O·I·Analytical

Analysis of Chlorinated Pesticides Using Gas Chromatography with a Halogen Specific Detector

Application Note 10790798

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Introduction

One of the common environmental analytical problems is the determination of chlorinated pesticides in a variety of sample matrices. Chlorinated pesticides have been widely used and occur in many areas. Some of the common analyses of chlorinated pesticides include foods, drinking water, waste water, industrial sites, and waste sites. The sample matrix and the sample preparation for the analysis of the chlorinated pesticides vary greatly, but there are some common requirements for the detection of the pesticides in all these types of matrices. In most cases, the pesticides are present in low concentration, especially in foods, so the detector must be very sensitive. In addition, most of the sample matrices listed above are complex with many potentially interfering compounds, so the detector must also be highly selective for halogenated compounds.

Chlorinated pesticides are commonly analyzed using gas chromatographic methods. The detectors commonly used are the electron capture detector (ECD), the mass spectrometer (MS), and the electrolytic conductivity detector (ELCD). The most commonly used detector for this analysis is the electron capture detector. The ECD is the most sensitive detector in common use and is more sensitive to halogenated compounds than to aliphatics, but the ECD does have some significant limitations. The ECD is a nonlinear detector, so the calibration range for the detector is relatively narrow. The response of the ECD is also very compound dependent, so equal masses of different analytes give widely varying responses. Finally, the ECD is subject to significant interferences. Any compound with a significant electron capture cross section will produce a response on an ECD. Oxygenated, nitrogenous, and other heteroatomic compounds as well as high concentrations of hydrocarbons will produce a response on the ECD. Air or water passing through the column will affect the sensitivity of the ECD.

The mass spectrometer is a detector that is growing in popularity for the analysis of the chlorinated pesticides. The major advantage of the mass spectrometer is the ability to obtain a mass spectrum of the compounds of interest when operating in full scan mode. The main disadvantage to operating in scan mode is the lack of sensitivity compared to a conventional GC detector. The sensitivity of the mass spectrometer may be increased by operating in selected ion monitoring (SIM) mode, but the confirmation of identity by library matching is lost. Sensitivity for trace components is reduced when there is a co-eluting major component. The ionization efficiency is proportional to the number of atoms in the source,

so if a major component and a trace component are in the source simultaneously, the major component will be preferentially ionized. The initial method development is more complex than using conventional detectors, especially when SIM mode is used. This requires a highly skilled operator. In addition, there is more performance verification data required than with conventional detectors, for both initial setup and continuing performance verification.

The electrolytic conductivity detector is not as sensitive as the ECD, but it is a more selective detector. The ELCD pyrolyzes the organics in a GC effluent, and the pyrolyzed products are passed through a solvent. The change in the conductivity of the solvent is measured to determine if a halogenated species has passed through the GC. The major disadvantage of the ELCD for pesticide analysis is that it is a relatively high maintenance detector. The reaction tube requires periodic replacement, the resin cartridges must be changed, and the cell must be cleaned regularly. There are also some interfering compounds that will produce peaks. These are generally compounds such as phthalates which liberate carbon dioxide during pyrolysis and will change the conductivity of the solvent.

OI Analytical's new detector, the halogen specific detector (XSD™), has been developed to address the limitations of the current generation of pesticide detectors. The XSD operates as a thermal electron emission detector. The detector is shown in Figure 1. The major component of the detector is a probe consisting of a platinum bead and a platinum coil mounted on a ceramic probe and a high temperature reactor. The GC column effluent is combusted in a stream of air at 1000° to 1100°C. The combusted effluent is passed over the bead, which has been sensitized with alkali metal atoms released from the ceramic. The halide species in the combusted effluent react with the alkali metal atoms on the surface of the bead and an increase in thermal electron emission results. By measuring the electron emission current, the mass of halogen reacting with the probe may be determined and the concentration of the halogenated species determined.

The XSD offers several advantages over other detectors used for the analysis of chlorinated pesticides. The XSD is less subject to interferences than the other detectors. The XSD will give a peak if large masses of hydrocarbons are present, but significant peaks are observed only if the mass of hydrocarbon is greater than 1 microgram. For a significant detector response at typical GC masses, the molecule must contain one or more halogen atoms. The molar sensitivity to halogens is Cl > Br > F >I, with the molar sensitivity decreased by approximately an order of magnitude between each halogen. The response depends primarily on the mass of halogen present, so there is less compound dependence of the response than there is with an ECD. The XSD response is somewhat compound dependent, but at higher temperatures the compound dependence is reduced. There is no radioactive source as in an ECD, and the linear range of the XSD is wider than most ECDs.

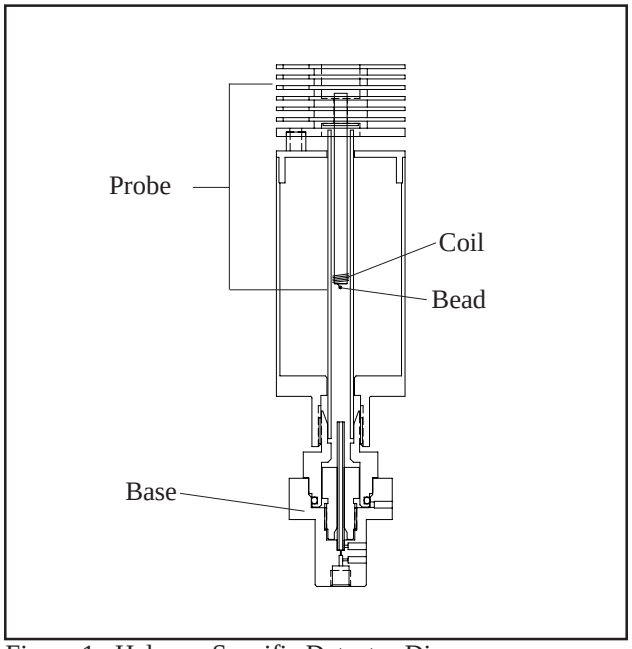

Figure 1. Halogen Specific Detector Diagram

Results and Discussion

Figures 2 and 3 illustrate the selectivity of the XSD. Figure 2 is an XSD chromatogram of a 16-component Method 608 chlorinated pesticide standard. The individual components of the mixture are present at levels ranging from 100 to 600 picograms of compound. Figure 3 is a chromatogram of the same sample spiked with 10,000 parts per million diesel. The response for some of the later eluting compounds is lower in the diesel spiked mixture and the baseline between the solvent peak and the first pesticide is noisier, but there are no interfering peaks that can be attributed to the hydrocarbons and sulfur compounds in the diesel. Other detectors would have detected a number of interfering peaks.

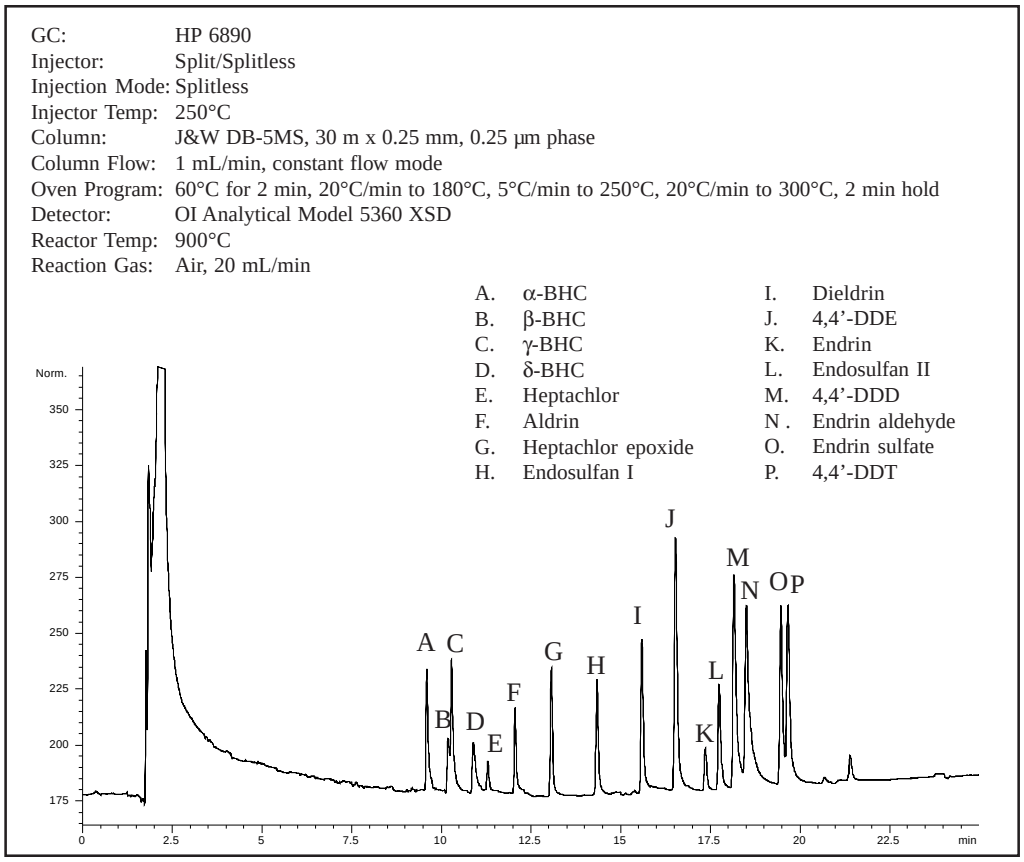

Figure 2. Method 608 Standard in *n*-Hexane

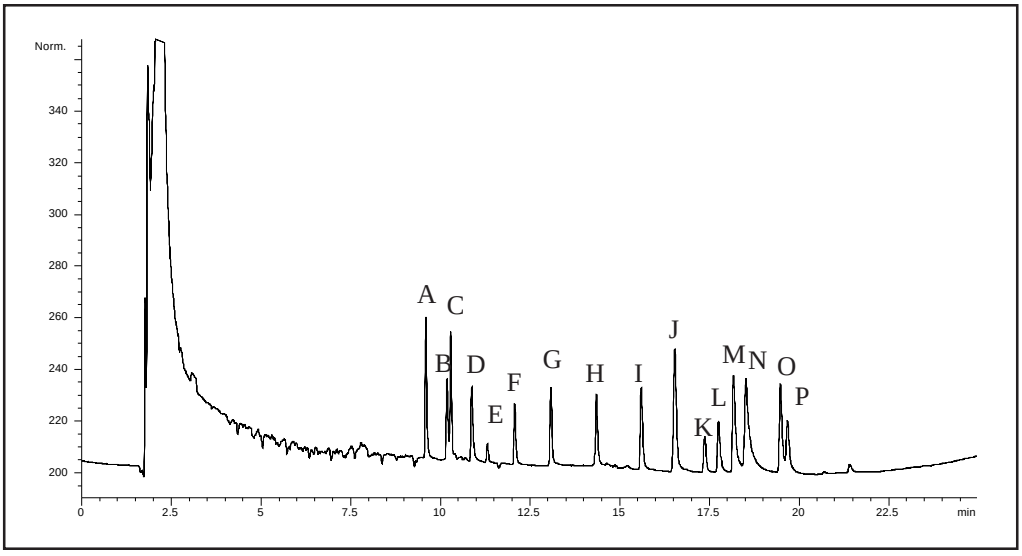

Figure 3. Method 608 Standard in *n*-Hexane with 10,000 ppm Diesel Fuel Added (same conditions as Figure 2)

The response of the XSD to the chlorinated pesticides is typically linear from 10 picograms of pesticide up to 1000 picograms of pesticide. Figures 4 and 5 are the response curves of gamma - BHC and heptachlor epoxide from 10 picograms to 1500 picograms. The response is linear up to 1000 picograms, then begins to decrease at higher concentrations. At high halogen concentrations the response of the XSD fits a second order curve well. Figures 6 and 7 are response curves of heptachlor epoxide and 4,4'-DDE demonstrating excellent linearity out to 1000 picograms.

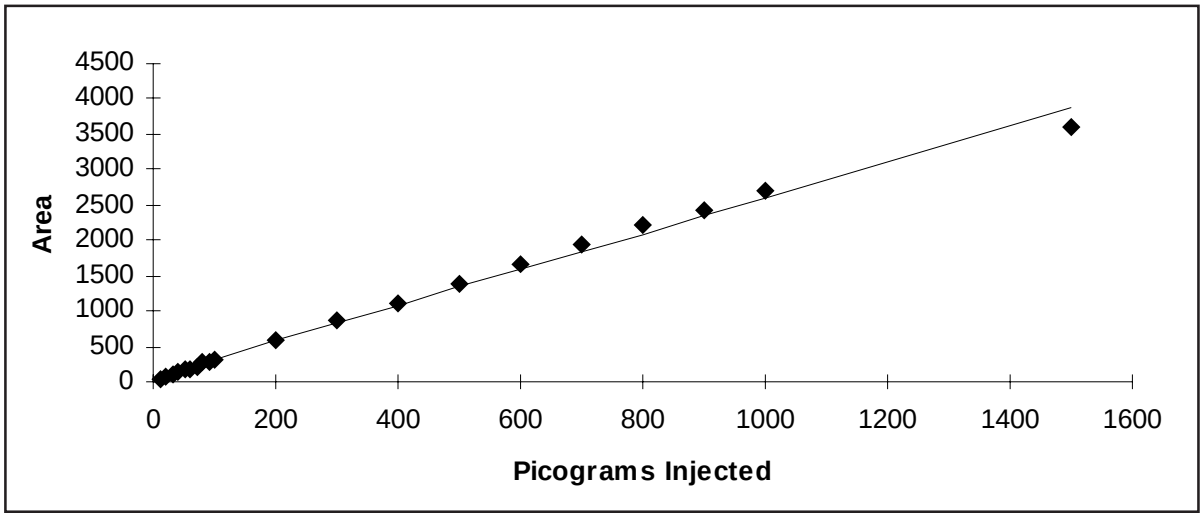

Figure 4. Response Curve for γ-BHC, 0–1500 pg

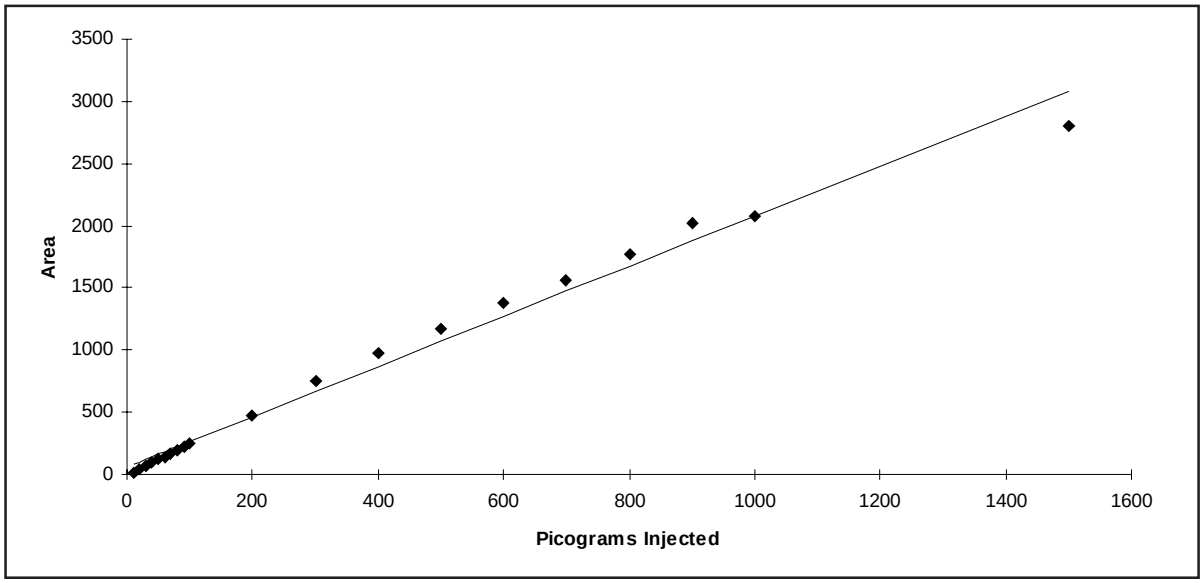

Figure 5. Response Curve for Heptachlor Epoxide, 0–1500 pg

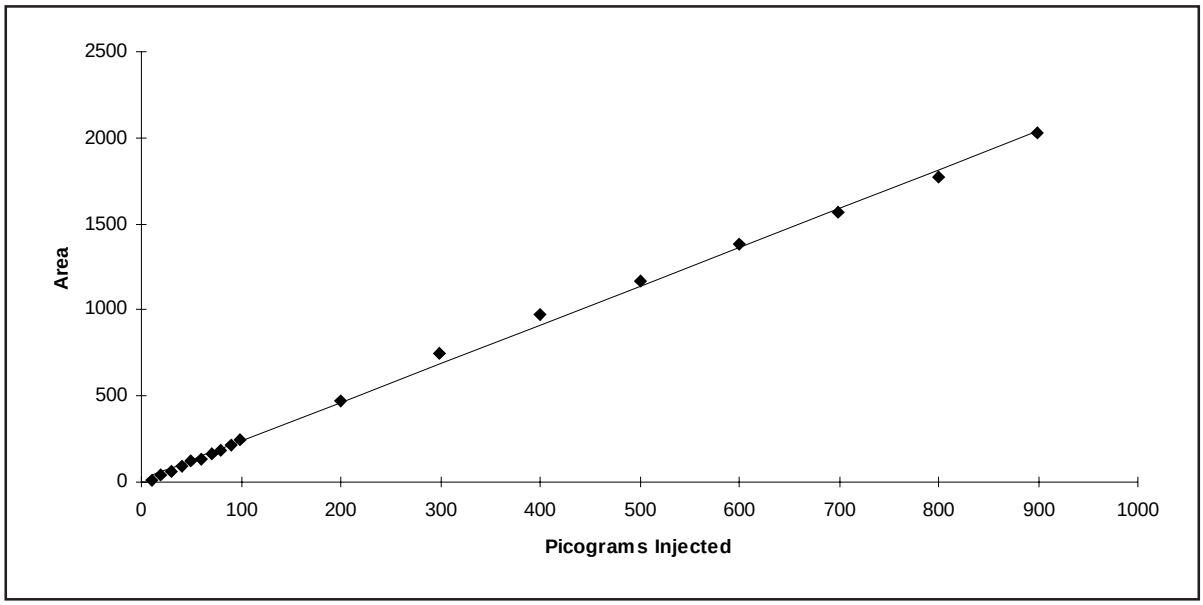

Figure 6. Response Curve for Heptachlor Epoxide, 0–1000 pg

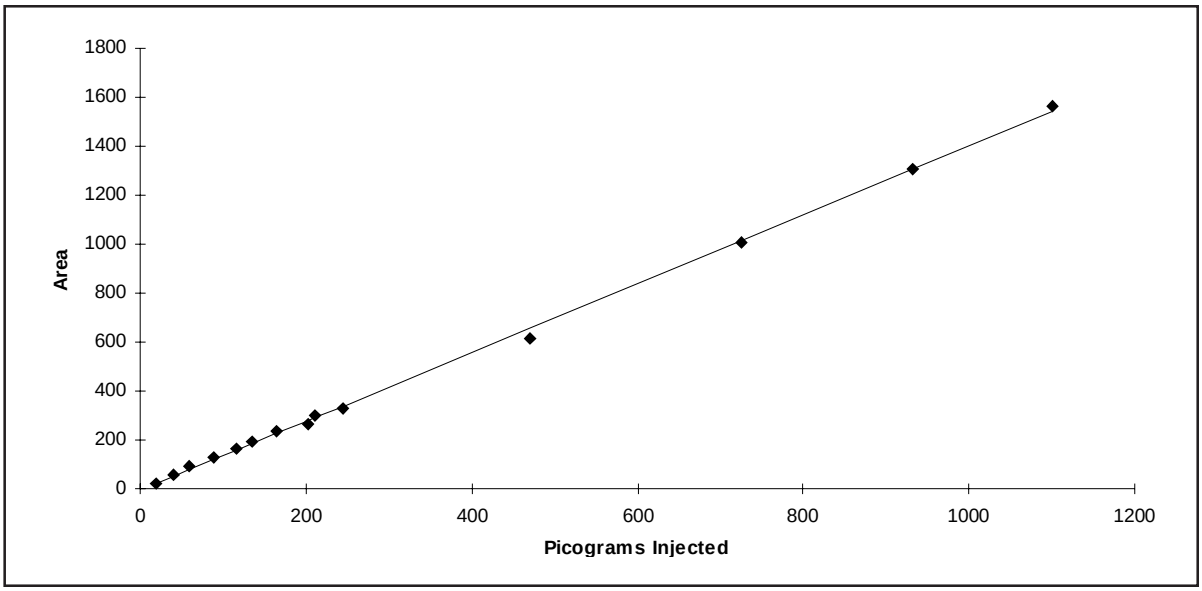

Figure 7. Response Curve for 4,4'-DDE, 0–1000 pg

Figures 8 and 9 show the compound dependence of the response of the XSD. These figures are response curves for 4,4'-DDT. 4,4'-DDT has a lower response at a given mass than 4,4'-DDE (see Figure 7). Note that even though 4,4'-DDT has a lower response per picogram the linear range for this compound is also larger.

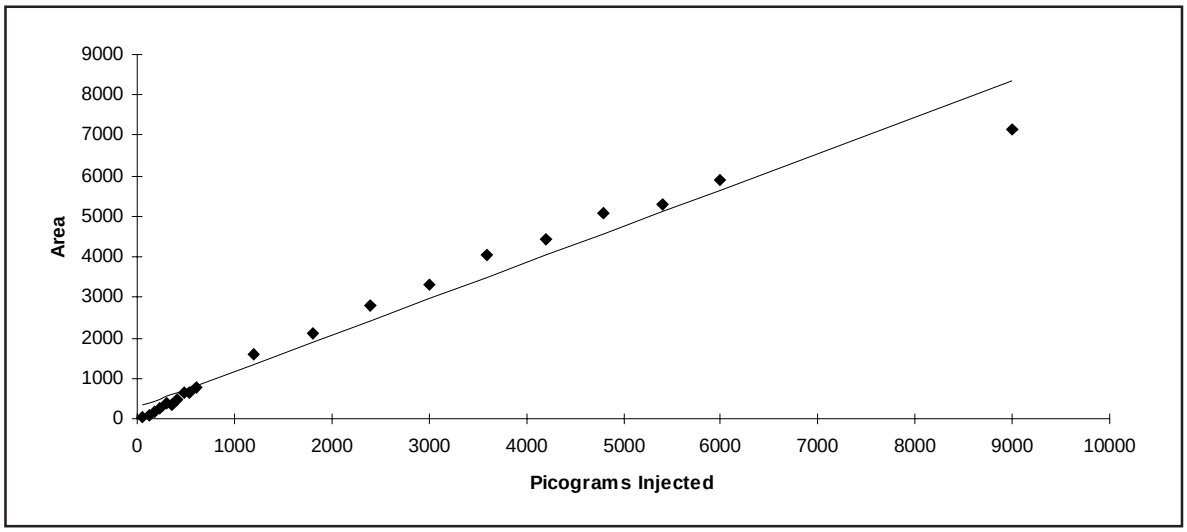

Figure 8. Response Curve for 4,4'-DDT, 0–9000 pg

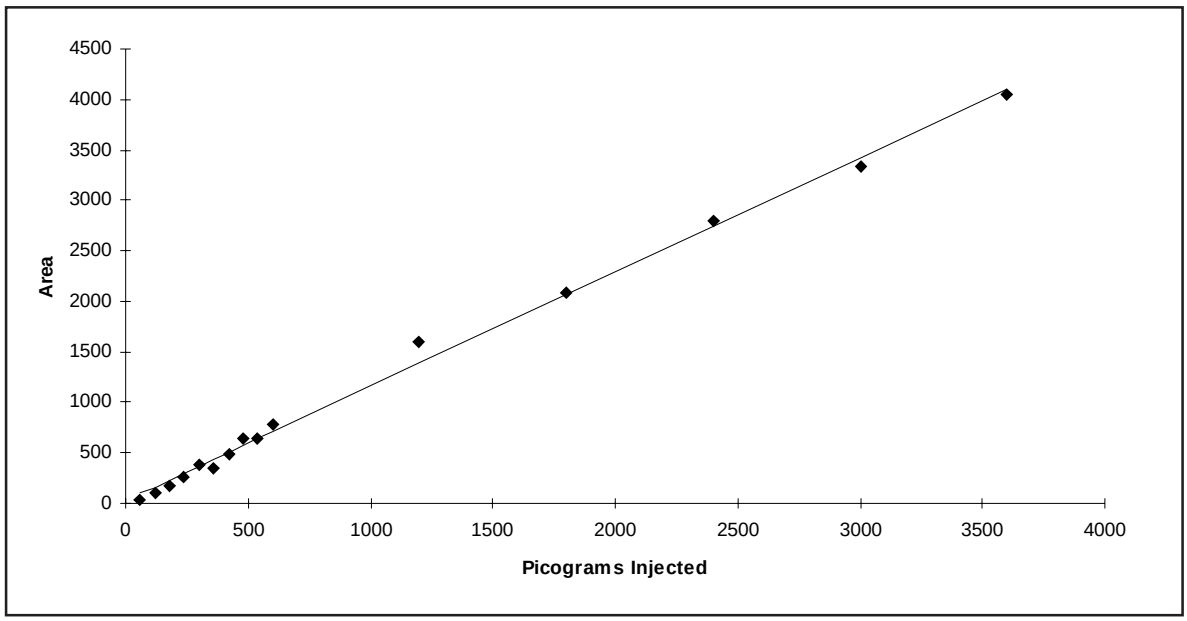

Figure 9. Response Curve for 4,4'-DDT, 0–3600 pg

Conclusion

The OI Analytical Model 5360 Halogen Specific Detector (XSD) is an excellent detector for chlorinated pesticides. The XSD has fewer interferences than the ECD, ELCD, and the mass spectrometer. The response for the XSD is also less compound dependent than the ECD. The linearity of the detector is excellent over at least three orders of magnitude for most compounds.

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