Chlorine speciation in complex hydrocarbon matrices using GC-ICP-MS/MS

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Fig. S

Table S

Table S1. List of the 13 chlorinated compounds used for calibration procedures with their raw formula, chlorine percentage, boiling points and observed retention times.

Compound	Raw formula	%Cl	Boiling point (°C)	RT (min)
2-chloro-2-methylpropane	C_4H_9Cl	38.3	51	2.64
1-chloropropane	C_3H_7Cl	45.14	47	3.05
1-chlorobutane	C_4H_9Cl	38.3	78	4.38
Carbon tetrachloride	CCl_4	92.19	77	5.32
1-chloro-2-methylbutane	$C_5H_{11}Cl$	33.26	86	5.77
Dichloromethane	CH_2Cl_2	83.48	40	6.64
1-chloropentane	$C_5H_{11}Cl$	33.26	108	6.86
Trichloroethylene	C_2HCl_3	80.95	87	8.16
Tetrachloroethylene	C_2Cl_4	85.51	121	8.84
1,2-dichloroethane	$C_2H_4Cl_2$	71.65	83	9.92
1-chloroheptane	$C_7H_{15}Cl$	26.33	159	11.42
Chlorobenzene	C_6H_5Cl	31.5	132	12.88
1,1,2-trichloethane	$C_2H_3Cl_3$	79.73	114	13.59

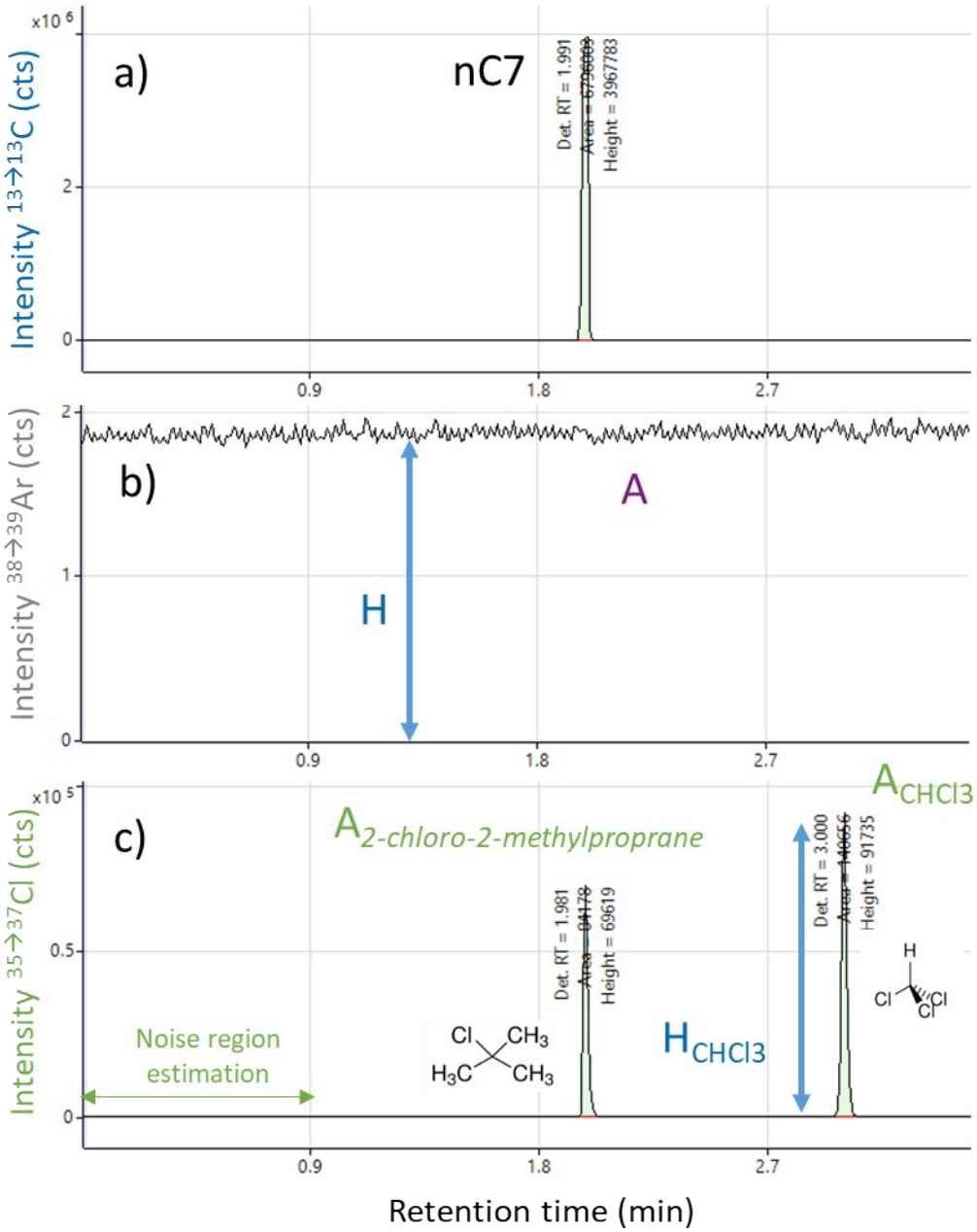


Fig. S 1

Chromatograms of the (a) carbon $^{13}\rightarrow^{13}C$, (b) argon $^{38}\rightarrow^{39}Ar$, (c) chlorine $^{35}\rightarrow^{37}Cl$ channels obtained for the injection of the optimization mix solution containing $CHCl_3$ and 2-chloro-2-methylpropane in n-heptane with CG = 0.1 and OG = 0.16 L min^{-1} (optimized conditions).

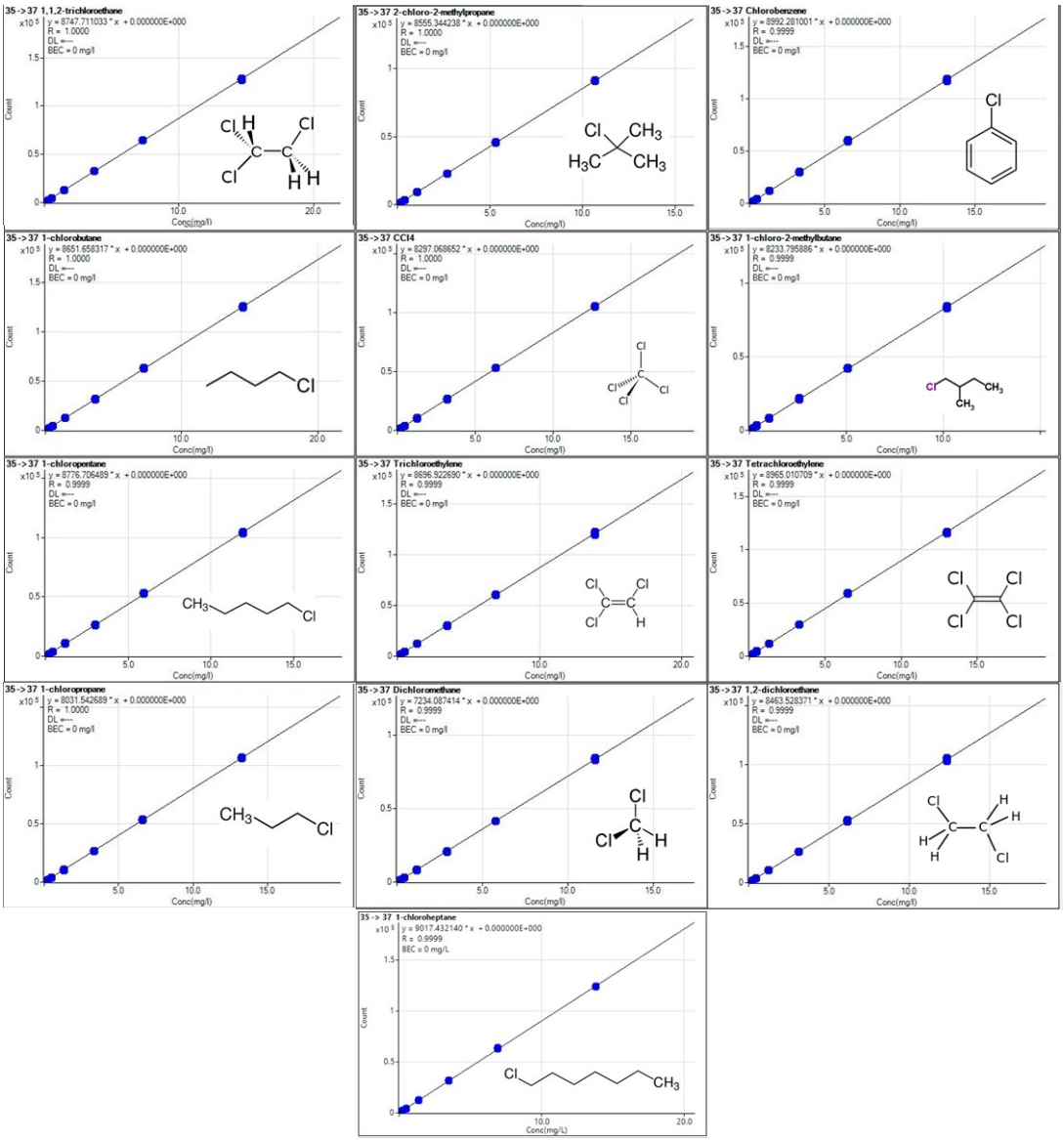


Fig. S 2 Calibration curves for 13 standard chlorinated compounds in n-heptane for Cl concentrations from 0.02 to 15 mgCl L^{-1} per compound. Every calibration standard was injected in three replicates.

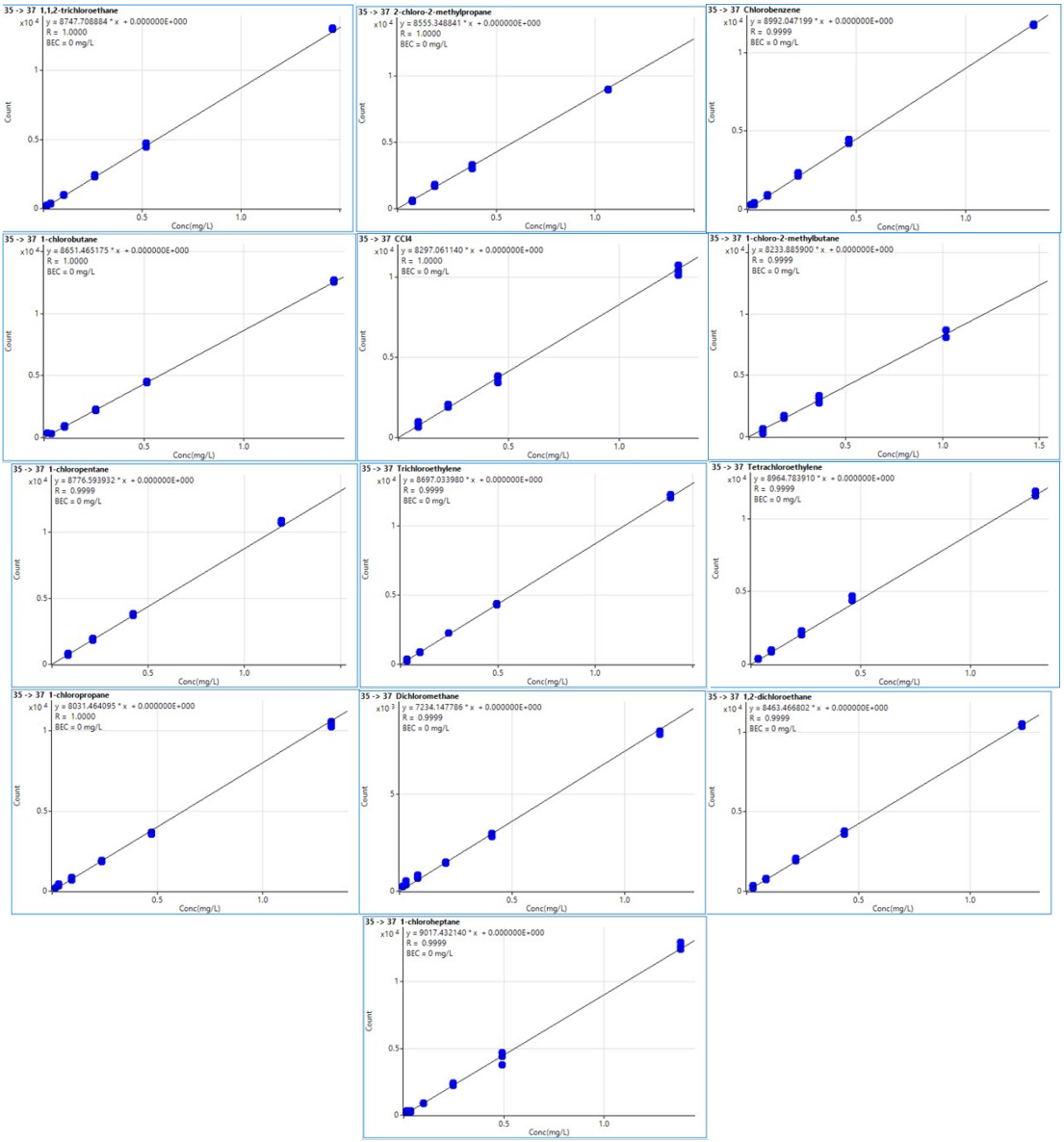


Fig. S 3. Calibration curves for 13 standard chlorinated compounds in n-heptane for Cl concentrations from 0.02 to 15 mgCl L^{-1} per compound. Every calibration standard was injected in three replicates. Zoom on concentrations below 1.5 mgCl L^{-1}.

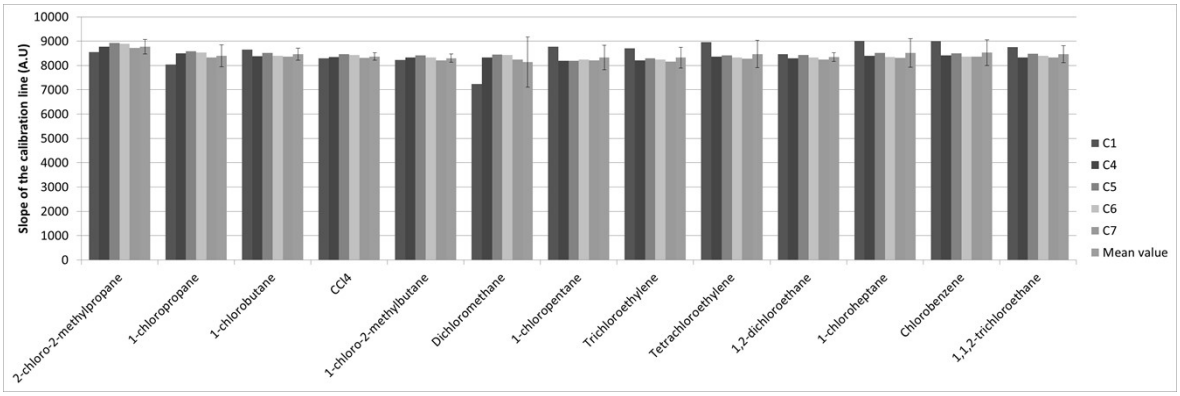


Fig. S 4. Slopes of 5 independent calibration curves obtained from 5 independently prepared standard solutions (C1, C4, C5, C6 and C7) containing 13 organochlorides in n-heptane.

Table S2. Relative response factors versus 1,2-dichloroethane in nC7 for 13 chlorinated standard compounds in optimized GC-ICP-MS/MS conditions in n-heptane and in 4 gasoline samples (G1 to G4).

Compound	n-heptane	G1	G2	G3	G4
2-chloro-2-methylpropane	1.05 +/- 0.04	0.95	0.93	0.90	0.86
1-chloropropane	1.01 +/- 0.05	0.89	0.90	0.87	0.83
1-chlorobutane	1.01 +/- 0.03	0.97	0.95	0.94	0.92
Carbon tetrachloride	1.00 +/- 0.02	0.96	0.94	0.94	0.92
1-chloro-2-methylbutane	0.99 +/- 0.02	0.98	0.96	0.95	0.95
Dichloromethane	0.97 +/- 0.12	0.79	0.84	0.80	0.76
1-chloropentane	1.00 +/- 0.06	0.99	0.97	0.96	0.95
Trichloroethylene	1.00 +/- 0.05	0.97	0.94	0.95	0.93
Tetrachloroethylene	1.01 +/- 0.07	0.99	0.96	0.97	0.95
1,2-dichloroethane	1.00 +/- 0.02	0.94	0.94	0.91	0.90
1-chloroheptane	1.02 +/- 0.07	1.04	1.01	0.99	0.98
Chlorobenzene	1.02 +/- 0.06	1.00	0.98	0.97	0.96
1,1,2-trichloroethane	1.01 +/- 0.04	0.97	0.96	0.94	0.93

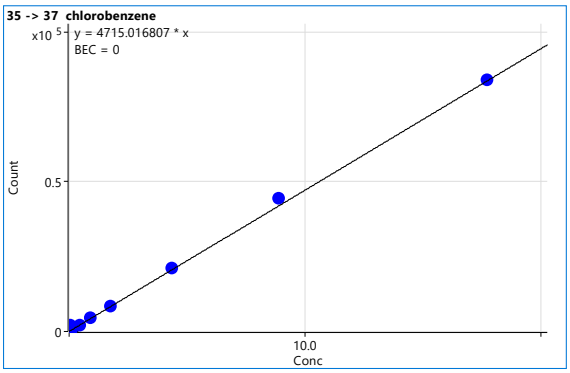
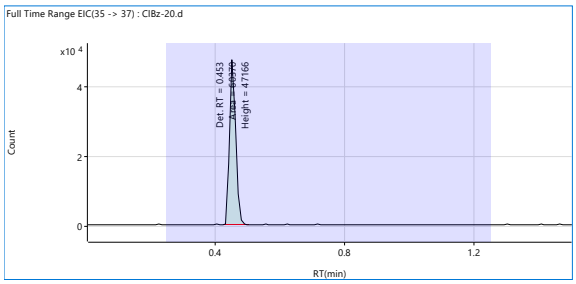


Fig. S 5. Calibration line for chlorobenzene in n-heptane on the HP-INNOWax column in the 1-20 mgCl L^{-1} range (slope = 4715).



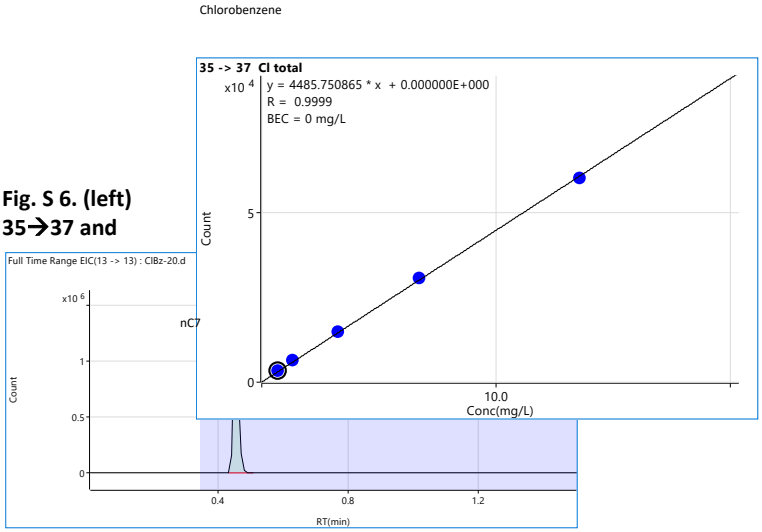


Fig. S 6. (left) 35→37 and 13→13 chromatograms for the analysis of chlorobenzene in n-heptane (13.5 mgCl L^{-1}) on a DB-1MS column (23.5 m, 0.25 mm, 0.25 µm) run at 340°C in isothermal mode and (right) obtained calibration line between 0.8 and 13.5 mgCl L^{-1} (slope = 4486).

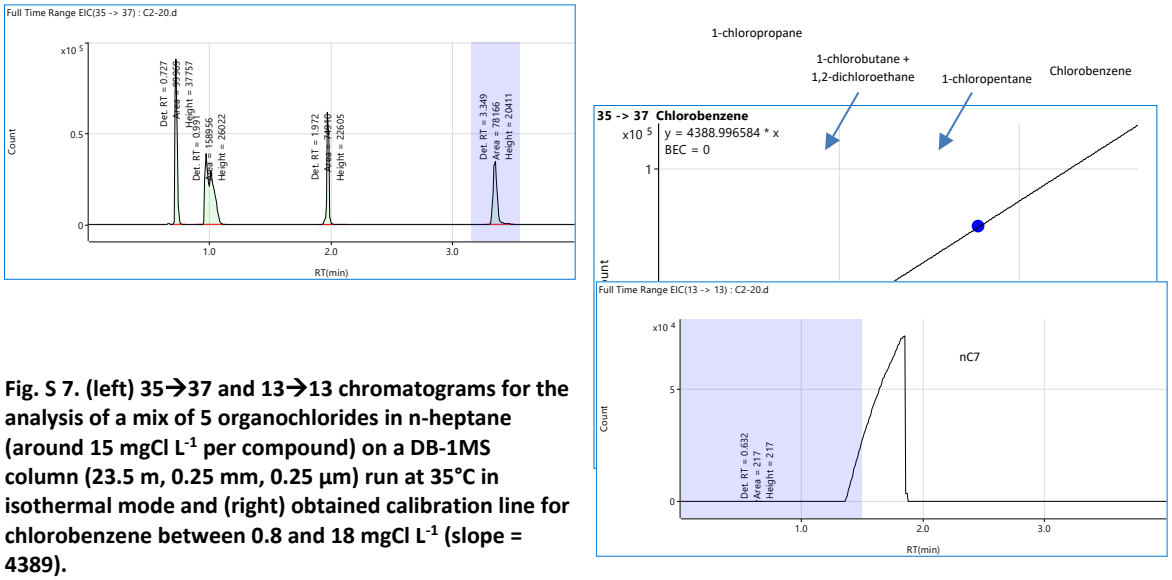


Fig. S 7. (left) 35→37 and 13→13 chromatograms for the analysis of a mix of 5 organochlorides in n-heptane (around 15 mgCl L^{-1} per compound) on a DB-1MS column (23.5 m, 0.25 mm, 0.25 µm) run at 35°C in isothermal mode and (right) obtained calibration line for chlorobenzene between 0.8 and 18 mgCl L^{-1} (slope = 4389).

Table S3. Percentage of recovery for 13 chlorinated compounds spiked in 4 gasoline samples for medium and high range concentrations.

Compound	Medium range					High range				
	[Cl] mgCl L^{-1}	G1	G2	G3	G4	[Cl] mgCl L^{-1}	G1	G2	G3	G4
2-chloro-2-methylpropane	1.1	100%	91%	92%	84%	10.9	95%	94%	90%	86%
1-chloropropane	1.4	91%	88%	88%	83%	13.5	89%	91%	87%	83%
1-chlorobutane	1.5	100%	94%	98%	92%	14.8	97%	95%	94%	92%
Carbon tetrachloride	1.3	102%	95%	94%	91%	13.0	96%	95%	94%	92%
1-chloro-2-methylbutane	1.0	101%	96%	97%	95%	10.4	98%	96%	95%	95%
Dichloromethane	1.2	85%	83%	80%	75%	11.8	79%	84%	81%	76%
1-chloropentane	1.2	99%	99%	99%	95%	12.2	99%	97%	96%	96%
Trichloroethylene	1.4	98%	93%	97%	93%	14.2	97%	94%	95%	93%
Tetrachloroethylene	1.3	105%	99%	98%	95%	13.3	99%	96%	97%	95%
1,2-dichloroethane	1.3	98%	93%	92%	89%	12.6	94%	94%	91%	90%
1-chloroheptane	1.4	103%	102%	101%	97%	14.1	104%	102%	99%	98%
Chlorobenzene	1.3	102%	99%	100%	97%	13.4	100%	98%	97%	96%
1,1,2-trichloroethane	1.5	99%	96%	96%	94%	15.0	97%	96%	94%	92%

Table S4. Quantitative results for chlorine speciation in the reformate sample by GC-ICP-MS/MS.

Compound [a]	1	2?	3	4?	5	6?	7?	8
RT (min)	2.64	3.93	5.83	6.15	6.78	8.35	8.59	8.87
[Cl] mg L^{-1} [b]	0.53 ± 0.03	0.51 ± 0.03	0.26 ± 0.04	0.06±0.03	0.24±0.03	0.12±0.03	0.07±0.08	0.16±0.14
Distribution (%)	29.3	27.8	14.7	3.7	12.3	3.8	3.0	5.3
Total Cl (sum of peaks)	1.93 ± 0.16 mg/L							

[a] The reference of the identified compounds are (1) 2-chloro-2-methylpropane; (3) 1-chloro-2-methylbutane; (5) 1-chloropentane and (8) Tetrachloroethylene. ? means "unknown chlorinated compound". [b] 3 replicates were taking into account