Using the Halogen Specific Detector (XSD™) as an Alternative to the ELCD in USEPA Methods

Application Note 16561101

Keywords
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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, to a lesser extent, 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 co-eluting compounds, including nonhalogenated interferences. A mass spectrometer may be used to identify co-eluting compounds, but in some cases, an MS does not have the sensitivity required for trace level analyses.

The Model 5360A Halogen Specific Detector (XSD™) was developed to address the need for a sensitive and selective detector for halogenated compounds. This detector operates by combusting the gas chromatograph (GC) column effluent in a stream of air. The combustion products of the halogenated compounds then react with alkali 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 selectively determined. Figure 1 illustrates this detector.

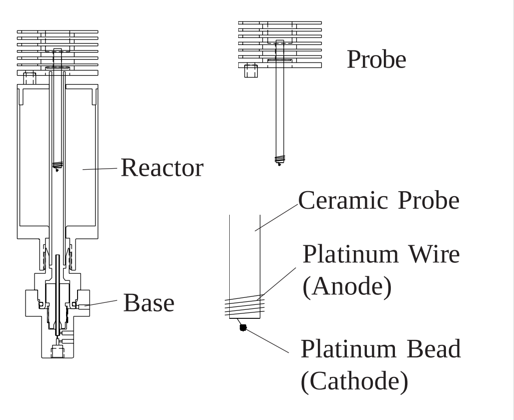


Figure 1. Model 5360A Halogen Specific Detector

This application note presents data comparing the performance of the XSD and ELCD for the analysis of pesticides and volatile organic compounds (VOCs), and it demonstrates some of the advantages that can be gained when using an XSD in USEPA methods.

Selectivity

Complex sample matrices present one of the most common problems associated with the analysis of environmental samples, particularly when analyzing for chlorinated pesticides. The resulting extracts typically contain an unusually high number of co-extractants as interferences. Figures 2 and 3 illustrate the selectivity of the XSD for halogenated compounds against a high petrochemical background.

Figure 2 is a chromatogram of a USEPA Method 608 pesticide standard with the concentration of the individual components varying between 100 and 600 picograms per microliter (ppb). Figure 3 is a chromatogram of the same standard solution with 10,000 ppm (1%) of diesel fuel spiked into the solution. There are only small baseline disturbances with the addition of the diesel fuel.

Food extracts present another challenging analysis in terms of co-eluting contaminants. Figure 4 is an ECD chromatogram of a garlic extract following Florisil cleanup. The presence of multiple sulfur co-extractives creates a complex ECD chromatogram, and it is impossible to discriminate between the target compounds and the background interferences. Figure 5 is an XSD chromatogram of the same extract. All of the interfering sulfur peaks have been eliminated, and the chlorinated pesticides are easily identified and quantitated.

GC:	Agilent 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:	1,000°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

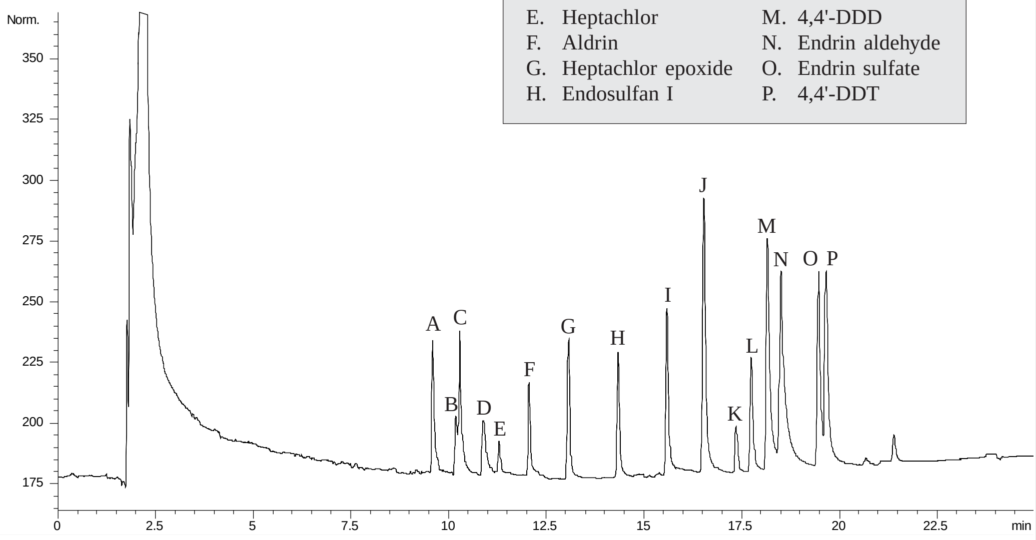


Figure 2. Chromatogram of Method 608 Standard in *n*-Hexane

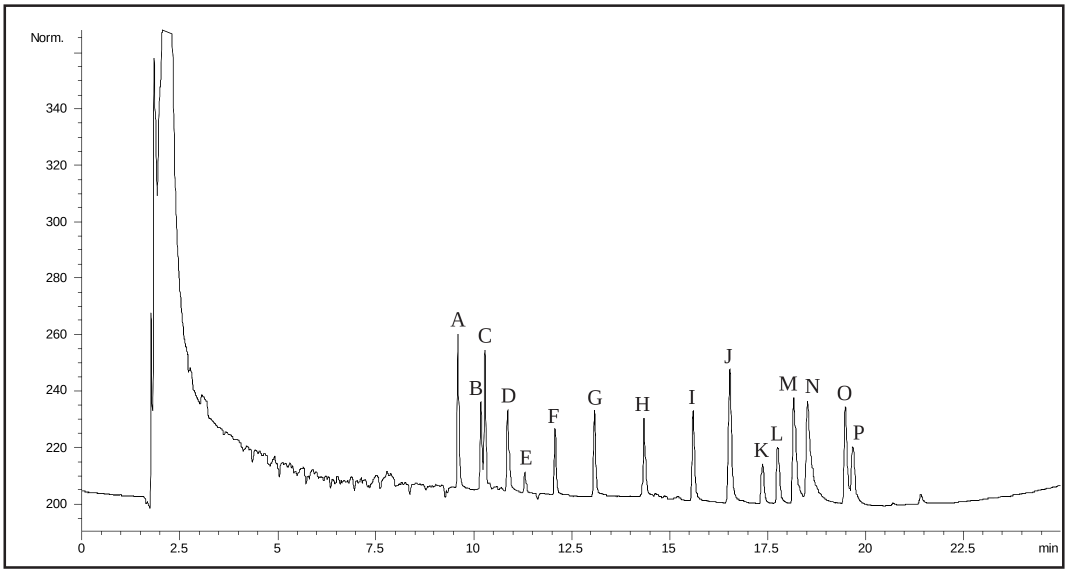


Figure 3. Chromatogram of Method 608 Standard in *n*-Hexane With 10,000 ppm Diesel Fuel Added (See Figure 2 for conditions.)

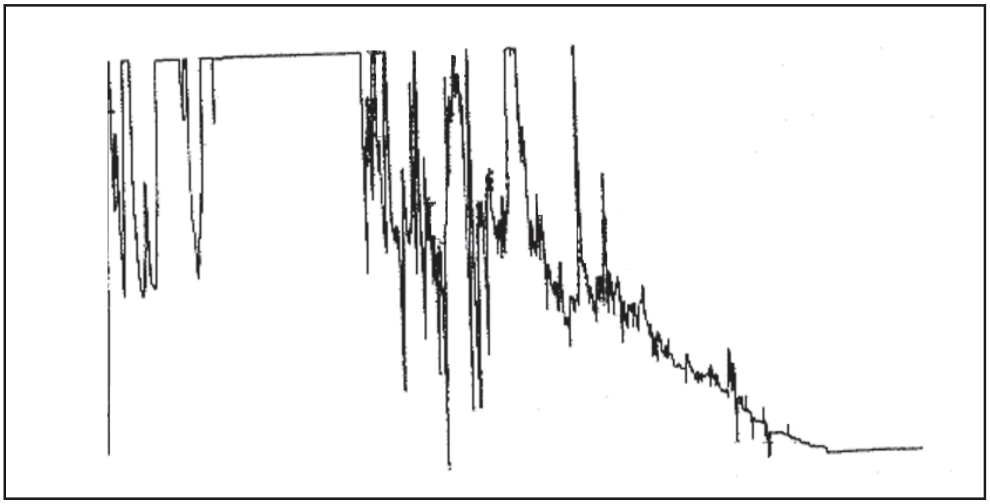
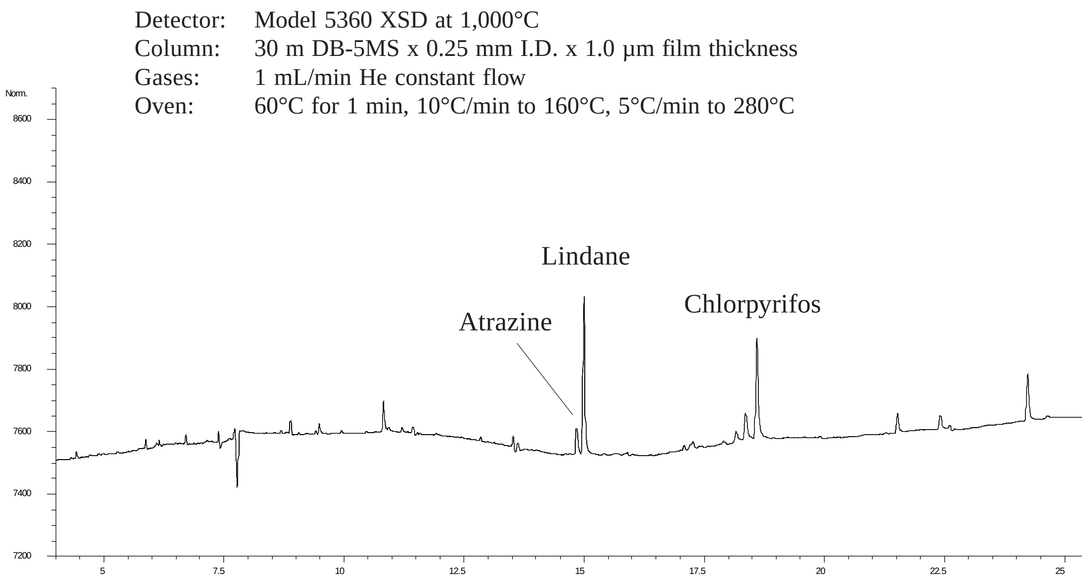


Figure 4. ECD Chromatogram of a “Worst Case” Garlic Extract Following Florisil Cleanup (1-µL injection, split 9:1)



Detector: Model 5360 XSD at 1,000°C
Column: 30 m DB-5MS x 0.25 mm I.D. x 1.0 µm film thickness
Gases: 1 mL/min He constant flow
Oven: 60°C for 1 min, 10°C/min to 160°C, 5°C/min to 280°C

Figure 5. Chromatogram of the Same “Worst Case” Garlic Extract Run on an OI Analytical Model 5360 Halogen Specific Detector (1-µL injection, split 9:1).

Compound Response

One fundamental question that must be considered when comparing the performance of two detectors is the response of the target compounds. Response curves were determined for the XSD and the ELCD by injecting five concentrations of a volatile organic standard (Method 502.2) into the GC (100 to 500 pg on column). The mean value of three replicate injections was used in constructing the response curves. Figure 6 is a representative ELCD chromatogram of the USEPA Method 502.2 standard used in this study with the compounds labeled. Figures 7, 8, 9, and 10 are the response curves from the XSD and the ELCD generated for this study. In all cases, the response curves for the two detectors were nearly identical, with no significant differences.

GC: Agilent 6890
GC Injector: Split/Splitless
Injection Mode: Splitless
Injector Temperature: 250°C
Column: Restek 502.2, 105 m x 0.53 mm, 3 µm phase
Column Flow: 6 mL/min
Oven Program: 35°C for 10 min, to 160°C at 4°C/min, to 230°C at 6°C/min, 2 min hold
Detector: OI Analytical Model 5320 ELCD

A. Chloromethane
B. Methylene chloride
C. Chloroform
D. Carbon tetrachloride
E. Dichloroethane
F. Tetrachloroethene
G. Dibromoethane
H. Chlorobenzene
I. 1,1,1,2-Tetrachloroethane
J. Bromoform
K. 1,1,2,2-Tetrachloroethane
L. Bromobenzene
M. 1,3-Dichlorobenzene
N. 1,4-Dichlorobenzene
O. 1,2-Dichlorobenzene
P. 1,2,4-Trichlorobenzene
Q. 1,2,3-Trichlorobenzene

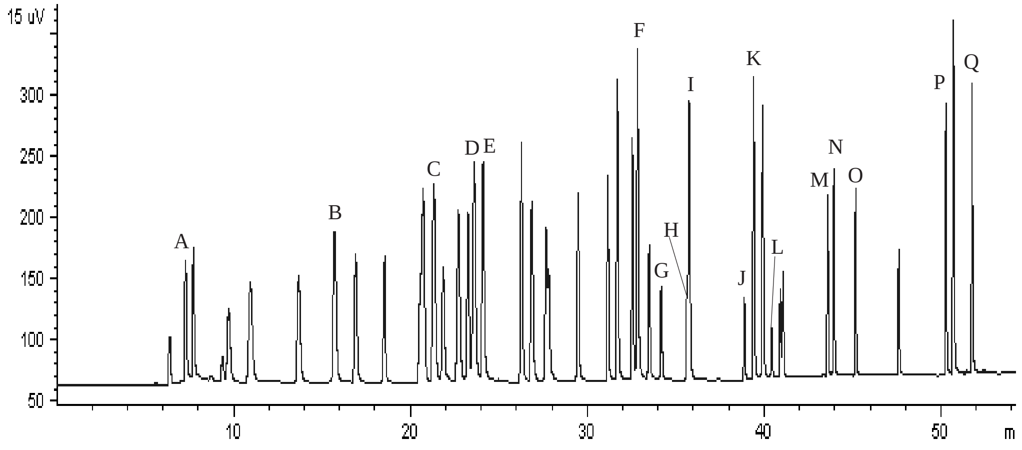


Figure 6. ELCD Chromatogram of Method 502.2 Standard, 500 pg of Each Component

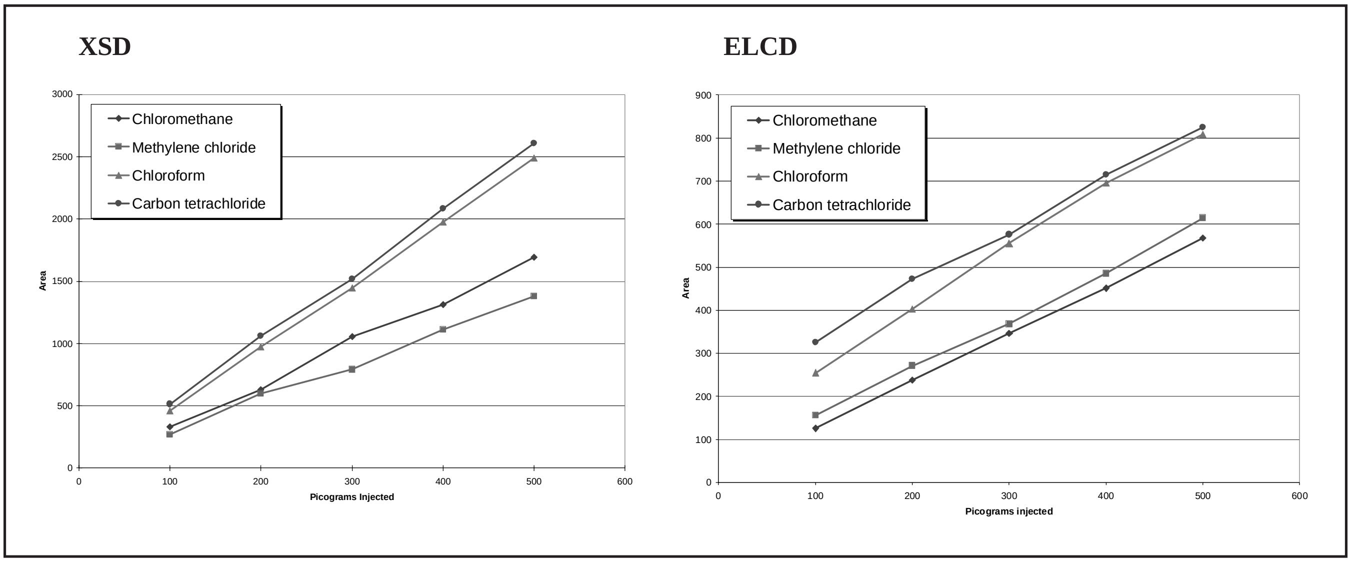


Figure 7. XSD and ELCD Response Curves for Chlorinated Methanes

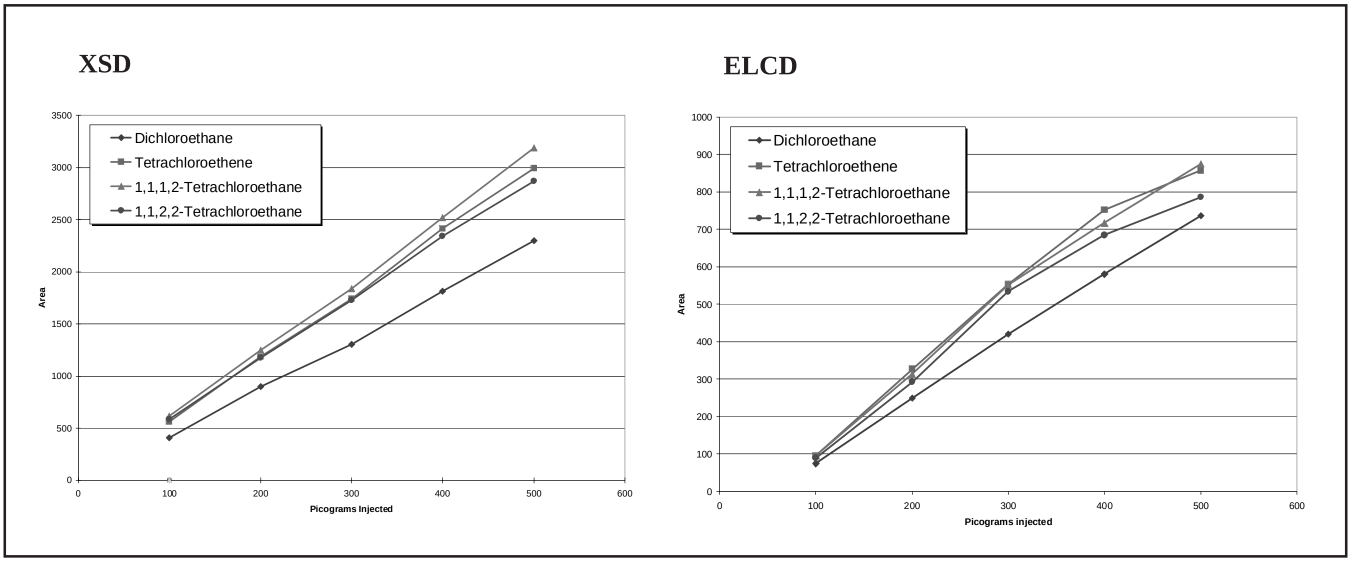


Figure 8. XSD and ELCD Response Curves for Chlorinated Ethanes and Ethene

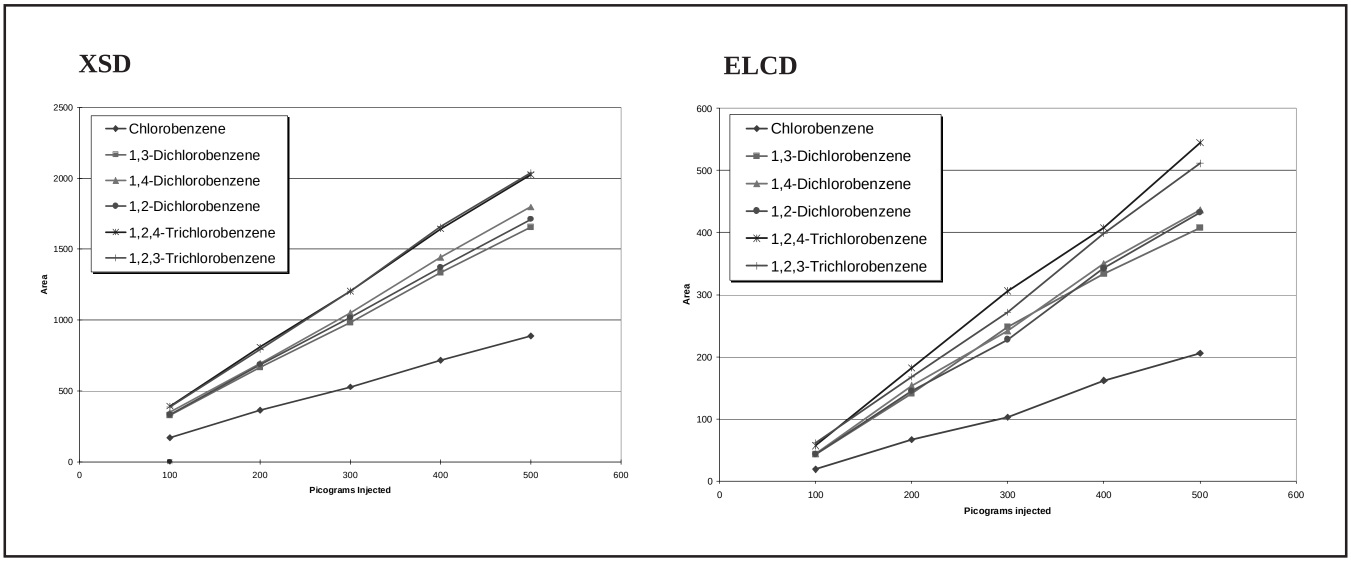


Figure 9. XSD and ELCD Response Curves for Chlorinated Benzenes

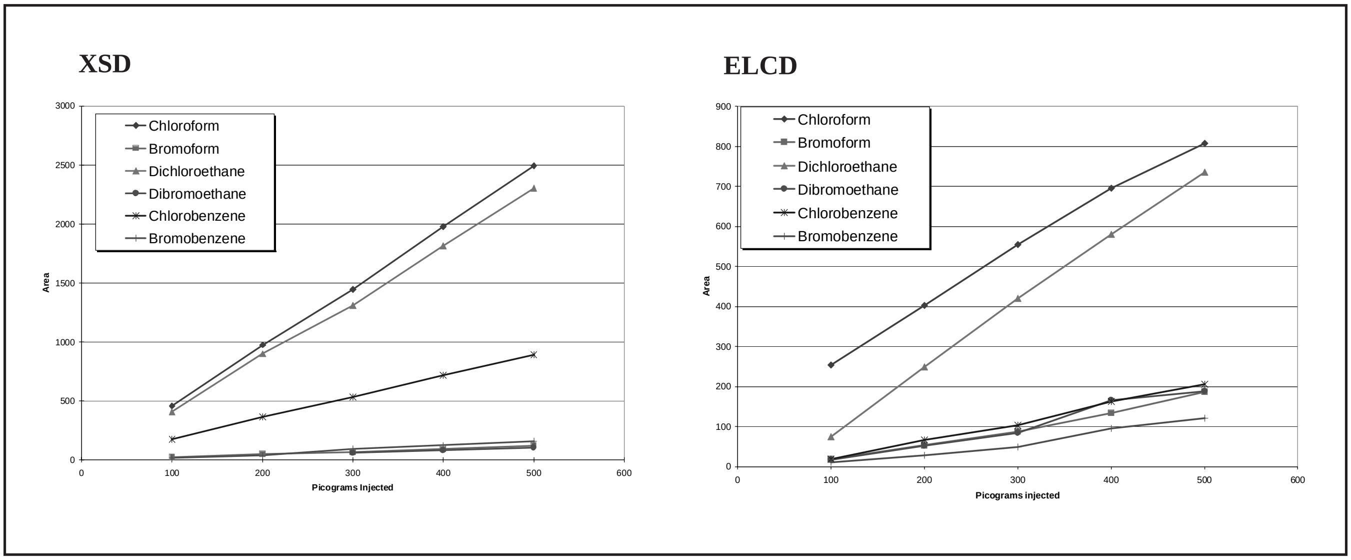


Figure 10. XSD and ELCD Response Curves for Chlorinated and Brominated Compounds

Table 1 lists the XSD and ELCD response factors for the compounds in this study. The response factors are calculated first in area counts per picogram of compound, then as area counts per femtomole of compound, and finally as area counts per femtomole of halogen.

Table 1. XSD and ELCD Response Factors

Compound	**Response per Picogram Compound**		**Response per Femtomole Compound**		**Response per Femtomole Halogen**	
	XSD	*ELCD*	*XSD*	*ELCD*	*XSD*	*ELCD*
Chloromethane	1.1	1.2	0.05	0.06	0.05	0.06
Methylene chloride	1.4	1.3	0.12	0.11	0.06	0.06
Chloroform	1.9	2.0	0.23	0.24	0.08	0.08
Carbon tetrachloride	1.7	2.2	0.27	0.34	0.07	0.08
1,1,1,2-Tetrachloroethane	1.9	1.6	0.33	0.27	0.08	0.07
1,1,2,2-Tetrachloroethane	1.9	1.5	0.32	0.25	0.08	0.06
Tetrachloroethene	1.8	1.6	0.30	0.27	0.08	0.07
Chlorobenzene	0.7	0.3	0.08	0.04	0.08	0.04
1,2-Dichlorobenzene	1.0	0.7	0.15	0.11	0.08	0.05
1,3-Dichlorobenzene	1.0	0.7	0.15	0.11	0.07	0.05
1,4-Dichlorobenzene	1.0	0.8	0.14	0.10	0.07	0.05
1,2,4-Trichlorobenzene	1.2	0.9	0.22	0.17	0.07	0.06
1,2,3-Trichlorobenzene	1.2	0.9	0.23	0.16	0.08	0.05
Chloroform	1.9	2.0	0.23	0.24	0.08	0.08
Bromoform	0.1	0.3	0.03	0.07	0.01	0.07
Dichloroethane	1.7	1.3	0.15	0.11	0.08	0.06
Dibromoethane	0.1	0.3	0.02	0.06	0.01	0.03
Chlorobenzene	0.7	0.3	0.08	0.04	0.08	0.04
Bromobenzene	0.05	0.18	0.01	0.03	0.01	0.03

Several trends become apparent on both detectors when examining the various responses.

- *Response factor tends to increase with increasing halogen substitution*. For example, the methane and benzene series show an increase in response with the addition of extra chlorines (response per picograms or femptomole of compound).

- *Compounds of similar structure and with the same number of halogen atoms have a similar response factor.* For example, the three dichlorinated benzenes all have comparable response factors, as do the three tetrachlorinated ethanes (response per picogram or femptomole of compound).

- *Response factors on the XSD are slightly higher than on the ELCD*, indicating a greater sensitivity for chlorine.

- *Brominated compounds had a significantly lower response than their chlorinated counterparts on both detectors.* However, even at these lower response levels, these compounds can still be analyzed as specified in most USEPA VOC methods.

- *Both detectors demonstrated approximately equimolar response to the chlorinated compounds*, as indicated by the response per femtomole of halogen.

- *There is approximately one order of magnitude sensitivity decrease from chlorine to bromine on the XSD.*

Calibration

Calibration curves were generated for all 17 chlorinated volatile compounds looked at in this study. The calibration range was from 50 pg to 50 ng on column, which is the equivalent of 10 ppt to 10 ppb in a 5-mL water sample. All of the ELCD calibration curves were linear throughout the entire range, with linear R^2 values ranging from 0.9966 for chloromethane to 0.9997 for methylene chloride and chloroform. The XSD was linear up to approximately 2 ng on column, with comparable R^2 values. For concentrations above 2 ng the calibration curves became nearly quadratic as expected with the XSD. Figures 11 and 12 illustrate representative calibration curves for two volatile chlorinated compounds using the ELCD and XSD.

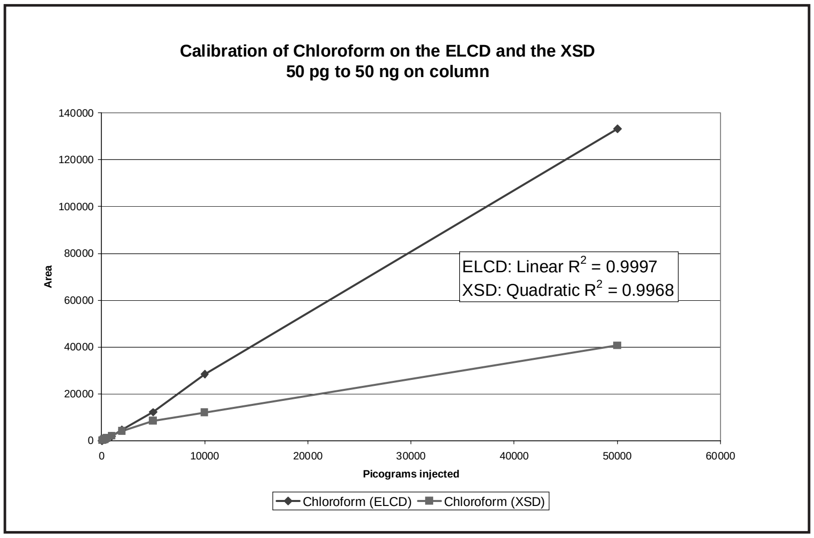


Figure 11. Calibration Curves for Chloroform on the ELCD and XSD

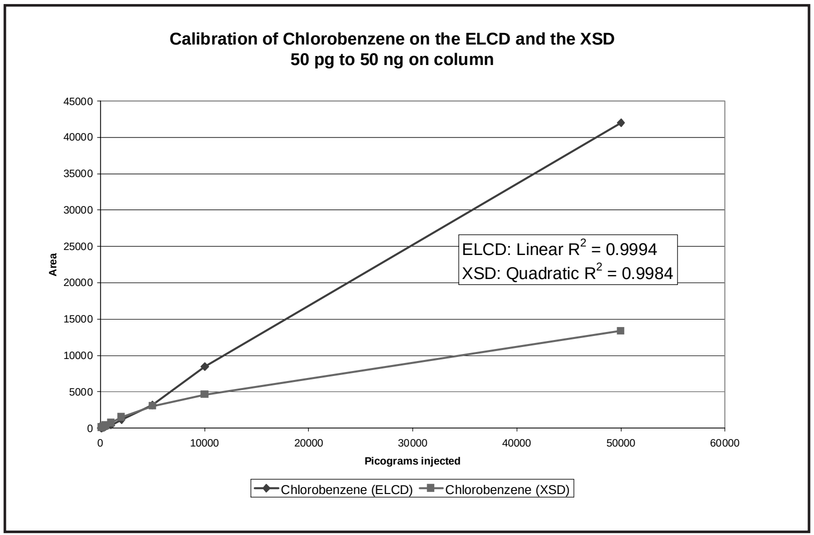


Figure 12. Calibration Curves for Chlorobenzene on the ELCD and XSD

Chromatography

One of the known limitations of the ELCD is tailing peaks. The tailing is noticeably reduced, and the peak shape improved significantly using the XSD, as illustrated by Figure 13. The XSD will exhibit increased tailing at the higher concentration ranges (>50 ng).

The trade-off for improved peak shape on the XSD is an early baseline disturbance from the water and methanol (MeOH) in VOA standards. Figure 14 is a chromatogram of a 100 ppt Method 502.2 standard run on the XSD using a purge-and-trap sample concentrator. The large “hump” maximizing at 10 minutes results from the presence of water and MeOH in the sample. This distrubance is more pronounced in the XSD than the ELCD because the XSD is less selective than the ELCD (>10^2). The water/methanol peak co-elutes with four or five of the six light gases and makes it difficult to quantify them at low levels. None of the nongas components are affected.

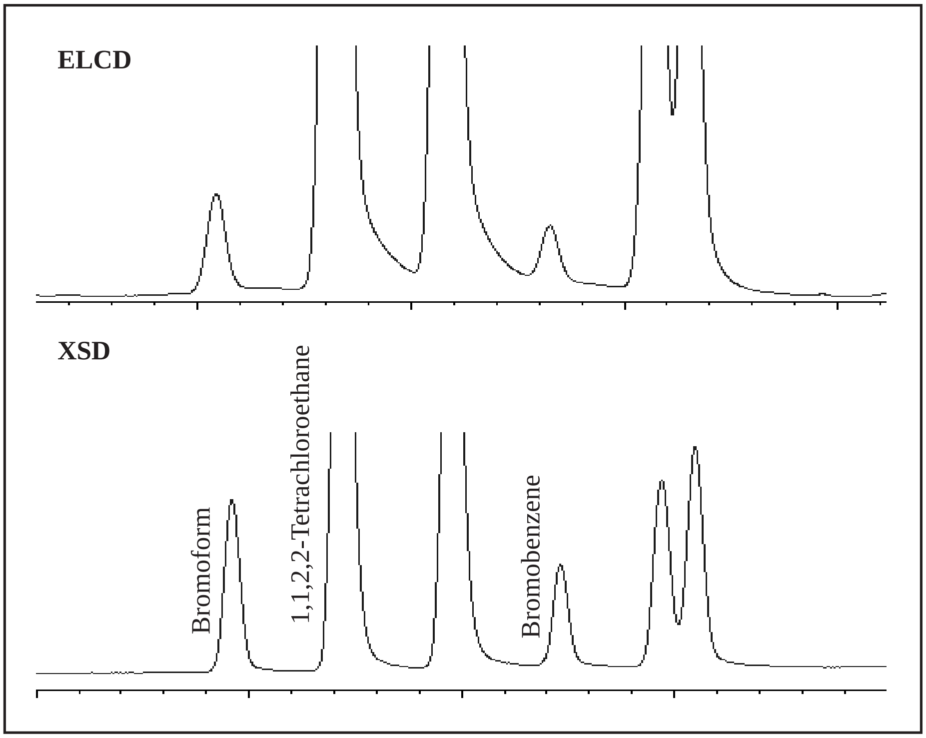


Figure 13. Chromatograms from the ELCD and the XSD, Showing Reduced Tailing and Improved Peak Shape with the XSD (Splitless, 1-µL injection of a 500 ppb 502.2 standard)

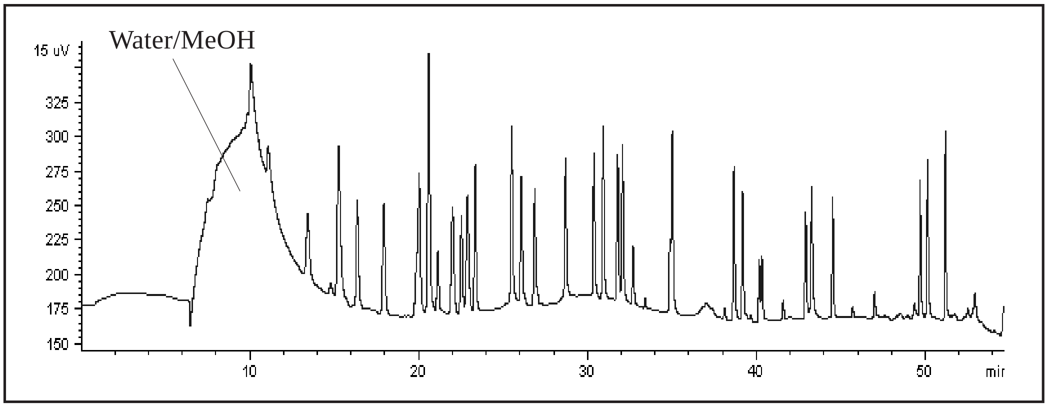


Figure 14. Chromatogram of 100 ppt Method 502.2 Standard Run on the XSD Using a Purge-and-Trap Sample Concentrator

Relative Halogen Sensitivity

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. The injection of the halobenzene standard (Figure 15) 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 detector sensitivity increases 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.

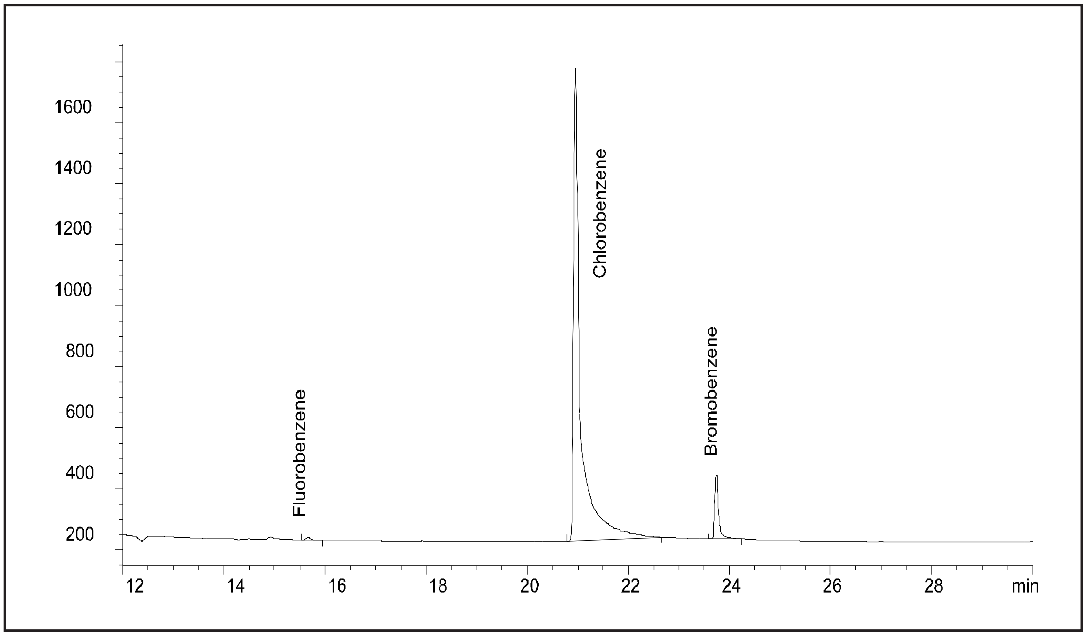


Figure 15. Chromatogram of Halobenzenes, 10 ng of Each Component, Iodobenzene Not Detected

Conclusions

The XSD is a very selective detector for the analysis of halogenated pesticides, and it is not subject to interference from co-extractants present in complex matrices such as environmental and food samples.

Both detectors display similar trends with regard to response factors, with the XSD response factors slightly higher than on the ELCD. Response factors tend to increase with increasing halogen substitution; compounds of similar structure and with the same number of halogen atoms have a similar response factor; and both detectors demonstrate approximately equimolar response to the halogenated compounds. The XSD is most sensitive to chlorinated compounds, with brominated compounds approximately one order of magnitude lower in sensitivity.

The additional advantages of improved chromatography and low maintenance make the XSD an excellent alternative for the analysis of halogenated pesticides and volatiles by USEPA methods.

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