

# Chlorinated Compounds in Hydrocarbon Streams Using a Halogen Specific

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## 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.<sup>1</sup> 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.



Figure 1. Model 5360A XSD

## 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

Table 1. Instrument Configuration & Operating Conditions

### Agilent 7890A GC & OIA 5360 XSD

|          |  |
|----------|--|
| Detector | Detector Base: 300 °C<br>Detector: 1100 °C<br>Air: 65 mL/min |
| Inlet    | 240 °C   |

## 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.

Table 2. XSD Calibration table

| Compound | Analyte  | Retention Time (minutes) | Linear Regression (R <sup>2</sup> ) |
|----------|--|--------------------------|-------------------------------------|
| 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-Dichloroethane                         | 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                              |

### Sample Analysis

A variety of petrochemical samples were analyzed in the baseline in locations where the hydrocarbon effect if interference with a chlorinated compound. Some samples contained solvents such as Methylene chloride, Toluene, Benzyl chloride may catalytic reforming process. (Figures 2-13)

Figure 2. 5 ppm Standard

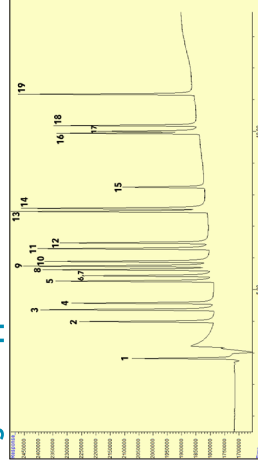


Figure 5. Paint Thinner

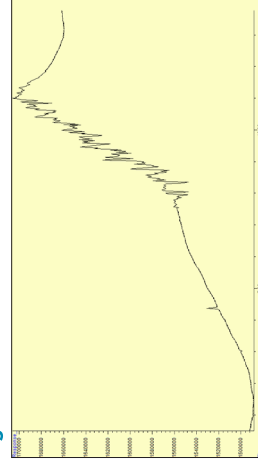


Figure 8. Washed Naptha (2015)

