O·I·Analytical

Halogen and Compound Dependence of a Halogen Specific Detector for Gas Chromatography

Application Note 10480798

Keywords
Compounds
Gas Chromatography
Halogen
Halogen Specific Detector
XSD

Presented at the 1997 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy
Atlanta, GA
March 16–21, 1997

Introduction

Many different detectors are used for the gas chromatographic analysis of halogenated compounds. These detectors range from the very nonselective detectors such as flame-ionization detectors (FID) and mass spectrometers (MS) to very selective detectors like the electrolytic conductivity detector (ELCD) and the electron capture detector (ECD). Most of these detectors exhibit serious interferences from other compounds. An FID or an ECD identifies compounds only on the basis of retention time, so it is difficult to identify coeluting compounds, including nonhalogenated interferences. A mass spectrometer may be used to identify coeluting compounds, but in some cases an MS does not have the sensitivity required for trace level analysis.

A new halogen specific detector (XSD™) has been developed to address the need for a sensitive and selective detector for halogenated compounds. This detector operates by combusting the gas chromatograph column effluent in a stream of air. The combustion products of the halogenated compounds then react with alkali metal atoms on the surface of an electrically charged platinum bead. The bead functions as an electron emitter when the reaction takes place, and by measuring the current, halogenated species can be determined. Figure 1 illustrates this detector.

Figures 2 and 3 illustrate the selectivity of the XSD for halogenated compounds. Figure 2 is a chromatogram of a USEPA Method 608 standard with the concentration of the individual components varying between 100 and 600 picograms per microliter. Figure 3 is a chromatogram of the same standard solution with 10,000 parts per million of diesel fuel spiked into the solution. There are only small baseline disturbances (from a small HC response for these high HC concentrations) with the addition of the diesel fuel.

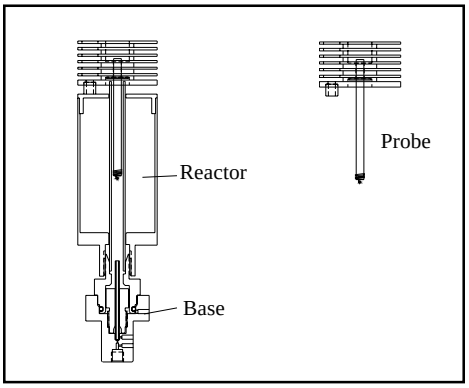

Figure 1. Halogen Specific Detector

GC:	HP 6890
GC Injector:	Split/Splitless
Injection Mode:	Splitless
Injector Temperature:	250°C
Column:	J&W DB-5ms, 30 m x 0.25 mm, 0.25 µm phase
Column Flow:	1 mL/min, constant flow mode
Oven Program:	60°C for 2 min, to 180°C at 20°C/min, to 250°C at 5°C/min, to 300°C at 20°C/min, 2 min hold
Detector:	OI Analytical Model 5360 XSD
Reactor Temperature:	1000°C
Reaction Gas:	Air, 25 mL/min

A. α-BHC	I. Dieldrin
B. β-BHC	J. 4,4'-DDE
C. γ-BHC	K. Endrin
D. δ-BHC	L. Endosulfan II
E. Heptachlor	M. 4,4'-DDD
F. Aldrin	N. Endrin aldehyde
G. Heptachlor epoxide	O. Endrin sulfate
H. Endosulfan I	P. 4,4'-DDT

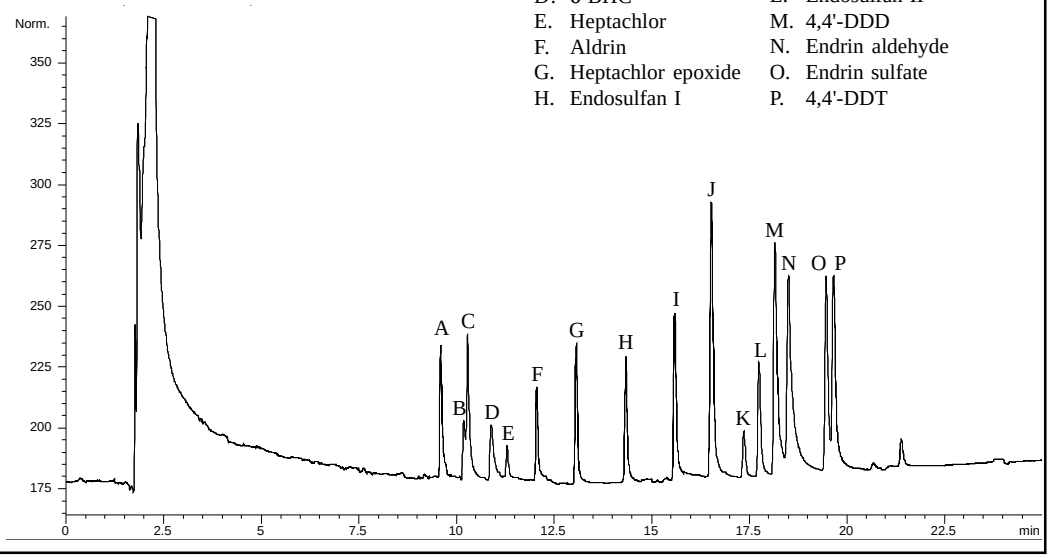

Figure 2. Chromatogram of Method 608 Standard in *n*-Hexane

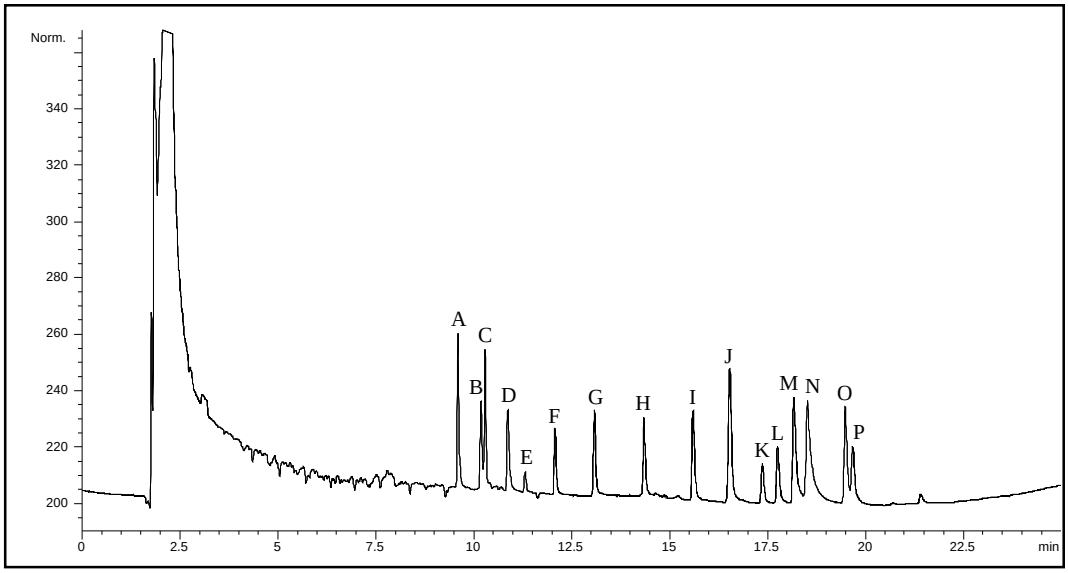

Figure 3. Chromatogram of Method 608 Standard in *n*-Hexane With 10,000 ppm Diesel Fuel Added (See Figure 2 for conditions.)

Selectivity is very important in the analysis of halogenated compounds, but another factor to be considered is the compound dependence of the detector response. An FID gives a very similar response for the same mass of any hydrocarbon. In contrast, the response of an ECD is very compound dependent. An investigation was undertaken to determine the factors affecting the response of the XSD.

Experimental

Standards used in this study were made up in methanol from the neat compounds or were purchased from Accustandard, New Haven, CT. All working standards were prepared in methanol from the methanol stock solutions.

The gas chromatograph (GC) used for this study was a Hewlett-Packard (HP) Model 6890 GC fitted with an OI Analytical Model 5360 XSD. The data was collected and processed using HP ChemStation software. Samples were injected using an OI Analytical Model 4105 Liquid Autosampler. One-microliter injections were made in splitless mode.

A solution containing 10 nanagrams per microliter of fluorobenzene, chlorobenzene, bromobenzene, and iodobenzene was injected to obtain an estimate of the relative responses of the halogens.

Response curves were determined by injecting five concentrations of a volatile organic standard (Method 502.2 standard) into the GC. The mean value of three replicate injections was used in constructing the response curves.

Results

The injection of the halobenzene standard (Figure 4) indicated approximately an order of magnitude sensitivity decrease from chlorine to bromine, and another order of magnitude decrease from bromine to fluorine. The iodobenzene was not detected, indicating an extremely low response factor. In contrast, the sensitivity of an ECD depends on the electron capture cross section of the element, so sensitivity increases on-going from chlorine to bromine to iodine. In addition, since the XSD is a thermal electron emission detector, the temperature of the detector will affect the response ratios of the various halogens.

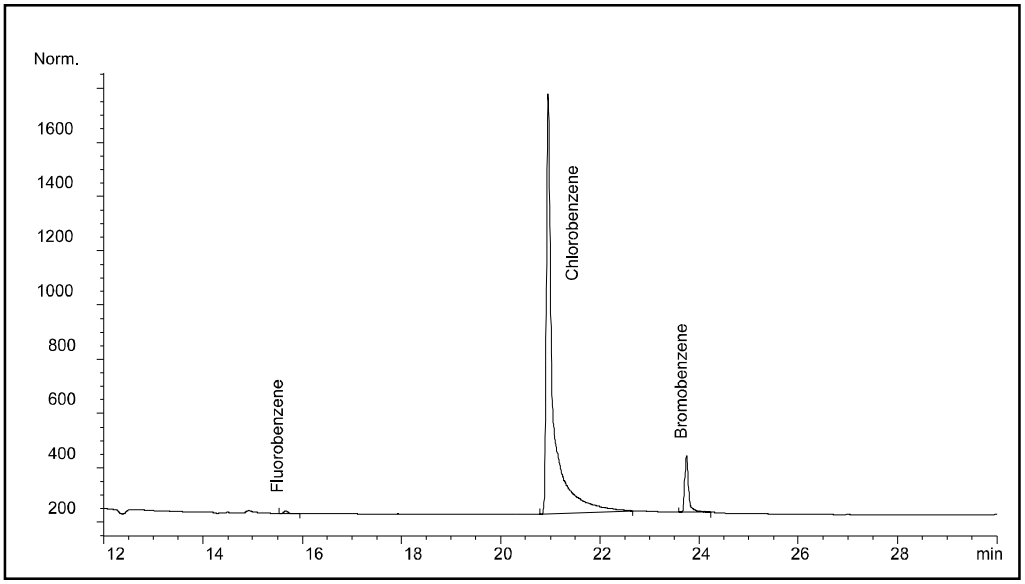

Figure 4. Chromatogram of Halobenzenes 100 ng of Each Component, Iodobenzene Not Detected

Figure 5 is a representative chromatogram of the USEPA Method 502.2 standard used in this study. The compounds used in this study are labeled. Figures 6, 7, 8, and 9 are response curves of the compounds used for this study. This linearity of the response is good for all the compounds. Figures 6, 7, and 8 show that the response tends to increase as the number of halogen atoms in the compound increases. Figures 7 and 8 also show that compounds with similar molecular weights and the same number of halogen atoms will have similar responses, e.g. all the dichlorobenzenes have an almost identical response curve.

Figure 9 illustrates the response differences between chlorinated compounds and the corresponding brominated compounds. In all cases, the brominated compounds have a much lower response than the chlorinated compounds verifying the results obtained from the monohalobenzene chromatogram.

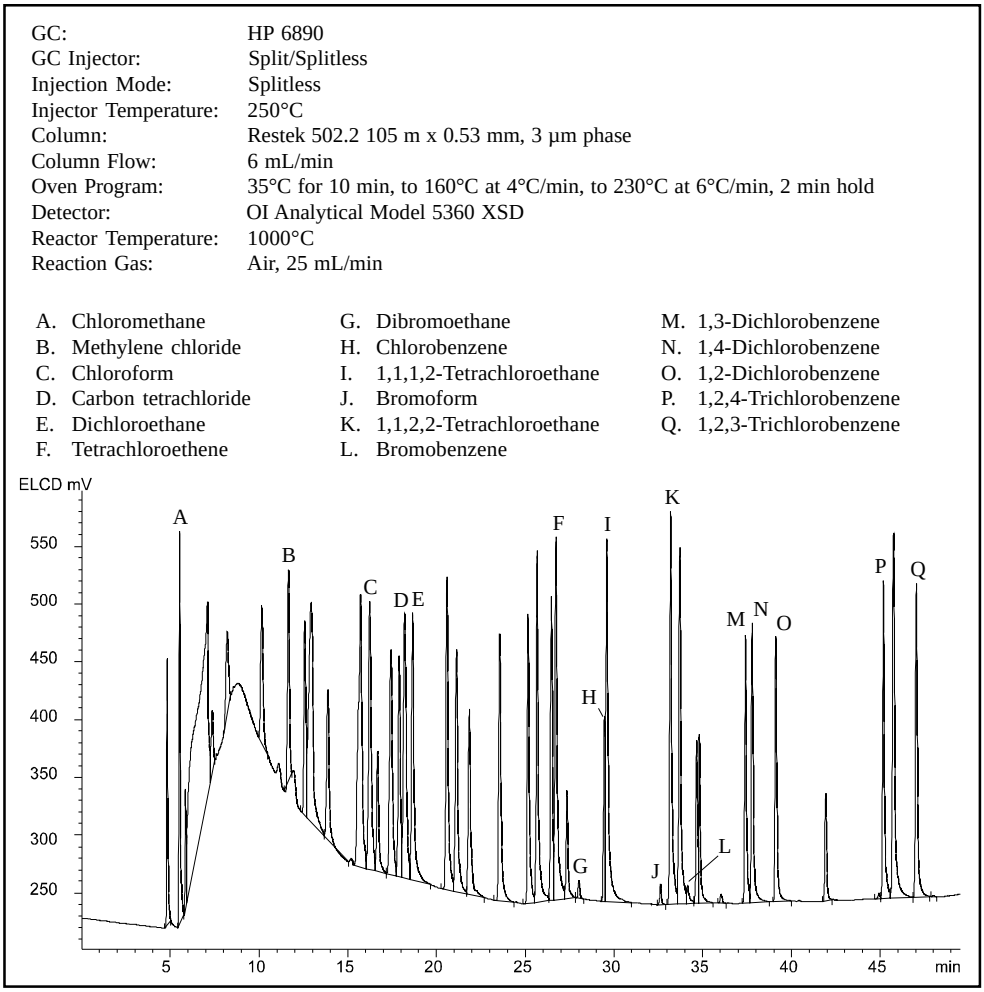

Figure 5. Chromatogram of Method 502.2 Standard, 500 pg of Each Component

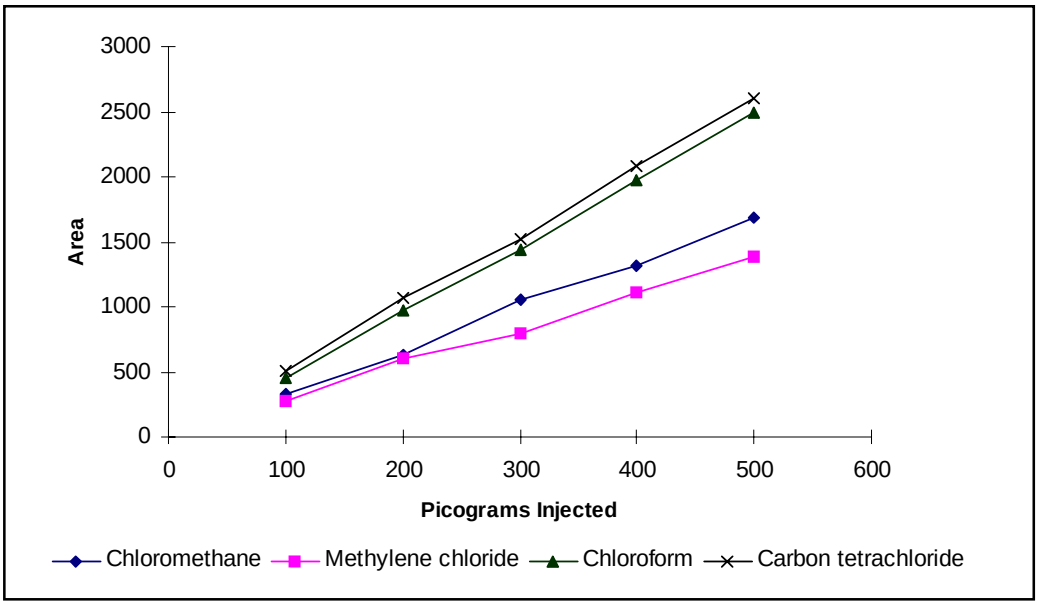

Figure 6. Response Curves of Chlorinated Methanes

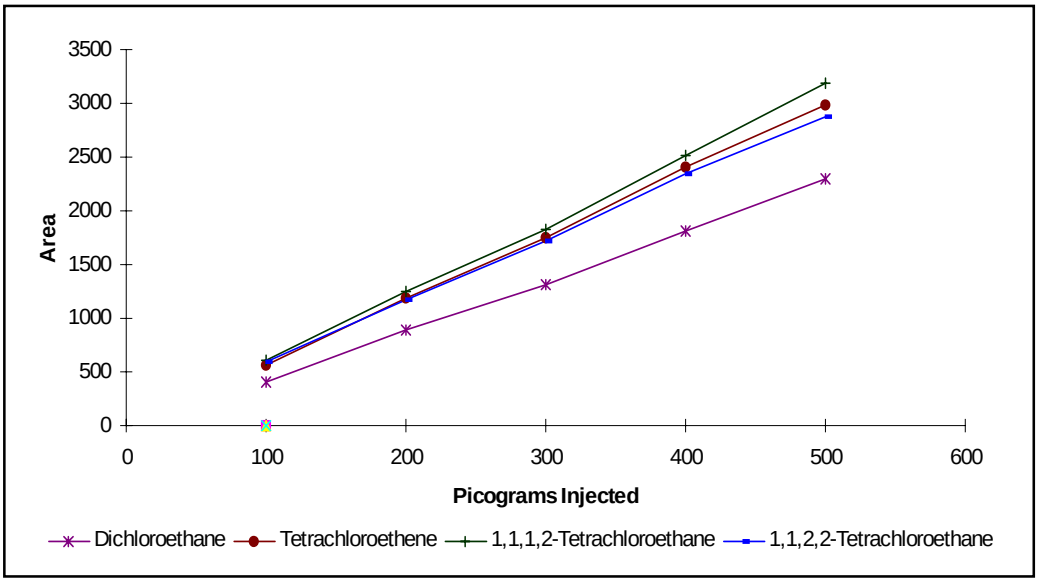

Figure 7. Response Curves of Chlorinated Ethanes and Ethene

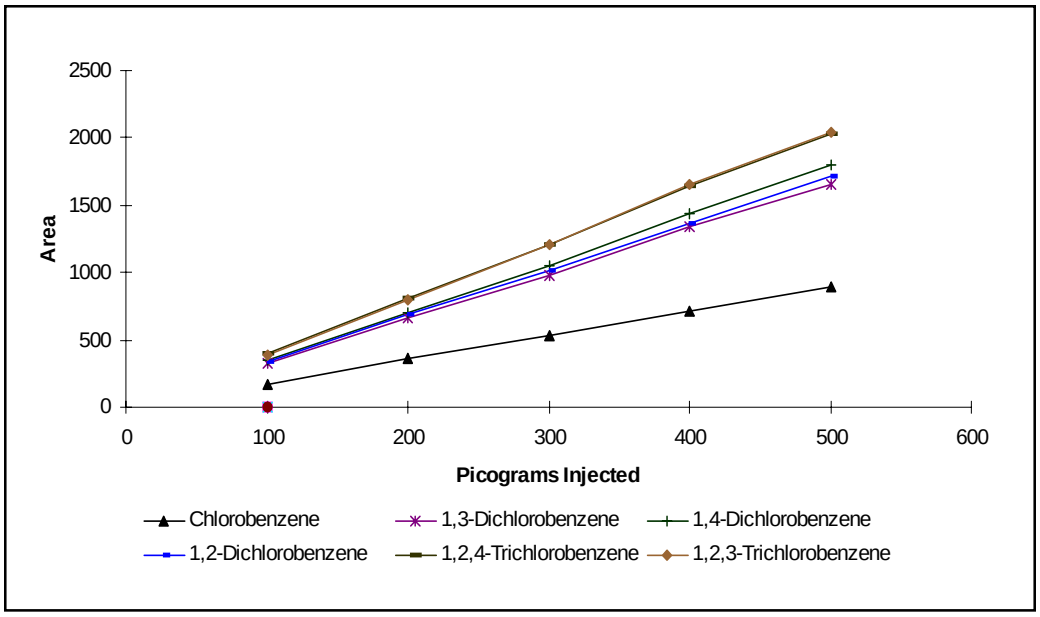

Figure 8. Response Curves of Chlorinated Benzenes

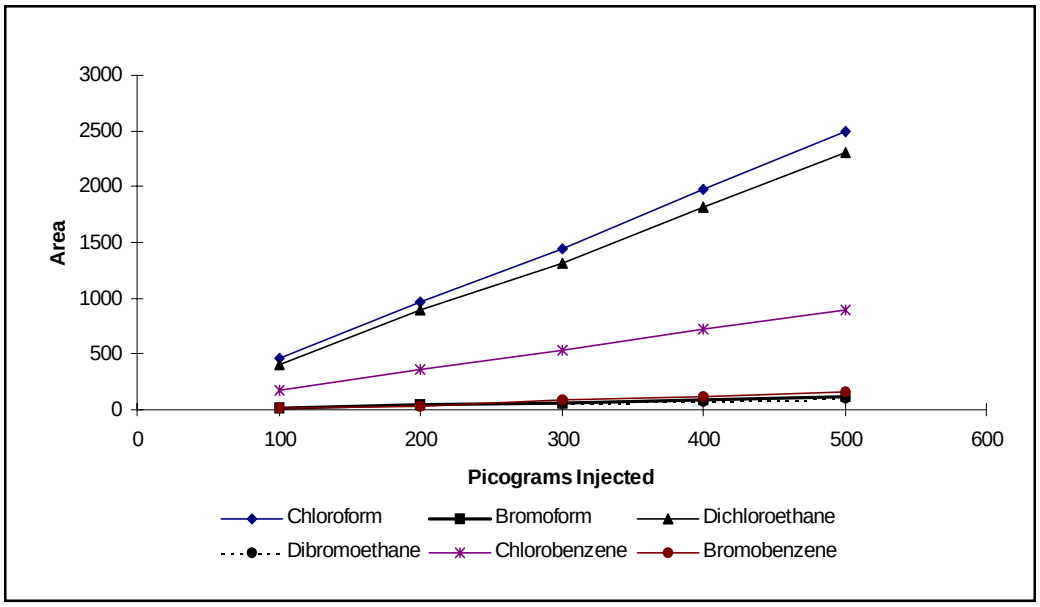

Figure 9. Response Curves of Chlorinated and Brominated Compounds

Table 1 lists the response factors for the compounds in this study. The response factor is calculated first in area counts per picogram of component, then as area counts per femtomole of component, and finally as area counts per femtomole of halogen. Several trends become apparent when examining the response per femtomole of halogen. First, compounds of similar structure and the same number of halogen atoms have a similar response factor. Second, the response factor tends to decrease with increasing halogen substitution. Finally, excluding chloromethane the molar halogen response factor for all the chlorinated compounds varied by less than a factor of two. The response factor for chloromethane is high because the formation of the stable carbene radical will tend to drive the elimination of HCl to completion.

Table 1. Detector Response

Compound	Area per Picogram Compound	Area per Femtomole Compound	Area per Femtomole Halogen
Chlorobenzene	1.8	15.9	15.9
1,2-Dichlorobenzene	3.4	23.4	11.7
1,3-Dichlorobenzene	3.3	22.6	11.3
1,4-Dichlorobenzene	3.6	24.8	12.4
1,2,4-Trichlorobenzene	4.1	22.6	7.5
1,2,3-Trichlorobenzene	4.2	23.0	7.7
Chloroform	5.1	42.5	14.2
Dichloroethane	4.7	47.5	23.8
Chlorobenzene	1.8	15.9	15.9
Bromoform	0.2	0.9	0.3
Dibromoethane	0.2	1.2	0.6
Bromobenzene	0.4	2.3	2.3
Chloromethane	3.4	67.3	67.3
Methylene chloride	2.7	32.1	16.1
Chloroform	5.1	42.5	14.2
Carbon tetrachloride	5.2	33.9	8.5
1,1,1,2-Tetrachloroethane	6.4	38.2	9.6
1,1,2,2-Tetrachloroethane	5.7	34.1	8.5
Tetrachloroethene	6.1	36.7	9.2

Conclusions

The XSD is a very selective detector for the analysis of halogenated compounds. The detector is most sensitive to chlorinated compounds, with brominated compounds approximately an order of magnitude lower in sensitivity and fluorinated compounds approximately a factor of 100 lower in sensitivity than the corresponding chlorinated compounds.

The XSD response is much less compound dependent than most other detectors. The detector response is primarily a function of the molar quantity of halogen present. Although the XSD does not display true equimolar response, a semiquantitative estimate of the chlorine content of an unknown compound may be obtained by using the response factor of a known compound. The deviations from equimolar response can be explained by considering the reaction chemistry. If there are more halogen atoms attached to a molecule, it is more difficult to eliminate all halogen. If a stable radical is formed, the response will tend to be higher than average.

P.O. Box 9010
College Station, Texas 77842-9010
Tel: (979) 690-1711 • FAX: (979) 690-0440 • www.oico.com