O·I·Analytical

Application Note 03570194

Introducing an Improved Electrolytic Conductivity Detector for Gas Chromatographic Analysis of Pesticides

Keywords
ELCD
Electrolytic Conductivity Detector
Gas Chromatography
Pesticides

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Objective

Pesticide analysis by gas chromatography (GC) can be impeded when analyzing unclean samples, particularly multiresidue extracts. If the detector used is not a compound-class selective detector, any species present can appear on a chromatogram. This limits the detector's ability to provide meaningful information, the response due to the matrix may be greater than or co-elute with the response of the desired analyte.

The electrolytic conductivity detector (ELCD) is exceptionally well suited for pesticide analysis because of its selectivity. It is capable of eliminating much of the matrix response, allowing unimpeded identification of the desired analyte. While the detection mechanism of the ELCD is relatively simple, ELCDs are not regarded as particularly user friendly. This perception is due in part to the time-consuming maintenance requirements of the ELCD and to ambiguity in setting controls (e.g., solvent flow rates, temperatures).

In this study, we introduce a technologically-advanced ELCD. The new Model 5220 ELCD (5220) has an input filter that removes high-frequency noise while still registering the analyte's signals. This feature produces better signal-to-noise ratios. Because this ELCD is specifically designed for capillary columns (packed columns may be used with an optional base), packed-to-capillary column adapters are not necessary. The ELCD's digital input controlling system provides accurate and precise control of parameter settings.

The chromatographic performance of the ELCD is demonstrated by identifying several pesticides in various sample matrices. Additionally, the ELCD was used in a dual column, dual detector (with an electron capture detector (ECD)) GC system.

Introduction

In GC pesticide analysis, interferences due to matrix extract are easily overcome by employing a selective detector such as an ELCD. The 5220 operates on the same principles as OI Analytical's previous ELCD[1] but contains several features that enhance performance and ease of use. The new ELCD has three modes of operation that are based on chemical characteristics and electronic signal-handling functions: halogen (X), nitrogen (N), and sulfur (S). In each mode, the compound of interest is oxidized or reduced to the desired reaction product in a high-temperature reaction tube. The reaction product is then carried to the detection cell, which has a continuously running flow of deionized solvent. When the reaction product comes in contact with the solvent, a portion of the

ionizable gas dissolves into the liquid. This increases the electrolytic conductivity of the mixture, which in turn is measured by two electrodes that constantly monitor the mixture's conductivity.

The 5220 is comprised of three primary components: the reactor assembly, the cell-solvent assembly, and the 5200 Detector Controller (Figure 1). The reactor assembly (Figure 2) includes the reactor, reactor base, catalytic reaction tube, and vent valve. The manifold serves as the source for either hydrogen or air reaction gas, which is directed into the bottom of the reactor to the column-reaction tube interface. The base is designed to directly accept any size of fused-silica capillary column (0.53-mm I.D. or less) without needing special adapters. The reaction gas (added at the column exit) acts as the makeup gas. In older detector designs, the makeup gas was added separately. The catalytic reaction tube fits into the reactor with a brass and a graphite/Vespel® ferrule, eliminating the contamination problems caused with graphite ferrules. The reactor is capable of heating the nickel reaction tube up to 1,100 °C, allowing complete oxidation or reduction of the more thermally-stable compounds such as polychlorinated biphenyls (PCBs).

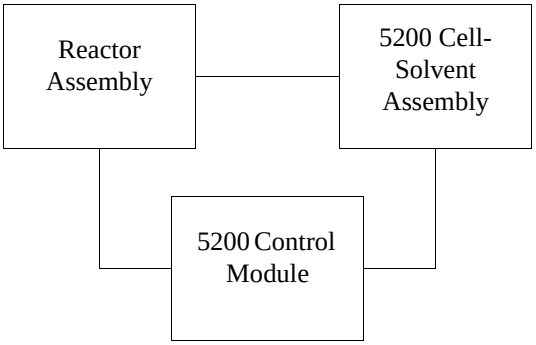


Figure 1. Model 5220 ELCD principal components

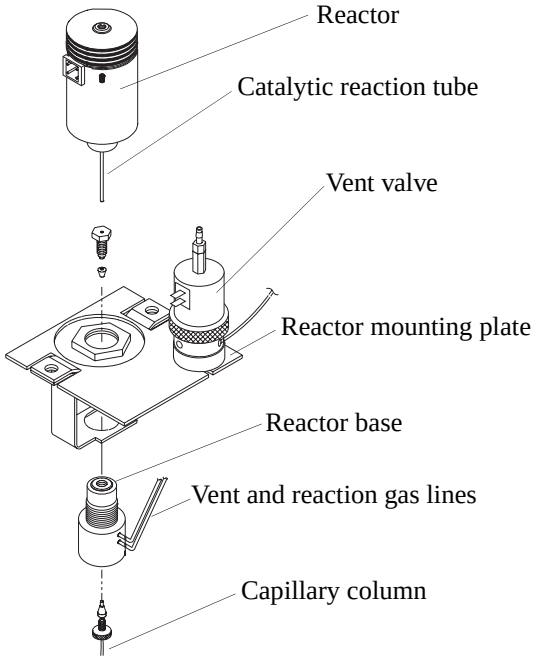


Figure 2. ELCD reactor assembly

Reactor maintenance is minimal. Periodically, the nickel reaction tube must be changed due to fouling or catalyst poisoning. This can be accomplished with the new reactor design in under 10 minutes. The reactor itself has a replaceable reaction core that extends the life of the reactor and reduces ownership costs.

The cell-solvent assembly includes the conductivity cell, solvent pump, conductivity amplifier, and fluid-flow and electrical lines (Figure 3). The "quick connect" feature of the new cell design greatly reduces difficulties in changing the cell. With the new disposable spring-loaded resin cartridge, resins may be changed within seconds. The conductivity amplifier digitizes the signal, which allows signal processing. This enables the 5220 to remove most high-frequency noise without signal loss. The amplifier also gives the operator the option of linearizing a non-linear signal, which is useful for some N and S compounds.

The 5200 Detector Controller converts the signal from the conductivity cell to a one-volt analog output and controls various components of the detector. The 5200 is capable of controlling two ELCDs simultaneously or one ELCD and an OI Analytical Photoionization Detector (PID). The push-button keypad provides greater programming accuracy. The vent valve of the reactor can be programmed by sequencing the method of the 5200 with that of a GC run. In addition to the vent valve times, other ELCD parameters such as reaction temperature and solvent flow rate can be stored into a file. The 5200 can store up to 14 of these files. Also, any file may be started from any other file, allowing such advanced capabilities as a "weekend standby mode" that activates the detector after a set period of inactivity.

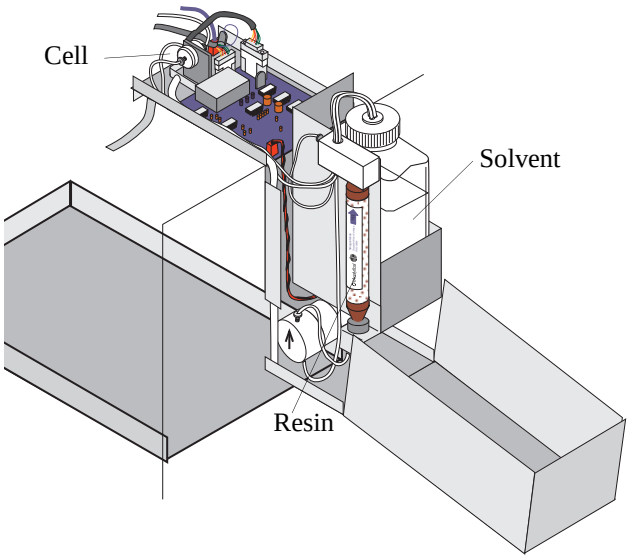


Figure 3. Cell-solvent assembly

Experimental

All of the experiments were performed on a Hewlett-Packard (HP) 5890 Series II GC. The detectors configured on the GC were an OI Analytical Model 5220 ELCD, an OI Analytical 4420 ELCD, and an HP Electron Capture Detector. Data was accumulated on an HP 3396A Integrator and an HP ChemStation. All neat standards were purchased from Chem Service, Inc. (West Chester, PA) and were made up in acetone or hexane. Samples were received from Primus Laboratories (Santa Maria, CA) and the Texas Department of Agriculture Extension Laboratory (Brenham, TX).

A dual-column, dual-detector system was developed using an SGE Variable Outlet Splitter System OSS-2 (Austin, TX) (Figure 4). An inert fused-silica (0.53 mm I.D.) precolumn, 20 cm in length, was used between a packed column injection port and the SGE splitter. The flow was split to two 10-cm inert fused-silica precolumns (0.32 mm I.D.). These columns were connected to a DB-5, 30 m x 0.53 mm column and a DB-17, 30 m x 0.53 mm column using presstight connectors (J&W Scientific, Inc. Folsom, CA). The DB-5 column was connected to the Model 4420 ELCD; the DB-17 column was connected to the ECD. The flow going to the ELCD was always higher to cause a preferential split to the relatively less sensitive detector. The flow to the ECD could be stopped completely by closing the outlet splitter system's valve.

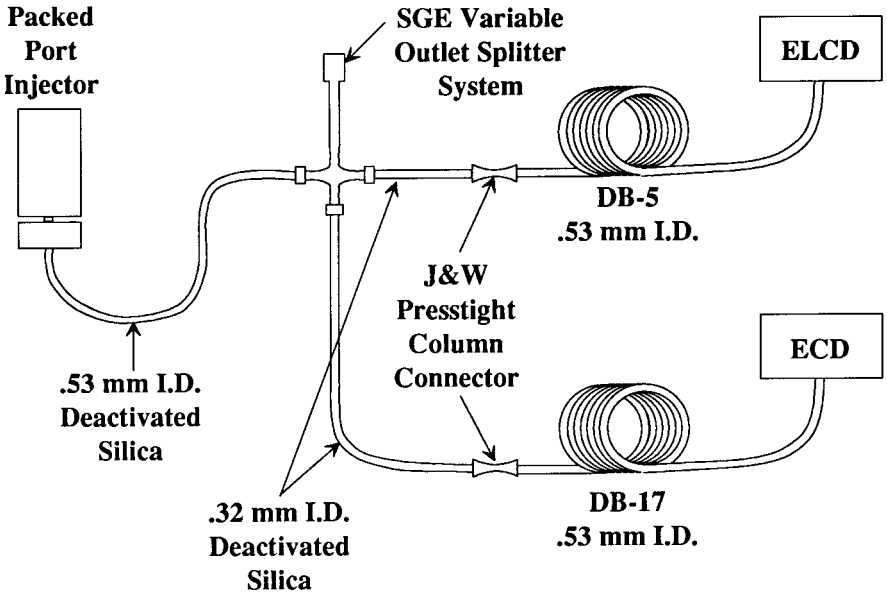


Figure 4. Diagram of the dual-column, dual-detector GC system

A split/splitless injector in the splitless mode was used for the linearization studies. The temperature program was 65 °C for one minute, 20 °C/minute to 260 °C for 10 minute. A DB-5 was used in the X mode. For analyte levels at the 1 pg level, a 20 m x 0.18 mm column was used. For analyte levels greater than 1 pg, a 30 m x 0.53 mm column was used. The S and N modes were run using a 30 m x 0.053 mm Rtx-5 column (Restek Corp., Bellefonte, PA).

A modified inlet was used for the remaining analyses[2] (Figure 5). All items were purchased and used as described in Reference 2 with the exception of the presstight connectors, which were substituted for the butt connector recommended by Hopper. The fused-silica was connected to a 30 m Megabore, Rtx-35 column. The column was connected to the 5220 using a knurled nut and a graphite/Vespel ferrule. The liner provided an inert medium on which nonvolatiles commonly encountered in pesticide residue extracts could collect after injection. Maintenance was facilitated with the easily-replaceable column inlet liner.

a. Column inlet liner
b. Glass wool
c. Column packing
d. On-column liner
e. Reducing union
f. Retention gap
g. Presstight connection
h. Wide-bore, fused-silica column
i. Reaction gas inlet
j. Detector

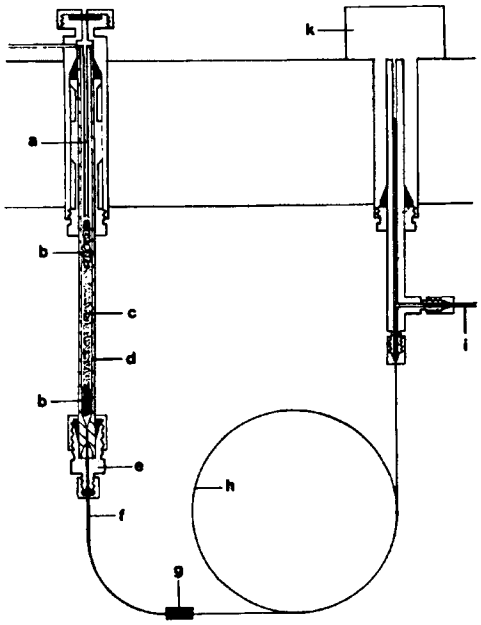
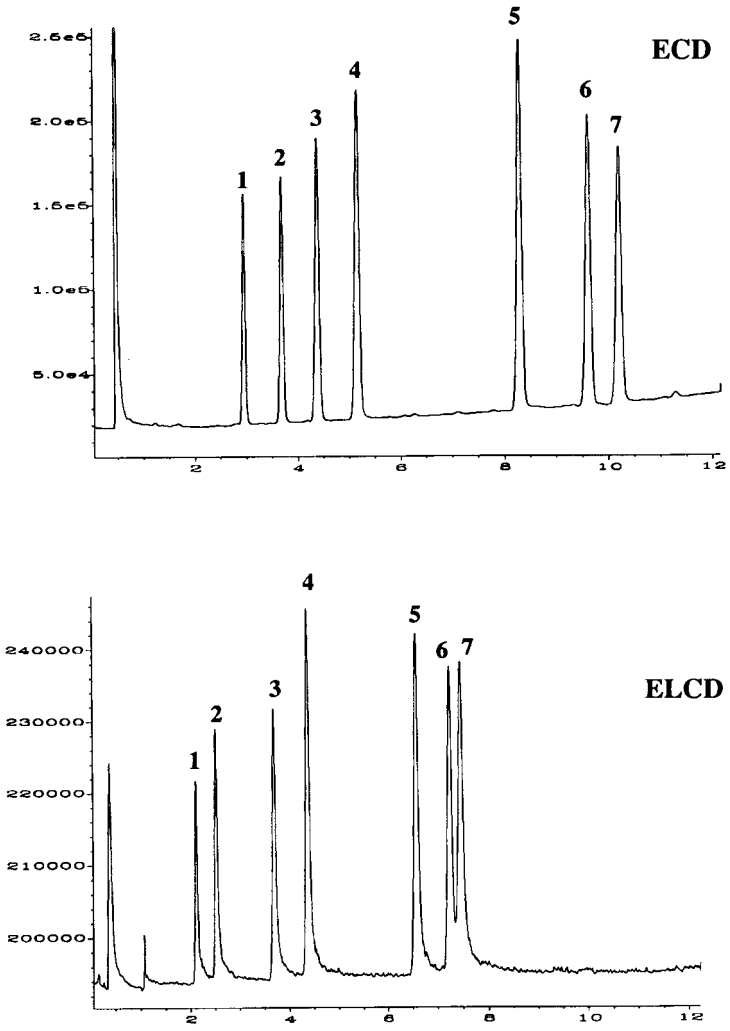


Figure 5. Components used in the direct vaporization injection system

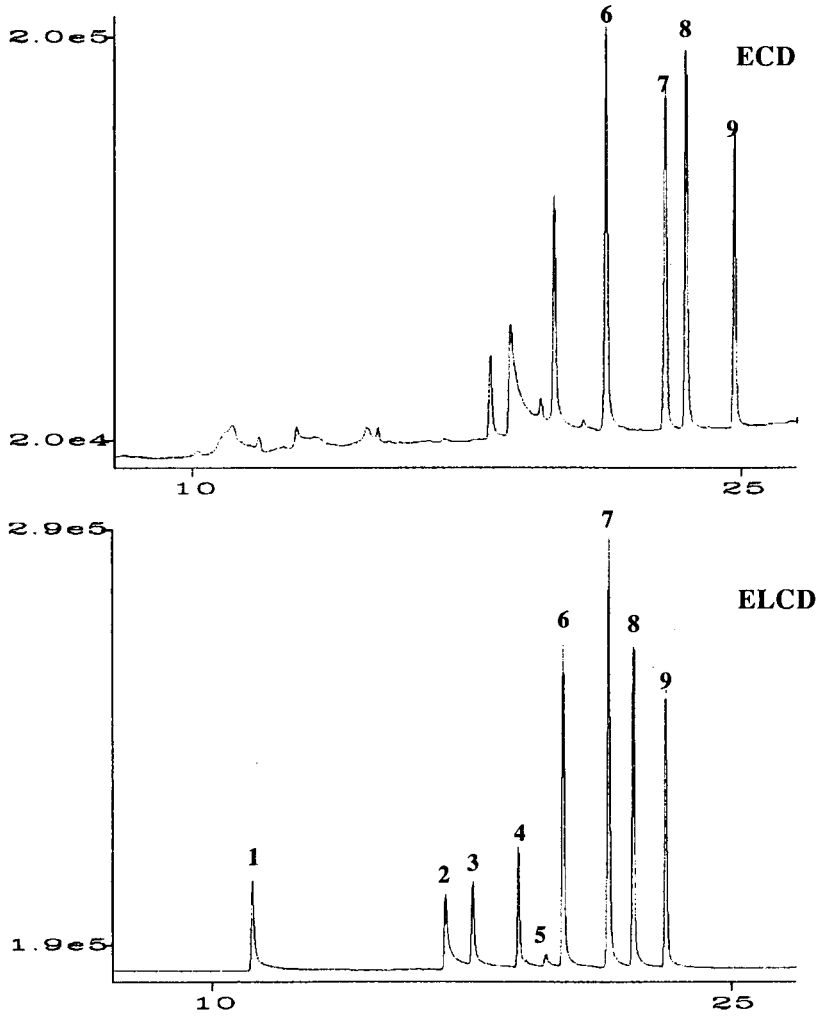
Results and Discussion

The dual-column, dual-detector GC system was an extremely high-maintenance system because the splitter was especially susceptible to contamination. Although not designed for this particular application, marginal success was achieved when running clean sample matrices (i.e., neat standards). The apparatus appeared to be chemically inert to reactive compounds such as endrin, showing no degradation products during analysis. However, after analyzing only a few crop sample extracts, the splitter needed cleaning. In order to clean the splitter, it had to be removed from the GC system, rinsed, and sonicated. This became time-consuming and outweighed the advantages of being able to easily adjust the split ratios. Chromatograms that show some of the contamination problems of this system can be seen in Figure 6 and Figure 7.



1. α-BHC
2. β-BHC
3. Heptachlor
4. Aldrin
5. *p,p´*-DDE
6. Endrin
7. Endosulfan

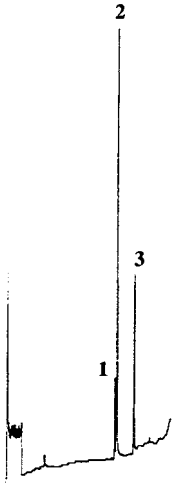
Figure 6. Dual-column analysis of a nominal 0.5-ng halogenated pesticide mix. The ECD used a DB-17 column, 30 m x 0.53 mm, and the ELCD (4420) used a DB-5 column, 30 m x 0.53 mm.
The temperature program was 200 °C/1/5 °C//270 °C/1.



1. Dichlobenil
2. Dichloran
3. Pronamide
4. Vinclozolin
5. Linuron
6. DCPA
7. *o*,*p*-DDE
8. *p*,*p*-DDE
9. *p*,*p*-DDD

Figure 7. Dual-column analysis of a 1-ng halogenated pesticide mix. The ECD used a DB-17 column, 30 m x 0.53 mm, and the ELCD (5220) used a DB-5 column, 30 m x 0.53 mm. The temperature program was 65 °C/1/8 °C//275 °C/20.

A pesticide mix containing atrazine, lindane, and chlorpyrifos was run at decreasing levels to show linearity in the X mode (Figure 8). The log of the concentration versus the log of the areas was graphed for each of the compounds (Figure 9). In each case, the best fit line matched the theoretical sloped line with correlation coefficients greater than 0.997.



1. Atrazine
2. Lindane
3. Chloropyrifos

Figure 8. Halogenated pesticide mix (100 pg) used for the linearity study run on a DB-5 column, 30 m x 0.53 mm. The temperature program was 65 °C/1/20 °C//260 °C/10, attn 2.

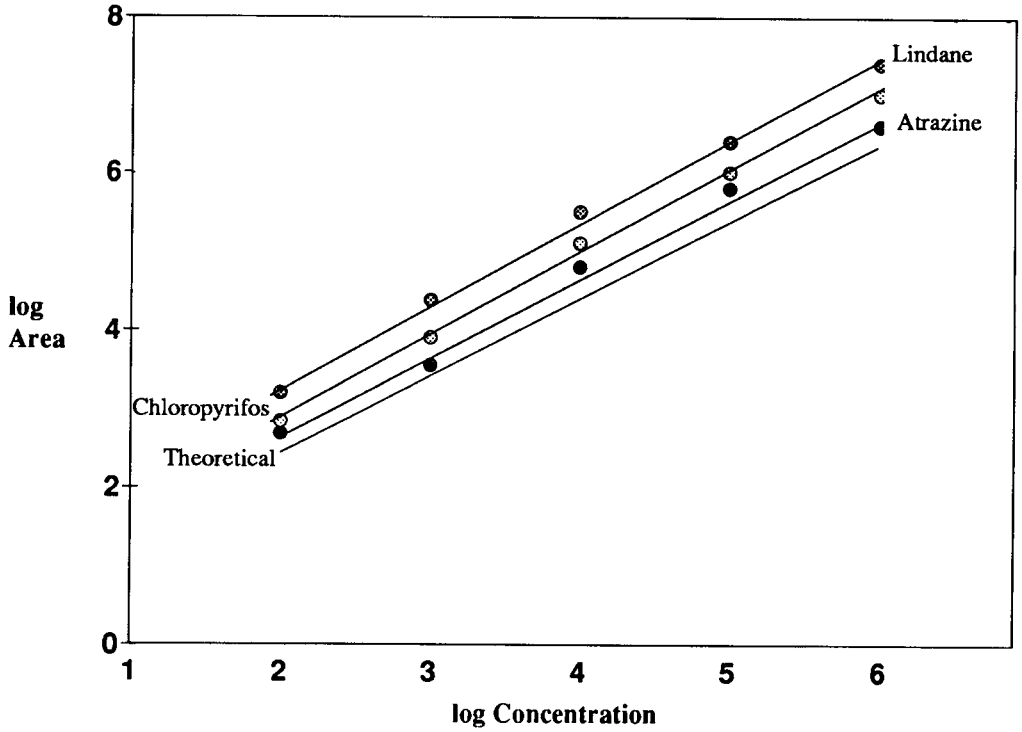
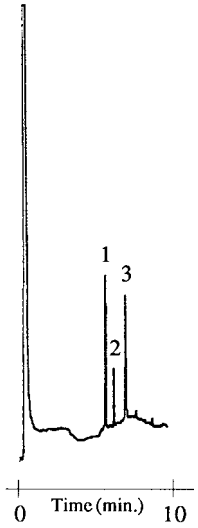


Figure 9. Linearity for three halogenated pesticides (10 pg–100 ng)

Thimet and atrazine were used to study the instruments' ability to linearize data in the S and N modes, respectively. A neat pesticide standard was run at various concentrations in both the S and N modes (Figure 10 and Figure 12). The log of the concentrations versus the log of the areas is shown in Figure 11 (S mode) and Figure 13 (N mode). The same graphs show the Model 5220's linearization of the curves and a theoretical line. The linearized data fit the theoretical sloped line with a correlation coefficient of 0.999 for the S mode and 0.993 for the N mode.

Figure 14 shows a chromatogram of a spinach extract fortified with 200 pg of the halogen pesticide mix shown in Figure 7. Figure 15 and Figure 16 show chromatographic runs with the modified inlet. The initial results of this system showed excessive peak broadening as compared to direct injection to the packed port adapted to 0.53-mm columns. The Ultrabond packing was removed, leaving the on-column liner and the upper-column inlet liner to aid in trapping nonvolatiles in sample matrices. A cilantro extract was run and then fortified with 50 pg of the halogenated pesticide mixture shown in Figure 6. The low-level spike was unimpeded by the sample matrix due to the Model 5220's exclusive selectivity to halogen species present (i.e., spiked pesticides).



1. Thimet
2. Chloropyrifos
3. Diazinon

Figure 10. Sulfur pesticide mix (1 ng) used for a linearity check run on an Rtx-5 column, 30 m x 0.53 mm

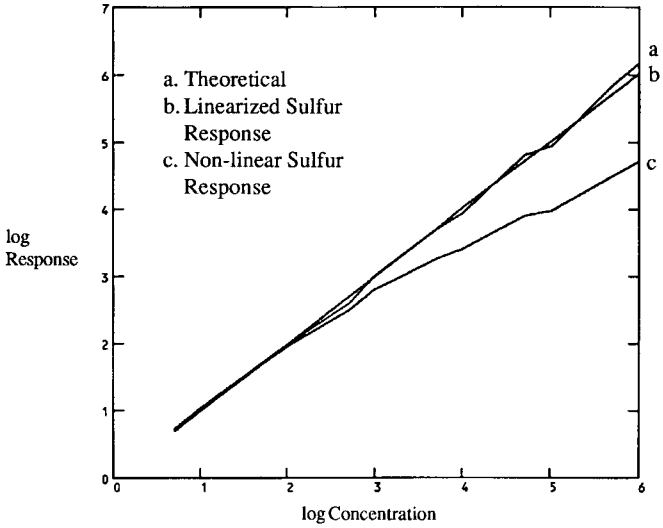
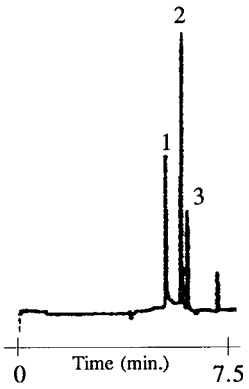


Figure 11. Response curve for thimet



1. Atrobenzene
2. Atrazine
3. Chloropyrifos

Figure 12. Nitrogen pesticide mix (1 ng) used for a linearity check

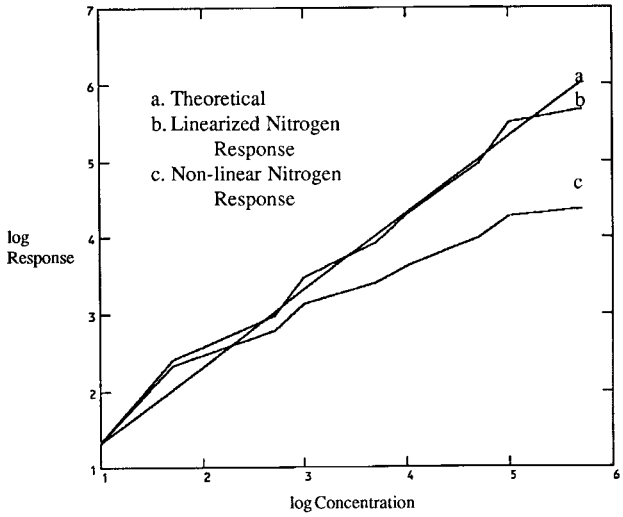
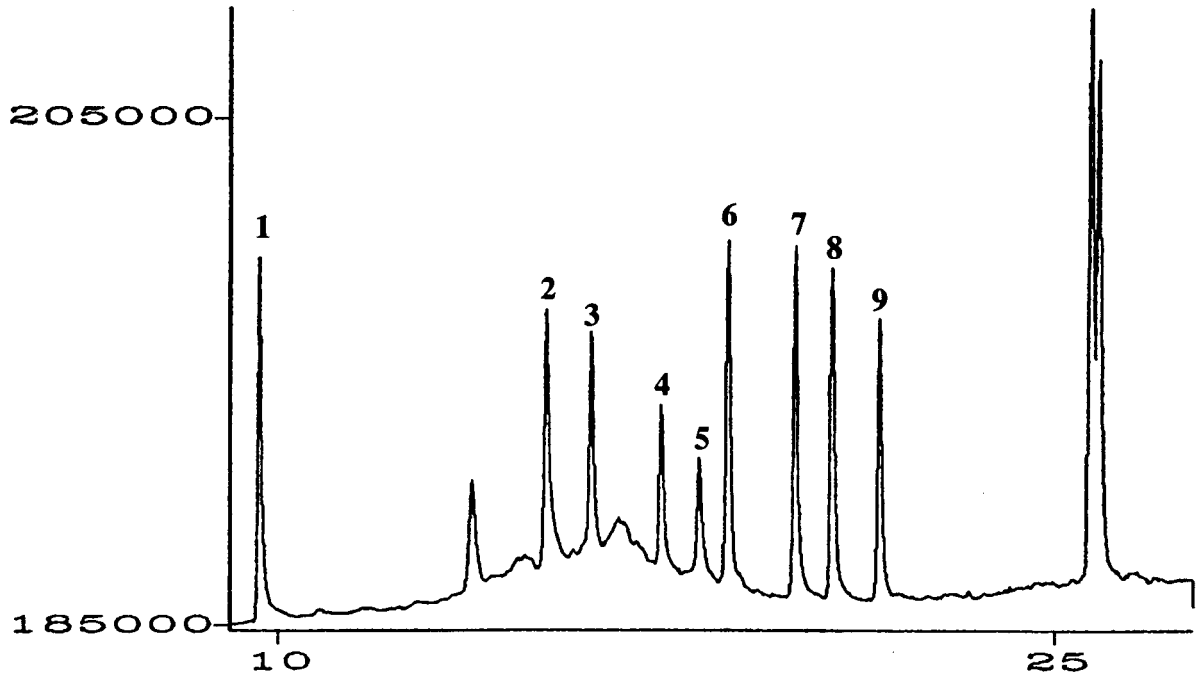


Figure 13. Response curve for atrazine



1. Dichlobenil
2. Dichloran
3. Pronamide
4. Vinclozolin
5. Linuron
6. DCPA
7. *o,p*-DDE
8. *p,p*-DDE
9. *p,p*-DDD

Figure 14. Spinach extract spiked with pesticide mix (Figure 7) to 200 pg/µL run on a DB-5 column, 30 m x 0.53 mm. The temperature program was 65 °C/1/8 °C//275 °C/20.

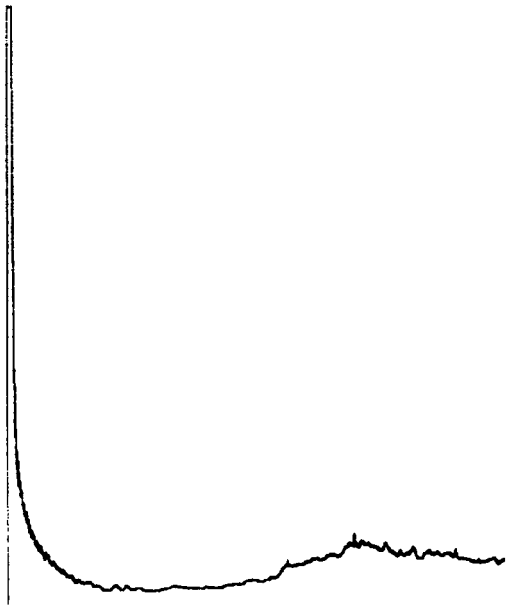


Figure 15. Cilantro extract before spiking run on an Rtx-35 column, 30 m x 0.53 mm. The temperature program was 160 °C/2/8 °C//275 °C/10.

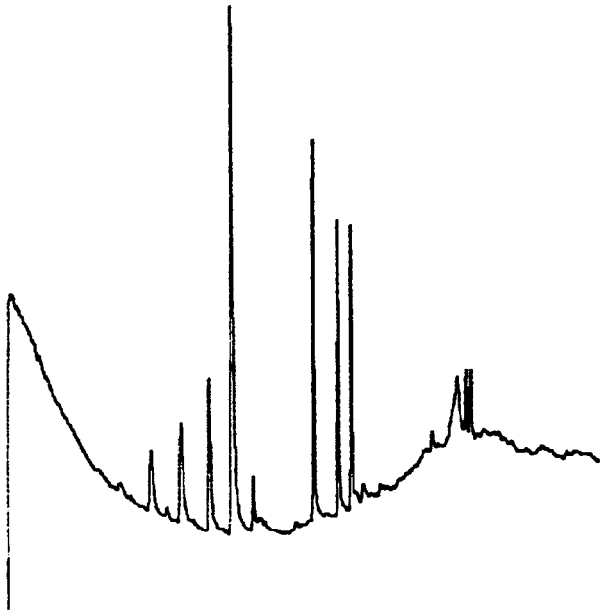


Figure 16. Cilantro extract spiked with 200 pg of pesticide mix run a an Rtx-35 column, 30 m x 0.53 mm. The temperature program was 160 °C/2/8 °C//275 °C/5.

Conclusion

These data show that the OI Analytical Model 5220 ELCD is well suited for the analysis of pesticides. Major design improvements of the Model 5220 include optional linear response correction (S and N modes), baseline correction, newly-designed and easily-maintained reactor design, easily-changeable disposable resin cartridge, and an operator-friendly control module.

References

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