Chlorinated Compounds in Hydrocarbon Streams Using a Halogen Specific Detector (XSD)

Introduction

There has been an increase in concern for the detection and removal of organic chloride species from crude aromatic, naphtha, and other hydrocarbon streams. One process called catalytic reforming uses organic chloride to condition the catalyst which results in low level chloride contamination downstream. This can take the form of hydrogen chloride (HCl) and organic chlorides. The chloride species can cause a number of problems in the various refining processes including formation and deposition of ammonium chloride, corrosion, poisoning of catalysts, and fouling of product.[1] Since reformates and other aromatic and naphtha streams are used to make gasoline blending stock, aromatic bulk chemicals, and raw materials for plastics, determining and removing contaminants is essential. Chlorides can also be introduced by sample handling and equipment degreasers so identifying the specific chlorinated species is important to pinpoint the source of the contamination. Analysis by the halogen specific detector (XSD) can be useful in the detection of organic chlorides. This detector offers advantages over other halogen selective detectors such as it contains no radioactive source, doesn't use organic solvents, and is simple to operate. This poster will show a method for organic chloride analysis with a representative compound list with a calibration range of 0.1 to 10 ppm.

Model 5360A XSD

O·I·Analytical
a xylem brand

Instrumentation and Methodology

The instrumentation used was an Agilent 7890A Gas Chromatograph and OI Analytical 5360A XSD. The XSD operates as a thermionic emission detector optimized for the detection of halogen compounds. The detector assembly consists of a ceramic probe with a platinum coil and bead inserted into a high temperature reactor. The GC column effluent is combusted in a stream of air and passed over the bead. The elevated temperature of the reactor causes alkali metals atoms to be released from the ceramic probe and deposited on the bead. The halogenated compounds in the effluent react with the alkali metal atoms on the surface of the bead which results in an increase in thermal electron emission. The measured emission current is proportional to the mass of halogen produced.

A calibration was analyzed for a representative group of halogenated compounds by manually injecting 1 µl of standard prepared in methanol. Instrument conditions are shown in Table 1.

Table 1. **Instrument Configuration & Operating Conditions**

Agilent 7890A GC & OIA 5360 XSD	
Detector	Detector Base: 300 °C Detector: 1100 °C Air: 65 mL/min
Inlet	240 °C Split mode Split ratio 100:1 4 mm precision liner with wool
GC Column	Restek Rxi – 624 SIL MS 30-m x 0.25-mm ID x 1.4 µm df Helium carrier gas, 0.8 mL/min constant flow
Oven Program (Agilent 7890A)	40 °C for 1 minute 18 °C / minute to 180 °C 40 °C / minute to 300 °C Hold for 2 minutes* Total run time 13.8 minutes

* Final hold may need to be adjusted according to the matrix.

Results & Discussion

Calibration

A six-point calibration was performed which included the range of 0.1 ppm to 10 ppm for all compounds except for 1-Bromopropane. The calibration for this compound was 1.0 ppm to 100 ppm. The response for a brominated compound is approximately 10 times less than that of a chlorinated compound on the XSD. The Agilent Chemstation OpenLab software was used to generate calibration curves using linear regression. Please see Table 2.

Sample Analysis

A variety of petrochemical samples were analyzed. Some samples had very high hydrocarbon concentrations, such as naphtha, which caused dips in the baseline in locations where the hydrocarbons eluted. It may be necessary to dilute or run some samples at a higher split in order to avoid this effect if interference with a chlorinated compound is suspected.

Some samples contained solvents such as Methylene chloride, 1- Bromopropane, and Trichloroethene that may come from sample handling or the catalytic reforming process. Benzyl chloride may come from the use of corrosion inhibitors or a reaction of a chlorinated compound with Benzene and Toluene. (Figures 2-13)

Table 2. **XSD Calibration table**

Compound	Analyte	Retention Time (minutes)	Linear Regression (R^2)
1	Vinyl chloride	2.81	0.9998
2	1,1-Dichloroethene	3.98	0.9999
3	Methylene chloride	4.36	0.9999
4	trans-1,2-Dichloroethane	4.57	0.9999
5	cis-1,2-Dichloroehtne	5.26	1.0000
6,7	1-Bromopropane & Bromochloromethane (co-elute)	5.42,5.43	0.9994, 0.9993
8	1,1,1-Trichloroethane	5.62	0.9999
9	Carbon tetrachloride	5.74	0.9999
10	1,2-Dichloroethane	5.88	1.0000
11	Trichloroethene	6.29	0.9999
12	1,2-Dichloropropane	6.47	0.9999
13	1,1,2-Trichloroethane	7.46	0.9992
14	Tetrachloroethene	7.57	1.0000
15	Chlorobenzene	8.24	0.9998
16	1,4-Dichlorobenzene	9.94	0.9987
17	Benzyl chloride	10.00	0.9996
18	1,2-Dichlorobenzene	10.18	0.9993
19	1,2,4-Trichlorobenzene	11.17	0.9988

Figure 2. 5 ppm Standard

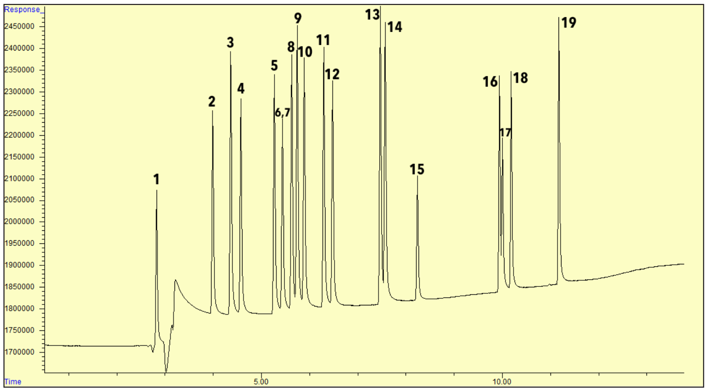


Figure 3. Lacquer Thinner

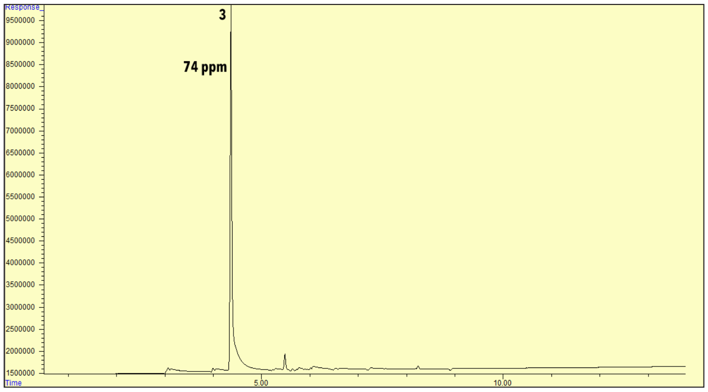


Figure 4. Kerosene Alternative

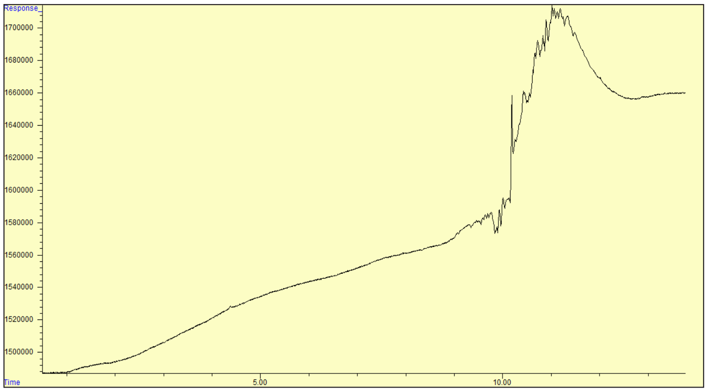


Figure 5. Paint Thinner

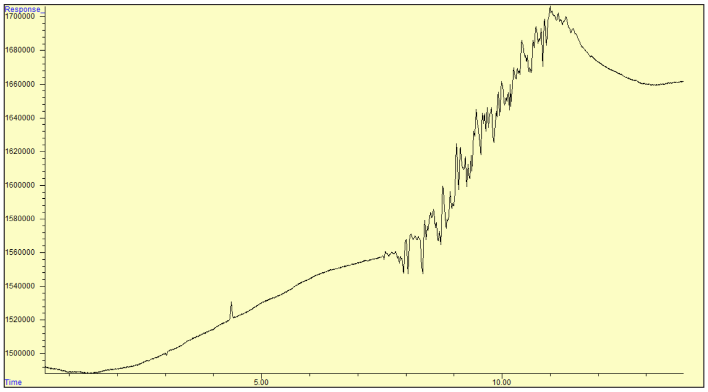


Figure 6. Crude Oil Diluted 100x

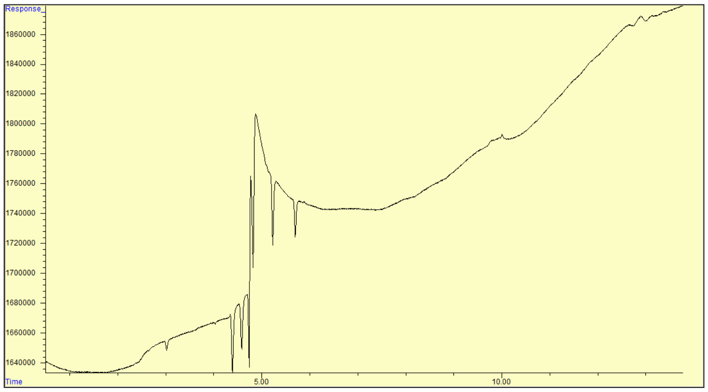


Figure 7. Naptha

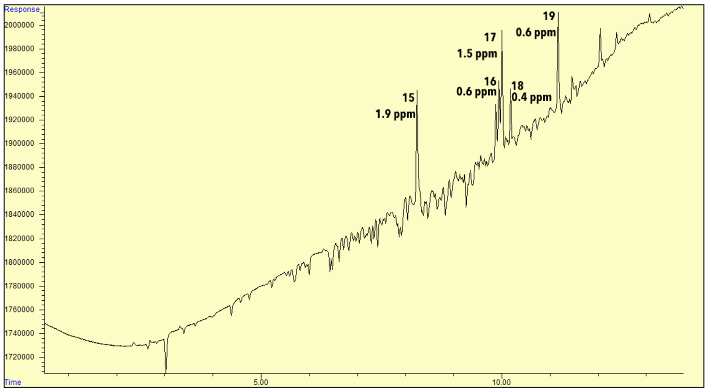


Figure 8. Washed Naptha (2015)

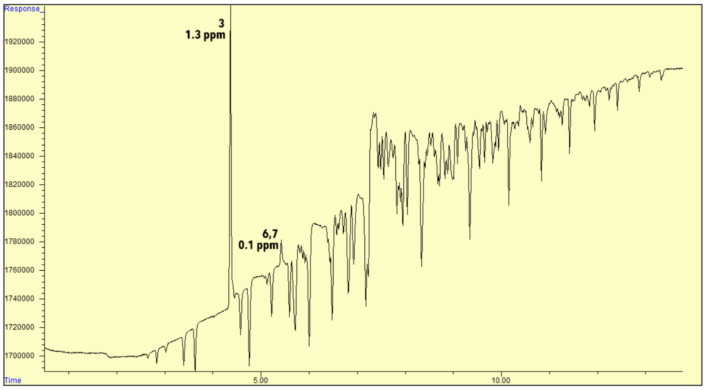


Figure 9. Unwashed Naptha (2015)

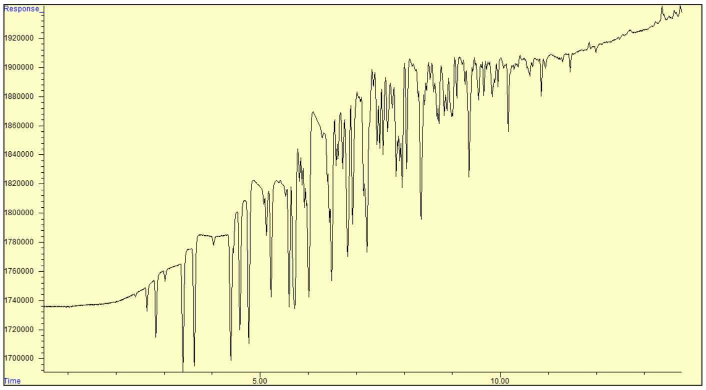


Figure 10. Washed Naptha

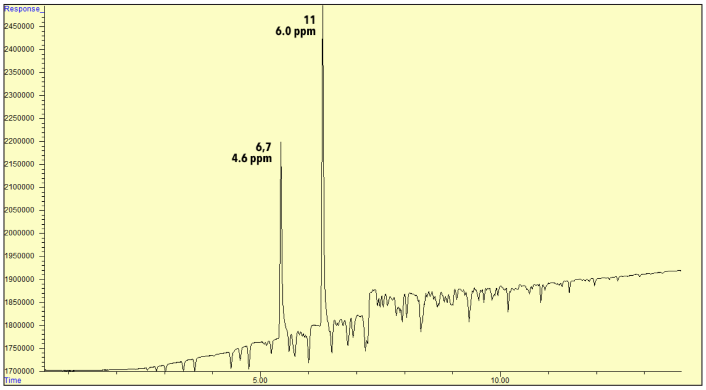


Figure 11. Naptha

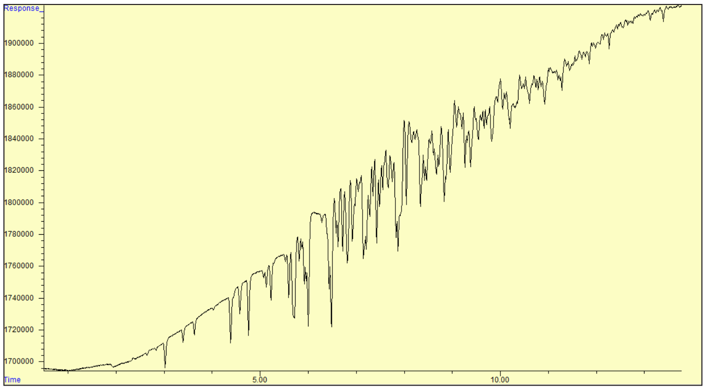


Figure 12. Reformate

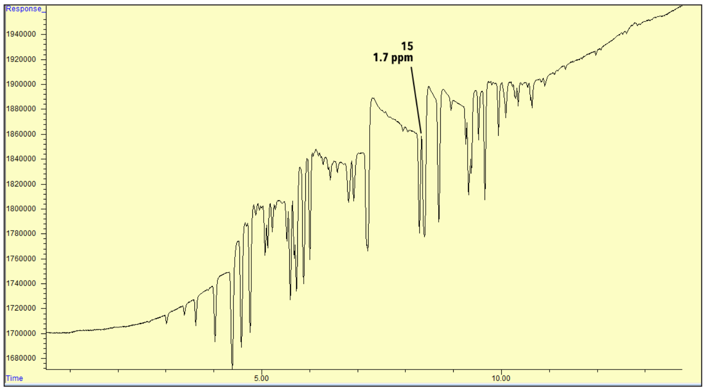
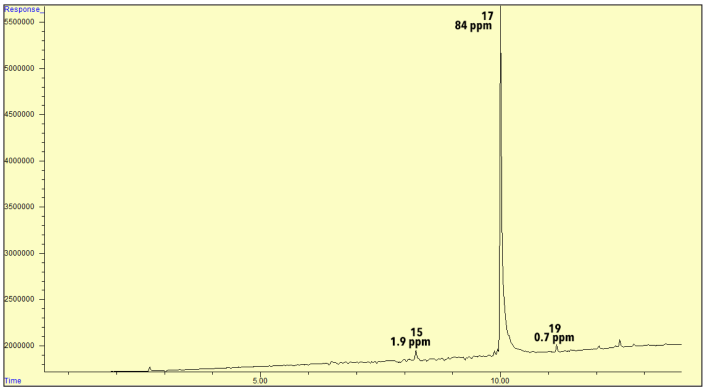


Figure 13. Naptha with Corrosion Inhibitor



Conclusions

Refineries have become more aware of the need for the detection and removal of chlorinated species from their refinery streams. A critical factor in removing the chlorides is detecting them in samples.[2] Many refineries use gas tube detection methodologies which are not very effective at detecting low chloride concentrations.[3] The XSD provides data which may help the refineries accurately measure and pinpoint the source of chlorinated compounds in their streams. The presented method is fast, easy to use, and utilizes an easy to maintain detector.

References

1. Digitalrefining.com, Removal of Chloride Compounds, April 2003.
2. Digitalrefining.com, Chloride Removal in Refineries, March 2011.
3. Digitalrefining.com, Close Guard Against Chloride Issues, August 2017.

Conclusions

Thank you to Restek for the analytical column used for this work.

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