

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

Vincent Souchon<sup>a</sup>, Marc Maleval<sup>a</sup>, Fabien Chainet<sup>\*a</sup>, Charles-Philippe Lienemann<sup>a</sup>

<sup>a</sup>IFP Energies Nouvelles, Rond-point de l'échangeur de Solaize, BP 3, F-69360 Solaize, France

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

Compound	Raw formula	%Cl	Boiling point (°C)	RT (min)
2-chloro-2-methylpropane	C <sub>4</sub> H <sub>9</sub> Cl	38.3	51	2.64
1-chloropropane	C <sub>3</sub> H <sub>7</sub> Cl	45.14	47	3.05
1-chlorobutane	C <sub>4</sub> H <sub>9</sub> Cl	38.3	78	4.38
Carbon tetrachloride	CCl <sub>4</sub>	92.19	77	5.32
1-chloro-2-methylbutane	C <sub>5</sub> H <sub>11</sub> Cl	33.26	86	5.77
Dichloromethane	CH <sub>2</sub> Cl <sub>2</sub>	83.48	40	6.64
1-chloropentane	C <sub>5</sub> H <sub>11</sub> Cl	33.26	108	6.86
Trichloroethylene	C <sub>2</sub> HCl <sub>3</sub>	80.95	87	8.16
Tetrachloroethylene	C <sub>2</sub> Cl <sub>4</sub>	85.51	121	8.84
1,2-dichloroethane	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	71.65	83	9.92
1-chloroheptane	C <sub>7</sub> H <sub>15</sub> Cl	26.33	159	11.42
Chlorobenzene	C <sub>6</sub> H <sub>5</sub> Cl	31.5	132	12.88
1,1,2-trichloroethane	C <sub>2</sub> H <sub>3</sub> Cl <sub>3</sub>	79.73	114	13.59

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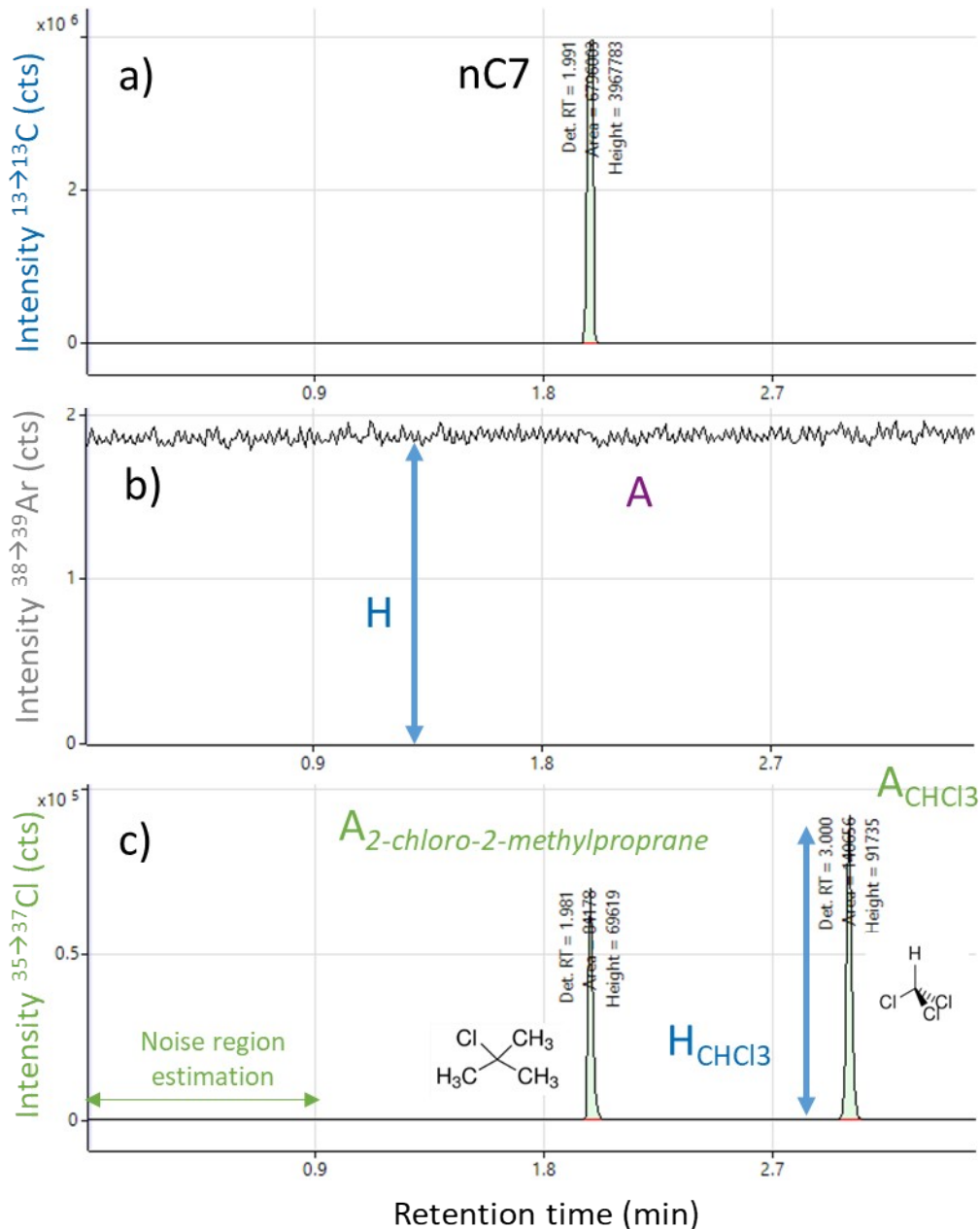


Fig. S 1

90 Chromatograms of the (a) carbon  $^{13}\text{C}$ , (b) argon  $^{39}\text{Ar}$ , (c) chlorine  $^{37}\text{Cl}$  channels obtained for the injection  
91 of the optimization mix solution containing  $\text{CHCl}_3$  and 2-chloro-2-methylpropane in n-heptane with  $\text{CG} = 0.1$  and  
92  $\text{OG} = 0.16 \text{ L min}^{-1}$  (optimized conditions).

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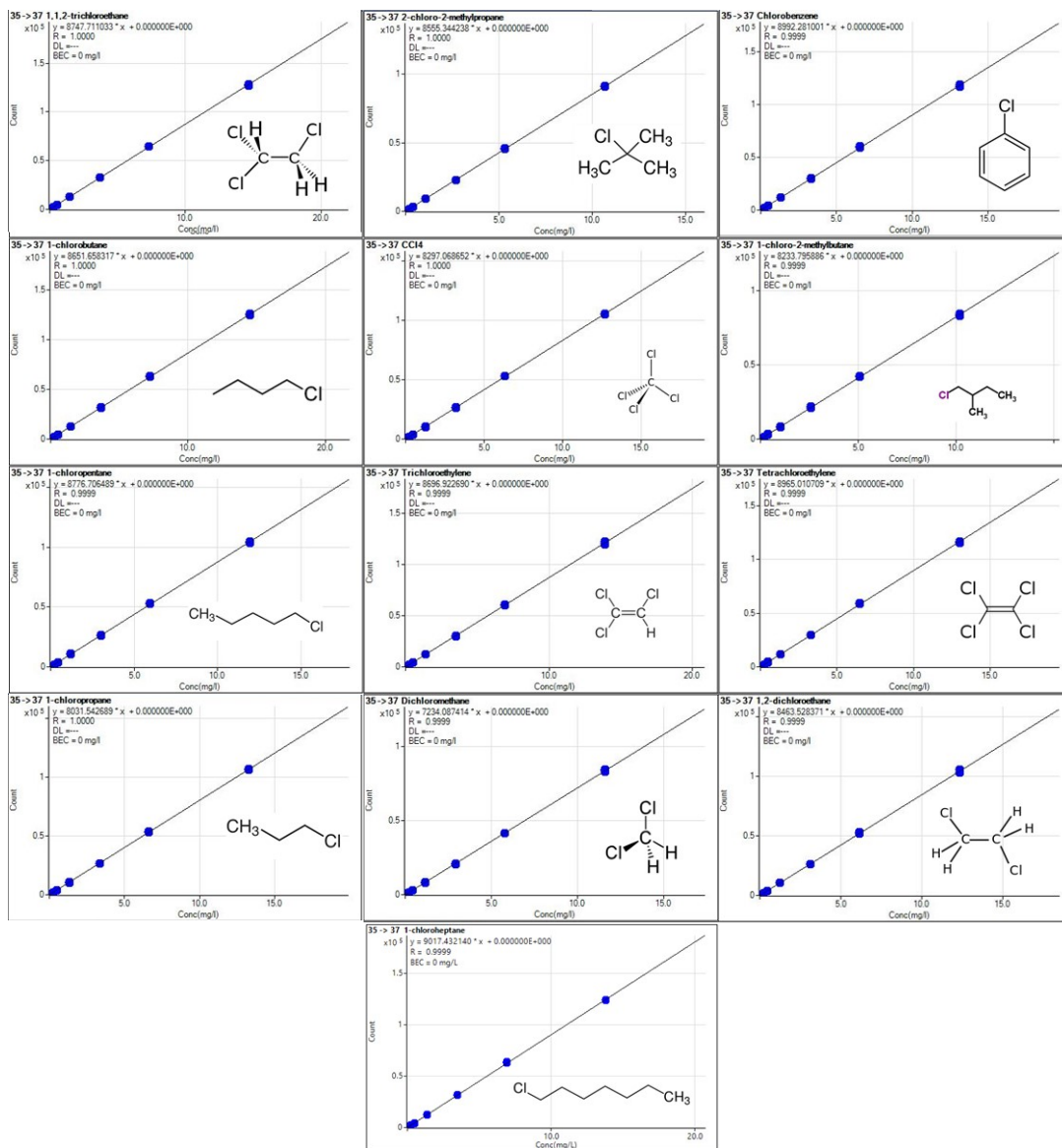
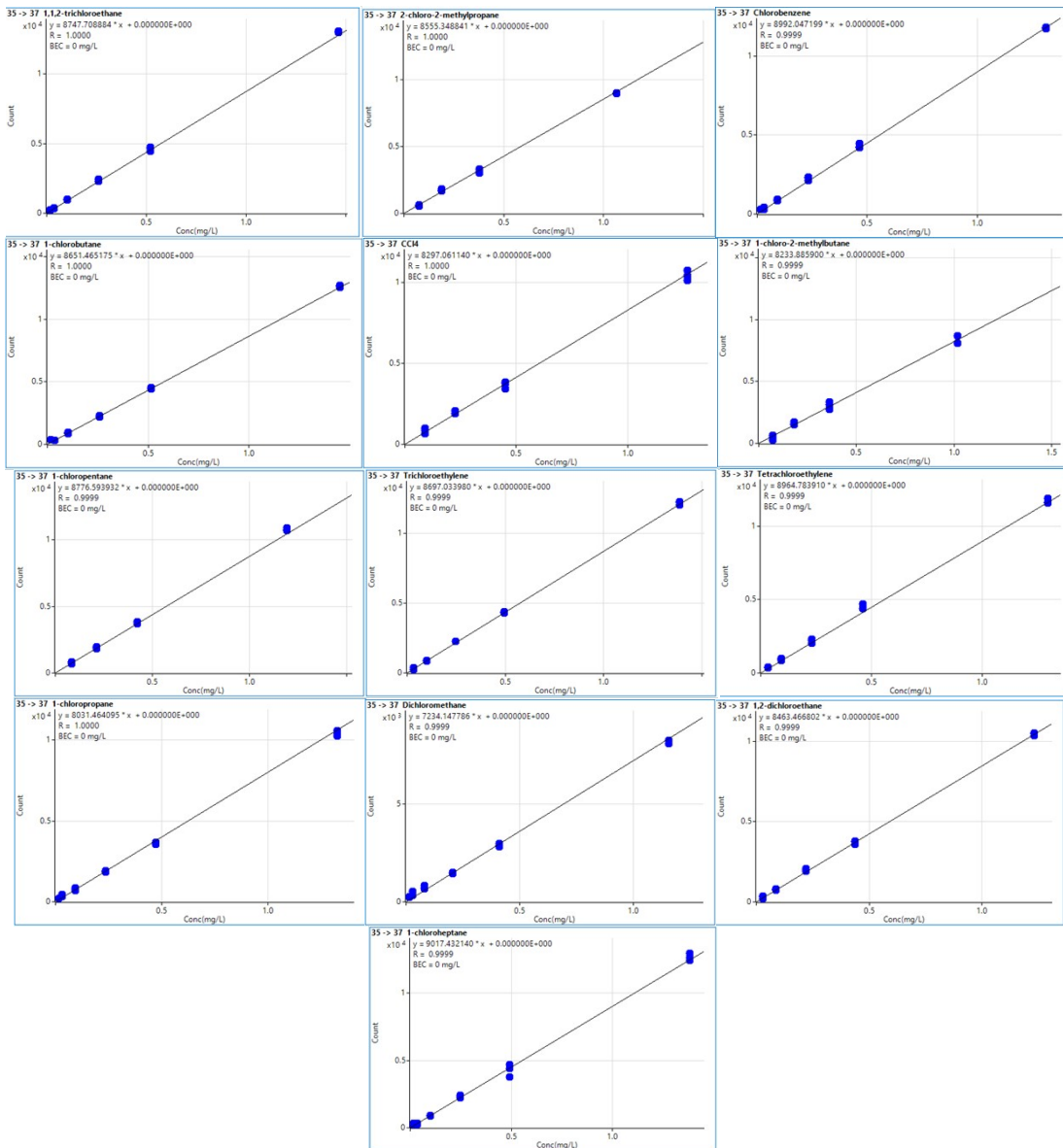


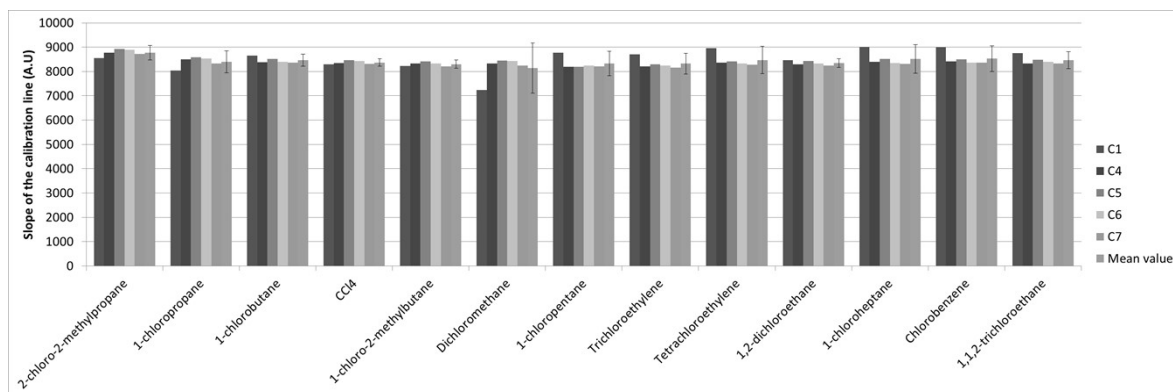
Fig. S 2 Calibration curves for 13 standard chlorinated compounds in n-heptane for Cl concentrations from 0.02 to 15 mgCl L<sup>-1</sup> per compound. Every calibration standard was injected in three replicates.



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

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188 Fig. S 4. Slopes of 5 independent calibration curves obtained from 5 independently prepared standard solutions

189 (C1, C4, C5, C6 and C7) containing 13 organochlorides in n-heptane.

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193 **Table S2. Relative response factors versus 1,2-dichloroethane in nC7 for 13 chlorinated standard compounds in**  
 194 **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

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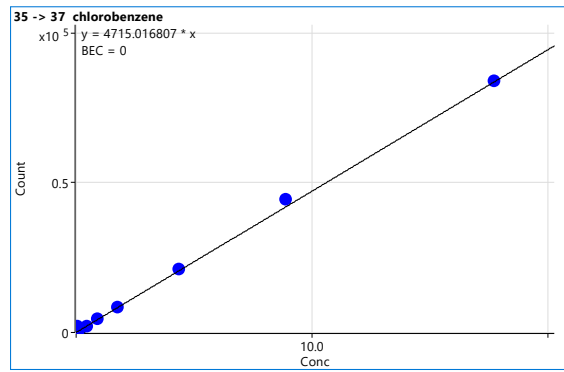
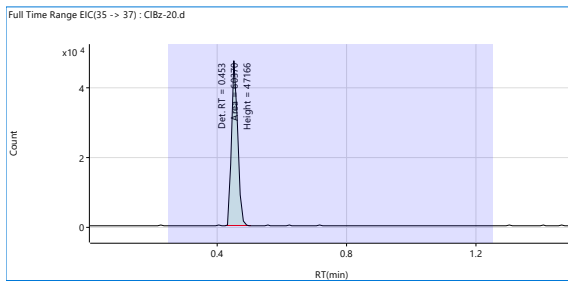


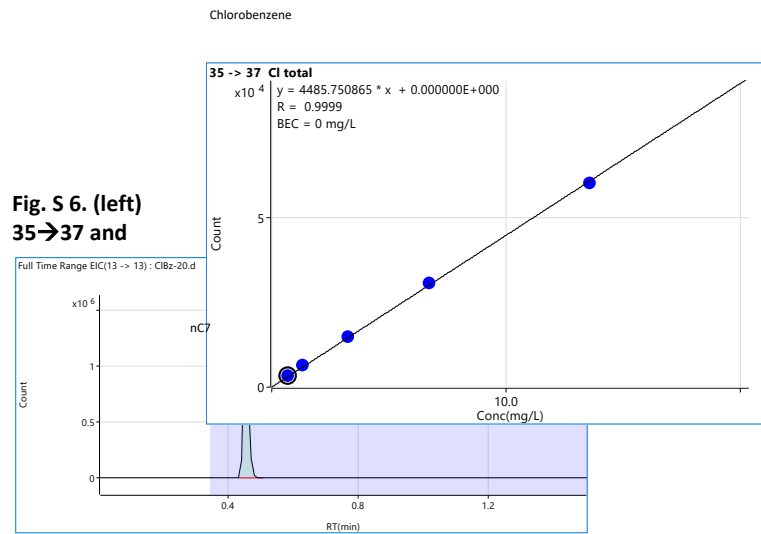
Fig. S 5. Calibration line for chlorobenzene in n-heptane on the HP-INNOWax column in the 1-20 mgCl L<sup>-1</sup> range (slope = 4715).



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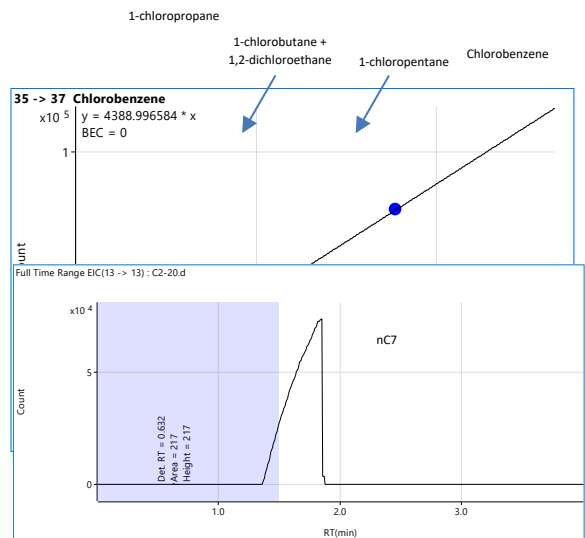
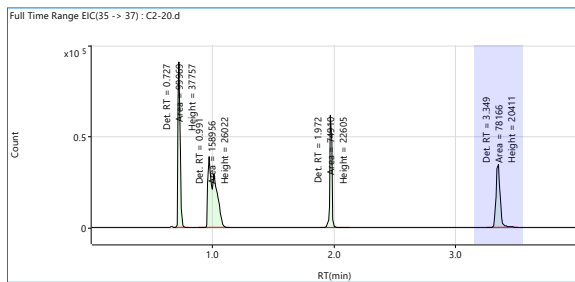


**13→13 chromatograms for the analysis of chlorobenzene in n-heptane (13.5 mgCl L<sup>-1</sup>) on a DB-1MS column (23.5 m, 0.25 mm, 0.25 μm) run at 340°C in isothermal mode and (right) obtained calibration line between 0.8 and 13.5 mgCl L<sup>-1</sup> (slope = 4486).**



**Fig. S 6. (left) 35→37 and**

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294 **Fig. S 7. (left) 35→37 and 13→13 chromatograms for the**  
295 **analysis of a mix of 5 organochlorides in n-heptane**  
296 **(around 15 mgCl L<sup>-1</sup> per compound) on a DB-1MS**  
297 **column (23.5 m, 0.25 mm, 0.25 μm) run at 35°C in**  
298 **isothermal mode and (right) obtained calibration line for**  
299 **chlorobenzene between 0.8 and 18 mgCl L<sup>-1</sup> (slope =**  
300 **4389).**

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

Compound	Medium range					High range				
	[Cl] mgCl L <sup>-1</sup>	G1	G2	G3	G4	[Cl] mgCl L <sup>-1</sup>	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%

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

Compound <sup>a</sup>	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 <sup>-1</sup> <sup>b</sup>	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							

<sup>a</sup> 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". <sup>b</sup> 3 replicates were taking into account

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