

# Determination of Organic Chlorides in Petroleum Products Using a Halogen Specific Detector (XSD)

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## Introduction

Recently there has been interest in the detection and removal of organic chloride species in petroleum products. Crude oil is distilled to form naphthas, and then with continued refining, these products can go through catalytic reforming to produce reformates. Reformates are used for many products including gasoline blending stock and aromatic bulk chemicals, so the process is crucial.<sup>1</sup> During this process catalysts are conditioned with organic chlorides. If these are not removed they may form hydrogen chloride and various organic chlorides which can cause operational problems such as corrosion and poisoning of downstream catalysts, as well as product specification issues.<sup>2</sup> Though they do not occur naturally in crude oils, the presence of organic chlorides can be the result of contamination caused by equipment cleaning or chlorinated solvent used in dewaxing pipelines.<sup>3</sup> Refineries see the need for a more comprehensive approach to the challenges that organic chlorides present in their processes.<sup>4</sup> The ability to sample at various points in the process and speciate the organic chlorides is important to determine where the contamination is coming from and aids in evaluating processes and chloride removal. This poster will present a simple gas chromatographic method utilizing a halogen specific detector (XSD) to determine chlorinated organic compounds in various petroleum samples.

## Instrumentation and Methodology

The instrumentation used was an Agilent 7890A Gas Chromatograph with an OI Analytical 5360A Halogen Specific Detector (XSD). The XSD is a thermionic emission-based GC detector which specifically responds to electronegative elements such as chlorine and bromine. The detector assembly consists of a ceramic probe with a platinum coil and bead inserted into a high-temperature reactor. The halogenated compounds eluting from the column into the reactor combust between the jet outlet and the bead surface. The halogenated species react with the alkali on the platinum bead surface and produce an increase in thermionic emission from the bead. This emission is collected and the measured current is proportional to the mass of halogen in the halogenated compound. High halogen selectivity vs. hydrocarbon (Cl: HC > 10<sup>4</sup>) simplifies analyses and minimizes or eliminates sample preparation.

A calibration was analyzed by injecting halogenated compounds prepared in methanol. Instrument conditions are shown in Table 1.

Table 1. Instrument Parameters

XSD	5360A
Base	300 °C
Reactor	1000 °C
Air	65 ml/minute
Gas Chromatograph	Agilent 7890A
Column	Restek Rxi - 624Sil MS 30 meter, 0.25 mm, 1.4 µm
Carrier Gas	Zero grade helium
Inlet Temperature	240 °C
Inlet Liner	Topaz 4 mm precision with wool
Column Flow Rate	0.8 mL/min constant flow
Split Ratio	120
Oven Program	Hold at 40 °C for 2.0 min 16 °C/minute to 200 °C 30 °C/minute to 300 °C Hold at 300 °C for 2.0 min Total GC Run is 17.33 min

## Results and Discussion

### Calibration

A six-point calibration from 1 to 50 ppm was performed. The response of Bromoform is much less than that of the chlorinated compounds. In general, the response of brominated compounds is approximately nine times less than chlorinated compounds on the XSD. Calibration curves were generated using Agilent OpenLab software and linear regression was used for quantitation. Please see Table 2.

Table 2. Calibration

Compound	Analyte	Retention Time (minutes)	Linear Regression	Response Factor
1	Vinyl chloride	3.09	0.996	1.52
2	1,1-Dichloroethene	4.60	0.996	2.48
3	Methylene chloride	5.09	0.996	3.24
4	trans-1,2-Dichloroethene	5.36	0.996	2.68
5	cis-1,2-Dichloroethene	6.24	0.997	3.11
6	Bromochloromethane	6.44	0.996	2.11
7	Chloroform	6.51	0.997	4.20
8	1,1,1-Trichloroethane	6.68	0.996	3.27
9	Carbon tetrachloride	6.81	0.996	3.81
10	1,2-Dichloroethane	7.00	0.996	3.13
11	Trichloroethene	7.49	0.996	3.26
12	1,2-Dichloropropane	7.70	0.997	2.74
13	Bromodichloromethane	7.90	0.997	2.10
14	1,1,2-Trichloroethane	8.87	0.997	3.52
15	Tetrachloroethene	8.98	0.997	3.74
16	Chlorodibromomethane	9.22	0.999	1.13
17	Chlorobenzene	9.75	0.997	1.37
18	Bromoform	10.46	0.999	0.38
19	1,4-Dichlorobenzene	11.82	0.997	2.16
20	Benzyl chloride	11.91	0.998	1.56
21	1,2-Dichlorobenzene	12.15	0.998	2.25
22	1,2,4-Trichlorobenzene	13.48	0.998	4.32

### Sample Analysis

A variety of petrochemical samples were analyzed without any sample preparation. The samples contained high hydrocarbon concentrations which caused dips in the baseline where the hydrocarbons eluted. It may be necessary to run samples at a higher split or dilute if interference with a chlorinated compound is suspected. In order to test this effect, naphtha and reformat samples were spiked at 10 ppm. Recoveries in the naphtha sample ranged from 88-142% recovery and in the reformat sample, 87-142%. Please see Table 3.

Table 3. Spike Recovery

Compound	Analyte	Reformat Spike % Recovery	Naphtha Spike % Recovery
1	Vinyl chloride	87.2	136
2	1,1-Dichloroethene	104	141
3	Methylene chloride	101	105
4	trans-1,2-Dichloroethene	105	88.5
5	cis-1,2-Dichloroethene	105	142
6	Bromochloromethane	110	137
7	Chloroform	106	126
8	1,1,1-Trichloroethane	91.4	117
9	Carbon tetrachloride	84.7	119
10	1,2-Dichloroethane	103	125
11	Trichloroethene	113	137
12	1,2-Dichloropropane	108	132
13	Bromodichloromethane	115	132
14	1,1,2-Trichloroethane	122	138
15	Tetrachloroethene	120	135
16	Chlorodibromomethane	111	129
17	Chlorobenzene	141	132
18	Bromoform	116	117
19	1,4-Dichlorobenzene	110	130
20	Benzyl chloride	116	118
21	1,2-Dichlorobenzene	121	125
22	1,2,4-Trichlorobenzene	118	122

## Conclusions

Refineries are more aware of the need for the detection and removal of chlorinated species from their hydrocarbon streams. The XSD provides data which may help refineries accurately measure and pinpoint the source of chlorinated compounds in their streams minimizing costly operational problems and product specification issues. The method presented is straightforward, easy to use, and utilizes an easy to maintain detector. If the impact of the coeluting HC matrix is problematic with the quantitation of the halogenated hydrocarbons a more selective detector, such as an Electrolytic Conductivity Detector (ELCD), can be considered as an option.

## References

1. Wikipedia.org, Catalytic Reforming, May 2017.
2. Digitalrefining.com, Removal of Chloride Compounds, April 2003.
3. ASTM D8150, Standard Test Method for Determination of Organic Chloride Content in Crude Oil, 2017.
4. Digitalrefining.com, Chloride Removal in Refineries, March 2011

## Acknowledgement

Thank you to Spectrum Standards in Houston, Texas for some of the samples used in this study.

SEE PAGE 2 FOR FIGURES 1 - 8.

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Figure 1. 10 ppm Standard

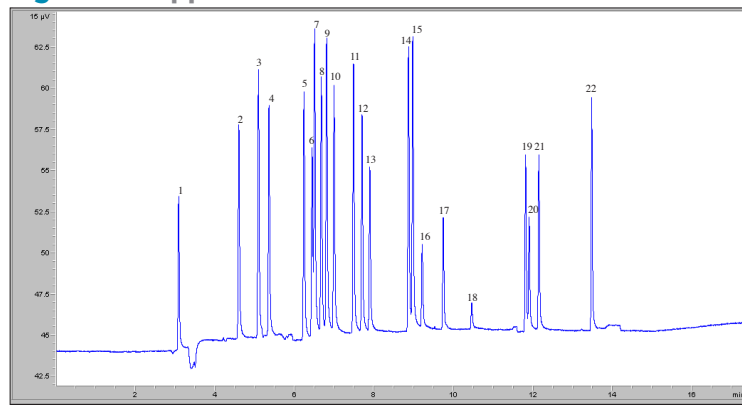


Figure 2. 20 ppm Standard

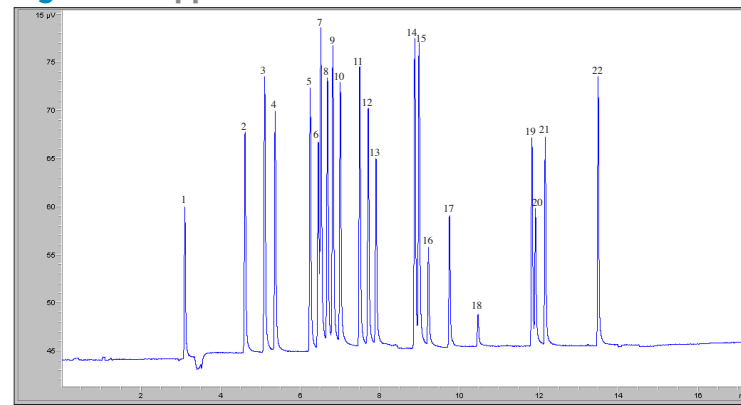


Figure 5. Naphtha

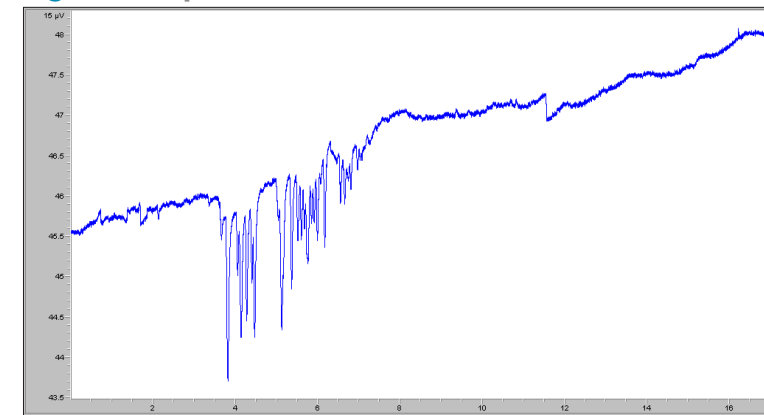


Figure 6. Naphtha Spike

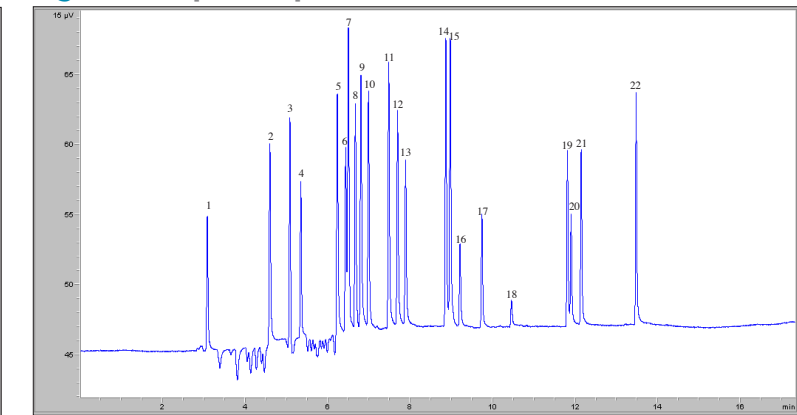


Figure 3. Reformate

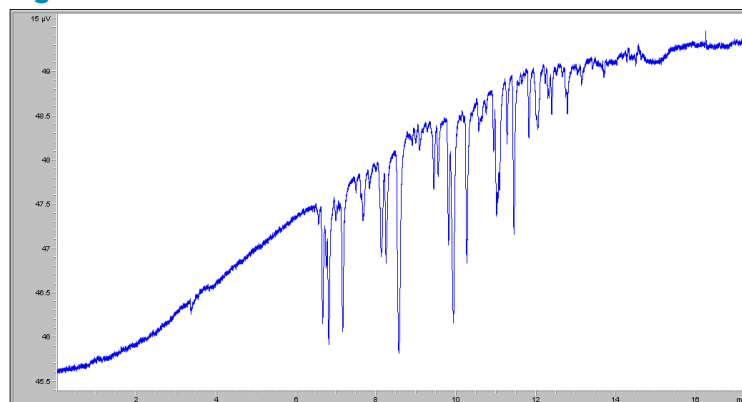


Figure 4. Reformate Spike

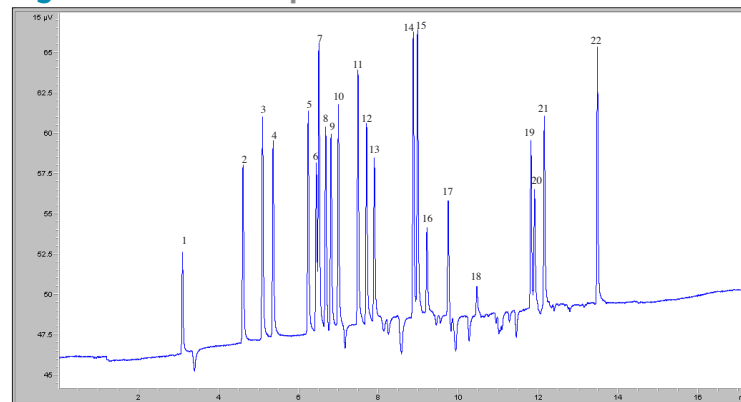


Figure 7. 2015 Unwashed Naphtha

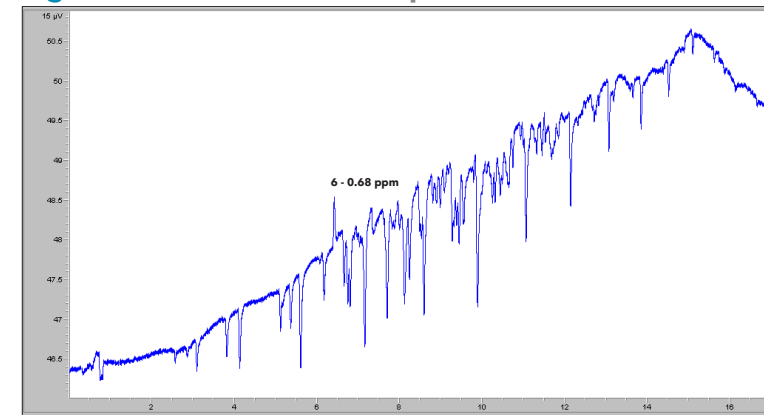


Figure 8. 2015 Washed Naphtha

