CHEMICAL & ENERGY ANALYSIS

SPECIATION OF CHLORINATED HYDROCARBONS IN REFORMATE USING THE AGILENT 7200 GC/Q-TOF

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ABSTRACT

The presence of chlorine in petroleum products can be harmful to equipment and refining processes. In addition to total chlorine determination, hyphenated techniques are needed to identify and quantitate the different chlorinated species. Speciation of chlorinated hydrocarbons in reformate was performed using the Agilent 7200 GC/Q-TOF high resolution mass spectrometer. Using extracted ion chromatograms at accurate mass, excellent selectivity and sensitivity were achieved, enabling the detection and quantitation of chlorinated hydrocarbons in the very complex reformate matrix. These compounds were determined at concentrations below 2 pg on-column, corresponding to 0.5 ppm (mg/kg) in the reformate matrix.

INTRODUCTION

The presence of chlorine in the petroleum industry is of considerable importance because of the potential formation of hydrogen chloride in liquid or gas streams [1]. This chloride-containing gas can deactivate downstream catalysts and cause undesired reactions. Chlorine is a poison recovered on Pd/Al_2O_3 catalysts during selective hydrogenation [2]. The presence of HCl in a hydrocarbon matrix leads to the formation of chlorinated hydrocarbons and can also promote the polymerization of olefins to produce "green" oils, mainly containing C6-C18 hydrocarbons [3]. Even if the concentration of HCl is relatively low, it can still interfere with operating processes that use hydrogen and can also cause corrosion problems in equipment such as pipes, valves and compressors.

In addition, HCl is considered a hazardous material and must be eliminated before release to the environment [1]. Recently, a review on total chlorine determination was published by Doyle et al. [4]. Chlorine can be measured using X-ray fluorescence (XRF) with a quantitation limit (LOQ) of 4 mg/kg in petroleum products and derivatives [5], by ICP-OES [4] and also by ICP/MS [6]. Micro-coulometric methods are currently the most widely used techniques for the determination of total chlorine, using standard test methods ASTM D4929 [7] or NF EN 14077, with an LOQ of around 1 mg/kg (ppm).

However, these methods determine the total chlorine concentration rather than identifying specific organochlorine compounds. In the petroleum industry, speciation of chlorine is necessary as these compounds need to be identified and quantitated, in order to develop systems for trapping these molecules. To our knowledge, there are no speciation methods for chlorine in petroleum products available in the literature.

Typically, chlorinated organic compounds are analyzed by gas chromatography (GC) and liquid chromatography (LC) coupled to mass spectrometry or specific detectors such as electron capture detector (ECD), atomic emission detector (AED) and inductively coupled plasma mass spectrometry (ICP/MS). GC-ECD lacks specificity and the ECD detector response is strongly dependent on the organic molecule [8, 9]. Chlorobenzene, for instance, gives a very low response in ECD. GC-AED can also be used, but chlorine detection is not very sensitive and the co-elution of hydrocarbons at very high levels (3-4 orders of magnitude higher than the chlorine compounds) exceeds the selectivity of the detector [10]. Despite spectral interferences at *m/z* 35 and low ionization potential for chlorine, GC-ICP/MS can be performed, as shown by Peters et al. [11], for the detection of three compounds (dichloromethane, trichloroethane and trichloroethylene) in pentane with LODs around 2 mg/L. However, GC-ICP/MS configurations are not widely available.

Due to the complexity of reformate samples, containing about 250 hydrocarbon species, and the chlorine concentration at low (or sub-) ppm level, selective and sensitive techniques must be used. Compound specific analysis can be performed using two-dimensional GC (heart-cutting) [12] or GC-MS/MS in multi-reaction monitoring (MRM) mode [13]. However, these techniques can only be applied to selected target compounds that are available as standards and for which retention time and mass spectra (MRM transitions) can be determined. In organochlorine speciation, the availability of a screening (non-target) method that allows for the detection and quantitation of chlorinated hydrocarbons (alkanes and aromatics) in gasoline, naphtha or reformate samples at low ppm levels would offer interesting possibilities for the petrochemical industry.

In this application note, the use of the Agilent 7200 GC/Q-TOF high resolution mass spectrometer for the analysis of chlorinated hydrocarbons in reformate is described. Ion extraction at accurate masses is used for detection and quantitation of the target compounds.

EXPERIMENTAL

Samples: A reformate sample from IFP Energies Nouvelles (Solaize, France) was used as the test matrix. Basic properties of this reformate are listed in Table 1. A stock solution of 10 chlorinated hydrocarbons was prepared in heptane at a concentration of 100 mg/kg (ppm). The reference compounds are listed in Table 2. A diluted stock solution was also prepared in heptane at 10 ppm. Spiked matrix solutions at concentrations between 0.5 and 20 ppm (per chlorinated compound) were prepared by spiking the reformate test matrix with the stock solution.

GC/Q-TOF instrument:

Analyses were performed on an Agilent 7890B GC equipped with a split/splitless inlet. Injection was performed using an Agilent 7693 ALS. The GC was coupled to an Agilent 7200 Q-TOF mass spectrometer.

Analytical conditions:

0.2 µL of sample was injected in split mode (1/50) at 250°C. Separation was performed on a 100 m x 0.25 mm ID x 0.5 µm HP-PONA column (19091Z-530). The carrier gas was helium at 1.5 mL/min constant flow. The oven was programmed from 35°C (5 min) at 4°C/min to 250°C (10 min). The transfer line was set at 280°C.

The 7200 Q-TOF was operated in MS mode using electron impact (EI) ionization. The source temperature was 230°C. The scan rate was 5 Hz in HR (high resolution) mode and the mass range was 50 to 300 amu. No internal mass referencing was used, but the instrument was mass calibrated before each run using the keyword command (MassCal) in the sequence.

RESULTS AND DISCUSSION

The total ion chromatogram obtained for the analysis of the diluted calibration stock (10 ppm) is shown in Figure 1. Taking into account the injection volume (0.2 µL) and the split ratio (1/50), the injected amount corresponds to 40 pg per compound on-column. Seven compounds were easily detected. However, compounds 2, 3 and 4 were masked by the heptane solvent peak. For the detected compounds, accurate mass spectra were obtained and searched against the standard NIST library. The chloroalkanes from chloropentane to chlorononane, all have the ion at *m/z* 91.031 in common.

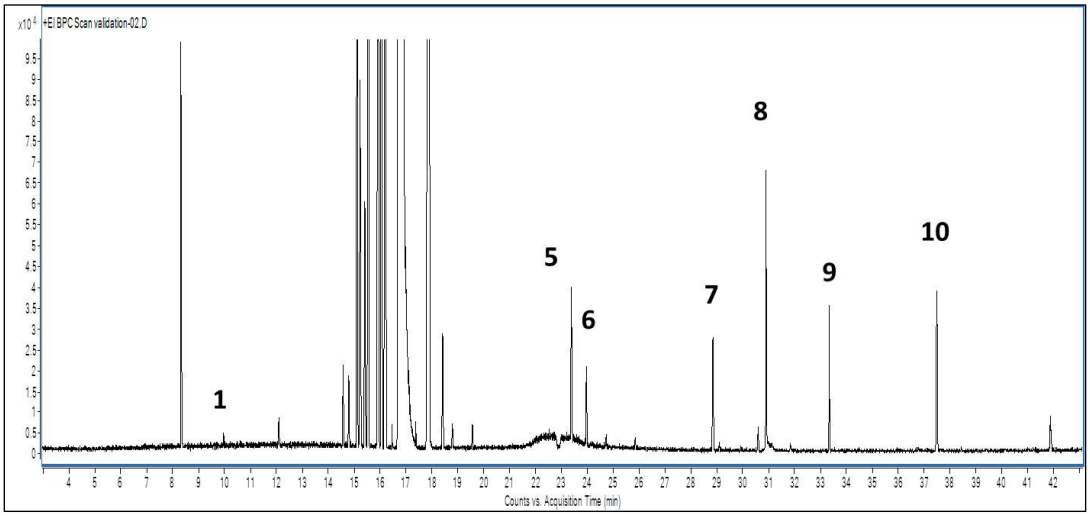

Fig 1: Base Peak Chromatogram of the analysis of a test solution containing chlorinated hydrocarbons in heptane (10 ng/µL concentration, 40 pg on-column).

Using the formula generator option, this fragment ion was correctly identified as $[C_4H_8Cl]^+$, as illustrated by the high resolution mass spectrum of chloroheptane (compound 7) in Figure 2. At *m/z* 93.028 the chlorine isotope peak is detected. For these ions, the mass error was found to be lower than 4 ppm.

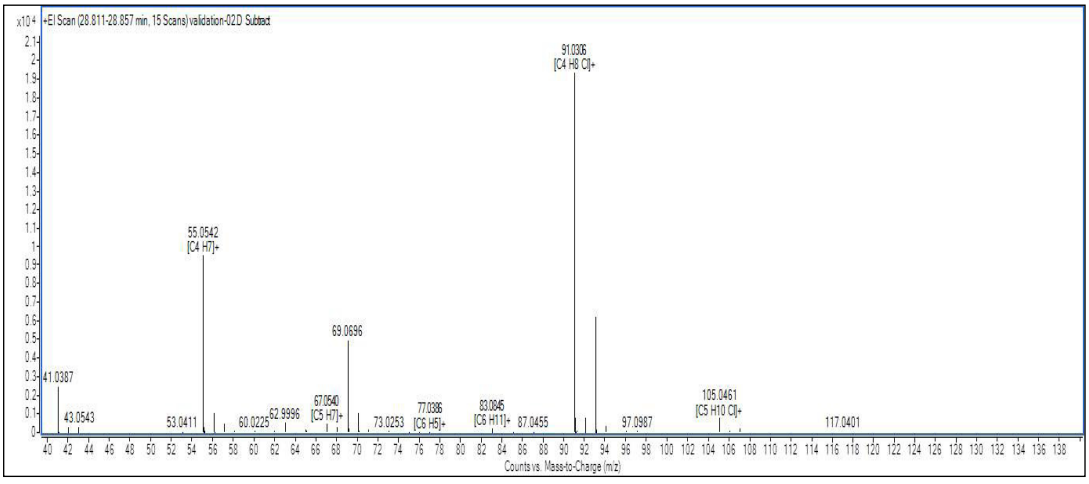

Fig. 2: High resolution accurate mass spectrum of peak 7 (1-chloroheptane)

Using extracted ion chromatograms at accurate mass, very high selectivity can be obtained. This is illustrated in Figure 3. In Figure 3A, the total ion chromatograms are compared for a reformate sample (top) and the same reformate sample spiked at 1 ppm level with the chloroalkanes (bottom). These profiles show the high complexity of the reformate sample, mainly containing aromatic hydrocarbons (toluene, xylenes, C3-, C4-, C5- benzenes) and paraffins. If the ion chromatograms are extracted using a window of +/- 0.5 amu, as is done on low resolution instruments such as a single quadrupole or a triple quadrupole instruments, the chloroalkane compounds cannot be selectively detected in the spiked sample.

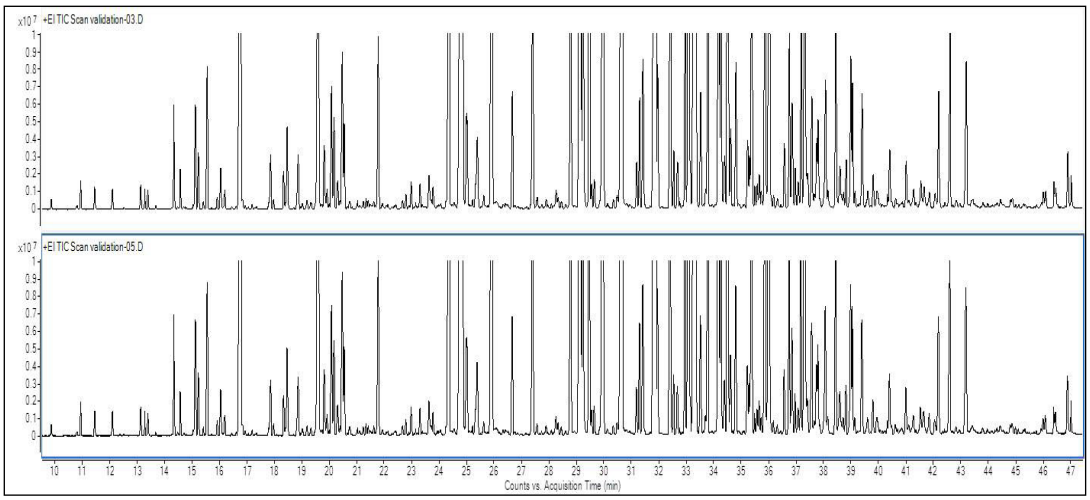

Fig. 3A: Comparison of TIC obtained for reformate sample (top) and reformate sample spiked at 1 ppm level with chlorinated hydrocarbons (bottom).

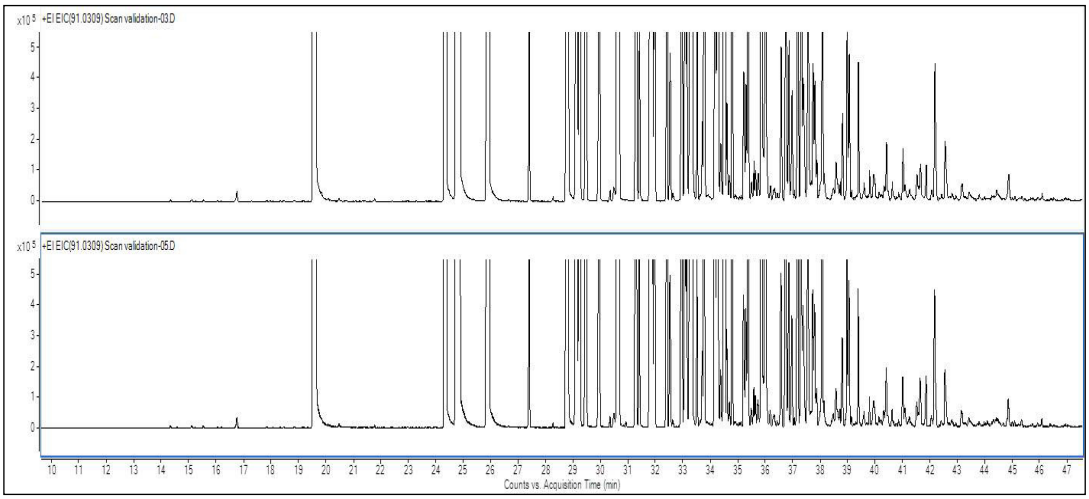

Fig. 3B: Comparison of EIC obtained for reformate sample (top) and reformate sample spiked at 1 ppm level with chlorinated hydrocarbons (bottom). EIC performed at unit mass resolution (91.0309 +/- 0.5 amu)

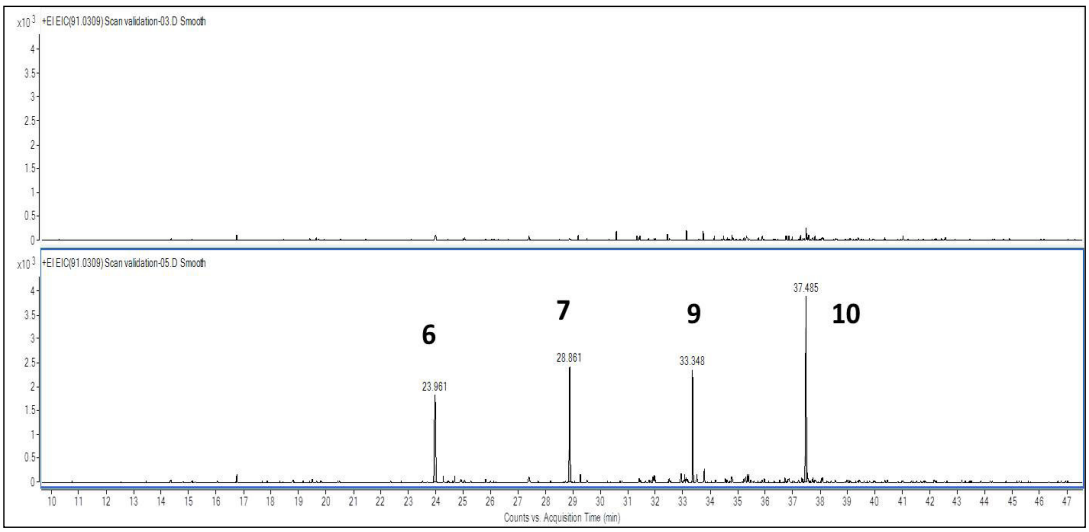

Fig. 3C: Comparison of EIC obtained for reformate sample (top) and reformate sample spiked at 1 ppm level with chlorinated hydrocarbons (bottom). EIC performed at high mass resolution (91.0309 +/- 20 ppm)

This is illustrated in Figure 3B, showing the EIC at *m/z* 91.0309 +/- 0.5 amu. No difference can be observed between the sample (top) and the spiked sample (bottom). The main peaks detected in these EICs are the aromatic hydrocarbons that give the well know tropylium ion at *m/z* 91 in their mass spectra. This fragment corresponds to $[C_7H_7]^+$ and the exact mass is 91.0542. The first 4 peaks correspond to toluene (19.5 min), ethylbenzene, m- and p- xylene and o-xylene (24 - 26 min). These compounds all have the tropylium ion as the most abundant ion in their mass spectra and low resolution MS is unable to differentiate the tropylium ion from the $[C_4H_8Cl]^+$ ion. If ions are extracted at a mass accuracy of +/- 20 ppm, the target compounds can be selectively detected, as illustrated in Figure 3C. In the unspiked sample, no chloroalkanes were detected (top chromatogram), while compounds 6, 7, 9 and 10 were detected in the spiked sample.

The EIC signals at accurate mass for a standard (10 ppm of compounds in heptane, corresponding to 40 pg on-column) and for a spiked matrix sample (10 ppm compounds in matrix) are compared in Figure 4. The peak areas are quite similar, indicating that no quenching or ion suppression occurs in the matrix. Only slight differences are noted in retention time and peak width, caused by matrix effects on the chromatography (solvent effects).

Using this method, all chlorinated compounds were detected at low ppm or even sub-ppm levels in the matrix (low ppb levels on column). To take maximum advantage of the selectivity, the ions chosen for EIC extraction all contained chlorine (see Table 2). Even though in some cases chlorine-containing ions were of relatively low abundance in a compound spectrum, it allowed efficient detection of the compounds in the very complex matrix. This is illustrated in Figure 5 for chlorobenzene using the ion at 112.007 and in Figure 6 for benzylchloride using the ion at *m/z* 126.023. Ion chromatograms were extracted at +/- 20 ppm *m/z* window. The high resolution mass spectra are shown in these figures and the mass accuracy was calculated using the formula generation option. Chlorobenzene showed a mass error of -3.03 ppm and benzylchloride a mass error of -3.17 ppm. It should be emphasized that these mass errors were obtained in the complex reformate matrix.

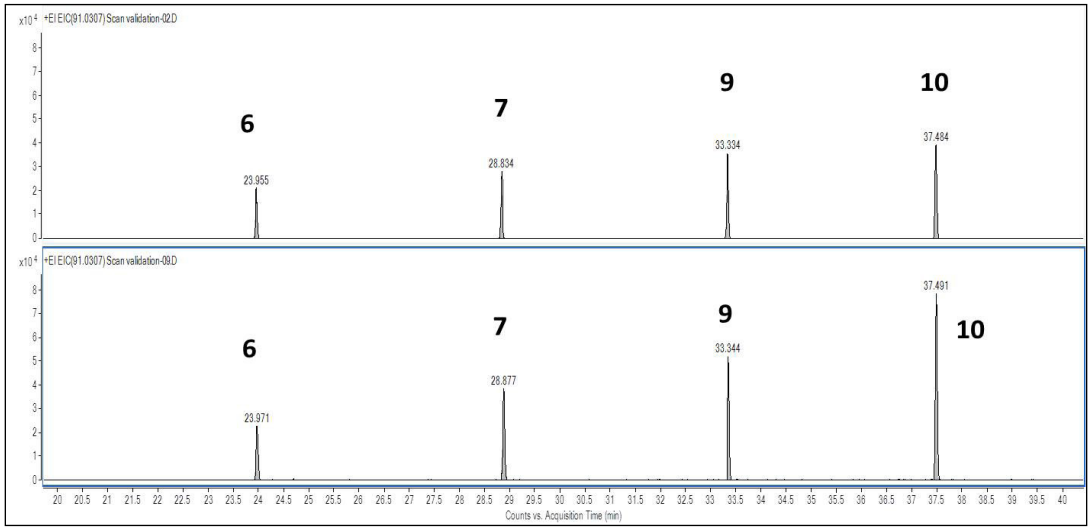

Fig. 4: Comparison of EIC obtained for a 10 ppm standard solution (top) and reformate sample spiked at 10 ppm level with chlorinated hydrocarbons (bottom). EIC performed at high mass resolution (91.0309 +/- 20 ppm)

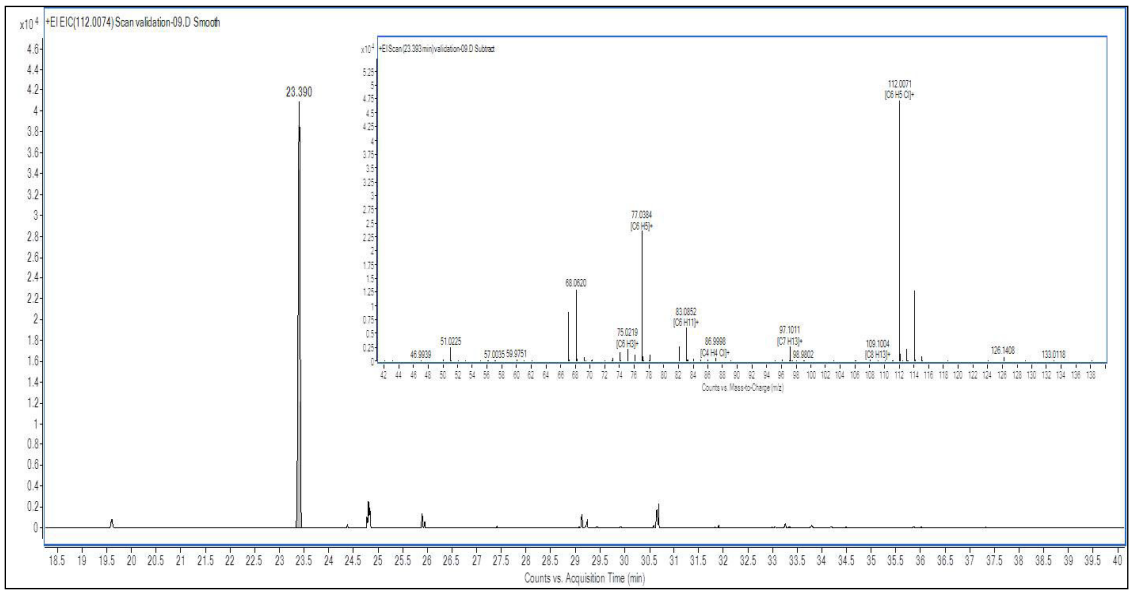

Fig. 5: Detection of chlorobenzene in reformate (spiked at 10 ppm level) - EIC @112.0074 +/- 20 ppm
Mass spectrum is given in insert

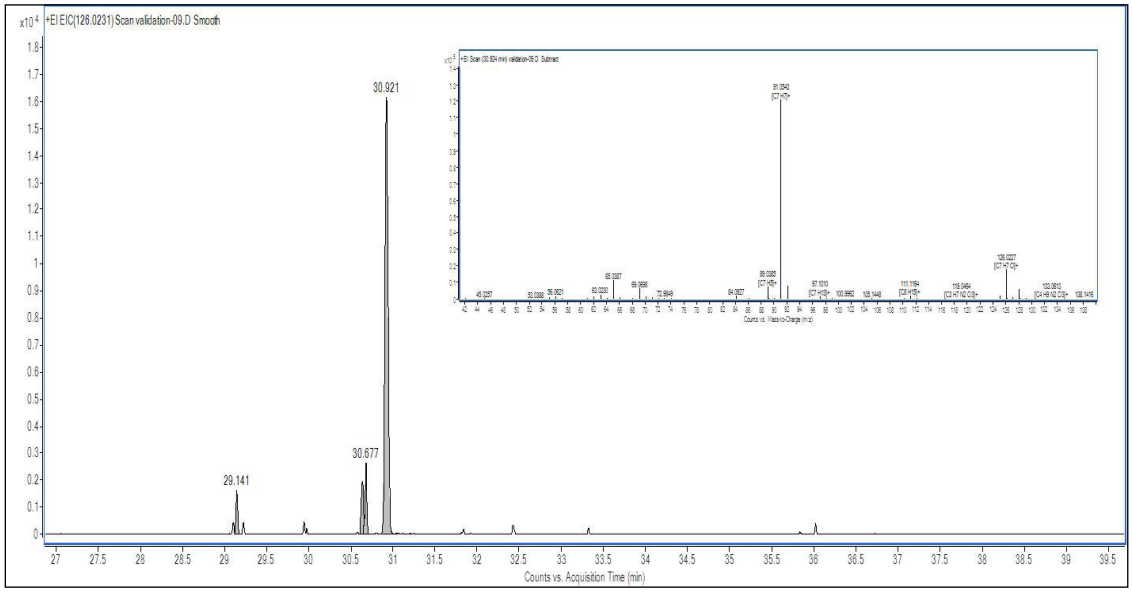

Fig. 6: Detection of benzylchloride in reformate (spiked at 10 ppm level) - EIC @126.0231 +/- 20 ppm
Mass spectrum is given in insert

PROPERTIES	METHODS	VALUES
Density (g/cm3)	NF EN ISO 12185	0.8316
Boiling range (◦C)	ASTM D2887	82-197
RON	IFPEN 9302	101
Paraffins (%wt)		5.0
Isoparaffins (%wt)		14.7
Naphthenes (%wt)		1.1
Aromatics (%wt)		78.4
Olefins (%wt)		0.8
Chlorine (mg/kg)	NF EN 14077	< 2

Table 1

PEAK	TR (MIN)	SOLUTE	FORMULA	MW	EXACT MASS	FRAGMENT
1	9.949	2-chloro-2-methylpropane	C_4H_9Cl	92	77.0158	C_3H_6Cl
2	16.463	1-chloro-2-methylbutane	$C_5H_{11}Cl$	106	62.9996	C_2H_4Cl
3	16.747	2-chloro-pentane	$C_5H_{11}Cl$	106	62.9996	C_2H_4Cl
4	18.784	1-chloropentane	$C_5H_{11}Cl$	106	62.9996	C_2H_4Cl
5	23.390	chlorobenzene	C_6H_5Cl	112	112.0074	C_6H_5Cl
6	23.955	1-chlorohexane	$C_6H_{13}Cl$	120	91.0309	C_4H_8Cl
7	28.834	1-chloroheptane	$C_7H_{15}Cl$	134	91.0309	C_4H_8Cl
8	30.921	benzylchloride	C_7H_7Cl	126	126.0231	C_7H_7Cl
9	33.334	1-chlorooctane	$C_8H_{17}Cl$	148	91.0309	C_4H_8Cl
10	37.484	1-chlorononane	$C_9H_{19}Cl$	162	91.0309	C_4H_8Cl

Table 2

CONCLUSION

Sub-ppm chlorinated hydrocarbons can be analyzed in reformate samples using GC/Q-TOF high resolution MS analysis. The high selectivity offered by accurate mass ion extraction allows the target compounds to be detected and quantified in this extremely complex matrix. Sensitivity is better than 2 pg on column, corresponding to 0.5 ppm (mg/kg) in the reformate matrix.

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