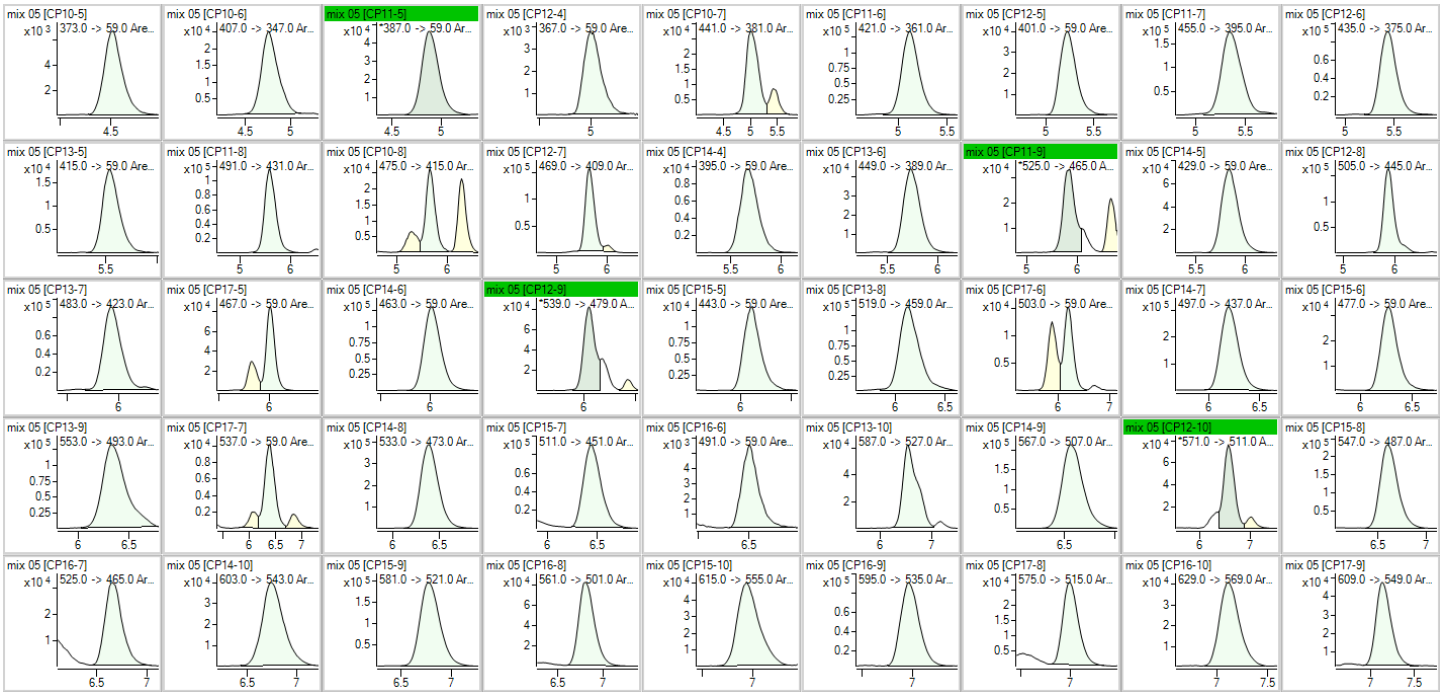

Figure 3. Chromatograms of MCCP and SCCP congeners at 5 mg/L of ΣMCCPs and ΣSCCPs using ZORBAX RRHD StableBond CN column.

Chromatographic performance

The chromatograms of 5 mg/L SCCP and MCCP solutions showed good separation with effective desolvation of target ions using the AJS ion source (Figures 4 and 5).

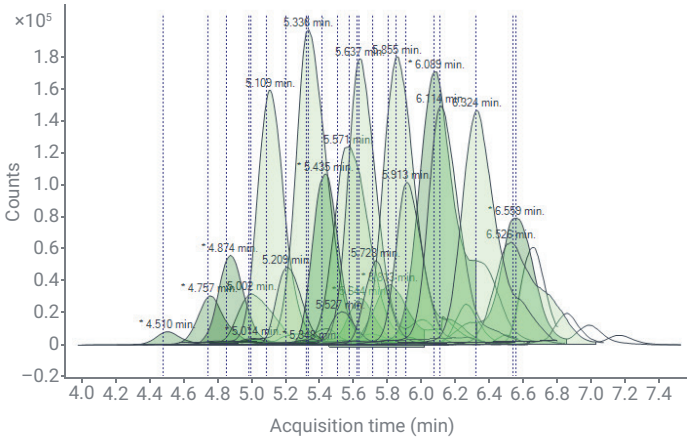

Figure 4. LC/TQ chromatogram of ΣSCCPs at 5 mg/L

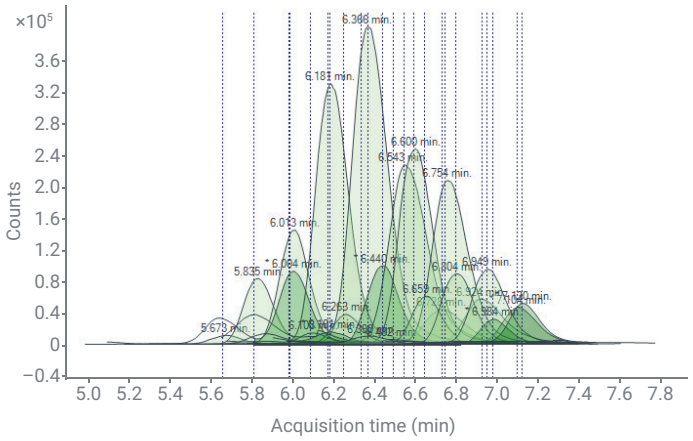

Figure 5. LC/TQ chromatogram of ΣMCCPs at 5 mg/L

Calculation and method validation

The standard was a mixed technical standard of SCCPs (CP_{10} to CP_{13}) and MCCPs (CP_{14} to CP_{17}), and there was no information on the percentage of each congener in the mixed standard. Therefore, concentrations of SCCPs and MCCPs were reported to the sum of SCCP congeners (ΣSCCPs) and the sum of MCCP congeners (ΣMCCPs) respectively.[1]

The term + ΣSCCPs is defined as the sum of SCCPs, calculated as C_{10} to C_{13} based on at least the sum of all corresponding Cl_5 to Cl_9 congeners (five most abundant homologue groups for the LC instrument).[1]

The term + ΣMCCPs is defined as the sum of MCCPs, calculated as C_{14} to C_{17} based on at least the sum of all corresponding Cl_6 to Cl_{10} congeners (five most abundant homologue groups for the LC instrument).[1]

In this application note, we referred to the percentage of individual SCCP and MCCP congener in the mixed standard according to the published calculation results of McGrath *et al.*[4], to calculate the concentration of each specific MCCP and SCCP congener.

The workflow performance criteria were verified based on linearity, sensitivity, recovery, and repeatability.

Linearity range

The calibration curves (Figure 6) were found to be linear over a concentration range of ΣMCCPs and ΣSCCPs from 0.5 to 5 mg/L with 1/x weight. As shown in Table 4, calibration curves of both individual congeners, ΣMCCPs and ΣSCCPs showed good linearity (R^2 ≥0.995). Accuracy of all MCCP and SCCP congeners, and ΣMCCP and ΣSCCP content at the lowest concentration, was in the acceptable range of 80 to 110% (Table 4).

Table 4. Linearity and accuracy of MCCPs and SCCPs.

Compound	R^2	% Bias STD1
CP10-5	0.9993	4.5
CP10-6	0.9993	3.8
CP10-7	0.9999	0.1
CP10-8	0.9976	1.7
CP11-5	0.9994	4.7
CP11-6	0.9999	0.5
CP11-7	0.9999	1.3
CP11-8	0.9995	3.4
CP11-9	0.9972	9.9
CP12-4	0.9982	8.1
CP12-5	0.9996	1.6
CP12-6	0.9995	1.8
CP12-7	0.9987	6.2
CP12-8	0.9974	9.8
CP12-9	0.9990	5.9
CP12-10	0.9997	0.7
CP13-5	0.9987	1.6
CP13-6	0.9997	3.1
CP13-7	0.9982	7.5
CP13-8	0.9979	9.2
CP13-9	0.9973	10.4
CP13-10	0.9990	6.3
ΣSCCPs	0.9994	4.8

Compound	R^2	% Bias STD1
CP14-4	0.9974	2.3
CP14-5	0.9995	3.2
CP14-6	0.9983	7.3
CP14-7	0.9985	6.6
CP14-8	0.9989	5.8
CP14-9	0.9996	3.1
CP14-10	0.9994	4.2
CP15-5	0.9965	11.9
CP15-6	0.9980	8.9
CP15-7	0.9991	4.6
CP15-8	0.9991	5.1
CP15-9	0.9995	1.5
CP15-10	0.9993	4.9
CP16-6	0.9994	4.4
CP16-7	0.9988	1.5
CP16-8	0.9997	0.5
CP16-9	0.9996	1.5
CP16-10	0.9993	4.9
CP17-5	0.9995	4.1
CP17-6	0.9986	6.8
CP17-7	0.9981	5.8
CP17-8	0.9988	6.5
CP17-9	0.9994	4
ΣMCCPs	0.9995	3.7

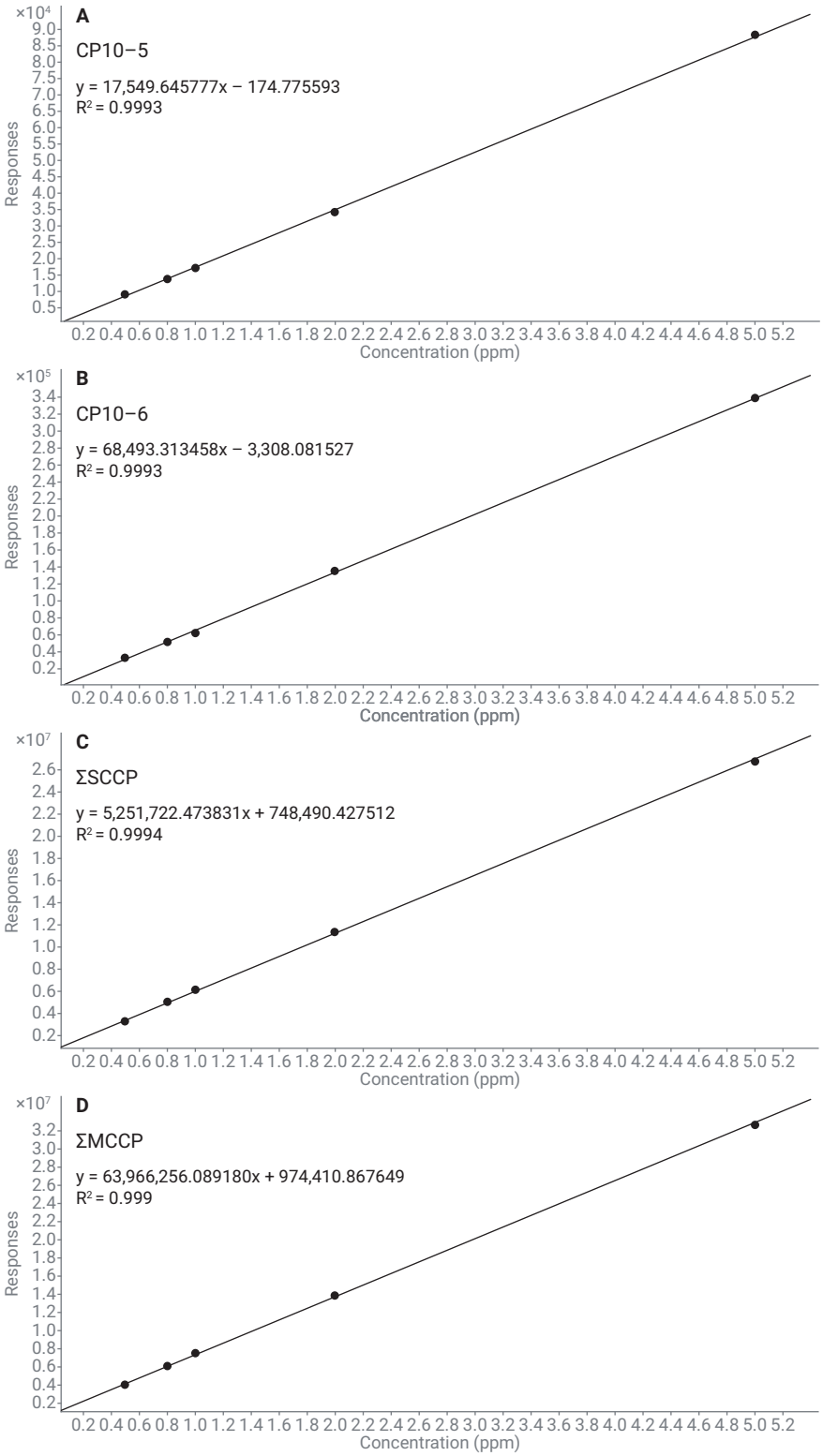

Figure 6. Calibration curves of ΣMCCPs, ΣSCCPs, CP10-5, and CP10-6

Instrument detection limit (IDL)

The IDL was estimated based on the standard deviation (SD) of the seven replicate injections of ΣMCCPs and ΣSCCPs standard at 0.5 mg/L in methanol.

The calculated IDL values of all individual MCCP and SCCP congeners were less than 0.004 mg/L and the IDLs of ΣMCCPs and ΣSCCPs were less than 0.006 mg/L with %RSD <5% (Table 5 and Figure 7). These values indicated a good response of MCCPs and SCCPs on LC/TQ.

Table 5. Calculated IDL and %RSD of seven replicates of ΣMCCPs and ΣSCCPs at 0.5 mg/L.

Compound	IDL (mg/L)	RSD (%)
CP10-5	0.011	1.37
CP10-6	0.011	1.34
CP10-7	0.009	1.05
CP10-8	0.022	2.80
CP11-5	0.012	1.46
CP11-6	0.012	1.45
CP11-7	0.008	0.98
CP11-8	0.014	1.81
CP11-9	0.036	4.61
CP12-4	0.018	2.33
CP12-5	0.018	2.30

Compound	IDL (mg/L)	RSD (%)
CP12-6	0.012	1.53
CP12-7	0.021	2.83
CP12-8	0.018	2.45
CP12-9	0.030	3.94
CP12-10	0.017	2.00
CP13-5	0.028	3.63
CP13-6	0.032	4.11
CP13-7	0.037	4.64
CP13-8	0.019	2.28
CP13-9	0.010	1.31
CP13-10	0.019	2.37
ΣSCCPs	0.005	0.64

Compound	IDL (mg/L)	RSD (%)
CP14-4	0.033	4.34
CP14-5	0.024	3.05
CP14-6	0.014	1.71
CP14-7	0.014	1.75
CP14-8	0.010	1.29
CP14-9	0.008	1.06
CP14-10	0.030	3.37
CP15-5	0.038	4.63
CP15-6	0.032	4.59
CP15-7	0.021	2.63
CP15-8	0.018	2.28
CP15-9	0.014	1.82

Compound	IDL (mg/L)	RSD (%)
CP15-10	0.020	2.26
CP16-6	0.030	3.74
CP16-7	0.019	2.26
CP16-8	0.022	2.56
CP16-9	0.024	2.90
CP16-10	0.012	1.40
CP17-5	0.021	2.52
CP17-6	0.036	4.34
CP17-7	0.031	4.36
CP17-8	0.042	5.00
CP17-9	0.032	4.00
ΣMCCPs	0.006	0.75

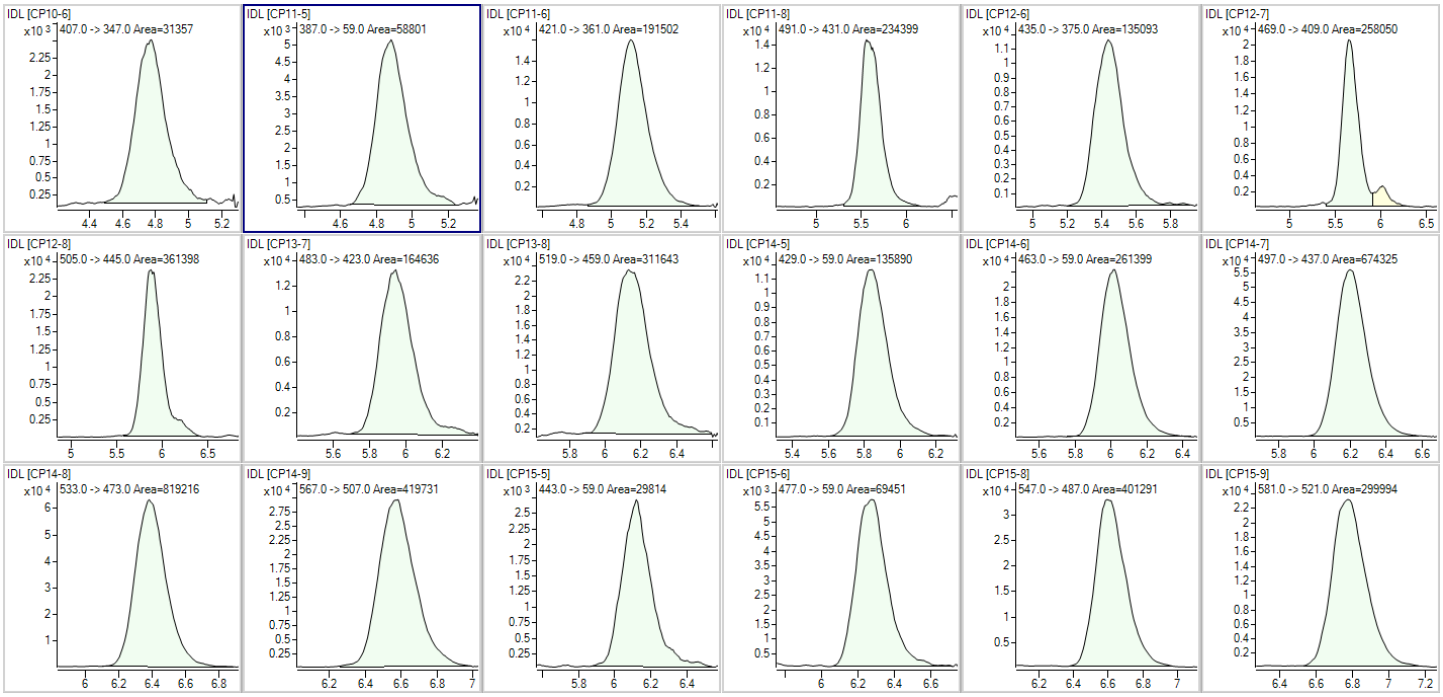

Figure 7. Chromatograms of MCCP and SCCP congeners at estimated IDL, 0.5 mg/L of ΣMCCPs and 0.5 mg/L of ΣSCCPs.

Method detection limit (MDL)

The MDL was estimated based on the standard deviation (SD) of the analysis results of nine spiked samples prepared on 3 different days at 2 mg/kg of ΣMCCPs and 2 mg/kg of ΣSCCPs.

The estimated MDL of each MCCP and SCCP congener in both textile and leather matrices was less than 0.4 mg/kg. Also, the MDL of ΣMCCPs and ΣSCCPs in the textile matrix and leather matrix was less than 0.14 mg/kg (Table 6).

The calculated relative standard deviations (RSDs) of all corresponding SCCP congeners (Cl_5 to Cl_9) and MCCP congeners (Cl_6 to Cl_{10}) in both textile and leather samples was below 10% (Table 6).

The extremely low detection limits met the requirements of MCCPs and SCCPs residue analysis in textile and leather samples.

Table 6. Method detection limit (MDL) and %RSDR of MCCPs and SCCPs in the textile matrix and leather matrix.

Compound	MDL (mg/kg)		RSD_R (%)	
	Textiles	Leather	Textiles	Leather
CP10-5	0.20	0.15	4.53	3.36
CP10-6	0.23	0.25	5.13	5.49
CP10-7	0.27	0.42	6.08	9.43
CP10-8	0.16	0.13	3.32	2.62
CP11-5	0.12	0.23	2.61	4.81
CP11-6	0.08	0.23	1.76	4.89
CP11-7	0.17	0.23	3.85	5.15
CP11-8	0.13	0.16	2.91	3.49
CP11-9	0.21	0.15	5.12	3.68
CP12-4	0.15	0.20	3.24	4.19
CP12-5	0.15	0.19	3.30	4.12
CP12-6	0.19	0.24	3.95	4.84
CP12-7	0.24	0.13	5.26	2.66
CP12-8	0.15	0.11	3.57	2.63
CP12-9	0.27	0.25	6.52	6.22
CP12-10	0.14	0.23	3.60	5.52
CP13-5	0.06	0.12	1.21	2.53
CP13-6	0.11	0.16	2.32	3.37
CP13-7	0.16	0.11	3.28	2.27
CP13-8	0.20	0.28	4.42	6.07
CP13-9	0.20	0.20	5.10	5.16
CP13-10	0.15	0.15	3.83	3.78
CP14-4	0.08	0.11	1.59	2.17
CP14-5	0.07	0.08	1.50	1.69
CP14-6	0.09	0.13	1.78	2.62
CP14-7	0.20	0.18	4.44	3.94
CP14-8	0.22	0.13	5.62	3.36
CP14-9	0.11	0.13	2.72	3.31
CP14-10	0.08	0.16	1.96	3.83
CP15-5	0.09	0.06	1.83	1.19
CP15-6	0.33	0.25	7.52	5.55
CP15-7	0.17	0.21	4.33	5.15
CP15-8	0.13	0.13	3.20	3.33
CP15-9	0.11	0.12	2.65	2.85
CP15-10	0.10	0.12	2.22	2.75
CP16-6	0.27	0.37	6.21	8.27
CP16-7	0.16	0.20	3.80	4.76
CP16-8	0.09	0.10	2.20	2.48
CP16-9	0.22	0.22	5.19	5.32
CP16-10	0.17	0.15	3.72	3.28
CP17-5	0.21	0.11	4.47	2.30
CP17-6	0.27	0.23	6.08	4.87
CP17-7	0.29	0.14	7.23	3.54
CP17-8	0.17	0.07	4.15	1.61
CP17-9	0.23	0.24	5.12	5.56
ΣSCCPs	0.09	0.13	2.13	2.88
ΣMCCPs	0.12	0.11	2.75	2.66

Recovery, repeatability, and reproducibility

The recovery, repeatability, and reproducibility were evaluated based on the results of nine spiked samples prepared on three different days at 2 and 20 mg/kg.

The recoveries of MCCPs and SCCPs in textile and leather samples at two different concentrations (2 and 20 mg/Kg) ranged from 82.5 to 107.4%, as shown in Tables 7 and 8, which satisfied recovery requirements (80 to 110%). In addition, the calculated RSDR of all MCCPs and SCCPs at 2 and 20 mg/kg in both textile and leather samples were below 12% (Table 7 and Table 8).

Table 7. %RSDR, % Recovery of MCCPs and SCCPs at 2 mg/kg of ΣMCCPs and ΣSCCPs spiked textile matrix and leather matrix sample.

	RSD_R (%)		Recovery (%)	
Compound	Textiles	Leather	Textiles	Leather
CP10-5	4.53	3.36	97.1	98.3
CP10-6	5.1	5.49	97.2	100.2
CP10-7	6.08	9.43	95.2	97.6
CP10-8	3.32	2.62	102.1	105.3
CP11-5	2.61	4.81	100.4	102.2
CP11-6	1.76	4.89	97.6	100.2
CP11-7	3.85	5.15	98.5	98.8
CP11-8	2.91	3.49	98.8	100.0
CP11-9	5.12	3.68	86.8	89.6
CP12-4	3.24	4.19	102.1	103.9
CP12-5	3.30	4.12	96.5	98.3
CP12-6	3.95	4.84	102.8	105.7
CP12-7	5.26	2.66	98.7	103.9
CP12-8	3.57	2.63	92.0	94.6
CP12-9	6.52	6.22	90.1	88.8
CP12-10	3.60	5.52	86.5	88.7
CP13-5	1.21	2.53	107.3	104.2
CP13-6	2.32	3.37	105.2	105.6
CP13-7	3.28	2.27	103.0	103.8
CP13-8	4.42	6.07	96.4	99.5
CP13-9	5.10	5.16	86.7	85.5
CP13-10	3.83	3.78	87.5	88.8
CP14-4	1.59	2.17	107.8	107.4
CP14-5	1.50	1.69	107.4	107.4

	RSD_R (%)		Recovery (%)	
Compound	Textiles	Leather	Textiles	Leather
CP14-6	1.78	2.62	105.2	106.5
CP14-7	4.44	3.94	95.5	97.0
CP14-8	5.62	3.36	85.5	84.1
CP14-9	2.72	3.31	85.9	85.9
CP14-10	1.96	3.83	92.3	93.2
CP15-5	1.83	1.19	106.2	107.4
CP15-6	7.52	5.55	95.7	98.6
CP15-7	4.33	5.15	85.9	87.1
CP15-8	3.20	3.33	86.4	85.7
CP15-9	2.65	2.85	89.4	90.1
CP15-10	2.22	2.75	94.2	93.9
CP16-6	6.21	8.27	94.2	97.3
CP16-7	3.80	4.76	90.4	92.2
CP16-8	2.20	2.48	88.1	90.4
CP16-9	5.19	5.32	92.1	90.3
CP16-10	3.72	3.28	96.5	95.9
CP17-5	4.47	2.30	103.8	104.6
CP17-6	6.08	4.87	96.8	100.6
CP17-7	7.23	3.54	87.1	85.7
CP17-8	4.15	1.61	90.1	91.8
CP17-9	5.12	5.56	96.0	94.2
ΣSCCPs	2.13	2.88	95.4	97.0
ΣMCCPs	2.75	2.66	91.5	91.7

Table 8. %RSDR, % Recovery of MCCPs and SCCPs at 20 mg/kg of ΣMCCPs and ΣSCCPs spiked textile matrix and leather matrix sample.

Compound	RSD_R (%)		Recovery (%)	
	Textiles	Leather	Textiles	Leather
CP10-5	4.09	7.13	85.9	89.9
CP10-6	2.80	8.64	85.8	91.3
CP10-7	3.96	6.68	86.0	89.4
CP10-8	3.86	7.32	87.2	90.1
CP11-5	2.82	8.81	87.0	93.4
CP11-6	3.39	7.97	85.5	89.6
CP11-7	4.13	4.96	87.8	88.8
CP11-8	2.45	2.23	87.1	86.2
CP11-9	12.19	4.05	92.1	83.7
CP12-4	3.80	9.05	87.5	91.0
CP12-5	3.68	6.71	86.7	88.4
CP12-6	3.19	5.66	87.4	89.4
CP12-7	3.94	7.00	86.4	90.4
CP12-8	2.98	4.72	83.9	84.8
CP12-9	6.22	4.47	89.9	85.3
CP12-10	5.50	10.68	87.9	87.8
CP13-5	3.37	10.88	86.1	93.9
CP13-6	3.21	4.11	88.0	88.8
CP13-7	7.17	6.01	89.0	87.6
CP13-8	4.54	4.08	88.3	84.6
CP13-9	3.16	2.34	83.6	82.5
CP13-10	3.48	4.26	83.8	84.4
CP14-4	2.92	5.24	90.4	93.7
CP14-5	1.02	3.99	84.3	87.8
CP14-6	2.34	8.08	83.3	87.5
CP14-7	2.28	4.05	84.2	83.8
CP14-8	5.48	1.97	85.7	83.1
CP14-9	4.08	4.08	86.0	83.6
CP14-10	2.96	3.23	86.2	85.0
CP15-5	2.91	8.52	87.2	90.8
CP15-6	1.39	4.72	83.4	86.4
CP15-7	4.14	2.88	84.9	84.0
CP15-8	5.58	4.15	87.0	86.1
CP15-9	1.92	3.00	84.2	84.4
CP15-10	2.30	4.75	85.2	86.0
CP16-6	6.39	7.04	87.6	90.6
CP16-7	3.97	3.86	87.3	86.3
CP16-8	2.67	3.73	85.1	84.8
CP16-9	4.11	2.99	85.3	84.7
CP16-10	3.15	3.77	84.8	85.4
CP17-5	2.47	4.66	86.8	88.9
CP17-6	7.15	7.87	89.1	89.8
CP17-7	5.05	2.86	85.5	84.0
CP17-8	5.14	4.01	88.2	84.9
CP17-9	2.55	2.20	84.6	84.8
ΣSCCPs	3.15	3.28	86.6	87.1
ΣMCCPs	2.93	2.17	85.3	84.8

Conclusion

A fast, sensitive, and accurate LC/TQ method for identification and quantification of MCCPs and SCCPs in textiles and leather was presented. This method used an Agilent 1290 Infinity II LC system coupled to an Agilent 6470B triple quadrupole LC/MS with Agilent MassHunter Workstation software.

The Agilent ZORBAX RRHD StableBond CN column used in this study provided good separation efficiency and peak shape. The evaluation has demonstrated that this method can achieve excellent specificity, linearity, and accuracy.

References

1. Kerstin, K; *et al.* Guidance Document on the Analysis of Chlorinated Paraffins. "Sample Preparation and Quantification in Food and Feed", v 1.9, **2021**.
2. ISO 18219-1:2021, Leather — Determination of Chlorinated Hydrocarbons in Leather
3. ISO 22818:2021, Textiles — Determination of Short-Chain Chlorinated Paraffins (SCCP) and Middle-Chain Chlorinated Paraffins (MCCP) in Textile Products Out of Different Matrices by Use of Gas Chromatography Negative Ion Chemical Ionization Mass Spectrometry (GC-NCI-MS)
4. McGrath, T. J. *et al.* Short- and Medium-Chain Chlorinated Paraffins in Polyvinylchloride and Rubber Consumer Products and Toys Purchased on the Belgian Market. *Int. J. Environ. Res. Public Health* **2021**, *18*, 1069. https://doi.org/10.3390/ijerph1803106

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